Module-I Electrochemistry and Energy storage systems

Use of free energy in chemical equilibria

Electrochemistry is the branch of chemistry, that deals with the interconversion of electrical and chemical energies during spontaneous oxidation and reduction reactions.

An important class of chemical reactions is oxidation-reduction reactions.

In oxidation: a species loses one or more electrons resulting in an increase in its oxidation number.

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

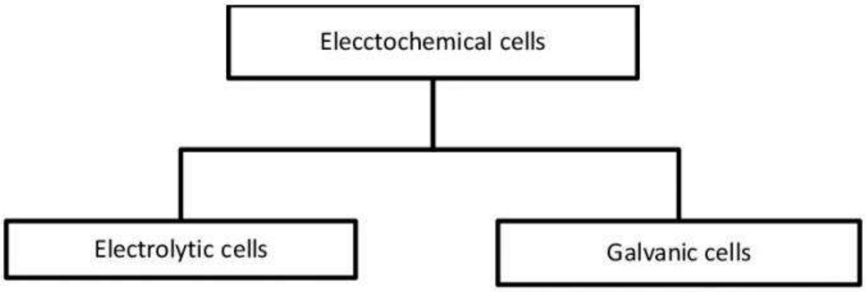
In reduction: the species gains one or more electrons; there is a decrease in oxidation number.

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

A reduction process necessarily accompanies an oxidation process since electrons can be lost by a species only when there is a counterpart to receive them. Redox reaction forms the basis of electrochemical cells.

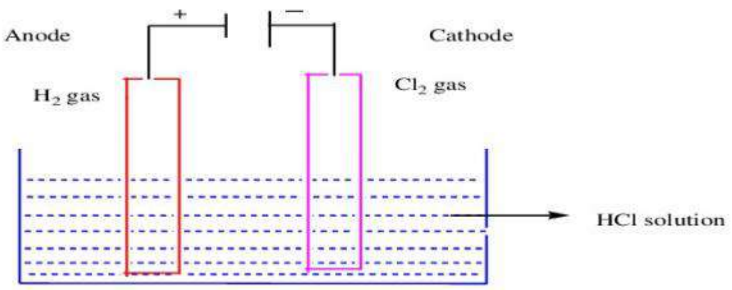
Electrochemical Cells: Electrochemical cells are the device which converts chemical energy into electrical energy or electrical energy into chemical energy due to spontaneous oxidation and reduction reactions.

Types of electrochemical cells



Electrolytic Cells: These are electrochemical cells in which electrical energy is applied from the external source to bring about certain chemical changes.

The redox reaction in an electrolytic cell is non-spontaneous. Electrical energy is required to induce the electrolysis reaction. An example of an electrolytic cell is shown below, in which aqueous HCl is electrolyzed to form hydrogen and chlorine gas. The hydrogen ions migrate toward the cathode, where they are reduced to hydrogen gas. Similarly, chloride ions migrate to the anode and are oxidized to form chlorine gas.



Electrolysis of HCl

$$\text{At anode} \quad 2Cl^- \longrightarrow Cl_2 + 2e^- \quad \text{Oxidation}$$

$$\text{At cathode} \quad 2H^+ + 2e^- \longrightarrow H_2 \quad \text{Reduction}$$

Note: common electrolyte is used during electrolysis. Salt bridge is not required

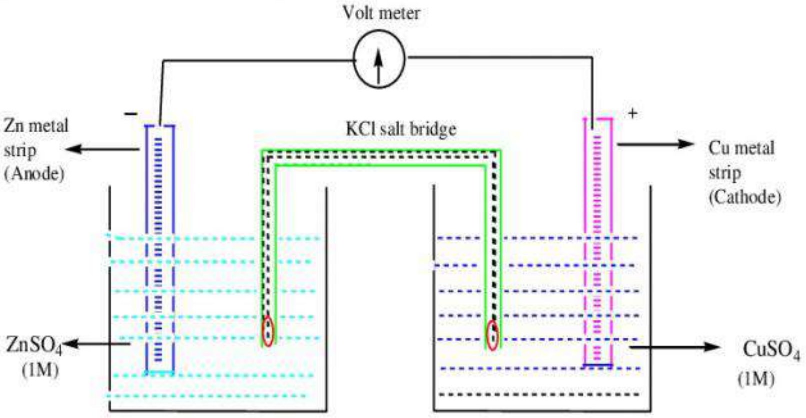
Galvanic cell: These are the electrochemical cells which convert chemical energy into electrical energy during spontaneous redox reactions inside it. The redox reaction in a galvanic cell is spontaneous.
Ex: Daniell cell, Leclanche cell etc.

Construction and working of Galvanic cells:

Ex: Daniell cell:

A galvanic cell is formed when two electrodes dipped in two electrolyte solutions are connected externally by conducting material (Metallic wire) and internally ionic solutions are connected by a salt bridge and thereby produces an electric current.

It consists of two beakers one of which contains zinc rod immersed in zinc sulphate solution and the other one contains copper rod in copper sulphate solution. A salt bridge (U-tube) containing KCl or KNO_3 connects the solutions of two beakers. The zinc and copper rods are connected externally by means of metallic through the voltmeter. On completing the circuit the following changes are observed.



Cell representation $Zn_{(s)} / ZnSO_4\ (1M) // CuSO_4\ (1M) / Cu_{(s)}$

- At anode, zinc metal starts dissolving to form Zn^{2+} ions by leaving negative charge.
- At cathode, Cu^{2+} ions get deposited to form copper metal by leaving positive charge.
- Zinc sulphate solution becomes more concentrated with respect to Zn^{2+} ions
- Copper sulphate solution becomes more dilute with respect to Cu^{2+}
- Migration of ions takes place within the salt bridge to maintain electrical neutrality takes place in solution.

  Electrode reactions:

$$\text{At anode} \quad Zn_{(S)} \longrightarrow Zn^{2+}_{aq} + 2e^- \quad \text{(Oxidation)}$$

$$\text{At cathode} \quad Cu^{2+}_{aq} + 2e^- \longrightarrow Cu_{(S)} \quad \text{(Reduction)}$$

$$\text{Net cell reaction} \quad Zn_{(S)} + Cu^{2+}_{aq} \longrightarrow Zn^{2+}_{aq} + Cu_{(S)}$$

Note Salt Bridge- A U- tube filled with a solution of salt composed of ions not involved in the cell reaction. The tube has porous plugs at the ends prevent the solution from pouring out while still allowing the bridge to exchange ions with the solutions of the half cells.

- Often KCl or KNO_3 as the electrolyte in the salt bridge.
- The negative ions diffuse from the salt bridge into the copper half-cell or Cu^{2+} ions leave the solution into the salt bridge to help maintain a neutral solution in the half cell.
- Positive ions from the salt bridge can enter the cell to keep the half cell neutral.

Differences between Galvanic cells and electrolytic cells

Electrochemical cell (Galvanic Cell)	Electrolytic cell
A Galvanic cell converts chemical energy into electrical energy.	An electrolytic cell converts electrical energy into chemical energy.
A spontaneous redox reaction occurs and is responsible for the production of electrical energy.	The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction.
The electrodes are made of dissimilar metals	The electrodes used may be dissimilar metals or same metals
The two half-cells are set up in different containers.	Both the electrodes are placed in a same container in the solution of common electrolyte.
The electrolytic solutions connected through the salt bridge.	Salt bridge is not required
Here the anode is negative and the cathode is the positive electrode. The reaction at the anode is oxidation and that at the cathode is a reduction.	Here, the anode is positive and the cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is a reduction.

Thermodynamic functions: Free energy and work function – concepts.

When we talk about our chemical system losing or gaining energy, we need to introduce a quantity which represents the total energy of the system. It may be chemical, electrical, and mechanical or any other type of energy you may think of, the sum of all these is the energy of the system.

In order to find out the spontaneity of a process, we have to see the change in entropy of the system as well as surroundings. It is difficult to find out entropy of the surrounding every time. So new thermodynamic functions are introduced, which can be determining more conveniently.

Gibbs free energy: In thermodynamics, the **Gibbs free energy** or **Gibbs energy** or **Gibbs function**; also known as **free enthalpy** is a thermodynamic potential that can be used to calculate the maximum of reversible work that may be performed by a thermodynamic system at a constant temperature and pressure (isothermal, isobaric).

Gibbs energy is an important thermodynamic property which automatically accounts for the enthalpy and entropy of the system. It was introduced by American physicist J.W. Gibbs and is therefore, called Gibbs energy function denoted by symbol *G* in the honour of the scientist. Gibbs energy function is defined by

$$G = H - TS$$

Where H = Enthalpy of the system

S = Entropy of the system

T = Temperature on kelvin scale

For a small change.

$$\Delta G = \Delta H - T\Delta S$$

The thermodynamic **Free energy** is the amount of work that a thermodynamic system can perform.

Or The **free energy** is the internal **energy** of a system minus the amount of **energy** that cannot be used to perform work.

The Gibbs free energy ($\Delta G° = \Delta H° - T\Delta S°$) (J in SI units) is the maximum amount of non-expansion work that can be extracted from a thermodynamically closed system this maximum can be attained only in a completely reversible process. When a system transforms reversibly from an initial state to a final state, the decrease in Gibbs free energy equals the work done by the system to its surroundings, minus the work of the pressure forces.

The Gibbs free energy, originally called available energy, was developed in the 1870s by the American scientist Josiah Willard Gibbs.

Characteristics of Gibbs energy *(G)*

1. Gibbs energy is an extensive property. Its value depends on the amount of the system.
2. Gibbs energy of a system is a state property. For a known amount of the system it depends only on the state Variables (T, P, V). If the state variables are changed the Gibbs energy is also changed.
3. The change in Gibbs energy (ΔG) does not depend on the path by which the final state of the system is reached.
4. The change in Gibbs energy of the system is related to the entropy change of the universe
5. For a spontaneous process there is decrease in Gibbs energy and ΔG system < 0
6. In an isothermal reversible process the decrease in Gibbs energy is equal to the net useful work that can be obtained from the system.

ENTROPY (S)

Entropy is a Greek word which stands for *trope* meaning change; a prefix 'en' is written to identify it as a thermodynamic property which belongs to the family of energy and enthalpy. This term was introduced by Clausius. He denoted entropy by the symbol S

Entropy, S: At this point, we introduce another thermodynamic function, entropy denoted as S. It is a measure of the disorder or randomness of a system. Entropy increases as the number of possible microstates increases

S (gas) > S (liquid) > S (solid)

Characteristics of entropy

1. Entropy is an extensive property. Its value depends upon the amount of the substances Present in the system.
2. Entropy of a system is a state function. It depends only on the state variables (T, P, V, n). Thus, the change of entropy is given by $\Delta S = S$ (final) – S (initial)
3. Entropy change of system (ΔS system) does not depend on the path followed by the change, but the entropy change of the surroundings (ΔS surronndngs) depends upon the path.

4. The total entropy change of an isolated system is equal to the sum of the entropy change of system and the entropy change of the surroundings.

ΔS total = ΔS system + ΔS surroundings

The total entropy change of an isolated system is also called the entropy change of the ***Universe*** (ΔS universe)

5. In a reversible process ΔS system = – ΔS surroundings

6. In an irreversible process $\Delta.S$ total > 0. This implies that in spontaneous changes there is increase of entropy of universe.

Entropy is the ratio of heat and temperature. Since heat is expressed as joule (J) and temperature is expressed in kelvin (K), therefore, the entropy and change in entropy is expressed as Joules per kelvin ≡J $K.^{-1}$

Electrochemical sign conventions:

i) Sign of electrode potential:

a) The electrode where oxidation occurs is called anode and has negative electrode potential.

$$M \longrightarrow M^{n+} + ne^- \qquad E_{M^{n+}/M} = -ve$$

b) The electrode where reduction occurs is called cathode and has positive electrode potential.

$$M^{n+} + ne^- \longrightarrow M \qquad E_{M^{n+}/M} = +ve$$

ii) Representation of an electrode and cell

a) The electrode (Half cell) at which oxidation occurs is always written on LHS (Left Hand Side) in the order M/M^{n+} Ex: Zn/Zn^{2+} / ⟶ Single vertical line indicates phase boundary.

b) The electrode (Half cell) at which reduction occurs is always written on RHS (Right Hand Side) in the order M^{n+}/M Ex: Cu^{2+}/Cu / ⟶ Single vertical line indicates phase boundary.

c) The two electrodes are joined to a salt bridge represented as double vertical line as //

d) Concentration of the solution should be mentioned in bracket as (XM)
Consider general cell representation Ex: M/M^{n+} (XM) // (YM) M^{n+}/M
Ex: Zn/Zn^{2+} (1M) // (1M) Cu^{2+}/Cu

Electrode and cell reactions:

For any electrochemical cell, the two electrode reactions are

At anode $M_1 \longrightarrow M_1^{n+} + n\,e^-$ (Oxidation)

At cathode $M_2^{n+} + ne^- \longrightarrow M_2$ (Reduction)

Net cell rection $M_1 + M_2^{n+} \longrightarrow M_1^{n+} + M_2$

iv) EMF of a cell:

It is defined as the potential as the potential difference between cathode and anode causes the flow of electrons from one electrode to another electrode. It is represented as EMF or emf or E_{cell}

It is expressed in volts.

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

a) If E_{cell} =+ve ⟶ Maximum work is done by the cell.
b) If E_{cell} =-ve ⟶ Minimum work is done by the cell.
c) If E_{cell} = 0 ⟶ System is in equilibrium

Electrode: When metal in contact with a solution of its own ion is known to as a single electrode or half- cell. Electrode consists electric conducting metal and electrolyte solution, an interface at which electrode process occurs.

Electrode Potential (E): The potential developed when a metal is in equilibrium with its own ions in solution is electrode potential or half cell potential. Or

The tendency of an electrode to either loose or gain electrons when it is in contact with the solution of its own ions is called electrode potential/ single electrode potential.

Standard Electrode Potential (E^o): The potential developed when a metal is in equilibrium with its own ionic solution of unit concentration (1M) at 298K is called standard electrode potential. If the system involves gaseous substances pressure should be one atmosphere (101.325Kpa).

Nernst Equation:

Nernst Equation is derived on the basis of thermodynamic considerations. It relates the relation between electrode potential of the metal and metal ion concentration with the temperature.

Consider the generally reversible electrode reaction undergoing the spontaneous process.

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

The equilibrium constant for the above electrode reversible reaction may be written by applying law of mass action as

$$K = \frac{[M]}{[M^{n+}]} \qquad (1)$$

Maximum work done for electrochemical cell is the movement of charge at equilibrium and is expressed as

$$W_{max} = n\,F\,E \qquad (2)$$

Maximum work done at any electrode is due to spontaneous reaction is the decrease in the free energy,

$$W_{max} = -\Delta G \qquad (3)$$

Equating equations (2) and (3), we get

$$-\Delta G = nFE \quad \text{and} \quad -\Delta G^o = nFE^o$$

Or

$$\Delta G = -nFE \quad \text{and} \quad \Delta G^o = -nFE^o \qquad (4)$$

Where

ΔG is the free energy change ΔG^o is the standard free energy change

E is the electrode potential E^o is standard electrode potential

n is the number of electrons involved in the redox reaction

F is tha Faraday constant

F=Charge on electron x Avogadros number $F=1.6 \times 10^{-19} C \times 6.023 \times 10^{23}\ mol^{-1}$
$=96{,}500\ C\ mol^{-1} = 96{,}500\ J\ V\ mol^{-1}$
$=96.5 kJ\ V\ mol^{-1}$

Note: Faraday constant: It is the quantity of electric current required to discharge or deposit one gram equivalent of the element during electrolysis.

Free energy change and equilibrium constant are related by Vant Hoff's reaction isotherm equation.

$$\Delta G = \Delta G^{o} + RT \ln K \qquad (5)$$

Substitute the values of K, ΔG and ΔG° from equations (1) and (4) in equation (5).

$$-nFE = -nFE^{o} + RT \ln \frac{[M]}{[M^{n+}]} \qquad (6)$$

Dividing equation (6) on both sides by -nF

$$E = E^{o} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]} \qquad (7)$$

∵ M is Metal and [M]=1

$$E = E^{o} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]} \qquad (8)$$

$$E = E^{o} + \frac{RT}{nF} \ln [M^{n+}]$$

∵ ln= 2.303 $\log_{10}$

$$\therefore E = E^{o} + \frac{2.303\,RT}{nF} \log_{10} [M^{n+}] \qquad (9)$$

Equation (9) is Nernst equation for the calculation of electrode potential of the given electrode at given temperature.

At 298K temperature, the equation (9) becomes by substituting the values, T=298K,

R=8.314 J/K/mol and F=96,500 C/mol

$$\therefore E = E^{o} + \frac{0.0591}{n} \log_{10} [M^{n+}] \qquad (10)$$

Equation (10) is called Nernst's equation at 298K.

Note: The cell potential may be calculated by using the equation.

$$E_{cell} = E^{o}_{cell} + \frac{2.303\,RT}{nF} \log_{10} \frac{[M^{n+}]_{Cathode}}{[M^{n+}]_{Anode}}$$

Or

$$E_{cell} = E^{o}_{cell} + \frac{0.0591}{n} \log_{10} \frac{[M^{n+}]_{Cathode}}{[M^{n+}]_{Anode}}$$

ELECTROCHEMICAL ENERGY SYSTEM

Indicator electrodes:

The electrodes whose potential is dependent upon the concentration of the ion to be determined are called indicator electrodes.

Ex: Metal-Metal ion electrode, Glass electrode etc.

Reference electrodes:

Reference electrodes are the electrodes whose potential is known and with reference to those, the electrode potential of any other electrode can be measured.

There are 2 types of reference electrodes

1) Primary reference electrode 2) Secondary reference electrode:

Secondary reference electrodes:

Since a standard hydrogen electrode is difficult to prepare and maintain, it is usually replaced by other reference electrodes, which are known as secondary reference electrodes. These are convenient to handle and are prepared easily. The most widely used reference electrodes in electrochemical cells and maintains constant potential, these are the electrodes having constant electrode potential value and their potential is known with respect to SHE, hence they are called as secondary reference electrodes.

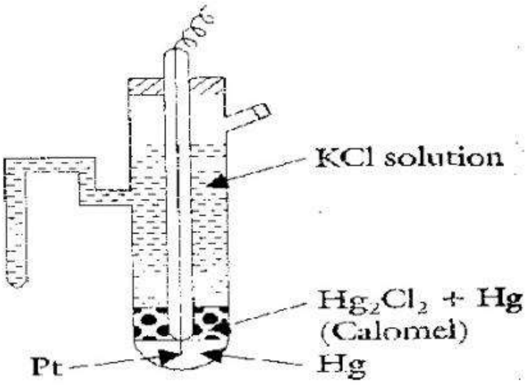
For the sake of simplicity and to overcome the difficulties of SHE, there was a need for the development of secondary reference electrodes.

Ex 1. Calomel electrode 2. Ag-AgCl electrode.

Advantages of secondary reference electrodes:

a. The electrodes can be constructed easily.
b. The electrodes are not bulky and space occupying.
c. These electrodes are not poisoned by the impurities.
d. The electrode potential is not changed by a change in pH.
e. These electrodes have constant and stable potential value at given temperature.

Calomel electrode:



Construction:-

Calomel electrode is a secondary reference electrode. It consists of a long glass tube having two side tubes as depicted in the figure. The small tube is used to fill the KCl solution into a long glass tube and other bent tube helps to make a connection through the salt bridge with another electrode. Highly pure mercury (Hg) is placed at the bottom of the tube and is covered by a paste of mercurous chloride (Hg_2Cl_2) and KCl solution. The electrical connection is made by means of platinum wire sealed into another small glass tube having little mercury at the bottom.

Calomel electrode is represented as $Hg_{(l)}/Hg_2Cl_{2(s)},KCl_{(s)}$

Electrode reactions

At anode

$$2\,Hg_{(l)} \longrightarrow Hg_2^{2+} + 2e-$$

$$Hg_2^{2+}{}_{(aq)} + 2Cl^-_{(aq)} \longrightarrow Hg_2Cl_2$$

$$2Hg_{(l)} + 2Cl^-_{(aq)} \longrightarrow Hg_2Cl_{2(s)} + 2e^-$$

At cathode

$$Hg_2Cl_2 \longrightarrow Hg_2^{2+}{}_{(aq)} + 2Cl^-_{(aq)}$$

$$Hg_2^{2+} + 2e- \longrightarrow 2\,Hg_{(l)}$$

$$Hg_2Cl_{2(S)} + 2e^- \longrightarrow 2Hg_{(l)} + 2Cl^-_{(aq)}$$

The electrode potential of calomel electrode depends on KCl solution with which the tube is filled.

$$E_{calomel} = E^o - 0.0591 \log[Cl^-]$$

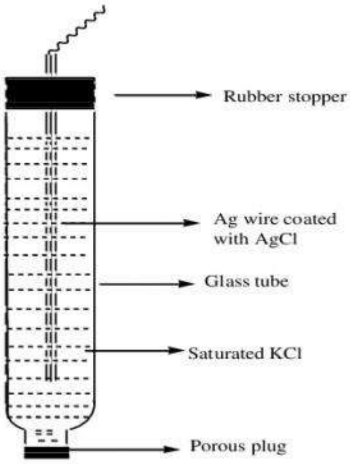
0.1NKCl solution ⟶ 0.334 V (Decinormal Calomel electrode)
1NKCl solution ⟶ 0.280 V (Normal Calomel electrode)
Saturated KCl solution ⟶ 0.2422 V (Saturated Calomel electrode)

Advantages and applications of calomel electrodes

- Simple to construct
- Maintains constant potential
- It is used as reference electrode to measure the pH of given solution

Silver-Silver chloride electrode:

In recent time Ag-AgCl electrode has been frequently used as a reference electrode for the accurate determination of standard electrode potential of the electrodes.



Construction: Silver-chloride electrode consists glass or plastic tube containing a silver wire coated with thin layer of silver-chloride either by electroplating or by dipping wire in molten silver-chloride. Finally, it is immersed in KCl(Saturated) solution. Silver-chloride electrode is represented as $Ag_{(s)}/AgCl_{(s)}/$ KCl.

Electrode reactions:

At anode

$$Ag_{(s)} \longrightarrow Ag^{+} + e^{-}$$

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \longrightarrow AgCl_{(s)}$$

$$Ag_{(\,l)} + Cl^{-}_{(aq)} \longrightarrow AgCl_{(s)} + e^{-}$$

At cathode

$$AgCl_{(S)} \longrightarrow Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$$

$$Ag^{+}{}_{aq} + e^{-} \longrightarrow Ag_{(s)}$$

$$AgCl_{(S)} + e^{-} \longrightarrow Ag_{(s)} + Cl^{-}_{(aq)}$$

The electrode potential of Ag-AgCl electrode depends on KCl solution with which the tube is filled.

$$E_{calomel} = E^{o} - 0.0591 \log[Cl^{-}]$$

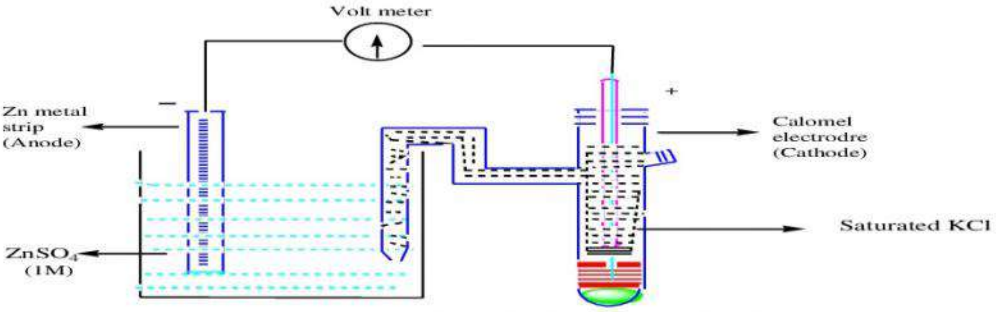
0.1NKCl solution → 0.288 V (Decinormal Ag-AgCl electrode)
1NKCl solution → 0.223 V (Normal Ag-AgCl electrode)
Saturated KCl solution → 0.199 V (Saturated Ag-AgCl electrode)

Advantages and applications of Ag-AgCl electrodes

- Simple to construct
- Maintains constant potential
- It is simple to use, inexpensive and used above 130 °C
- It is used as a reference electrode to measure the pH of given solution, photography films, and plate.

Measurement of single electrode potential using calomel electrode:

a) Measurement of electrode potential of anode: - To measure the electrode potential of Zn^{2+}/Zn, i.e., Zinc electrode is coupled with standard calomel electrode. In this cell, zinc electrode acts as an anode and the reference calomel electrode acts as a cathode. As the potential of calomel electrode is known, the potential of zinc electrode can be calculated.



Cell representation: $Zn_{(s)}/ ZnSO_4\ (1M)//KCl\ (Sat)/Hg_2Cl_{2(s)}/Hg_{(l)}$

Electrode reactions

$$\text{At anode:- } Zn_{(s)} \longrightarrow Zn^{2+}_{(1M)} + 2e^-$$

$$\text{At cathode:- } Hg_2Cl_{2(s)} + 2e^- \longrightarrow 2Hg_{(l)} + 2Cl^-_{(aq)}$$

$$\text{Net cell reaction } Zn(s) + Hg_2Cl_{2(s)} \longrightarrow Zn^{2+}_{(1M)} + 2Hg_{(l)} + 2Cl^-_{(aq)}$$

EMF of cell

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

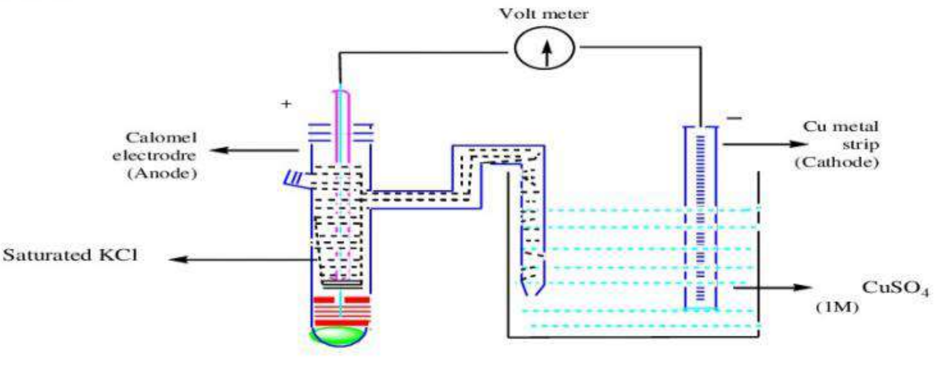
$$= E_{Calomel} - E_{zn2+/Zn}$$

$$- E_{zn^{2+}/Zn} = E_{cell} - E_{calomel}$$

$$E_{zn^{2+}/Zn} = E_{calomel} - E_{cell}$$

$$E_{zn^{2+}/Zn} = 0.2422 - E_{cell}$$

b) Measurement of electrode potential of cathode: - To measure the electrode potential of Cu^{2+}/Cu, i.e., a copper electrode is coupled with standard calomel electrode. In this cell, Copper electrode acts as a cathode and the reference calomel electrode acts as an anode. As the potential of calomel electrode is known, the potential of the copper electrode can be calculated.



Cell representation: $Hg_{(l)} / Hg_2Cl_2\,(s)/\ KCl\ (Sat)\ //CuSO_4\,(1M)/Cu_{(s)}$

Electrode reactions

At anode:- $2Hg_{(l)} + 2Cl^-_{(aq)} \longrightarrow Hg_2Cl_{2(s)} + 2e^-$

At cathode:- $Cu^{2+}_{(1M)} + 2e^- \longrightarrow Cu_{(s)}$

Net cell reaction: $Cu^{2+}_{(1M)} + 2Hg_{(l)} + 2Cl^-_{(aq)} \longrightarrow Cu_{(s)} + Hg_2Cl_{2(s)}$

EMF of cell $E_{cell} = E_{cathode} - E_{anode}$

$= E_{Cu^{2+}/Cu} - E_{Calomel}$

$E_{Cu^{2+}/Cu} = E_{cell} + E_{calomel}$

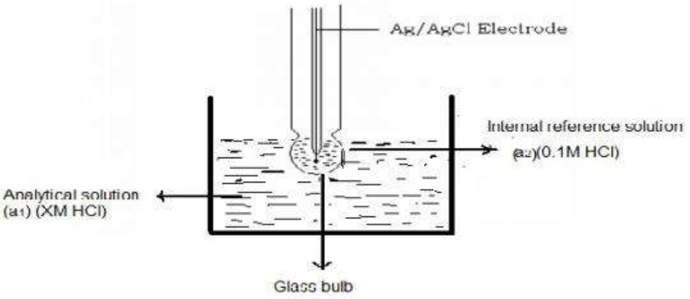
$E_{Cu^{2+}/Cu} = E_{cell} + 0.2422$

Ion-selective electrode:

The electrodes, which responds to specific ions only and develops a potential against that ions while ignoring the other ions present in the solution are called **ion-selective electrodes.** In other words, the potential developed only on the concentration of specific species or ions. For Ex. Glass electrode is only H^+ ions selective.

Construction:

The glass electrode is constructed by immersing Ag-AgCl internal reference electrode in a glass bulb containing 0.1M HCl solution. The glass bulb is made up of a long glass tube with a thin highly conducting glass membrane at the bottom. The glass membrane is selective to H^+ ions in the solution and is made up of silicate glass having a composition of 72% SiO_2, 22% Na_2O and 6% CaO.



Analytical soluron(a1)	Glass	Internal ref rence solution

A glass electrode is quite hygroscopic and takes a significant amount of water forms water layer across the membrane. The bulb of the glass electrode is dipped into any solution containing hydrogen ions. If the hydrogen ion concentrations of the solution inside and outside the glass membrane are different then the potential develops across the glass membrane. The probable reaction is

$$\underset{\text{Glass Membrane}}{NaG} + \underset{\text{In solution}}{H^+} \longrightarrow \underset{\text{On the surface of glass membrane}}{HG} + \underset{\text{In solution}}{Na^+}$$

When a thin glass membrane is placed between two solutions of different pH values, a potential difference develops across the glass membrane is known as boundary potential or junction potential

When a thin-walled glass bulb containing acid, H^+ solution is immersed in an acidic solution of different concentration $[a_1 > a_2]$ a boundary potential, E_b is developed across gel layers of the glass membrane. This potential E_b arises due to the difference in the H^+ ion concentration inside and outside the glass bulb i.e.

$$Eb = E_1 - E_2 = 0.0591 \log \frac{a_1}{a_2}$$

Since n=1 for H^+ ions

$$Eb = 0.0591 \log a_1 - 0.0591 \log a_2$$

Since the H+ on concentration inside the glass bulb is a constant, the term on RHS of the equation becomes constant,

$$Eb = 0.0591 \log a_1 + K \qquad \text{Since } K = -0.0591 \log a_2$$

$$= 0.0591 \log [H^+] + K$$

$$= -0.0591\, pH + K \qquad \text{Since } pH = -\log[H^+]$$

The overall potential of glass electrode includes also the potential of internal reference and asymmetric potential. The potential of glass electrode is

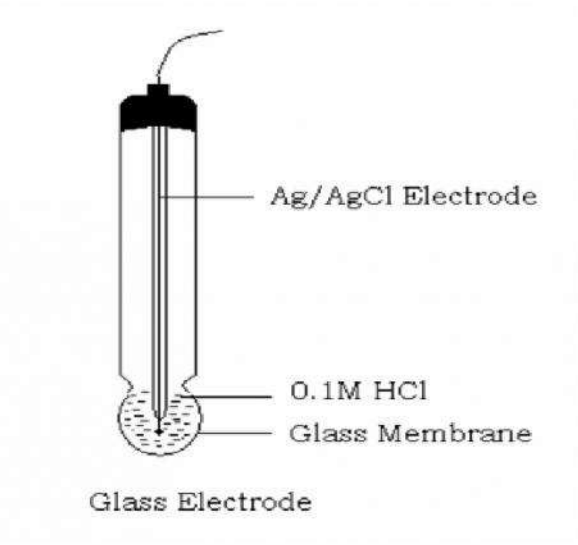
$$E_G = E_b + E_{ref} + E_{asy}$$

$$E_G = -0.0591 pH + K + E_{ref} + E_{asy} \qquad \text{Since } E^o_G = K + E_{ref} + E_{asy}$$

$$EG = E^o_G - 0.0591 pH$$

Note: $E_b=0$, when $C_1=C_2$. But in practice it is observed that small potential developed when $C_1=C_2$ is known as asymmetric potential (E_{asy}). This is due to the difference in the radius of curvature of glass membrane results on the two surfaces.

Construction of glass electrode:



Glass Electrode

Glass electrode is a pH sensitive electrode widely used for pH determinations. It is consisting of a long glass tube at the bottom of which a thin and delicate glass bulb, which made up of special type of glass (12 % Ba_2O, 6% of Cao, 72% of SiO_2) with low melting point and high electrical conductance is used. The glass bulb is filled with 0.1.M HCl and Ag – AgCl is used as a internal reference electrode. A platinum wire is used for electrical constant. The glass electrode can be represented

Glass electrode representation: Ag(s)/AgCl(s) /0.1M HCl /glass membrane.

Advantages:

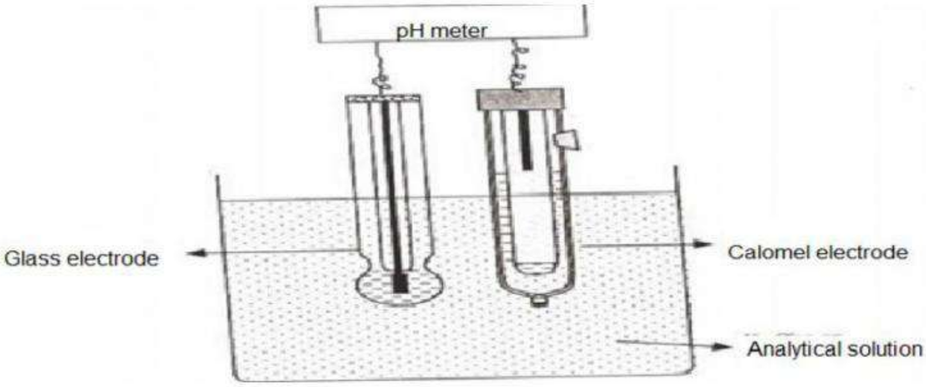
1. It can be employed in the presence of strong oxidizing agent or reducing agent or organic substances.
2. It is not poisoned easily.
3. Equilibrium reached quickly.
4. Requires small amount of solutions.
5. Simple to operate.

6. It is used in chemical, industrial, agricultural and biological laboratories for the measurement of pH.
7. It used to colored, turbid and colloidal solutions.
8. It can be used in solution with pH values ranging from 0 to 9.
9. It provides accurate results.

Limitations:

1. Glass electrode cannot be used in presence of fluoride ions.
2. It cannot be employed in pure ethyl alcohol and acetic acid.
3. Glass electrode cannot be used when P^H of the solution is above 9, as it introduces alkaline error.

Determination of pH of a solution using a glass electrode



The cell consists of glass electrode as an indicator electrode and calomel electrode as reference electrode, are immersed in a solution whose pH is to be determined. The cell The two electrodes are connected to potentiometer or pH meter. The combined electrodes can be represented as.

Cell representation

$Hg/Hg_2Cl_2,KCl_{sat/}$ //Analytical solution/Glass/(0.1M)HCl/AgCl/Ag

The pH value of the experimental solution can be calculated by using the following

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

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

$$E_{cell} =[E^{\circ}_G-0.0591pH]- E_{calomel}$$

$$-0.0591pH= E_{cell}- E^{\circ}_G- E_{calomel}$$

$$0.0591pH= E^{\circ}_G -E_{cell}- E_{calomel}$$

$$pH= \frac{E^{\circ}G - Ecell - Ecalomel}{0.0591}$$

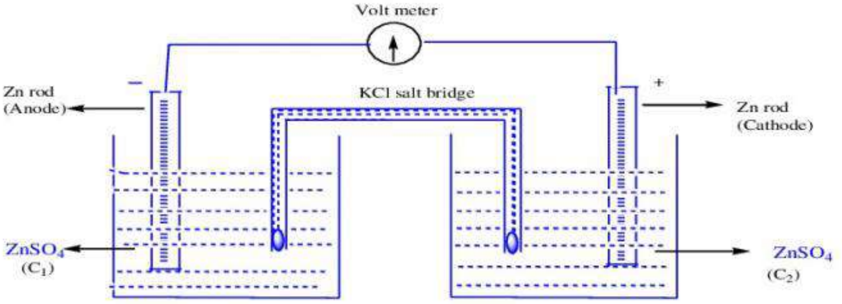
Or

$$pH= \frac{E^{\circ}G - Ecell - 0.2422}{0.0591}$$

Electrolyte Concentration Cells:

The two electrodes made up of the same element (metal) in contact with a same electrolytic solution of different concentrations are known as electrolytic concentration cells.

For example Zinc concentration cell consists of two half-cells, in which both electrodes are made up of Zinc metal dipped $ZnSO_4$ solution of different concentrations.



Zinc concentration cell consists of two half-cells, in which both electrodes are made up of Zinc metal dipped $ZnSO_4$ solution of different concentrations as shown in the figure. The half cell (electrode) having a lower concentration of Zn^{2+} ions has the tendency to get involved in an oxidation reaction and the electrode (half cell) possessing a higher concentration of Zn^{2+} ions has the tendency to get involved in the reduction reaction.

Concentration cell can be represented as

$$Zn_{(s)} / ZnSO_4 (C_1)//ZnSO_4 (C_2)/Zn \quad C_2>C_1$$

Electrode reactions:

At anode $Zn_{(S)} \longrightarrow Zn^{2+}(C_1) + 2e^-$ (Oxidation)

At cathode $Zn^{2+}(C_2)+2e^- \longrightarrow Zn_{(S)}$ (Reduction)

Net cell reaction $Zn^{2+}(C_2) \longrightarrow Zn^{2+}(C_1)$

EMF of cell reaction

$$E_{cell}=E^o_{Zn^{2+}/Zn}+\frac{0.0591}{n}\log_{10} C_2 - E^o_{Zn^{2+}/Zn}+\frac{0.0591}{n}\log_{10} C_1$$

Since $E^o_{cell}=E^o_{Zn^{2+}/Zn} - E^o_{Zn^{2+}/Zn} = 0$

$$E_{cell}=\frac{0.0591}{n}[\log_{10} C_2 - \log_{10} C_1]$$

$$E_{cell}=\frac{0.0591}{n}\log_{10}\frac{C_2}{C_1} \quad \text{Or} \quad E_{cell}=\frac{2.303RT}{nF}\log_{10}\frac{C_2}{C_1}$$

The following conclusions can be made by the above equation:

i) If $C_2=C_1$ $\log_{10}\frac{C_2}{C_1} = 0$ ∴ $E_{cell}=0$ ∴ Cell is in equilibrium

ii) If $C_2 > C_1$ $\log_{10}\frac{C_2}{C_1} = +ve$ ∴ $E_{cell}= +Ve$ ∴ Cell reaction is spontaneous

iii) If $C_2 < C_1$ $\log_{10}\frac{C_2}{C_1} = -ve$ ∴ $E_{cell}= -Ve$ ∴ Cell reaction is non spontaneous

Module-1

Chapter-2 BATTERY TECHNOLOGY

BATTERY: A Battery is an electrochemical cell or device with three basic components an anode (Negative electrode) a cathode (Positive electrode) and an electrolyte which converts chemical energy into electrical energy.

Uses: Batteries are used in calculators, watches and pacemakers for heart-beat hearing aids, computers, car engines, standby power supplies, emergency lighting in hospitals, electroplating industrial tractions and military and space applications.

Note: The size of the batteries ranges from a fraction of a cubic centimeter to several cubic decimeters.

Components of battery: The cell consists of four major components.

1. **The anode (Negative electrode):** The electrode at which oxidation of electrons takes place is known as anode. It gives electrons to the external circuit.

   A good anodic material, should possess the following characteristics such as

i) Easily oxidizable ii) Good conductivity iii) Easy to fabricate iv) Low cost v) Good stability vi) High columbic output Ex: Zn, Li etc.

2. **The cathode (Positive electrode):** The electrode at which reduction of electrons takes place is known as the cathode. It accepts electrons to the external circuit.

   A good cathodic material, should possess the following characteristics such as

i) High reduction potential and stability ii) Resistant electrolyte Ex: Cu, Ag, etc.

3. **The electrolyte (Ionic conductor):** Electrolyte is a material with high ionic conductivity between the anode and cathode of the cell. It is commonly a solution of acids, alkalis or salt of high ionic conductivity. Solid electrolyte with high ionic conductivity can also be used as an electrolyte. A good electrolyte should possess the following characteristics such as i) The electrolyte must have good ionic conductivity but not electrical conductivity.

   ii) The electrolyte should non reactive with the electrode materials and safe to handle.

4. **Separator:** The material that electronically isolates anode and cathode in a battery to prevent internal short circuiting**.** Ex: Cellulose vinyl polymer, Teflon, cellophane and nafion membranes are used for this purpose.

   A good separator should possess the following characteristics such as it should be permeable to the passage to the ions from anode to cathode and vice-versa.

Commercial importance of cells: A useful commercial cell should meet the following basic requirements.

1. Portability.
2. Should be compact and lightweight.
3. Should provide economically priced, continuous electric supply.
4. Should be capable of recharging.
5. Should have a long shelf life.

Battery characteristics: The performance characteristics of commercial batteries are given below.

1.Cell potential or Voltage: It is measure of the force or push given by the electrons in an electrical circuit. It may be also defined as measure of electrode potential.

According to Nernst equation at 298K

$$E_{Cell}=E^{o}_{cell} - \frac{2.303RT}{nF} \log Q \qquad \text{Where} \quad Q= \frac{[\text{Product}]}{[\text{Reactant}]}$$

The EMF of the battery depends on the following factors

i. The EMF of a battery largely depends on $E^{\circ}_{CELL} = E^{\circ}_{Cathode} - E^{\circ}_{Anode}$ the difference in the standard electrode potentials of the two electrodes. As E°_{CELL} increase the EMF also increases for a given value of Q at constant temperature.

ii. Increase in the value of Q marginally decreases the EMF. This is because Q decreases when [products] increases i.e when current is drawn from the cell.

iii. As the temperature increasing the voltage of the cell decreases.

iv. High potential is obtained by using high conductivity of the electrolyte.

2. Capacity: The capacity of a battery is the quantity of electrical charge in ampere hours (Ah) that can be withdrawn (obtained) from a fully charged battery or cell under specified conditions during discharge. It is. The capacity of a battery depends on

i) Size of a battery

ii) Discharge conditions

The capacity of a battery is to be determined by

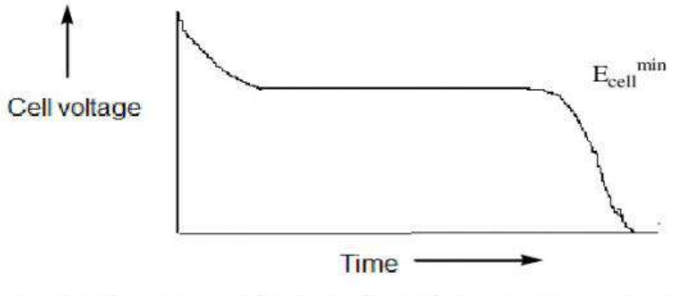
According to Faraday law $\quad \text{Capacity(C)} = \frac{WnF}{M}$

Where,

C -Capacity of battery (in Ah), W - Weight of the active material, n - number of electrons.

F - Faradays constant, M -Molar mass

It is measured by finding, for a fixed current discharge, the time t taken for the battery to reach a minimum voltage, when the cell is said to be dead. A plot of voltage against time at a fixed current discharge is shown in the fig. The variation of the battery voltage during discharge is shown by the flatness of the curve. The length of the flat portion of the curve is a measure of the capacity of the battery. Flatter and longer the curve better is the capacity.



3. Current: An electric current, which is the flow of charge, occurs when there is a potential difference between the electrodes. For a current to flow it require complete circuit.

Current (I) is measured in ampere (A) and it is the amount of charge flowing in coulomb per second.

$$I = \frac{q}{t} \qquad \text{with units } A=\frac{C}{Sec}$$

4. Electricity storage density: Electricity storage density is a measure of the charge unit weight stored in the battery. The weight includes the weight of the battery. The weight includes the weight of electrolyte, electrodes considered. High storage density indicates good battery.

In addition to the above requirement, the batteries should have long shelf life, tolerance at different conditions such as temperature, vibration and shock.

5. Energy efficiency: It is defined as the ratio of useful energy output to the total energy input. The battery should have high-energy efficiency. The percent energy efficiency for the battery is given by.

$$\% \text{ of energy efficiency} = \frac{\text{Energy released on discharge}}{\text{Energy required for charge}} \text{ X } 100$$

6. Cycle Life: Primary batteries are designed for single discharge and secondary batteries can be chargeable again and again.

The number of charge and discharge cycles that are possible in secondary batteries, before failure occurs is called cycle life.

The cycle life of batteries must be high. The factors which decrease the cycle life are:

i. For a secondary battery it is essential to charge and discharge cycle to reform the active material in a suitable state for further discharge. The cycle life depends upon how effectively this is achieved.

ii. Also depends upon the depth of each discharge attempts to discharge totally damaging to the electrodes.

7. Shelf life: The duration of storage under specified conditions at the end of which a cell or a battery retains its ability to a specified performance is called shelf life. A good battery should have more shelf life. It depends on self-discharge reactions and corrosion.

Classification of batteries.

The batteries are classified as

1.Primary battery or primary cells (Non rechargeable battery): A primary cell is the one in which electrical energy can be obtained at the expense of chemical energy only as long as the active materials are still present . i.e cells in which the cell reaction is not completely reversible. These are not rechargeable and once discharged have no further electrical use hence they are discarded.

Ex; Dry cell or Zn-MnO_2 Cell, Li-MnO_2 cell.

2. Secondary battery (Rechargeable battery): The cell reaction occurring in secondary cells is reversible and these are rechargeable. They are also referred to as storage cells or reversible batteries. After discharge, secondary batteries can be electrically recharged to their original condition by supplying current in the opposite direction to the discharge current.

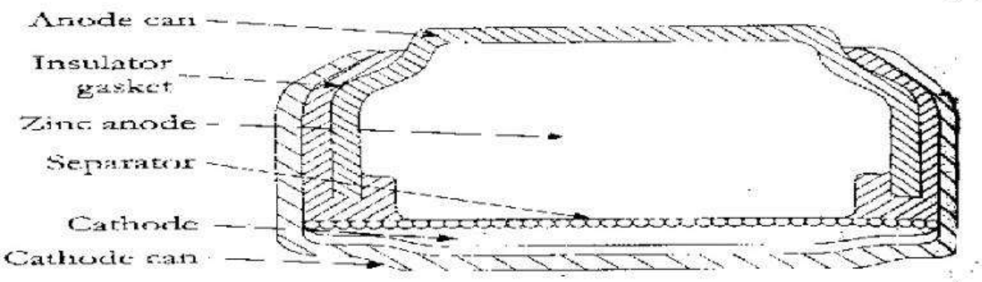
Ex. Lead-Acid storage cell, Ni-Cd cell and Ni-MH cell.

3. Reserve Batteries: In these batteries, a key component is separated from the rest of the battery prior to activation. Usually the electrolyte is the component that is isolated. In this condition, chemical deterioration or self- discharge is essentially eliminated and the battery is capable of long- term storage. These batteries are primarily used to deliver high power for short time after activation. Hence these batteries use in missiles and space applications.

- Batteries can be stored for a longer period.
- To prevent corrosion at contact points during storage.
- Self-discharging reactions during storage can be eliminated or avoided.
- They can be used whenever they are required.

  Egs: Magnesium water activated batteries (Mg-AgCl, Mg-CuCl), Zn–Ag_2O batteries etc.

Zinc -air battery



A schematic representation of a typical zinc air cell is **Zn|KOH (5M)|air,C**

- It is a metal –air battery, which use oxygen directly from the atmosphere to produce electrochemical energy.
- The zinc air cell consists of an anode, made up of loose granulated powder of zinc mixed with electrolyte 5M KOH and a gelling agent to immobilize the composite and to ensure adequate electrolyte contact with zinc granules.
- The air diffuses into the cell, as it is needed. The air cathode acts only as a reaction site and is not consumed. The catalyst layer contains porous carbon blended with oxides of manganese to form a conducting medium.
- The material is laminated with Teflon layer on one side and porous separating membrane is placed directly over air holes to ensure uniform distribution across the electrode and also avoids leakage.
- An air access hole on the positive terminal of a zinc air cell provides a path for oxygen to enter the cell and diffuse to the cathode catalyst site.
- The anode and cathode compartments are separated by a separator and both are encased in plastic or ebonite insulator.
- **Electrode reactions:**

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

$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2$

$Zn(OH)_2 \longrightarrow ZnO + H_2O$

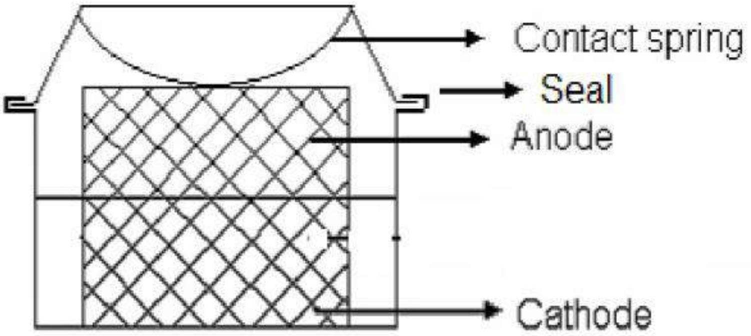
Overall reaction: $Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$

At the cathode: $\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

Cell reaction: $Zn + \frac{1}{2} O_2 \longrightarrow ZnO$

- The cell produces an open circuit potential of 1.45V.
- **ADVANTAGES:** 1.High energy density and capacity.
  2. Flat discharge voltage.
  3. Long shelf life.
  4. No ecological problems.
  5. Low cost.
  6. Operating temperature is 10 to 55°C.
- **DISADVANTAGES:** 1.Cell performance depends on the relative humidity.
  2. Pure oxygen is required. In the presence of CO_2 clogs the pores by forming carbonates.
  3. Short activated life.
- **Uses:** Uses as power source for hearing aids, electronics pagers, telemetry (voice transmitters) portable battery charges, finds applications in railways and military radio receivers.

Nickel-Metal hydride battery



A schematic representation of a typical cell is **MH|KOH (30%)|$Ni(OH)_2$|NiO(OH)**

- Nickel-Metal hydride battery is rechargeable battery.
- Nickel-Metal hydride battery is made up of anode containing metal hydride such as ZrH_2, VH_2 and TiH_2 with hydrogen storage metal alloy such as La Ni_5 or TiNi. The anode is highly porous structure using a perforated nickel foil or grid onto which the plastic bonded active hydrogen storage alloy is coated.
- The cathode containing highly porous nickel oxyhydroxide NiO(OH) compound is impregnated or pasted and converted into the active material by deposition.
- Both the compartments are separated by polypropylene as an insulator between two electrodes and medium for absorbing the electrolyte.
- An aqueous solution of 30% potassium hydroxide (KOH) as an electrolyte.
- Electrode reactions that occurs during discharge and charging are,

$$\text{At the anode: } MH + OH^- \longrightarrow M + H_2O + e^-$$

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

$$\text{Overall cell reactions} \quad MH + NiOOH \underset{\text{Charge}}{\overset{\text{Disharge}}{\rightleftharpoons}} M + Ni(OH)_2$$

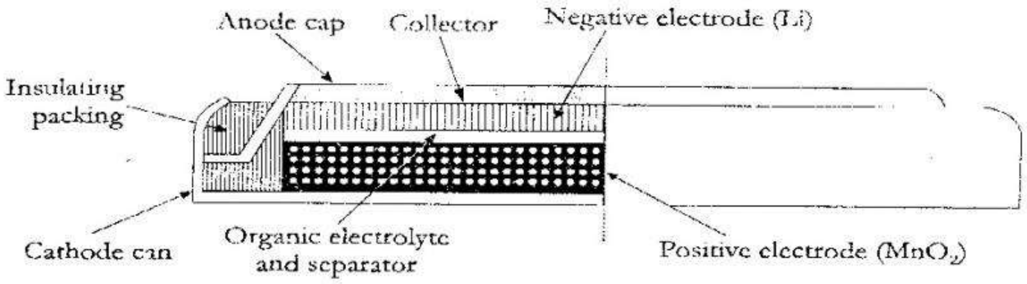
- Open circuit voltage of the cell ranges from-1.25 to 1.35 V
- **ADVANTAGES:** i) High capacity than Ni-Cd cell
  ii) Rapid recharge capability
  iii) Long Shelf and cycle life
  iv) Minimum environmental pollution.
- **DISADVANTAGES**: i) Poor performance as compared to Ni-Cd battery.
  ii) High cost
  iii) Poor charge retention.
- **Uses**: Used in computers, cellular phones and other portable and consumer electronic devices.

LITHIUM CELLS: Lithium metal is attractive as a battery anode material because of its lightweight, high voltage, high electrical equivalence and good conductivity. Because of these outstanding features, the use of lithium has predominated in the development of high performance primary and secondary batteries.

ADVANTAGES OF LITHIUM CELLS:

1. High voltage.
2. High energy density.
3. Operation over a wide range of temperature. Many of the lithium cells will perform over a temperature range from about 70-40°C.
4. Good power density.
5. Flat discharge characteristics.
6. Superior shelf life.

Lithium -Manganese dioxide cell:



- A schematic representation of Li-MnO_2 cell is- **Li, Non aq LiX| MnO_2**
- It is primary type of battery and available in many configuration like coil, bobbin, cylindrical, prismatic etc.
- Figure shows the illustration of a typical bobbin cell.
- Lithium manganese dioxide cell consisting of anode can containing lithium and the cathode can consisting of specially heat-treated manganese dioxide (MnO_2).
- Both anode and cathode are seperated by a separator made up of polypropylene impregnated with the electrolyte.(metal salt such as LiCl, LiBr, $LiAlCl_4$ which are mixed in a organic solvent such as 1,2 dimethoxy ethane, and propylene carbonate.)
- The cell delivers an emf of 3V.
- **The cell reactions.**

$$\text{Anode:}\quad Li \longrightarrow Li^+ + e^-$$

$$\text{Cathode:}\quad MnO_2 + Li+ + e^- \longrightarrow LiMnO_2$$

$$\text{The overall reaction is}\quad Li + MnO_2 \longrightarrow LiMnO_2$$

- Manganese dioxide is reduced from the tetravalent to the trivalent state by lithium. $LiMnO_2$ signifies that the Li^+ ion enters into the MnO_2 crystal lattice. The theoretical voltage of the total cell reaction is about 3.5V.
- **Advantages:** i) Highest energy density & Power density
  ii) Wider operating temperature use
  iii) Lowest self discharge
  iv) Good discharge performance.
- **Disadvantages:** Aqueous electrolyte cannot be used because lithium is highly reactive with water.
- **Applications:** Safety and security devices, watches, calculators, cameras, walkie-talkies, video games, many consumer electronic devices.

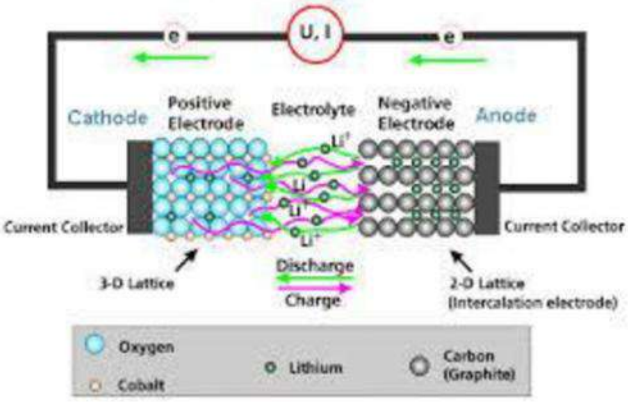
Lithium-ion battery (Li-ion Battery) Rechargeable batteries

Applications:

Li-ion batteries are now used in very high volumes in a number of relatively new applications, such as in mobile phones, laptops, cameras and many other consumer products. The typical Li-ion cells use carbon as the anode and $LiCoO_2$, $LiNiO_2$ or $LiMn_2O_4$ as the cathode.

Chemistry and construction

In order to overcome the problems associated with the high reactivity of lithium, the anode material is not purely the metal, it is a non-metallic compound, e.g. carbon, which can store and exchange lithium ions. A lithium ion-accepting material, for example Mn_2O_4, is then used as the cathode material, and lithium ions are exchanged back and forth between the two during discharging and charging. These are called intercalation (Insertion) electrodes. This type of battery is known as a "rocking chair battery" as the ions simply "rock" back and forth between the two electrodes.



Cathode materials

The most common compounds used for cathode materials are $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$. Of these, $LiCoO_2$ has the best performance but is very high in cost, is toxic and has limited lithium content range over which it is stable. $LiNiO_2$ is more stable, however the nickel ions can disorder. $LiMn_2O_4$ is generally the best value for money, and is also better for the environment.

Anode material

Graphite is by far the most common material for the negative electrode, but some other technologies are under development. The anode material is carbon (Graphite) based, usually with composition $Li_{0.5}C_6$. This lithium content is lower than would be ideal, however higher capacity carbons pose safety issues.

Electrolyte

Since lithium reacts violently with water, and the cell voltage is so high that water would decompose, a non-aqueous electrolyte must be used. A typical electrolyte is $LiPF_6$ dissolved in an ethylene carbonate and dimethyl carbonate mixture.

The following reactions take place upon discharge and charge:

At the anode: $Li_xC_6 \longrightarrow xLi^+ + 6C + xe-$

At the anode: $xLi^+ + LiMn_2O_4 + x\,e^- \longrightarrow Li_xMn_2O_4$

Net cell reaction: $Li_xC_6 + LiMn_2O_4 \underset{\text{charging}}{\overset{\text{disharging}}{\rightleftharpoons}} Li_xMn_2O_4 + 6C$

Or

$LiMO_2$ represents $LiCoO_2$ or $LiNiO_2$

At anode $LiC \longrightarrow xLi^+ + xe^-$

At cathode $xLi^+ + LiMO_2 + xe^- \longrightarrow Li_xMO_2$

Net cell reaction: $LiC + LiMO_2 \underset{\text{charging}}{\overset{\text{disharging}}{\rightleftharpoons}} Li_xMO_2 + C$

Advantages: The main advantage of lithium-ion batteries is their high energy density. They have a long cycle life, the cycle life of Li-ion batteries are between 500 to 1000 cycles and do not self-discharge rate. Li-ion batteries do not contain toxic heavy metals.

Disadvantages: The main disadvantage of Li-ion batteries is that they require careful attention to safety. Overcharging, overheating, or short-circuiting a charged Li-ion battery can result in fire or explosion. For a safe and long-lasting product, Li-ion-specific safety issues must be taken into account in product design.

Fuel cells

Fuel cell was discovered by a British judge, Sir William Grove. The research on fuel cell's got importance as we know conventional energy sources are depleting and also to reduce green house effect and global warming. The fuel cells play an important role in the next days as a source of energy in 21st century.

Fuel cells are like galvanic cell in which the chemical energy is converted to electrical energy by the continuous supply of chemical fuels and oxidant from the outside.

A fuel cell has two electrodes and an electrolyte. In fuel cells fuel and oxidizing agents are continuously supplied at respective electrodes, where electrochemical redox reactions are taking place to generate electrical energy. It is not recharging.

General representation of fuel cell

Fuel/ Electrode/ Electrolyte /Electrode /Oxidant

At anode, oxidation of fuel takes place

$$\text{Fuel} \longrightarrow \text{Oxidation products} + ne^-$$

At cathode, reduction of oxidant takes place

$$\text{Oxidant} + ne^- \longrightarrow \text{Reduction products}$$

Differences between a battery and fuel cell

Sl. No	Battery	Fuel cell
1.	Batteries store chemical energy	Fuel cells do not store chemical energy
2.	Reactants and products are stored in the cell	Reactants are supplied from the outside and products formed are removed simultaneously
3.	The electricity is generated till the active components present in the cell	The electricity is generated as long as fuel and oxidants are supplied from the outside.
4.	Harmful waste products are formed.	Harmful waste products are not formed.
5.	They can be recharged.	They cannot be recharged.

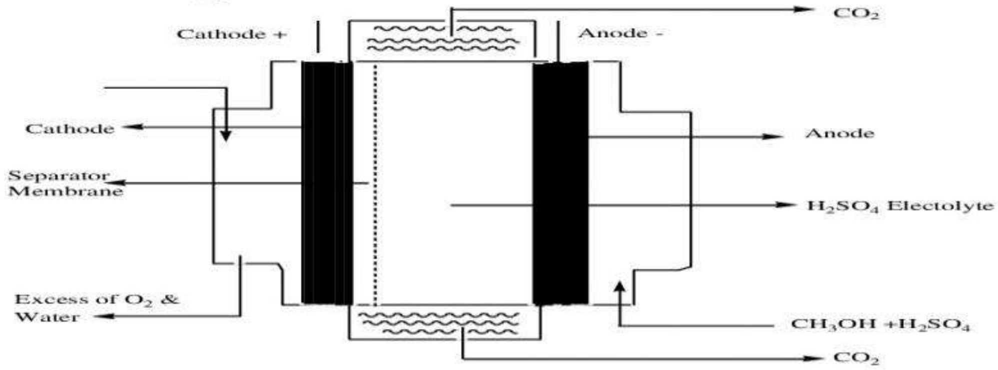
Advantages:

i. Power efficiency is high.
ii. Silent operation.
iii. Recharging is not required.
iv. No harmful waste products formed and products are eco-friendly.
v. Less attention is required.
vi. Produce direct current for long period at low cost.

Limitations:

The only disadvantage of the fuel cells associated with the cost. The two basic reasons are
i) High costs compared to other energy systems technology
ii) Fuel cells are slightly bigger compared with batteries.
iii) The technology is not yet developed.

Methanol- Oxygen Fuel cell



Construction: This fuel cell is operated below 100ºC. Methanol is one of the most organic fuel containing carbon and dilute H_2SO_4 is used as the electrolyte. It consists of anodic and cathodic compartments containing platinum electrodes. Methanol containing H_2SO_4 is passed through anodic compartment and oxygen is passed through cathodic compartment. Electrolyte consisting a membrane, which prevents diffusion of methanol into the cathode. The emf of the cell is 1.2V at 25ºC.

Electrode reactions:

$$\text{At anode : } CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$$

$$\text{At cathode: } \frac{3}{2} O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$$

$$\text{Overall cell reaction } \quad CH_3OH + \frac{3}{2} O_2 \longrightarrow CO_2 + 2H_2O$$

Uses: Methanol- Oxygen Fuel cell is used in military applications and in large scale power production.

Fuel cells

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2. Silent operation.
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5. Less attention is required.
6. Produce direct current for long period at low cost.

Solid Oxide Fuel Cell (SOFC)

Fuel: Hydrogen
Electrolyte: Ceramic compounds of metal oxides Ex: Calcium oxide or Zirconium oxide
Electrodes: Carbon or metal based.
Catalyst: Ceramic
operating temperature: 1000°C

Fuel cell reaction

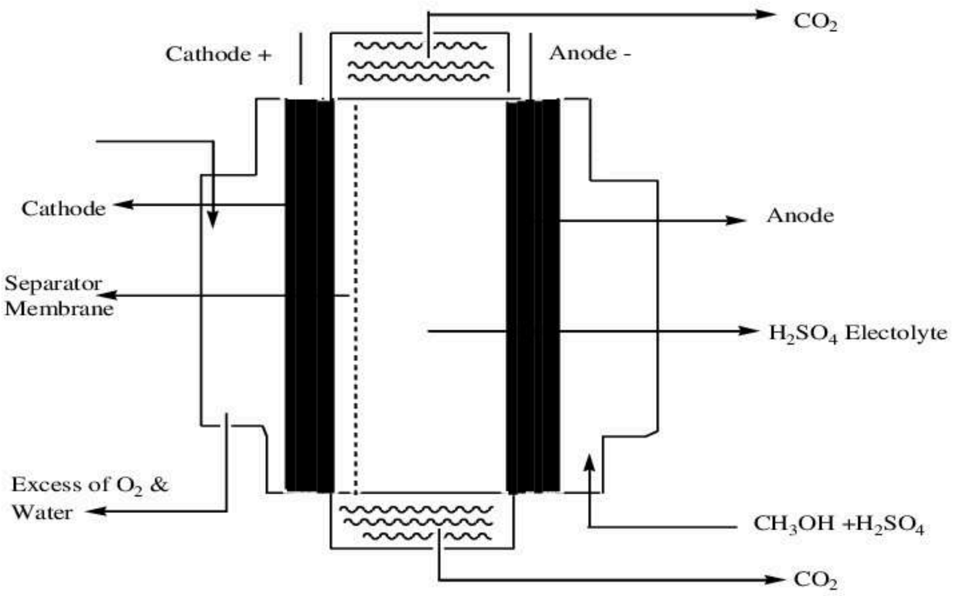
At anode $H_2 + O^{2-} \longrightarrow H_2O + 2e^-$

At cathode $\frac{1}{2} O_2 + 2e^- \longrightarrow O^{2-}$

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

Fuel cell efficiency:50- 60%
Uses: SOFC's are considered for large power plants and for industrial applications because of resistance nature of electrolyte to poisoning.

Methanol- Oxygen Fuel cell



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Uses: Methanol- Oxygen Fuel cell is used in military applications and in large scale power production.

Corrosion [illegible]

The Word corrosion is derived from the Latin corrode meaning to gnaw to piece. Several metal underge corrosion when exposed to air, water or other Substance. A typical example of corrosion is rusting of iron. Rusting weakens brid ship's hulls, iron railings and car bodies.

Def: corrosion can be defined as the destruction of metal by surrounding ~~en~~ environment through chemical or electroc -mical changes.

Why do metal to corrode?

Naturally ocuring compounds of metals are thermody namically stable, while the extracted metal from these ore have high energy state because of taking up of large amounts of. energy during its metallurgy. the metal thus obtained. when exposed to the natural environment will have a. tendency to go their stable lower energy state when ev an opportunity.

Types of corrosion:

The process of corrosion of metal depend on the environm -t to which the metal are exposed. The corrosion of metal can be either 1) dry corrosion ii) Wet corrosion.

Dry corrosion or Chemical corrosion or direct chemica attack.

The direct chemical action of atmospheric such as oxygen, halogens, sulphur dioxides and hydrogen sulphides with metals resulting in to formation of compounds such as oxides, halides, sulphates and sulphides is refered to as chemical or dry corrosion. It is mainly of three following.

1) corrosion by oxygen [oxidation corrosion].

2) Corrosion by other gas.

3) Liquide metal corrosion.

i) corrosion by oxygen [oxidation corrosion]

Atmospheric oxygen reacts with metal in the absence of moisture forming their respective oxides.

Alkali and alkaline earth metal are more prone and rapidly oxidised at low temperatures, ~~white like~~ where as all other metals [except Ag, Au and Pt] are oxidised at high temperature.

Ex: $Mg \rightarrow Mg^{+2} + 2e^{\ominus}$

$\frac{1}{2} O_2 + 2e^{\ominus} \rightarrow O^{-2}$

$Mg + \frac{1}{2} O_2 \rightarrow MgO$

It is observed that thin film metal oxide layers are formed on the surface of the metals. The nature of the tarnished layer or the thin film layer formed on the metal surfac decide further action with environment.

i) The stable oxide film formed on the surface metal protective and shields the metal from further corrosion. Since oxide film is rigidly adhered to the surface and is impervious in nature.

ii) The unstable oxide film formed decomposes back into metal and oxygen. for nobel metal like pt, Au etc corrosi is not possible because the oxide layer formed is very unst-ble and decompose back to metal and oxygen.

iii) When oxide film is porous in nature, the metal is attacke by oxygen through the pores and cracks the corrosion continues till the entire metal into oxide.

2) Corrosion by other gas:

In the absence of moisture of atmosphere, a few gases like SO_2, Cl_2, F_2 attack the metal by dry corrosion.

Ex: Dry Cl_2 attacks silver metals and form AgCl

$2Ag + Cl_2 \rightarrow 2AgCl.$

Liquid metal corrosion

This type of corrosion occurs when a molten liquide is continuously passed on solid metal surface or an alloy. This behaviour may be due to the fallowing

a) dissolution of molten liquide. or

b) penetration of the molten liquide into solid metal phase. Both these modes of corrosion cause weaking of the solid metal.

Ex: Na metal ~~Co [colant]~~ [coolant] leads to corrosion to Cd in nuclear reactor.

Electrochemical or Wet corrosion:

Corrosion is defined as the destruction of a metal or its alloy and consequent loss of metal, caused due to ~~dire~~ electrochemical reactions with environment.

This corrosion is explained by the electrochemical theory.

Electrochemical theory:

According to ~~electrical~~ electrochemical theory, corros. of metals occurs due to the fallowing changes, when they are exposed to environment.

1) A large number of minute galvanic cell are formed which act as anodic and cathodic area.

2) At anodic ~~re~~ region metal undergo oxidation and electrons are liberated which migrates towards cathodic region.

3) Oxygen of the atmosphere undergoes reduction at cathodic area in the presence of moisture forming hydroxyl ion at cathodic area.

Anodic reaction: At anode metal undergoes oxidation

$$M \longrightarrow M^{n+} + ne^{\ominus}.$$

cathode reaction: The electron released at anode migrate to cathodic area and fallowing reactions take place.

a) In acidic medium : ~~on~~ In acidic medium and in absence of oxygen, hydrogen ions ~~to~~ reduced to hydrogen gas.

$$2H^+ + 2e^{\ominus} \longrightarrow H_2.$$

b) In alkaline and in the absence of O_2. If the solution is alkaline and in the absence of oxygen cathodic reaction is.

$$2H_2O + 2e^{\ominus} \longrightarrow 2OH^{\ominus} + H_2.$$

c) In neutral and aerated mediums when the solution is neutral and aerated hydroxyl ions are formed.

$$2H_2O + O_2 + 4e^{\ominus} \longrightarrow 4OH^{\ominus}.$$

Metal ions are formed migrate ~~two~~ towards to Cathodic parts combines with negative ions and forms the product.

Rusting of Iron :

Def When Iron is exposed to moisture air reddish brown Coating of hydrated ferric oxide is formed. is called rust The phenomenon is known as rusting.

$$Fe \xrightarrow{moisture} Fe_2O_3 \cdot 3H_2O \text{ [rust]}$$

Resuting of Iron explained by electro chemical theory of corrosion.

a) Formation of galvanic cells anodic and cathodic areas are formed resulting in minute galvanic cells.

b) Anodic reaction: At the anodic area, oxidation takes place resulting in the corrosion of iron.

$$Fe \longrightarrow Fe^{+2} + 2e^{\ominus}.$$

c) cathodic reactions The electrons flow from the anodic to cathodic area and cause reduction.

i) If the solution is aerated almost neutral, oxygen is reduced in presence of water to $OH^{\ominus}$ ions according to the equation

$$O_2 + 2H_2O + 4e^{\ominus} \longrightarrow 4OH^{\ominus}.$$

ii) If the solution is deaerated neutral, water is reduced to H_2 and $OH^{\ominus}$.

$$2H_2O \longrightarrow 2H^{\oplus} + 2OH^{\ominus}.$$

$$\underline{2H^{+} + 2e^{\ominus} \longrightarrow H_2}$$

$$2H_2O + 2e^{\ominus} \longrightarrow H_2 + 2OH^{\ominus}.$$

iii) If the solution is dearated and acidic, the $H^{\oplus}$ ions are reduced to H_2.

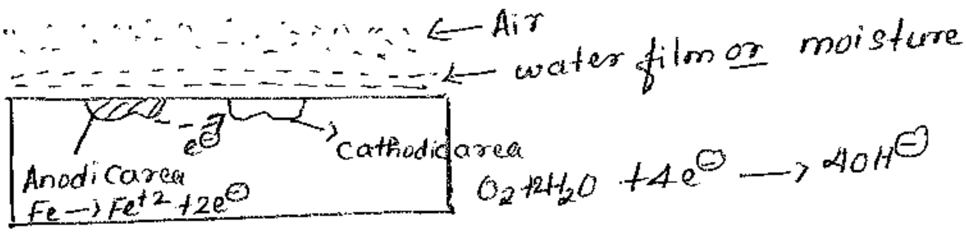
$$2H^{+} + 2e^{\ominus} \longrightarrow H_2.$$

The metal ions combine the $OH^{\ominus}$ ions to form the metal hydroxide and finaly hydrated ferric oxide.

~~At~~ $2Fe^{+2} + 4OH^{\ominus} \longrightarrow 2Fe(OH)_2$

$$2Fe(OH)_2 + O_2 + \underset{2}{(n-2)} H_2O \longrightarrow [Fe_2O_3 \cdot \underset{3}{n}H_2O]$$

oxide rust.



Note!

The cathodic and anodic process must occur at the same rate. If i_{corr} is the current [corrosion current] flowing, then the rate of corrosion of iron is given by the equation

$$\text{Rate of corrosion} = \frac{i_{corr}}{nF} \text{ grams per second.}$$

n = is the charge on the ion

F = is the faraday constant.

The total current due to cathodic reaction $[\Sigma i_c]$ must be equal, but opposite in sign, to the total current flowing out due to the anodic reaction $[-\Sigma i_a]$

$$i_{corr} = -\Sigma i_a = \Sigma i_c .$$

Differnce between Dry Corrosion and Wet corrosion

Dry Corrosion	Wet corrosion
1) It occurs in dry condition	1) It occurs in presence of moisture or electrolyte.
2) It involves the direct chemical attack on metal surface by environment	2) It involves the setting up of large number of galvanic cell
3) Explained by absorption mechanism.	3) Explained by mechanism of electrochemical reactions.
4) It occurs on both heterogeneous and homogeneous surface	4) It occurs only on heterogeneous metal surface
5) Corrosion is uniform	5) corrosion is not uniform
6) It is slow process	6) It is a fast process.
7) corrosion products accumalate at the place where corrosion occurs	7) corrosion take place at anode but products accumlate near to cathode.

Types of electrochemical corrosion:

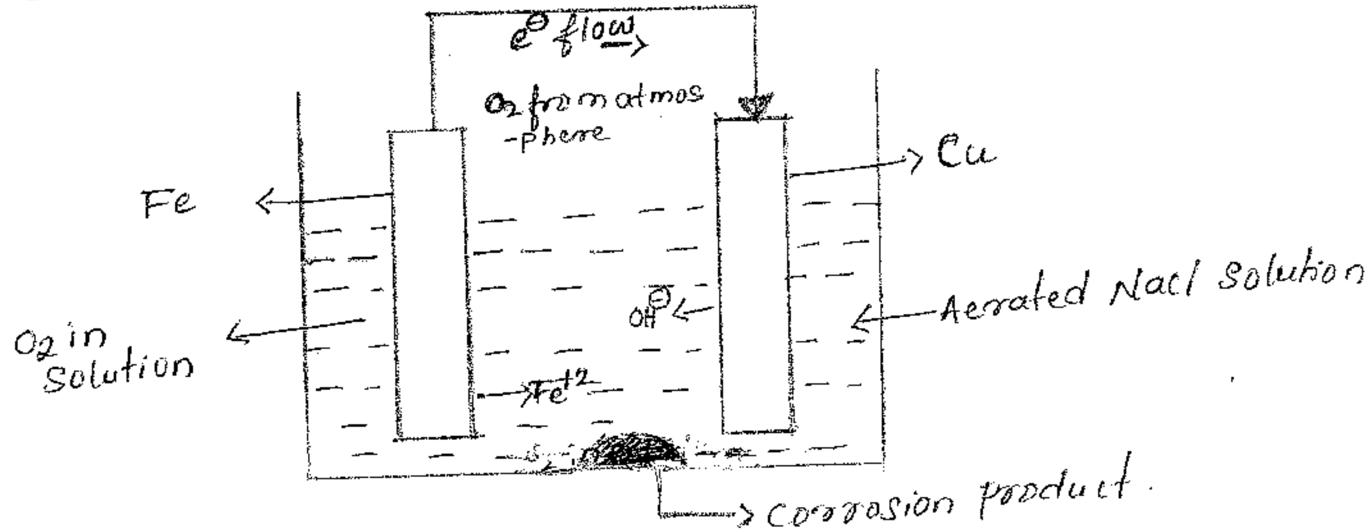
1) Differntial metal corrosion or Galavanic corrosion.

2) Differntial aeration corrosion or concentration cell corrosion.

Differential metal corrosion or Galavanic corrosion.

"When two different metal are in contact and jointly exposed to corrosive environment, the metal with lower reduction potential gets corroded. This type of corrosion is called galavanic corrosion"

In this type of corrosion the metal having less standard reduction potential value undergoes oxidation and liberates electrons, which migrates to the cathode. The other metal having higher standard reduction potential value act as cathode and reduction take place on its surface forming $OH^{\ominus}$ ions or any one kind of reduct reactions. The rate of corrosion depends on the potential differnce between the two metals. If differnce is more corrosion occurs faster and vice versa. Anodic metal underge corrosion and cathodic metal is protected.



$$2Fe^{+2} + 4OH^{\ominus} \longrightarrow 2Fe(OH)_2$$

$$2Fe(OH)_2 + O_2 + (n-2)H_2O \longrightarrow Fe_2O_3 \cdot nH_2O \text{ [rust]}$$

At anode: $M \longrightarrow M^{+} + 2e^{\ominus}$

At cathode: Depending on the nature of environment the cathodic reaction fallows.

1) $2H^{+} + 2e^{\ominus} \longrightarrow H_2$ [in acidic medium]
2) $H_2O + O_2 + 4e^{\ominus} \longrightarrow OH^{\ominus}$ [in neutral environment]

3) $2H_2O + 2e^{\ominus} \longrightarrow 2OH^{\ominus} + H_2$ [in alkaline environment]

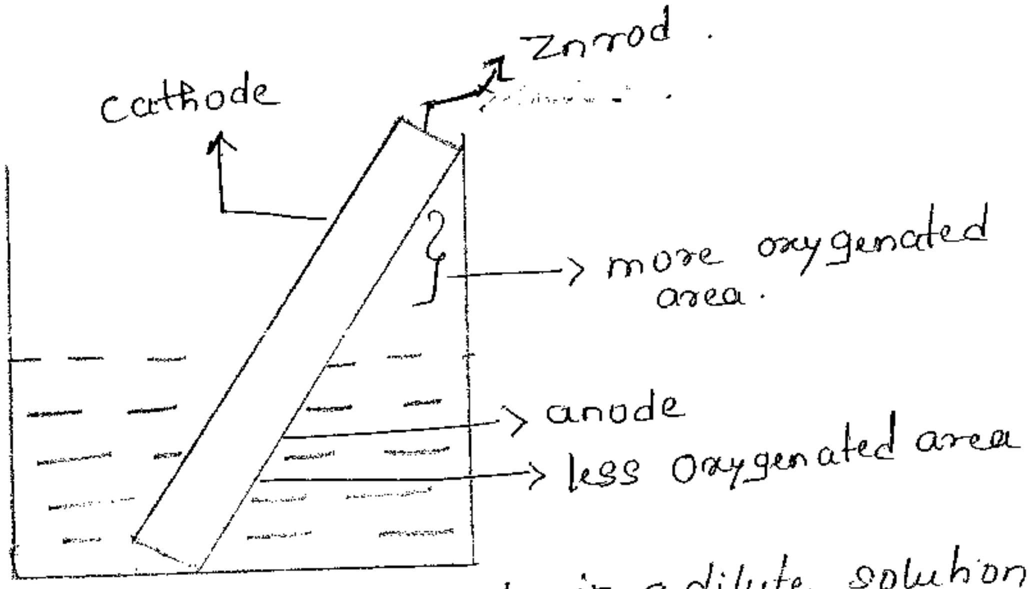
Example iron metal in contact with Copper. iron having lower reduction potential and its undergoes corrosion.

Differntial aeration corrosion:

"corrosion occurs due to differnce in the concentration of air over the surface of metal is called differntial ~~ae~~ aeration corrosion"

When metal surface is exposed to an electrolyte of varying concentration ~~of~~ or of varying aeration. It also occurs when one part of the metal is exposed to a different air concentration from the other part. It has been observed that poorly oxygenated parts become anodic and are corroded, where as more oxygenated portion act as cathode.

Ex:



When Zn rod partially immersed in a dilute solution of Nacl and solution is not aginated for long. The part of metal immersed in solution has less access to oxygen and act as anode, where ~~other~~ the part above and closely adjecent to the water line is more strongly aerated and act as cathode. So a differnce of potential is created which ~~becau~~ cause flow of electrons between two differntial aerated areas of the same metal

At anode $Zn \longrightarrow Zn^{+2} + 2e^{\ominus}$ (oxidation)

At cathode $\frac{1}{2} O_2 + H_2O + 2e^{\ominus} \longrightarrow 2OH^{\ominus}$ [reduction]

$Zn^{+2} + 2OH^{\ominus} \longrightarrow Zn(OH)_2$ [product]

Types of Differntial aeration corrosion.

Differntial aeration corrosion are classified fallowing types.

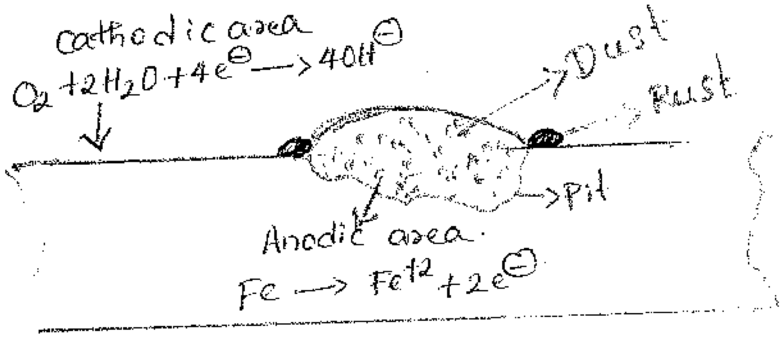
1) Pitting Corrosion:

Pitting corrosion occurs when small particle like dust, mud get deposited on metal surface. The portion of metal surface. The portion of metal covered by the dus or other particle is less aerated and act as anode. The other portion of the metal exposed to more oxygenat environment act as cathodic region. corrosion takes place at portion below dust and a small pit is formed. The rate of corrosion increases due to small anodic area.

At anode $Fe \longrightarrow Fe^{+2}$

At cathode $2Fe^{+2} + 4OH^{\ominus} \longrightarrow 2Fe(OH)_2$

$2Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 2[Fe_2O_3 \cdot 3H_2O]$ rust



$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 2[Fe_2O_3 \cdot 3H_2O]$

Water line corrosion:-

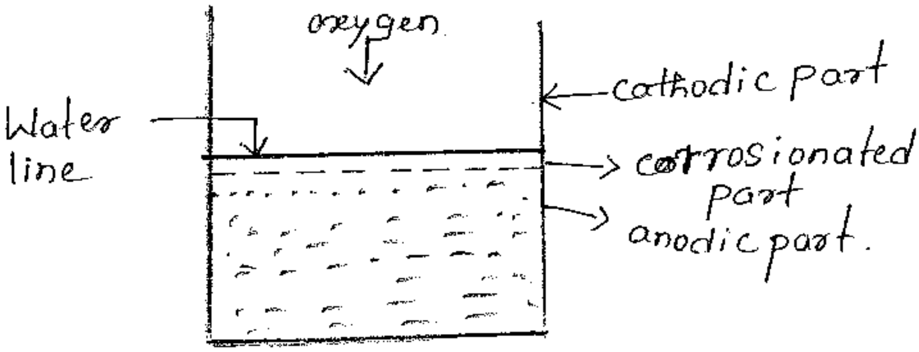
It is differntial aeration type of corrosion observed in water storage tanks, ships etc.

During Water line corrosion, the part of metal below the water line is exposed to less oxygen concentration. act as anode and undergoes corrosion than the other part which is more exposed to atmosphere oxygen act as ~~anode~~. cathode.

At anode: $Fe \longrightarrow Fe^{+2} + 2e^{\ominus}$

At cathode $2Fe^{+2} + 4OH^{\ominus} \longrightarrow 2Fe(OH)_2$

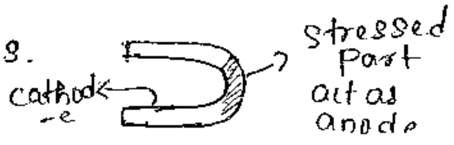
$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 2[Fe_2O_3 \cdot 3H_2O]$ rust.



Stress Corrosion:-

This type of corrosion is observed in fabricat article of certain alloys like Zinc, Nickel brass, Stainles steel, mild steel etc due to heavy working by rolling, drawing, bending, hammering. Stress caused by such action is the cause of increase of rate of corrosion when such article is exposed to corroding medium.

presence of stress gives rise to strain, which develops localized zones of higher electrode potential. The localized zone becomes very reactive chemically & may be attacked by even traces of corrosive environm -t results in the formation of cracks.



EX: Caustic embrittlement.

It is type of corrosion which is caused due to presen of alkaline water. In case of high pressure boilers, excess, Na_2CO_3 (Soda ash) added during lime soda process for removal of hardness causing impuritie hydrolysis to gives NaOH and makes water alkal

$$Na_2CO_3 + H_2O \longrightarrow NaOH + CO_2$$

This makes the boiler feed water slightly alkaline. When this dilute alkaline water ~~sto~~ solution flows in t the cracks in boiler walls, water evaporates and concentration of NaOH increases. The concentrated NaO dissolve iron as sodium ferroate. which decomposes as fallows.

$$3\,Na_2FeO_2 + 4H_2O \longrightarrow 6NaOH + Fe_3O_4 + H_2$$

$$6\,Na_2FeO_2 + 6H_2O + O_2 \longrightarrow 12NaOH + \underbrace{2Fe_3O_4}_{\text{Magnetite}}$$

Sodium hydroxide is regenerated and by formatio magnetite boiler walls become weak and This may leads to explosion of boiler.

Factors affecting the rate of corr.

1) Nature of Metal:

The rate and extent of corrosion of metals depends on the differnce of electrode potential or the position of the metal in the galvanic series. When dissimilar metal are in contact in a corrosive environment the more active metal [anodic metal] suffers corrosion with faster rate The rate of corrosion also depends upon the difference in their in position. Greater is difference, the faster is the corrosion of anodic metal or alloy.

For ex: Na corrodes faster than Mg, Zn corrodes faster than Fe.

2) Anodic to cathodic area:

The rate of corrosion is highly influenced by the relative area of anode and cathode. If metal has small anodic area and large cathodic area, the corrosion is mor intense and faster at anodic area. Because, the larger cathodic area has higher tendency to consume electro on the other hand if cathodic area is small the consu ption of electrons will be slower and the rate of corr -sion decrease.

Ex: In case of broken coating of tin on iron the Small exposed part of iron act as anode and rest of large tin coated area act as cathode. Because of small anodic to cathodic area the rate of corrosion is high.

3) pH of the medium:

Rate of corrosion increases with decrease in pH. If Ph 10, the rate of corrosion ceases due to the formation of protective coatings of hydrous oxides of the metal. If pH is between 3-10 presence of oxygen is essential for corrosi If PH<3 rate of corrosion is high even in the absence of air due to evolution of hydrogen at cathodic region.

In general, rule, acids are more corrosive than neutral or alkaline solution. However amphoteric metal such as Al, Zn and pb etc dissolve in alkaline solutions due to complexes ions formation.

4) **Conductance of medium:** If the medium conducting medium act as electrolyte and increase the rate of corrosion. This is because corrosion is an electrochemical phenomenon that involves the transfer of electron. The rate of Wet corrosion is far more greater than dry corrosion. Since wet corrosion is more conducting.

Ex: Fe undergoes corrosion faster in clay than in sandy soil's.

5) **Temperature;**

Corrosion increases with increase in temperature. because rate of chemical reaction increases with increase in temperature. Increase in temperature increases the conductance of medium and results in an increases in the diffusion rate. Hence corrosion ~~in~~ takes place faster.

~~To~~ When ~~acidi~~ medium is acidic, Increase in temperature, increases rate of hydrogen type of corrosion.

The rate of corrosion due to oxygen or oxidising agent decreases with increase in temperature due to decrease of solubility of gases like oxygen with temperature.

6) **Co. Nature of corrosion product:**

The corrosion product formed on the surface of metal largely decides the rate of further corrosion. If the corrosion product formed is insoluble, stable, uniform non-porous and non-volatile, it act as a protective. film and prevents further corrosion of metal becaus it act as barrier between the fresh metal surface and corrosive environment. on the other hand, if the product formed is soluble, unstable, non-uniform, porou and volatile then act as non-protective film. In suct the fresh metal is exposed for further attack

Ex: In case of metal like Fe, Zn and Mg the oxide film formed act as non-protective film and corrosion is continued till the metal is completely destroyed.

Corrosion control:

Corrosion is a surface phenomenon, the protection of the surface of the metal is the primary object to prevent corrosion.

The methods to control corrosion can be clasified as

1) Design and selection of material
2) Protective coating
3) Cathodic protection.

1) Design and selection of material:

Corrosion can be controlled by selecting suitable material which resist corrosion environment and designing them suitably during fabrication.

The fallowing point

1) ~~Galav~~ Galvanic corrosion can be controlled by reducing the use of two dissimilar metals. If their use is unavoidable the position of metal choosen should be as close as possible in the galavanic series.

X 2) Anode material must be larger as compared to cathode material i~~n ord~~er so that corrosion is minimised.

3) Stress corrosion can be controlled by annealing the equipments.

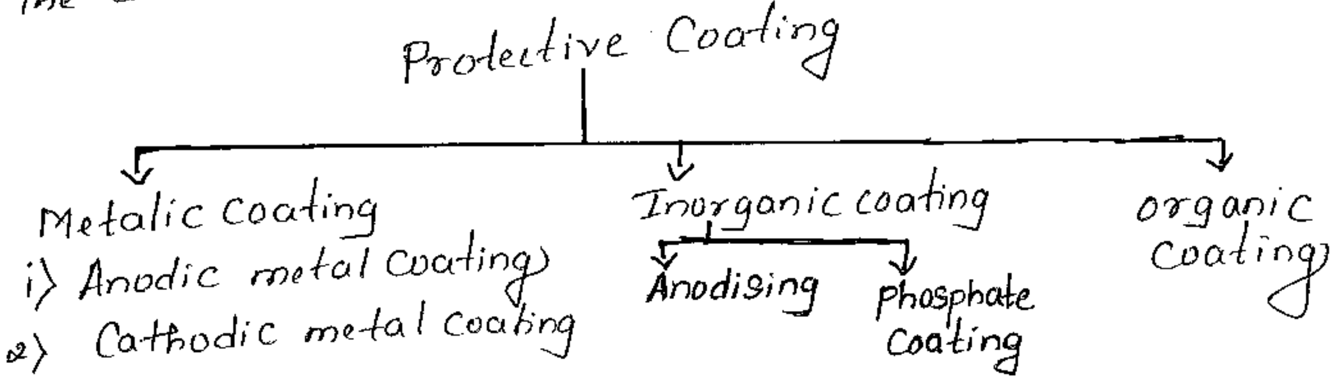
4) When metal are joined care should be taken not to leave gaps between them, where some liquids or air can be trapped resulting in differntial aeration corrosion

5) Proper design of the equipment will minimise the corrosion.

Protective coating:

Coating and linings play a significant role in corrosion prevention and are used extensively for this purpose.

A protective coating protects the metal from corrosion by acting as a barrier between the metal and the environment.



Metal coating :-

" The process of covering the base metal with a layer of protective metal is known as metal coating".

In this method more active or less active metal is coated over the substrate or base metal. Depending on the nature of metal coated over the substrate metal coating is devided in to two types.

1) Anodic metal coating.
2) Cathodic metal coating.

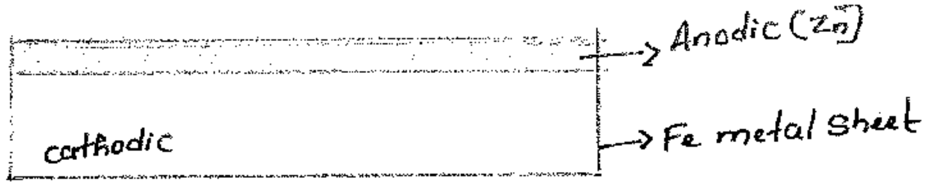
Anodic Metal Coating:

" It is the process of the metal coating which are anodic to the base metal is known as anodic metal coating"

In order to protect a metal from corrosion, any metal which is more reactive than the base metal is coated such as Zn, Mg, and Al.

Ex: Iron coated with more active metal Zinc. Zinc coating on iron act as anode and iron act as cathode.

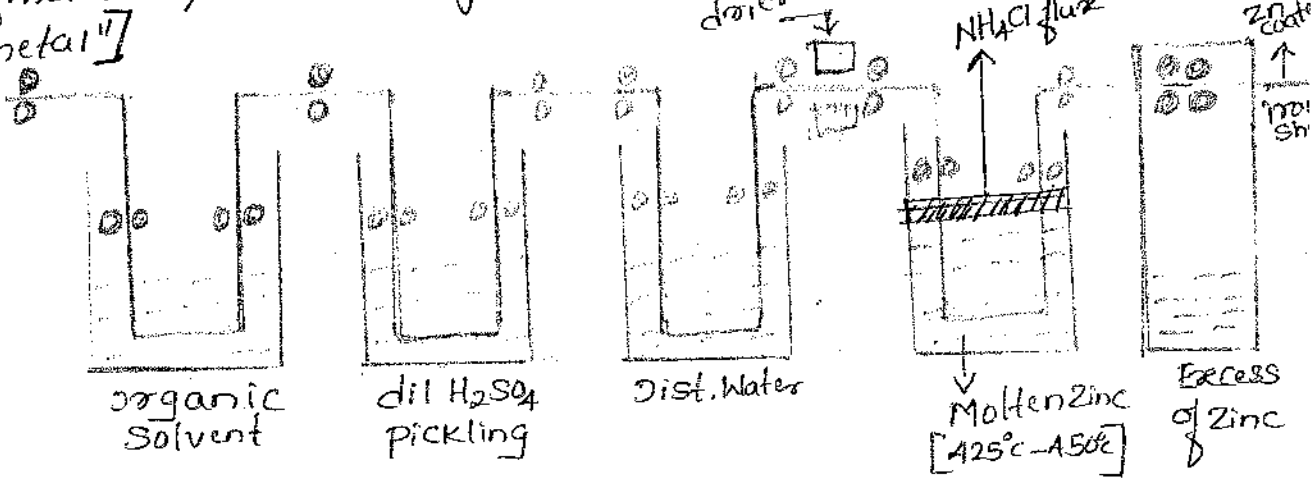
corrosion.



Galvanisation:

"The process of coating a basemetal with Zinc by hot dipping process is known as galvanisation"

Note: "The process of formation of thin film of uniform coatin of metal by immersing a clean metal in a bath of molten metal"]



The galavanisation process is carried out in the following steps:

Step1: The metal sheet is washed with organic solvent to remove oil, grease fatty substance etc.

Step2 Then the metal sheet is washed with dilute H_2SO_4 at 60-90°c inorder to remove old oxide ~~on~~ scale.

Step3: The metal sheet is passed in distilled water to remove trace of H_2SO_4 and dried.

Step4: The dried metal sheet is passed in molten zinc bath at 425-430°c. The surface of the bath covered with flux NH_4Cl to prevent the oxidation of Zinc.

Step 5: The Zinc coated metal sheet is passed through a pair of hot rollers to remove excess Zinc and prod
-ce a thin film of uniform thick ness.

Step6: Finally the metal sheet is annealed.

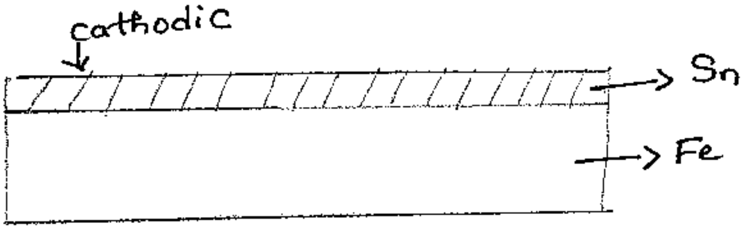
Uses:

1) For corrosion protection in roofing, sheet, wires, pipes nails etc.

Cathodic metal coating:

" The process of coating less active metal over the the base metal, whose tendency for corrosion is ~~lower~~ lower than the base metal".

The metal such as Cu, Ni, Sn and Ag are commonly which used as cathodic coating on steel.

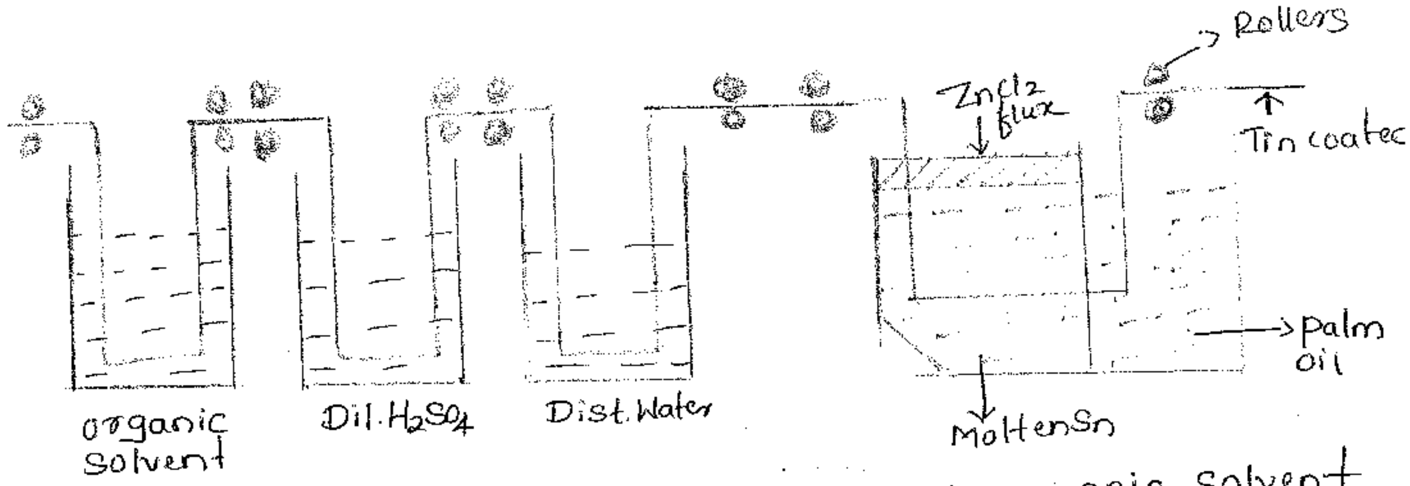


The coating metals are less reactive than the base metal and are less susceptible for corrosion. The surface of cathodic coating must be completely continuous otherwise there will be no effective protection of the base metal.

Tinning:

"The process of coating of tin on iron by hot dipping is called tinning."

The tinning of iron sheet involves the following steps.



step 1: The metal sheet is washed with organic solvent to remove oil, grease, and fatty substance.

Step 2: Then metal sheet is passed in dil H_2SO_4 at 60-90°c to remove old oxide scale.

Step 3: The metal is then passed in distilled water and dried.

Step 4: The dry metal sheet is passed through molten $ZnCl_2$ flux to improve adhesive capacity of metal.

Step 5: Now the metal sheet is passed in molten tin bath.

Step 6: Finally the metal sheet is passed through ~~pt~~ palm oil containing series of rollers.

palm oil prevents the oxidation of tin, the rollers remove excess tin and produces thin uniform tin coated metal sheet.

Uses:

1) Tin coated metal sheet are used in the manufacture of food storage container

2) In making cooking utensils and refrigeration equipment.

Inorganic Coating:

The chemical conversion coating in which surface of the metal is converted into its compounds, which inturn act as barries between the underlying metal and corrosive environment and protect the metal from corrosion are called inorganic coating. In practice, there are two types of inorganic coating techni-ques and the process of cating is described below.

1) Phosphate coating:

Phosphate ~~Cat~~ coating is a process in which a thin film of metal phosphate coating gets deposited on the metal surface due to the interaction of surface atoms of the base metals and certain metal phosphates in aqueous. Solution of phosphoric acid.

Phosphate coatings are generally used to coat iron Steel and zinc and to a lesser extent Al, Cd and tin. A chemical or electrochemical reaction between the phosph-ating solution and base metal results in the formation surface film. The surface coating obtained as a above. on metal surface do offer complete resistance to corrosi-n.

The phosphating bath is mixture of phosphorus acid. and Zn/Mn phosphate solution. Accelerators such as copper salts $[Cu(NO_3)_2]$, H_2O_2, nitrates, etc are used to enhance the rate of deposition. The pH of phosphating bath is to be maintained at 1.8 – 3.2. The electrodeposition of phosphate coating process is carried out at a temperature of 35 °C

Reaction

$$(M \longrightarrow M^{+2} + 2e^{\ominus}) \times 3$$

$M = Zn/Fe$

$$[H_3PO_4 \longrightarrow 3H^{\oplus} + PO_3^{-3}] \times 3$$

$3M + 2H_3PO_4 \longrightarrow M_3(PO_4)_2 + 3H_2$

Application

1) These applied frequently to iron, steel and Zinc and to small extent to Al, Cd and Sn.

2) Iron and Manganese phosphate coating are used to reduce wear due to friction piston ring, Cylinder lining of auto mobile.

Anodisation or anodized oxide film.

Anodisation is a process in which a protective passive oxide film is artificially ~~proced~~ produced. on certain metals [Non ferrous metals like Al, Zn, Mg etc] in oxidising acid bath.

It is carried out by passing moderate Dc Current through a bath in which the metal or alloy is Suspended form anode. The bath usualy contains H_2SO_4, phospheric acid, Chromic acid. After anodisizing, the oxide coating is sealed by immersing in boiling water.

Ex Anodizing Al: It is carried out by making it anode in electrolytic bath containing a suitable acid like chromic acid at 35-40°C. A plate of lead or stainless steel is made the cathode. When current of moderate density is passed, the O_2 liberated at anode. with it form oxide which takes the form of thick film. Al_2O_3 deposit on the surface of objet.

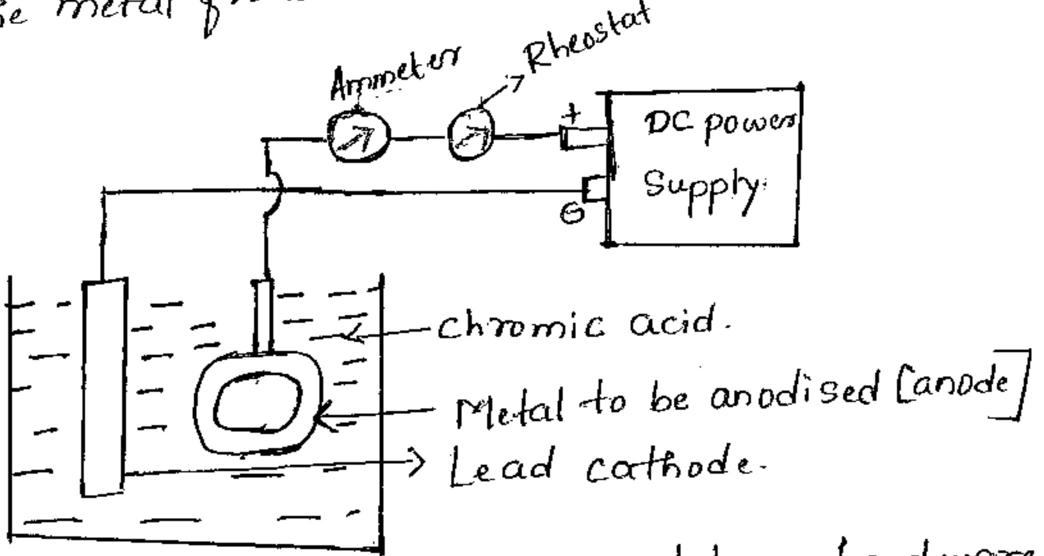
At anode : $2Al \longrightarrow 2Al^{+3} + 6e^{\ominus}$

At cathode : $6H^{\oplus} + 6e^{\ominus} \longrightarrow 3H_2$

$2Al + 3H_2O \longrightarrow Al_2O_3 + 3H_2\uparrow$

thickness of the deposit controlled by adjusting the current.

The coating is slightly porous and ~~seo~~ it is sealed by dipping in hot water.. Al_2O_3 get hydrated to $Al_2O_3 \cdot H_2O$ which occupies more volume and hence. protects the metal from corrosion.



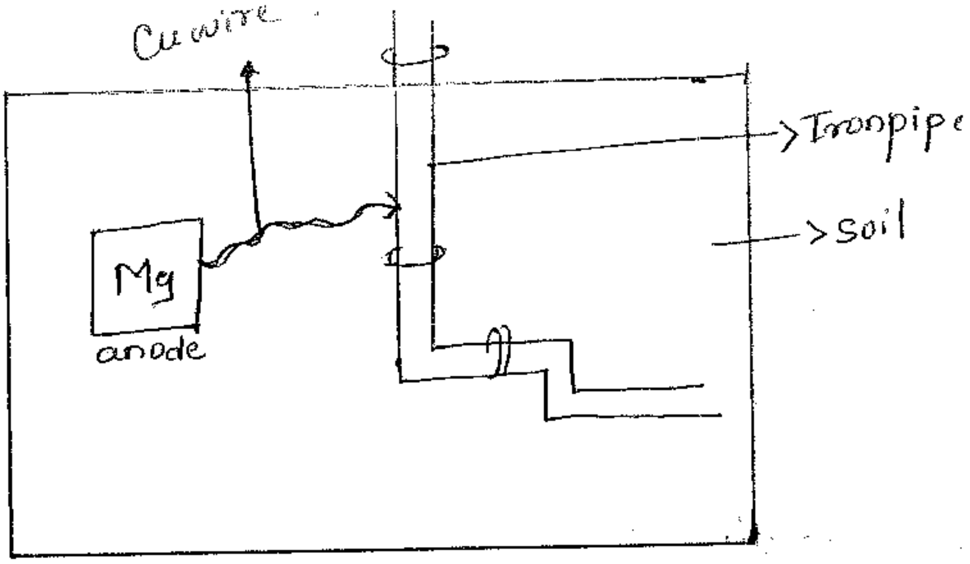
Uses· Application used for office partition, hardware, elevator, escalators etc.

Corrosion control by cathodic protection.

Protection of metals from corrosion by making them completely cathodic and no site of the metalic. object is allowed to act as an anode, obviously there can't be ~~anode~~ cathode without an anode. Hence to achive this, an auxilary anode is connected to the structure to be protected in corroding medium through external source of current. It is achieved by

1) Sacrificial anodic method

In this method metal structure to be protected is connected to a more active metal with the insulated copper wire. The metal structure act as cathode and the more active metal act as anode. Hence corrosion concentrates at anode which is ~~used~~ used up gradually due to more oxidation. The metal structure remain unaffected.



Advantage:
1) Method is simple and economical
2) No power supply required
3) Minimum maintenance cost.

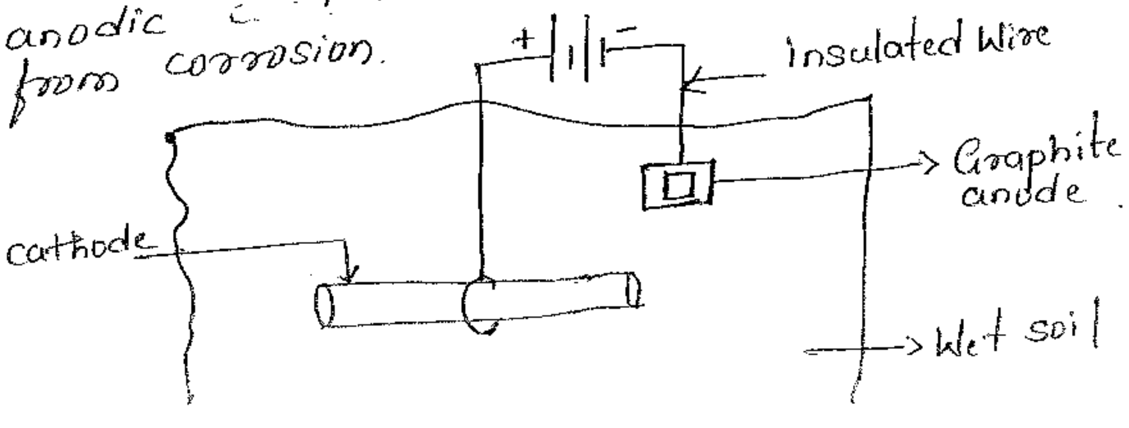
disadvantage
Loss of active metal

Application: Sacrificial anodic protection is used in the protection of oil tanks, ship hulls, underground cable etc.

2) Impressed Current Method :-

Corrosion occurs in metal to the environment to which it is exposed. The corrosion current always flows from anodic area to cathodic area of the metal.

In this method, an impressed external current is applied in opposite direction to the metal that is corro-ng to nullify the corrosion current. by doing so the metal subjected to corrosion is thus converted from anodic [illegible] to cathodic area. and protects the metal from corrosion.



Usualey graphite or platinum is used as inert anode along with back fill composed of coke, breeze. or gypsum which provide proper contact with surrounding soil.

Advantage.

1) Large area can be protected by single installation.

2) Applicable in high - resistivity environments.

Dis advantage:

1) Method is expensive due to the requirement of high. Current.

2) It is difficult to maintain uniform current over the. entire metal surface and as result localized corrosion may occur.

Application: This method is used for protection of. oil pipe line, towers, water tanks, condensers etc.

Reaction of Anodisation of Al :

$$Al \rightarrow Al^{+3} + 3e^{-}$$

$$2Al^{+3} + 3O^{-2} \rightarrow Al_2O_3$$

$$2Al^{+3} + 3OH^{-} \rightarrow Al_2O_3 + 3H^{+}$$

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^{+} + 6e^{-}$$

-: Metal finishing :-

A Kind of surface modification of metal is called metal finishing. In our daily life we use various metalic material such as refrigerator bodies, car components, window frames, electrical appliances, jewellery, automobile spare parts any more, require some basic needs such as corrosion resistance, wear resistance, electrical and thermal properties, ease of fabrication. But no single metal can fulfil all these ideal properties. Therefore metal finishing is one of the method employed for the purpose of improving their lacking properties.

Def " Metal finishing is the process carried out to modify the surface properties of metal by deposition of a layer of another metal or alloy or a polymer film on the substrate"

Ex: Electroplating of metal, electroless plating, etc.

Technogical Importance of metal finishing : It is used

1) To impart corrosion resistance.
2) Imparting improved abrasion and wear resistance.
3) To provide thermal and impact resistance.
4) To provide electrical or thermal conducting surface.
5) To enhance chemical resistance.
6) To impart hardness
7) To increase durability of metal.

Important techniques of metal finishing are.

1) electroplating of metal, alloys
2) Electroless plating of metal, alloys and composites.
3) Metal spraying
4) Metal clading etc.

Principles Governing process of metal finishing :

The fundametal principles governing metal finishing are.

a) Polarisation
b) Decomposition potential
c) Overvoltage.

Polarisation:

" It is the process ~~of~~ where in, there is a variation of electrode potential, due to the slow diffusion of metal ions from the bulk of the electrolytic solution to the vicinity of electrode"

The electrode potential is given by the Nernst's equation

$$E = E^0 + \frac{2.303\ RT}{nF} \log [M^{n+}]$$

Where E^0 = Standard electrode potential
R = gas constant T = Temperature.
$[M^{n+}]$ = Metal ion concentration
n = no of electrons involved in electrode reaction.
F = Faraday's.

M^{n+} is the concentration of metal ions surrounding
the electrode surface at equilibrium. When there is a passage
the electrode surface at equilibrium metal ion concentration in the vicinity of
of current, the metal ion concentration decreases owing to the reduction
the electrode surface decreases, there is a shift in the equilibrium
of metal ions. Therefore, there is a shift in the electrode potential. The concentratio
and a change in the electrode potential and the
-n gradiant between the bulk of the solution and the
area surrounding, the electrode surface leads to diffusion
of ions from the bulk of the solution towards the
electrode surface. This ~~reestablishment~~ reestablishes the.
equilibrium. If the diffusion is slow, the electrode
potential changes and electrode is now said to be polarise
-d.

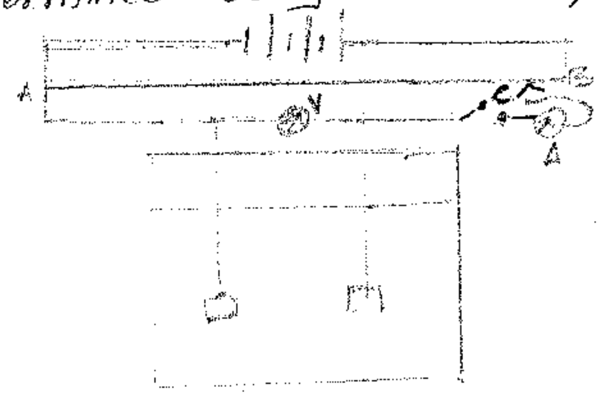
~~Se~~polarization depends up on
1) Nature i.e. size, shape, and the composition of the electro
-de
2) Electrolyte concentration and its conductivity.
3) products formed at electrode

4) Temperature

Decomposition potential (E_D):

"The minimum voltage required to bring about the electrolytic decomposition of the electrolyte without any interruption is called decomposition potential."

When a small voltage is applied between two platinum electrode immersed in 1M H_2SO_4, an apperciable current flows at the beginning. The current decreases rapidly and becomes almost equal to Zero in a short time. When the voltage is gradually increased, there is slight increase in the current. Beyond a certain voltage called the decomposition potential, the current abruptly increases due to commencement of electroly~~te~~sis. Below this voltage no electrolysis occurs. Decomposition potential is determined using an electrolytic cell.



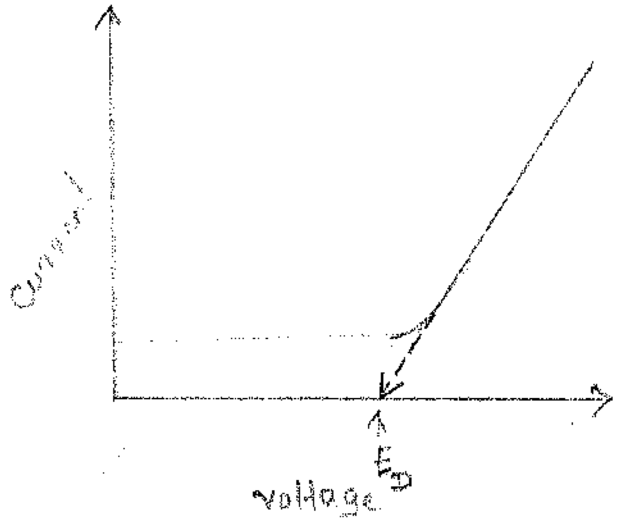
A = Ammeter
V = Voltametere.

Cell

The cell consists of two platinum electrodes immersed in a dilute solution of an acid or base. The voltage is varied by moving the contact maker 'C' along the wire AB and the current passing through the cell is ~~used~~ measured using an ammeter. At low voltage no reaction occurs and there is a very slight increase in the current. On increasing the voltage to slightly above 1.7v there is an abrupt increase in the current and sudden evolution of H_2 and O_2. The applied voltage of 1.7v is the decomposition voltage for dilute acids and bases.

A plot of the current flowing between the electrodes against the applied voltage. The decomposition voltage

E_d maybe obtained by extrapolation of the Curve as shown in the figure. There is very slight increase in the current at low voltages. Beyond the decomposition voltage electrolysis begins and there is abrupt increase in the current.



Overvoltage:

Continuous electrolysis take place when the applied voltage is slightly more than the decomposition potential E_D. In few cases the applied voltage has to exceed the theoretical value by at least 1v for continuous electrolysis. This is known as overvoltage or over potential represented by η. Over voltage is defined as

"The excess voltage that has to be applied above the theoretical decomposition potential for continuous electrolysis" is called overvoltage.

Or

The excess voltage that ha

$$\text{over voltage} = \text{Experiment } E_D - \text{Theorotical } E_D$$

$$\therefore E_D = E_{cathode} - E_{anode} + \eta$$

Overvoltage for given electrolyte depend on several factor.

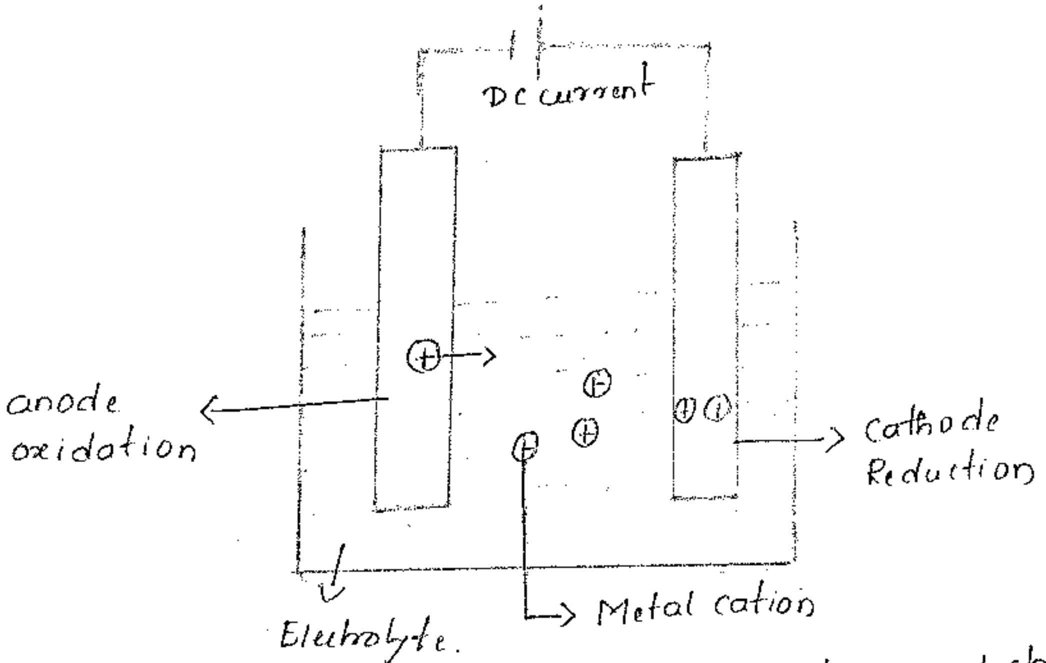
1) Nature and physical state of the metal electrode

2) Nature of the substance deposited.

3) current density
4) Temperature
5) Rate of stirring of electrolyte.

Electroplating :

" Electroplating is the process of deposition of a ~~metal~~ metal by electrolysis over the surface of a substrate"



Electroplating deposition is carried out by electrolyzing suitable salt solution of metal being plated. The substrate is the cathode and the pure metal is usually the anode. On electrolysis, the anode dissolve into the electrolytic bath and the metal ions from the bath solution are deposited as metal over cathode. The reactions taking place for an electrolyte MA are given below.

$$MA_{(aq)} \rightleftharpoons M^{+}_{(aq)} + A^{\ominus}_{(aq)}$$ ~~and~~

At anode electrode dissolve giving rise to M^{+} ions

$$M \longrightarrow M^{+}_{(aq)} + e^{\ominus}$$

At cathode metal ions get reduced and are deposited as metal

$$M^{+} + e^{\ominus} \longrightarrow M$$

The conditions of electrolysis are controlled in such a way that the current efficiency of the reactions are equal so that the concentration of M^+ remains constant in the electrolyte. However, when an inert metal is used as anode, the metal ions are supplied in the form of metal salt to maintain the concentration of electrolyte otherwise, oxygen will be evolved at the anode from the aqueous solution.

$$H_2O \longrightarrow \tfrac{1}{2}O_2\uparrow + 2H^+ + 2e^\ominus$$

Under acid conditions a side reaction involving of H_2 may take place

$$H^+ + e^\ominus \longrightarrow \tfrac{1}{2}H_2.$$

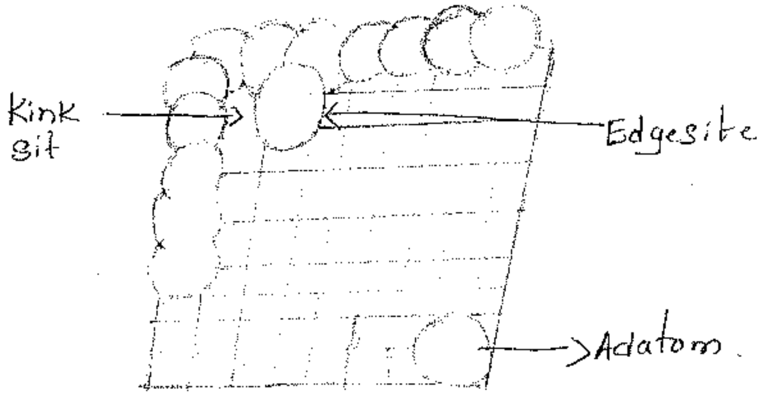
A highly conducting electrolytic solution and optimum current density are used to get a good deposition.

Mechanism of electrodeposition:

Deposition of metal is similar to crystal growth since metal have well defined crystal streetures. Electrodeposition take place in two stages

1) Formation of nuclei covering the electrode with a few atomic layers of metal.
2) Growth of deposit resulting in thicking of the layers into a macroscopic deposit.

The formation of nuclie require a high overvoltage. The nuclei once formed grow rapidly at a relatively low overvoltage. The atoms (adatoms) that are formed during the plating process on the crystal plane quickly move and occupy favourable sites. The most favourable site is a kink site where the atom can interact with three neighbours as shown figure. Atoms also occupy less favourable sites. Such as edge site (two neighbours or just remain as adatoms. The latter diffuse to more favourable site or redissolve.



Factors influencing the Nature of the deposit.

1) Current density :

Current density is defined as the current per unit area. Its unit Am^{-2} or $mAcm^{-2}$ of the electrode surface.

At low Current density: diffusion of ions on the surface is fast compared to the electron transfer and the adatoms find the most favourable positions resulting in a well formed deposit

At higher current density: Electron transfer predominates and surface diffusion becomes slow. Number nuclie formed increases and the add atoms may not move towards favourable sites. This results in a less ordered macroscopic deposit.

At higher current density [below limiting value]: Bulk transfer predominates along with electron transfer. surface diffusion is poor resulting in rough, powdery, non adhesive deposit.

At current density above limiting value: Hydroge evolution takes place resulting in a depletion of H^+ ion concentration in the ~~vicinity~~ vicinity of cathode. As a result metal hydroxide or oxide gets precipitated.

Hence optimum current density should be applied, to have better deposit.

2) Temperature: A good fine grain and smooth deposit is obtained at slightly higher temperature because at high temperature solubility and dissociation of metal salt increases, which in turns leads to higher

conductivity of the solution. A high temperature increases the mobility of the metal ions and decreases the viscosity of solution. But the disadvantage of maintaining the higher temperature are corrosion of process equipments hydrogen evolution at the cathode and decomposition of organic addition agents. Therefore moderate optimum temperature at range of 35 - 60°c is selected.

3) PH of the Bath:

For a good electrodeposit, the pH of the bath must be properly maintained by using buffer. At low pH, evolution of hydrogen at cathode occurs, resulting in a porous deposit. At high pH the insoluble metal hydroxide deposits on the article. Hence optimum pH range for most plating bath ~~so~~ should be from 4 to 8.

4) Plating Bath Solution

Plating bath consists of mixture of salts of metal being plated. It also containing complexing agents and other various organic additives. Metal ions are always added in high concentration to avoid rapid depletion in the vicinity of the cathode during electroplating. More soluble metals salts are used.

a) concentration of the metal ion and complexing agent:

The concentration of the metal ion should be low in order to have a smooth deposit. Therefore low metal ion concentration has to be maintained. This is achieved by addition of the compounds which have a common ion with metal salt, or by the adding complexing agent.
Eg: in the electrodeposition of copper, the concentration of Cu^{+2} ion is maintained low by adding sulphuric acid. The sulphate ion act as common ion and prevent the dissociation of copper sulphate. Thus maintained low Cu^{+2} ion.

$$\cancel{CuSO_4}\quad CuSO_4 \longrightarrow Cu^{+2} + SO_4^{-2}$$

$$H_2SO_4 \longrightarrow 2H^{+2} + SO_4^{-2}$$

The addition of complexing agent reduces the metal ion concentration by complex formation, which is less dissociated.

b) Concentration of metalic salt and electrolytes:

The metal salt concentration is usualy Kept high to ensure smooth deposit various electrolytes are also added to increase the conductance and cathodic efficiency. Thus firm and adherent deposits can be obtained with high electrolyte concentration.

c) Organic additives:

Wide ranges of organic compounds are added in relatively low concentration to modify the structure and properties of the deposits. Addition agents are clasified into several groups based on their mode of action.

i) **Brighteners:** These are added to give brightness and lustroous surface. They usualy cause the formation of even fine-grained deposits by modification of nucleation process.

Eg: thiourea, coumarin etc.

ii) Levellers: These are added to get level deposit. They produce a levelled deposit by preferentialy getting absorbed at the place where rapid deposition of metal take place. Generally plating take place rapidly on certain part such as on dislocations. The absorbed additives reduce the rate of deposition at those parts.

Eg: sodium alkyl sulphonate.

iii) structural modifier: These are added to modify the structure of the deposit in such a way as to alter the deposit properties and also to decrease stress on the surface of the metal.

Eg: Saccharin.

iv) Wetting agent: During electroplating in some cases there is simultaneous deposition of hydrogen and metal at the cathode. If bubbles of hydrogen adhere to the cathode Surface strongly, plating is prevented around.

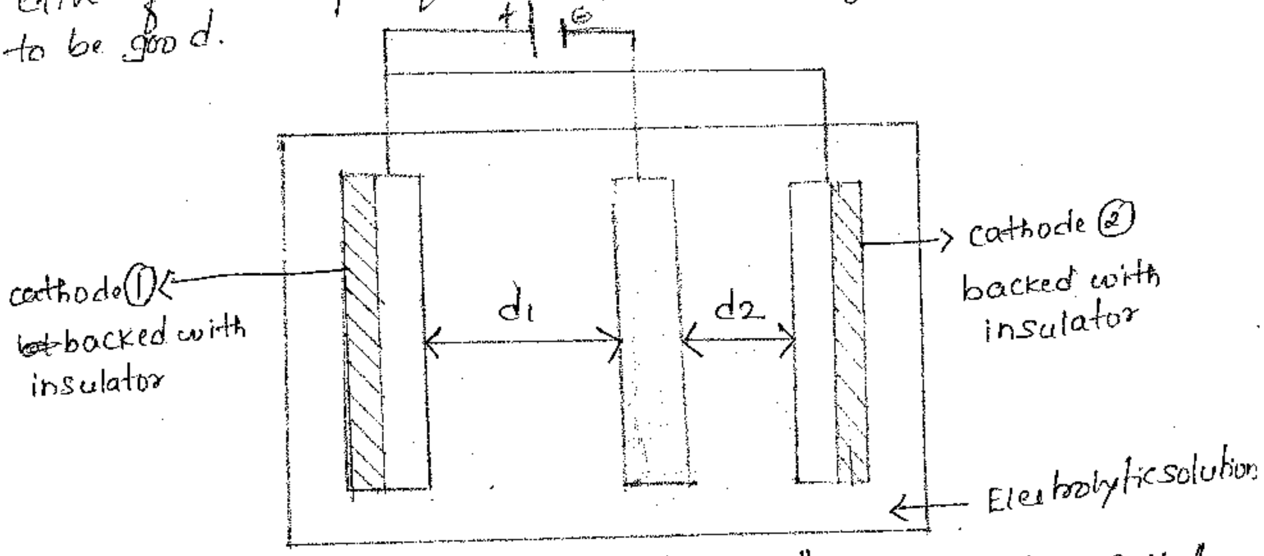
around the bubble and a pit is created in coating some surface active agents are added to detach absorbed hydrogen and eliminate pitting.

Eg: Sodium lauryl sulphate.

5) Throwing power of the plating plate:

" The ability of a plating bath to give an even deposit of metal is measured by its throwing power". It is the measure of uniformity of the deposit from high - current-density area to low - current - density areas.

When the distribution of the deposit is even, irrespective of the shape of the object throwing power is said to be good.



Throwing power can be determined by "Haring - Blum cell"

The cell contains plating bath solution whose throwing power is to be determined. It consists of two cathode (insulated at rear end) and an anode at the centre. Two cathodes are at different distance d_1 and d_2 from anode $(d_1 > d_2)$

The process of electroplating is carried out and weight $[W_1$ and $W_2]$ deposited at cathode (~~1&2~~) [1 and 2 respectively] are noted.

$$\therefore \quad \text{\% of throwing power} = \frac{100[x-y]}{(x+y-2]}$$

Where $x = d_1/d_2$ $Y = W_2/W_1$

When the amount deposited is same $[W_1 = W_2]$, irrespective of the placement of the electrodes, the throwing power is 100% and is considered to be very good.

When the calculated throwing power less than 100% then it is considered as very poor.

Surface preparation.

Before electroplating process the surface of the article is coated is cleaned in such a way as to remove the unwanted matter ~~such~~ such as oil, grease, oxide scale etc. Different cleaning methods are adopted for different metals and materials as follows.

1) Solvent cleaning: organic solvents [CCl_4, toluene, xylene trifluro ethane etc] are used to remove impurities like oil grease etc from the metal surface

2) Alkali cleaning: This is employed to remove oil old paint from the metal surface by using solution of NaOH sodium carbonate etc. A combination of alkalis with a proper surfactant, Che~~a~~lating agents such as EDTA makes the metal cleaning effectively.

3) Acid cleaning/pickling: After the removal of organic impurities, the substrate is immersed in 10% H_2SO_4. This removes any oxide scale on the surface. This type of cleaning also causes the electrochemical enhancement possible by making the surface more anodic.

4) Mechanical cleaning: Used to remove the oxide layer or rust and other inorganic deposists on the metal surface. The simple methods involve the hand cleaning with bristle brush, polishing tools, sand papers etc.

5) Electropolishing: In order to have a polished metal surface for electroplating, this method is used. In this method, the metal to be cleaned, is made as anode in a suitable solution. During the process, a surface layer of the metal gets dissolved along with the impurities.

Electroplating of chromium [Acid bath].

Chromium plating	Decorative chromium plating	Hard chromium plating
1) Anode	Insoluble anode like Pb, Pb-6% antimony Pb-7% Sn etc	Insoluble anode like Pb, Pb-6%, antimony Pb-7% Sn etc.
2) Cathode	object to be plated	object to be plated
3) Bath composition	100:1 chromic acid & H_2SO_4	100:1 chromic acid. and H_2SO_4.
4) Current density [$mAcm^{-2}$]	100-200	215-430
5) Temperature	45-55°c	43-66°c
6) Current efficiency	8-12	10-15
7) Application	Provide durable and good decorative finish on automobiles, surgical instruments. etc.	Hard, wear-resistant deposist.
8) pH	2-4	2-4.

Main reaction:

$$CrO_3 + H_2O \longrightarrow H_2CrO_4 \longrightarrow CrO_4^{-2} + 2H^+$$

$$2H_2CrO_4 \longrightarrow H_2Cr_2O_7 + H_2O \longrightarrow Cr_2O_7^{-2} + 2H^+ + H_2O$$

$$Cr_2O_7^{-2} + 14H^+ + 6e^{\ominus} \xrightarrow{\text{Catlyst } SO_4^{-2}} 2Cr^{+3} + 7H_2O$$

$$Cr^{+3} + 3e^{\ominus} \longrightarrow Cr.$$

Chromium anode are never used in Cr plating due to the fact that Cr metal passivates strongly in acid sulphate medium. Moreover, Cr anode on dissolution gives rise to Cr(III) ions which lead to the formation black Cr deposit.

In the plating bath, SO_4^{-2} ions from H_2SO_4 act as a catlyst Cr is present in the hexavalent state Cr(VI) as CrO_3 in the bath solution. In the presence of SO_4^{-2} ions Cr(VI) is converted to Cr(III) by a complex anodic reaction.

PbO_2 coating on the anode oxidize Cr(III) to Cr(VI) and thus ~~control~~ control the concentration of Cr(III) ions. in the presence of large excess of Cr(III) ions a black Cr deposit is obtained.

$$2Cr^{+3} + 3O_2 \xrightarrow{PbO_2} 2CrO_3 + 6e^{\ominus}.$$

Nickel plating [Watt's bath method].

Nickel plating	Watt's bath.
1) Anode	Ni pellets loaded to Ti basket/Ni rods
2) Nickel sulphate $[NiSO_4 \cdot 6H_2O]$	$240 - 300 g L^{-1}$
3) Nickel chloride $[NiCl_2 \cdot 6H_2O]$	$30 - 90 g L^{-1}$
4) Boric acid $[H_3BO_3]$	$30 - 45 g L^{-1}$
5) Temperature	40 - 60°C
6) pH	3.5 to 4.5.
7) Current density	$20-50 mA cm^{-2}$
8) Additives.	1) Sodium lauryl sulphate - Wetting agent 2) p-toluene sulphonamide as brightness.

	iii) Co, Zn allyl sulphonic acid. - as levellers.
9) current efficiency	95 to 100%
10) Electrode reaction	At anode $Ni \longrightarrow Ni^{+2} + 2e^{\ominus}$ At cathode $Ni^{+2} + 2e^{\ominus} \longrightarrow Ni$

Nickel sulphate is primary source of nickel $[Ni^{+2}]$ with nickel chloride a contri buting source. Nickel chloride has two major function i) apperciably increases solution conductivity ii) reduces the voltage requirements.

Boric acid is a buffer and has the major function of controlling the pH of solution.

Application

i) nickel plating used offer a high ~~but~~ luster finish corrosion protection and wear resistance.

2) It is also used for bright work on bicycles and motor cycles.

3) nickel plating used in automotive industry. nickel plating can be on bumbers, rims, exhust pipe.

Electroless plating :

"The controlled deposition of a continuous film of a metal from its salt solution on to a catalytically active surface by a suitable reducing agent without using electrical energy" is called electroless plating.

The reducing agent converts the metal ions $[M^{n+}]$ to metal $[M]$ which get plated over the catalytic surface.

$$M^{n+} + \text{Reducing agent} \xrightarrow[\text{Surface}]{\text{catlytic}} M + \text{oxidized product.}$$

Composition of electroless plating bath.
A typical electroless plating bath contains of the fallowing.

a) soluble electroactive metal salt, usually chloride components

b) Reducing agent [formaldehyde, sodium ~~boo~~borohydride, hydrazine].

c) complexing agent [eg: Citrate, tartrate etc]

d] Exalant [Eg: succinate, fluoride etc].

e] stabilizer [Eg: lead, calcium, thiourea]

f] Buffer

Advantage electroless plating:

1) No electrical power and electrical contact required.

2) plating may also be obtained on ~~insultar~~ insulator and semi conductor

3) Levellers are not required in electroless plating.

4) These coating posses unique mechanical, chemical and magnetic features.

5) There are no chance of hydrogen gas trap within the deposit in electroless plating.

6) Better throwing power compared to electro~~less~~ plating. consequently the intricate parts such as bends, recesses and inner parts of object with irregular shape.

Disadvantage of electroless plating

1) Electroless plating commonly generate more waste than other plating techniques.

2) Deposit is contaminated with oxidised product.

3) Rate of deposition is slow.

Distinctions between electroplating and electroless plating.

or

Differnce between electroplating and electroless plating.

Property	Electroplating	Electroless plating
1) Driving force	Electrical energy from external source	Autocatlytic redox reaction.
2) Site of anodic reaction.	Anodic reaction take place at separate anode used in the electrolytic cell	catalytic active surface of the article to be plated.
3) site of cathodic reaction	Article to be plated act as cathode	catalytic active surface of the article to be plated.
4) Anode	A separate anode is used which is connected to the terminal of battery	No separate anode is taken. anode reaction take place on the surface of article.
5) Reducing agent	Reduction is brought by electron	Reduction is brought by reducing agent on catalytic active surface.

6) Types of cathodic used for plating	plating is carried out on metal	plating may be carried out on metals, insulator and ~~Semis~~ Semiconductor.
7) Throwing power	Not satisfactory for intricate parts with irregular shape and inside of tube	Throwing power is satisfactory irrespective of the shape and inaccessibility of the parts.
8) Applicability	Applicable only on conductor	Applicable to conductors, semiconductors and insulator.

Electroless plating of Cu on PCB.

copper will deposit spontaneously in presence of a suitable reducing agent on metals such as gold, silver, platinum, iron. Insulator like plastic and glass are to be activated before subjecting to electroless plating.

An important application of electroless plating is in printed circuit board (pcb). In double side and multilayer boards where plating -through- holes is required. The base object in pcb is a plastic material such as a glass fibre epoxy or phenolic polymer over which a layer of copper is plated.

Pretreatment and surface activation:

The plastic board is degreased and etched in acid. It is activated by dipping in $SnCl_2$ / HCl at 25°c followed by dipping in $PdCl_2$.

Plating bath solution:

copper sulphate solution [12g/L]

Reducing agent - formaldehyde [8g/L]

Buffer - Sodium hydroxide

complexing agent and exaltant - EDTA (20g/L]

$pH = 11$

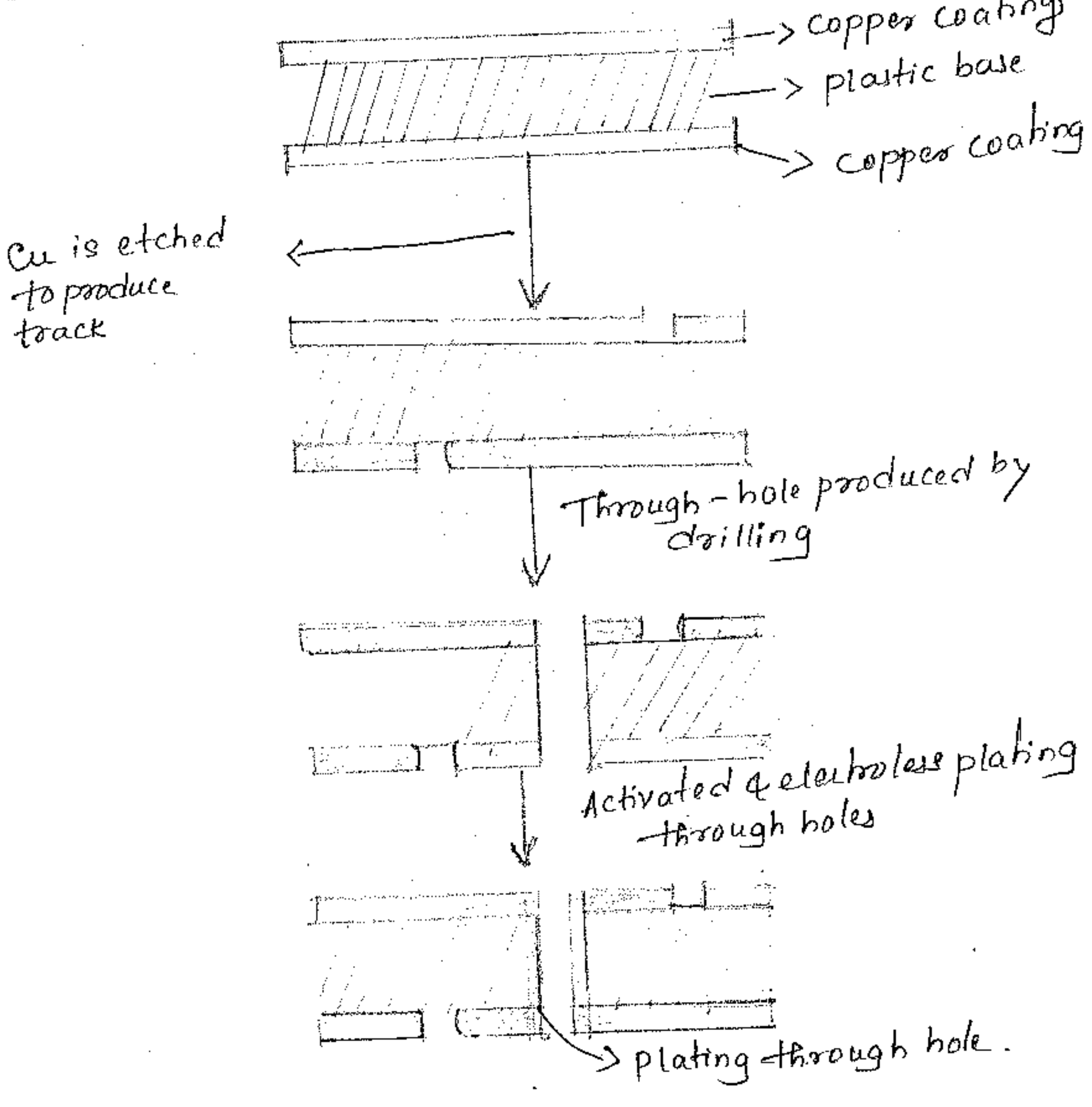
Reaction:

At anode: $Cu^{+2} + 2e^{\ominus} \longrightarrow Cu$.

At cathode: $2HCHO + 4OH^{\ominus} \longrightarrow 2HCOO^{\ominus} + H_2O + H_2 + 2e^{\ominus}$

$$Cu^{+2} + 2HCHO + 4OH^{\ominus} \longrightarrow Cu + 2HCOO^{\ominus} + 2H_2O + H_2$$

plating process:



Fuels:

Fuel: "A chemical fuel is a combustible substance containing carbon as the main constituent which may be burnt to supply heat for industrial and domestic applications without the formation of excessively objectionable byproducts"

OR

"A carbonacious combustible substance which on proper burning liberates large amount of heat is known as fuel."

Classification of fuel:

Depending on the origin fuels are classified as primary and secondary fuel.

Primary fuel are found in nature as such while. secondary fuels prepared or derived from the primary fuel

A complete classification of fuel is summarised below

Physical state	Primary fuel (Natural)	Secondary (Derived)
1) Solid	Wood, coal	Charcoal, coke
2) Liquid	petrolium	Gasoline, diesel etc
3) Gas	Natural gas	LPG, Biogas etc.

Characteristics of a good fuel:

1) It should have high calorific value
2) It should not pre-ignite easily
3) It should be easily available in natural or any other form
4) Storage, transportation and handling of fuel should be easy
5) It should have a low ignition temperature and burn ~~easily~~ efficiently.

6) For continous supply of heat fuel must burn with moderate vellocity. i.e fuel should have ~~moda~~ moderate velocity of combustion.

7) Low moisture content: moisture content reduces the calorific value of fuel. Hence fuel must have low moisture content.

8) products of combustion should not be harmful.

Calorific Value of fuel:

The calorific value of fuel is measured interms of the heating efficiency or the performance during its ignition in presence of oxygen.

"Calorific value of fuc is the total quanitity of heat liberated when a unit mass (or volume) of the fuel is burnt completely"

Generaly calorific value of fuel are expressed in two way

* Gross or Higher Calorific value [HCV or GCV]
* Net or Lower calorific Value [LCV or NCV]

Gross / Higher Calorific Value:

"Gross calorific value defined as the quanity of heat evolved by the complete combustion of unit mass/volume of the fuel in air or oxygen and products of combustion are cooled to room temperature"

Lower / Net calorific value: "Net heat produced when unit mass/volume of fuel is burnt ~~com~~ completely and the products of combustion are permitted to escape"

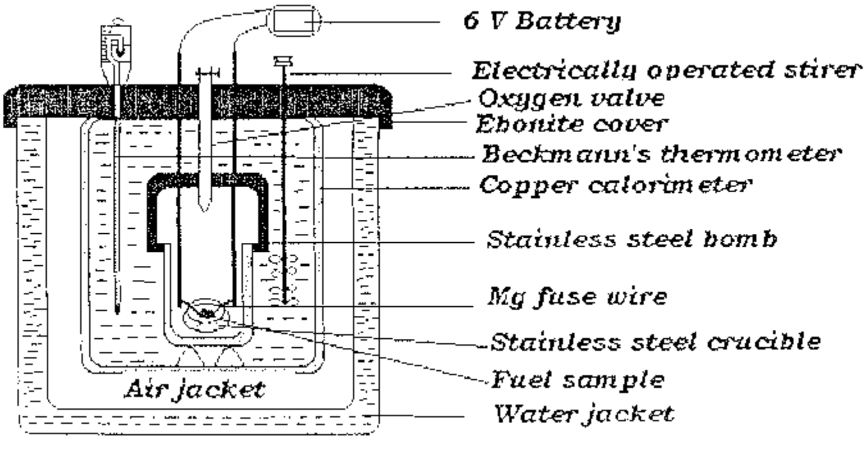
$$\left\{\begin{array}{c}\text{net or lower calorific}\\ \text{value}\end{array}\right\} = HCV - \left\{\begin{array}{c}\text{Latent heat of waters}\\ \text{vapours formed}\end{array}\right\}$$

∴ LCV = HCV − { Mass hydrogen x latentheat of steam }

The unit calorific value of a Solid or liquide fuel is $cal\,g^{-1}$ or $Kcal\,Kg^{-1}$ or JKg^{-1} or $KJKg^{-1}$

Determination of calorific value of a Solid or liquide fuel using Bomb calorimeter.

Principle: A known weight of a liquide or Solid fuel is completely burnt and liberated heat is absorbed by known weight of water. by recording the rise in temperature of water and knowing specific heat of water, calorific value is calcul



Bomb Calorimeter

Construction: Bombcalorimeter consists of an air tight Stainless bomb placed inside the or copper calorimeter. The calorimeter is surrounded by air and water jackets to prevent the heat loss to surrounding because of radiation. The copper calorimeter is also fitted with an electricaly operated stirrer to mix water, Magnesium fuse wire to start combution, an oxygen inlet to support combustion and Backmann's thermometer, which is capable of reading even a differnce of $1/100^{th}$

Working : A known weight of fuel ~~in the~~ taken in the crucible and placed inside the bomb. The bomb is kept inside a copper calorimeter containing a known weight of water. Initial temperature of water is noted after stirring. oxygen is pumped into bomb through oxygen ~~value~~ valve and the ignited using fuse wire and it is absorbed by water and calorimeter.

Calculation

1) weight of the fuel sample taken = m kg
2) weight of the water taken calorimeter = W_1 kg
3) Weight of water equivalent of calorimeter = W_2 kg
4) Initial temperature = t_1 °C
5) Final temperature = t_2 °C
6) Specific heat of water = S $Jkg^{-1}\,°C^{-1}$

a) If Q is gross calorific value than

Heat released by 'm' kg of fuel = {Heat gaine by water calorimeter} x {Heat gained by Cu}

$$Q \times m = (W_1 + W_2) \times S \times (t_2 - t_1)$$

$$Q = \frac{(W_1 + W_2)\, S\, (t_2 - t_1)}{m} \quad J/kg$$

b) Net C.V. of fuel

Let the fuel contains H % of hydrogen

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

i.e 2g of hydrogen produces 18 grm of water

$$\text{Water formed by 1kg of fuel} = \frac{18}{2} \times \frac{H}{100}$$
$$= 0.09\,H\,g$$

The latent heat of steam = 587 cal/g

∴ latent heat of water formed = 0.09 × H × 587 cal/g

∴ Lower (net) C.V. = HCV − (latent heat of water formation)

$$= HCV - (0.09H \times 587)\ cal/g$$

$$= HCV - \left[\frac{0.09H \times 587 \times 4.187}{10^{-3}}\right] J/kg$$

Cracking :

Cracking is defined as " Thermal or catalytic decomposition of bigger hydrocarbons into simple, low boiling hydrocarbons of lower molecular weight."

Eg : $C_{10}H_{22} \xrightarrow{Cracking} C_5H_{12} + C_5H_{10}$

Decane — n-pentane — Pentene

B.P = 174°C — B.P = 36°C

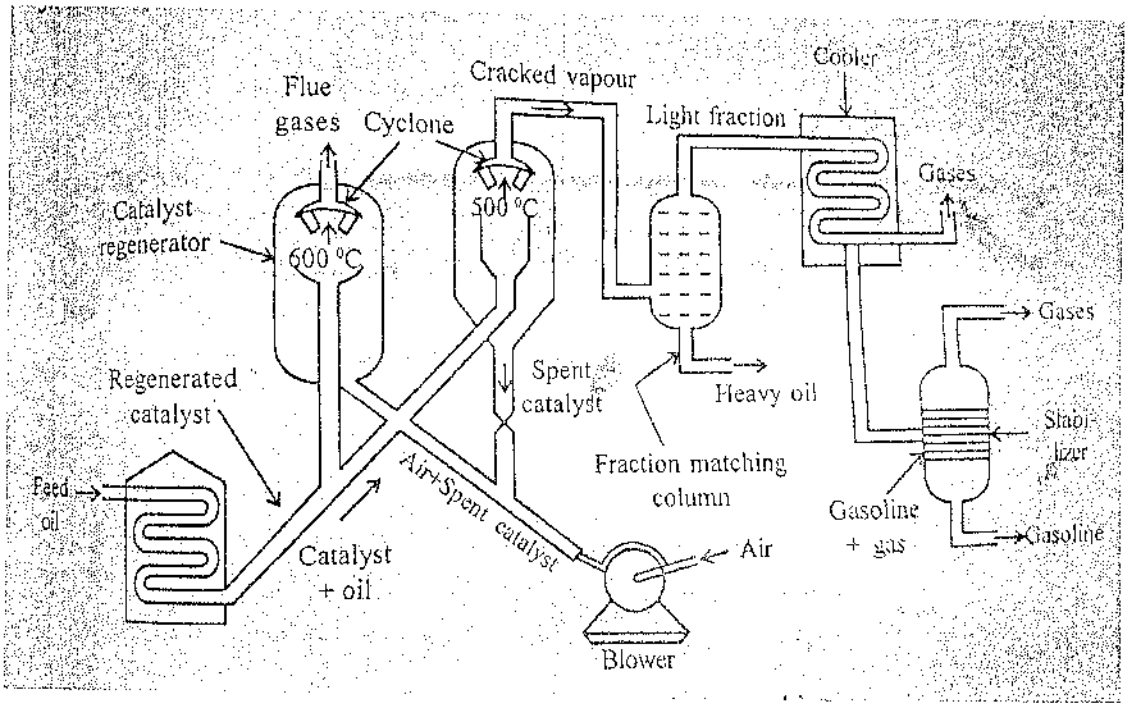
There are two methods of cracking :

1) Thermal cracking: In this method heavy oil subjected to high pressure and temperature (up to 700°C) in absence of air and oxygen.

2) Catalytic cracking : The cracking is carried out in presence of catalyst at milder condition [low temperature and pressure].

Fluidised [moving] Bed Catalytic Cracking :

Principle : In fluidized bed catalytic cracking, the finely devided catalyst is kept agitated by gas streams [cracking fuel] so that it can be handled like fluid system i.e. it can be pumped as a true liquide. There is good contact ~~in~~ ~~catalyst~~ between catalyst and reactant.



Conditions :

Stock : Heavy oil

Catalyst used : $Al_2O_3 + SiO_2$

Temperature : 500°c

The solid catalyst is finely devided, So that it behave almost as fluid and which can be circulated in gas stream The vapours of cracking stock [gas, heavy oil] mixed with fluidised catalyst is forced up into large reactor bed. in which cracking of heavies into lighter molecules occurs. At the top of reactor, there is centrifugal separator [called cyclones] which ~~alows~~ allows only the cracked oil vapours to pass on to fractinating column. but retains all the catalyst powder in the reactor it self. The catalyst powder gradualy becomes heavier, due to coating of carbon and ~~settes~~ settles to bottom. ~~cat~~ from where it is forced by an air blast to regenerator maintained at 600°c in order to regenerate catalyst.

Fischer Tropsch Process of Synthesis of Petrol:

In this process a mixture of pure water gas and hydrogen at ordinary pressure and at a temp of 200 - 300°C in presence of CO and Fe catalyst are converted to a mixture of alkanes & alkenes which resemble the crude oil. From this mixture gasoline is separated by fractional distillation.

$$_nCO + (2n+1)H_2 \longrightarrow C_nH_{2n+2} + nH_2O$$

$$_nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$$

Water gas required for this process is obtained from coal. The coal is converted into coke. The water gas is produced by the action of steam over red hot coke.

$$\underset{\text{coke}}{C} + \underset{\text{steam}}{H_2O} \longrightarrow \underbrace{CO + H_2}_{\text{Water gas}}$$

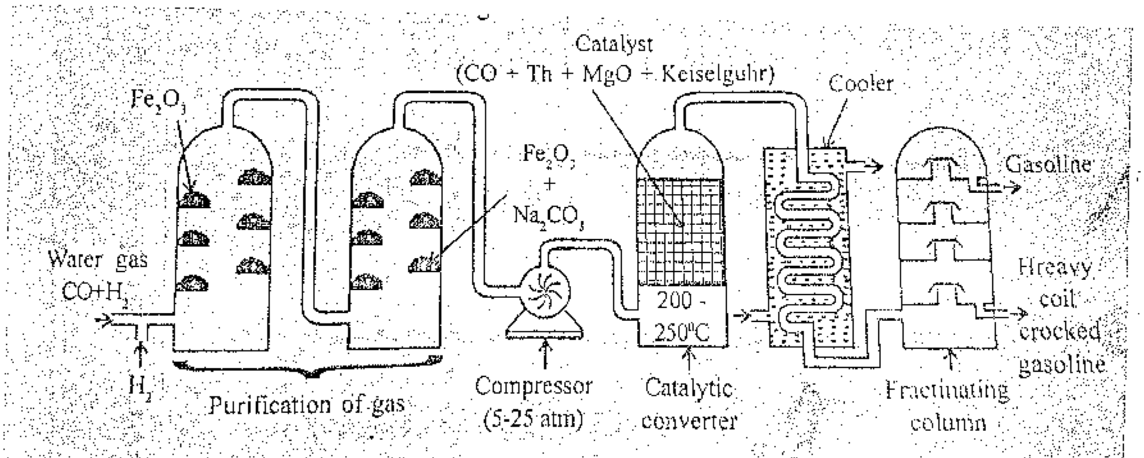


Fig. 5.3 : Fischer Tropsch Process

Water gas mixed with H_2 is passed over Fe_2O_3 to remove sulphur and its compounds. The mixture is further purified by passing over Fe_2O_3 mixed with Na_2CO_3 to remove organic compounds. The pure gas is the compressed to 5-25 atm and then passed to catalytic converter at 200-250°C containing a mixture of cobalt (100 parts), thourea (5 parts), magnesia (8 parts) and kieselguhr (200 parts) The reactions taking place in catalytic converter involving the formation of cobalt carbide and clevage of carbide by hydrogen to cobalt & methylene radicals. The methylene radicals so formed polymerises in presence of H_2 to form straight chain alkanes & alkenes. The product is condensed to separate the gases & the liquid is fractionated to get synthetic gasoline.

Reformation of petrol:

"The process of bringing about structural modification in the hydrocarbons without any change in number of carbon atoms in the straight run gasoline, to improve its anti-knocking characteristics"

Temperature: 470 - 600°c

Feed stock: Crude petrol

Pressure: 28 to 50 atmosphere.

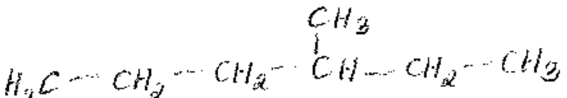
Following changes take place during reformation

1) Isomerisation: The straight chain hydrocarbon converted to branched chain hydrocarbon

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

n - hepatane

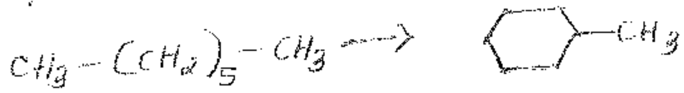
$\downarrow$



$H_3C-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3$

3-methyl hexane

2) Cyclisation: Straight or branched are converted to cyclo alkanes.

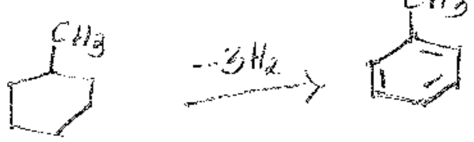


$CH_3-(CH_2)_5-CH_3 \longrightarrow$

n-heptane

methyl cyclohexane.

3) Dehydrogenation:



4) Hydrocracking: n-decane is cracked to n-pentane on mixing with ~~yet~~ hydrogen

$CH_3-(CH_2)_8-CH_3 \xrightarrow{\cancel{CH_2}}$

$CH_3-(CH_2)_8-CH_3 \xrightarrow{H_2} 2\ CH_3-(CH_2)_3-CH_3$

Decane. n-pentane

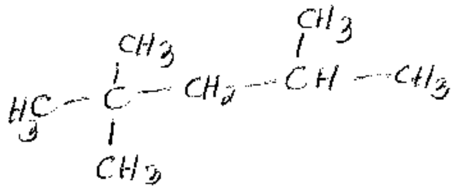
Octane number:

" Octane number of gasoline ~~may~~ defined as percentage of iso octane present in a mixture of iso-octane and n-heptane that has same knocking characteristics as that of fuel under test in standard cylinder engine operated under standard conditions".

$CH_3-(CH_2)_5-CH_3$

n-heptane

O.N = zero



$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{CH}-CH_3$

Iso-octane

O.N = 100

Ex: A fuel having O.N = 80, means which has the same combustion characterstics as that of 80:20 mixture at isooctane and n-heptane.

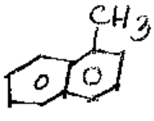
Cetane number:

The percentage by volume of n-cetane in mixture of n-cetane and α-methylnaphthalene ~~in~~ which is equivalent in ignition ~~to the~~ fu quality to the fuel under-test.

$CH_3-(CH_2)_{14}-CH_3$

n-cetane

C.N = 100



α-methylnaphthalene

C.N = Zero

Knocking in petrol engines:

In petrol engines the mixture of petrol and air is drawn in to the cylinder. The fuel-air mixture is compressed by the piston and is ignited by an electric spark.

As the flame front travels in the combustion chamber, rapidly expanding combustion products compress the remaining unburnt fuel and raise it's temperature. If the flame front travels rapidly at an optimum speed, the combustion of unburnt fuel takes place smoothly. On the other hand, if the flame front travels too slowly. the entire last portion of fuel mixture may get heated up beyond its ignition temperature & undergo instantaneous explosive combustion. This result in emission of a characteristic rattling sound called "Knocking."

Definition of knocking: knocking may be defined as the production of a shock wave in an IC engine as a result of an explosive combustion of fuel-air mixture, leading to a rattling sound.

Knocking in IC Engines

→ The power output and efficiency of an IC engine depends on the **Compression ratio** which is the ratio of the volume of the cylinder at the end of the suction stroke to the volume of the cylinder at the end of the compression stroke

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

→ Under ideal conditions, in an IC engine the petrol - air mixture drawn into the cylinder of the engine undergoes compression and then ignited.

→ The hydrocarbons in petrol undergo complete combustion and the flame propagates smoothly.

→ Sometimes due to deposits of carbon on the walls of the cylinder the hydrocarbons in petrol form peroxy compounds.

→ The accumulated peroxides decompose suddenly and burst into flames producing shock waves.

→ The shock wave hits the walls of the engine and the piston with a rattling sound. This is knocking.

→ The reactions that take place in an IC engine are given below (taking ethane as an example for the hydrocarbon present in petrol).

Under ideal conditions

$$C_2H_6 + 7/2\ O_2 \longrightarrow 2CO_2 + 3\ H_2O$$

Under knocking conditions

$$C_2H_6 + O_2 \longrightarrow CH_3-O-O-CH_3$$

(Dimethyl peroxide)

$$CH_3-O-O-CH_3 \longrightarrow CH_3CHO + H_2O$$

$$CH_3CHO + 3/2\ O_2 \longrightarrow HCHO + CO_2 + H_2O$$

$$HCHO + O_2 \longrightarrow H_2O + CO_2$$

Effects of knocking

1. Decreases life of engine
2. Causes Piston wrap.
3. Consumption of fuel is more

Knocking of Diesel Engine

Diesel fuel consists of straight chain hydrocarbons with very less branched chain hydrocarbons and aromatic hydrocarbons. Hence diesel fuel has low spontaneous ignition temperature as compared to gasoline and undergoes combustion with minimum induction lag.

In diesel engine, the fuel is ignited by the application of high pressure and heat. Here air is first drawn into the cylinder and compressed under high pressure. This compression produces heat in the cylinder. At this stage, fuel is injected into the cylinder filled with compressed air as small droplets by jets. The heat from compressed air ignites the diesel fuel and releases gases which pushes the piston. At the end, the cycle is completed by expulsion of hot gases from the cylinder

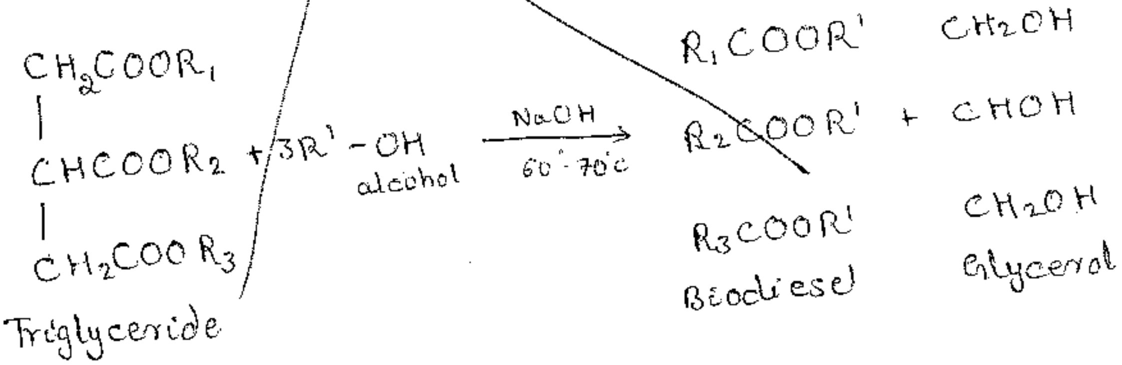
In diesel engine the air temperature and pressure are above the fuel's ignition point. Hence sponteneous ignition of fuel portion already mixed with air occurs. The interval between start of fuel injection and its ignition is called ignition delay or ignition lag. For proper fuctioning of diesel engine, ignition lag must be as small as possible

If the fuel has long ignition lag, then the injected fuel occomolate in the cylinder and when ignition take place it burnt violently with sudden increase in temperature & pressure. This produces a rattling sound & is know as knocking of diesel engine.

Biodiesel:

A fuel for diesel engine, that is produced from a variety of agricultural products such as soyabeans, rape, seeds, palm seeds etc. by transesterification is called biodiesel.

Chemically biodiesel is a long chain of fatty acid monoalkyl esters and is produced by transsesterification of vegitable oils of sunflower seed oil, soyabeans oil, palm oil, rape seed oil etc. These vegitable oil contain triglycerides. The transesterification of these triglycerides of vegitable oil with excess of methanol in presence of base catalyst to give "monomethyl ester of of long chain fatty acid" i.e. biodiesel and glycerine along with oil cake. By gravity method biodiesel is separated out. Oil cake is an excellent organic manure.



$$\begin{array}{l} CH_2COOR_1 \\ | \\ CHCOOR_2 \\ | \\ CH_2COOR_3 \end{array} + \underset{\text{alcohol}}{3R'-OH} \xrightarrow[60^\circ-70^\circ c]{NaOH} \begin{array}{l} R_1COOR' \\ R_2COOR' \\ R_3COOR' \end{array} + \begin{array}{l} CH_2OH \\ CHOH \\ CH_2OH \end{array}$$

Triglyceride, Biodiesel, Glycerol

Advantages:

1) It is produced from renewable energy sources.
2) It create lots self employment & encourage farming activities.
3) It is non-toxic & ecofriendly
4) It is biodegradable & reduces the depletion petroleum sources.
5) It produces highly useful biproducts.
6) It meets all the emission norms.

Antiknocking agents:

compounds that are added to gasoline in order to decrease the knocking tendency [to increase anti-knocking property] are called anti-knocking agent.

The common commercial antiknocking agents are

1) Tetra ethyl lead [TEL] --> $Pb(C_2H_5)_4$

2) Tetra methyl lead [TME] --> $Pb(CH_3)_4$

3) mixed methylethyl lead.

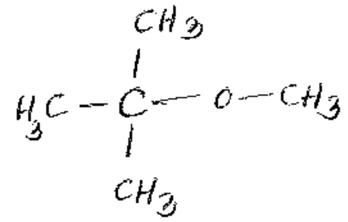
Among the antiknocks TEL is most widely used, since it is cheap and more effective in increasing the octane number of fuel.

During the combustion of gasoline, TEL forms Pb and PbO. These species act as free radical chain inhibitors and thus curtail the propagation of explosive chain reaction and thereby minimizing knocking. However, if TEL is used the species Pb and PbO may get deposited on engine parts and cause mechanical damage. In order to minimize the damage to engine parts, TEL always used along with ethylene dibromide or ethylene dichloride. The function of these halogen compounds is to convert the less voltaile Pb and Pbo into more voltaile $PbBr_2$ or $PbCl_2$ which escape in to air along with exhaust gases.

Unleaded petrol: The octane number of petrol may also increased by mixing the hydrocarbon with high octane number in petrol.

octane number is increased without addition of lead compounds by adding other compounds into it is called unleaded petrol

Unleaded petrol formed by petrol mixed with compounds like methyl tertiary butyl ether [MTBE] which also serve as antiknocking agents but not harmful



$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-O-CH_3$

MTBE

Advantage unleadedpetrol :

1) Increases efficiency of engine
2) It avoids the lead pollution in atmosphere.
3) It allows use of catalytic converter attached to the exhaust in automobile which reduces air pollution due to unburnt hydrocarbon and CO.

~~Power alo~~

Power Alcohol :

Ethyl alcohol is an important fuel. If it is used along ~~petrol in~~ with gasoline in I.C. engine. it is called power alcohol.

Generally gasoline and alcohol are present in the ratio of 4:1. The C.V. of alcohol is low, but it ~~is~~ has good antiknocking propertise with octane number 90. Alcohol mixes gasoline only in presence of ~~Because~~ ~~of~~ Benzene, tetraline or ether.

Advantage :

1) ~~Oct~~ octane number alcohol is high hence octane number fuel also increases.
2) posses ~~or~~ excellent antiknocking characterstics.

3) There is no considerable decrease in power output.

4) There is nostarting difficulty.

Disadvantage:

1) calorific value of alcohol is low, hence reduces. calorific value of petrol

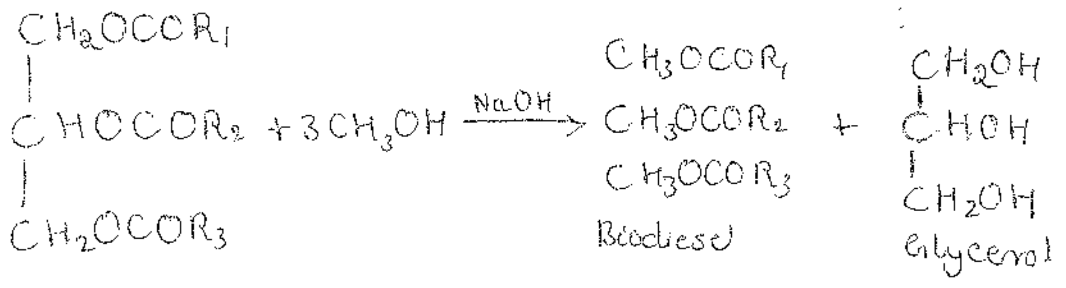
2) Alcohol is easily oxidised to acid and hence cause corrosion

3) Since, the air required for complete combustion of blend is less than air required for petrol. Therefore IC engine system shoud be modified.

Biodiesel:

A fuel for diesel engine, that is produced from a variety of agricultural products such as soyabeans, rape seeds, palm seeds etc. by transesterification is called biodiesel.

Chemically biodiesel is a long chain of fatty acid monoalkyl esters and is produced by transesterification of vegitable oils of sunflower seed oil, soyabeans oil, palm oil, rape seed oil etc. These vegitable oil contain triglycerides. The transesterification of these triglycerides of vegetable oil with excess of methanol in presence of base catalyst to give "monomethyl ester at of long chain fatty acid" i.e. biodiesel & glycerine along with oil cake. By gravity method biodiesel is separated out. Oil cake is an excellent organic manure.



$$\begin{array}{lcl} CH_2OCOR_1 & & \\ | & CH_3OCOR_1 & CH_2OH \\ CHOCOR_2 + 3CH_3OH \xrightarrow{NaOH} & CH_3OCOR_2 \;\; + & CHOH \\ | & CH_3OCOR_3 & CH_2OH \\ CH_2OCOR_3 & \text{Biodiesel} & \text{Glycerol} \end{array}$$

R_1, R_2 & R_3 are long chain fatty acid.

Advantages

- It is completely degradable, non-toxic & free from sulphur compounds.
- Non edible oils can be used.
- Eco friendly products are formed.

Biogas :

A combustible gas produced by an aerobic digestion of aqueous organic matter mixed with bacterial culture involving methane producers is called biogas and the process is known as "Biomethanation."

The biomethanation of organic matter is carried out in the absence of dissolved oxygen and oxygenated compounds like nitrates and sulphates. The mixed groups of bacterias already available in cow dung slurry. The bacterias decompose the organic matter in three stages and finally produce a gaseous mixture of CH_4 and CO_2.

Composition : 60-70% CH_4 + 30-40% CO_2
traces of H_2S, amonia, water vapour.

Density : 20% lighter than air

Ignition temperature : 650 - 750° C

Calorific value : 18.7 to 26 mJ/m^3

Chemistry of the production of biogas

ⓐ Large macro molecules in organic matter undergo decomposition through hydrolysis results in the formation of amino acids, fatty acids & sugars.

ⓑ Amino acids, fatty acids & sugars are fermented during acidogenesis, forms, volatile fatty acids such as butyric acid, lactic acid, propionic acid and valeric acid

ⓒ The fermented products (butyric acid, lactic acid, propionic ~~anc~~ acid and valeric acid) undergo acetogenesis, the bacteria produces acetic acid, carbon dioxide and hydrogen.

ⓓ Methanogenic organisms consume acetic acid, carbon dioxide and hydrogen and produce methane.

$$4\,CH_3OH + 6H_2 \longrightarrow 3CH_4 + 6H_2O$$

$$4\,CH_3COOH \longrightarrow 4CH_4 + 4CO_2$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

Solar Energy

Solar energy utilization and conversion can be of two types.

1) Direct solar power
2) Indirect solar power

Direct solar power: It involves only one step transformation into a usable form.

Eg: photovoltaic cell is used in generating electricity.

Indirect solar power: It involves more than one transformation to reach usable form.

Eg: Vegetation uses photosynthesis to convert solar energy to chemical energy.

Advantages:
1) Solar power is pollution free
2) Facilities can operate with little maintence
3) Solar power is economical.

Disadvantage:
1) It is only practical in certain areas with favourable cliamate
2) It is not avialable at night & is reduced when ~~there~~ there is cloud cover, decreasing the reliability of peak output performance.
3) Dc power output is obtained.

Solar grade silicon:

There are two types of silicon

a) Metallurgical grade silicon:- contain high concentration of intentional impurities like Boron and phosphorous and unintentional impurities like transition metal atoms are called killer impurities

b) Semiconductor grade silicon:
It is more refined and impurities lever are in ppb level but increase the cost of the solar cell.
Solar grade silicon with tolerable limits of impurities than in semiconductor grade have the same efficiency as like semiconductor grade Si.

~~production of solar grade Si:~~
Quartz and carbon are placed in a crucible. Two carbon electrodes are submerged in the crucible and an ~~electic~~ electric arc struck (1700°C). The mixture gets heated to a high temperature and following reaction take place

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

Silicon is obtained in the molten state from the bottom. CO is further oxidized to carbondioxide and released in to atmosphere.

Refining: Si obtained above needs refining before used in devises. Molten Si obtained above is treated with oxygen and slag forming additives, commonly silica sand. (The elements such as Al, Ca and Mg react with silica sand (SiO_2) to form slag and silicon.

$$4Al + SiO_2 \longrightarrow 3Si + 2Al_2O_3$$

$$2Ca + SiO_2 \longrightarrow Si + 2CaO$$

$$2Mg + SiO_2 \longrightarrow Si + 2MgO$$

$$Si + O_2 \longrightarrow SiO_2$$

Doping of Silicon by Diffusion Technique (n & p type)

Semiconductors are the prime materials used in solar cells. These materials exhibit very low conductivity at room temperature. However, these become conductive at higher temperature and by adding impurity element (doping).

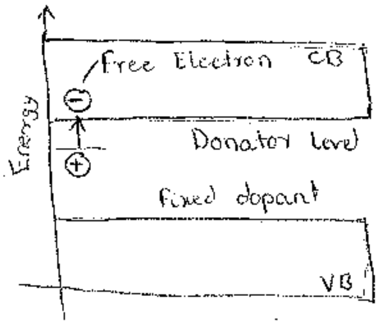
In this technique a region of a semi conductor material is incorporated with dopant atoms by the different impurity atom into the crystal of the material without actually melting it. By this technique the extent of impurity penetration can be controlled to a very small thickness of the material.

n-type Doping:

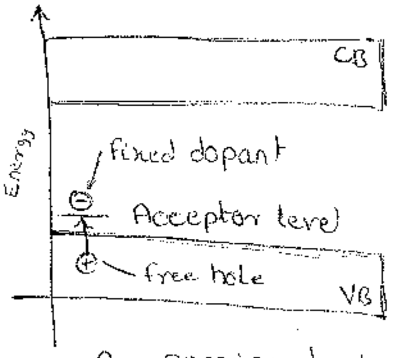
In n-type doping, silicon is doped with elements having fine valence electrons, such as Arsenic, Phosphorous etc Each atom of Arsenic when doped, replace silicon atom Of the five valence electrons of arsenic four will from bonds with silicon atom & one electron left free to conduct electric current. This type of semiconductors are called n-type semiconductor.

p-type Doping:

In p-type doping, silicon is doped with elements having three valence electrons such as Boron. Each atom of boron when doped, replace a silicon in structure. All the three valence electrons of boron will form covalent bonds with neighbouring silicon atom. One position left free & is called a hole which is positively charged. The electron of neighbouring silicon occupies hole and create movement. This type of semiconductors are p-type semiconductor.



n-semiconductor



p - semiconductor.

Purification of Silicon by Zone refining.

This metod gives ultra-pure Si

Principle: Impurities tend to concentrate in the liquid When a part of a solid is melted, the impurities concentrate in the molten zone. When the molten zone is moved along the solid, impurities also migrate. At the interface of the solid and the melt, there will be distribution of impurities. The distribution can be represented by distribution coefficient (kd).

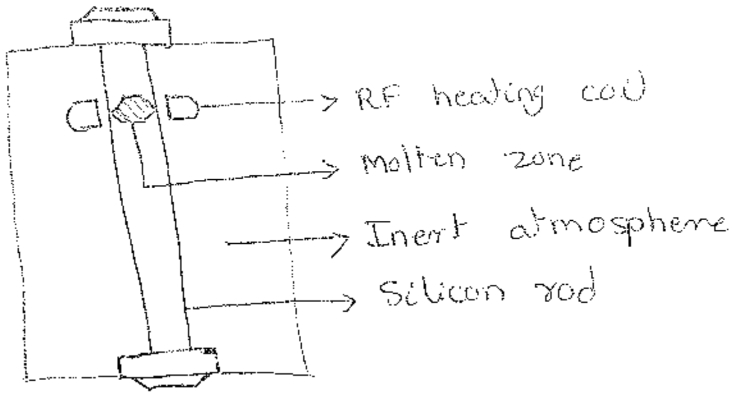
$$Kd = \frac{\text{concentration of impurity in solid phase}}{\text{concentration of impurity in molten phase}}$$

If $kd < 1/3$, concentration of impurities in molten phase is 3 times greater than that of solid phase.
Smaller the kd, better is the purification.

Process:

- A rod Si is clamped vertically and heated by a RF (Radio frequency) coil in a reducing atmosphere
- The RF coil is slowly moved from top to bottom.
- As the molten zone moves down, the impurities also swept down with the molten material.
- When the process is repeated, all the impurities concentration at the bottom portion of the rod. It is cut and removed.
- By this technique the impurities concentration can be decreased to 1 atom/10^{12} atoms of Si (Ultra pure). The purified Si rod is polycrystalline in nature.

It is cut into thin wafers doped suitably to get p-n junction.



Production of Solar grade Silicon by Union Carbide process:

Quartz and carbon are placed in crucible. two carbon electrode are submerged in the crucible and electric is struck (1700°C). The mixture gets heated to high temperature to get Silicon

$$SiO_2 + 2C \longrightarrow Si + 2CO.$$

The Si obtained above needs refining before used in device. Molten Si obtained above treated with oxygen and slag forming additives, commonly silica Sand. The elements such as Al, Ca, Mg react with silica sand to form silicon

$$Si + O_2 \longrightarrow SiO_2$$

$$2Al + SiO_2 \longrightarrow Si + 2Al_2O_3$$

$$2Mg + SiO_2 \longrightarrow Si + 2MgO$$

$$2Ca + SiO_2 \longrightarrow Si + 2CaO$$

The silicon obtained is called metallurgical silicon.

The metallurgical grade silicone obtained above is further processed in four stages to get Solar grade silicon.

Production Solar grade Silicon from metalurgical grad Si by Union carbide process this process developed by Union Carbide Chemicals in USA.

1) Synthesis of silicon hydride:

Metallurgical grade Silicon is treated with HCl gas at 300°C, pressure 40-50 in bar. in boiler bed reactor to form trichlorosilane and small amount of tetrachlorosilane

$$Si + 3HCl \longrightarrow HSiCl_3 + H_2$$

$$Si + 4HCl \longrightarrow SiCl_4 + 2H_2$$

$$SiCl_4 + H_2 \dashrightarrow HSiCl_3 + HCl$$

2) Purification of the silicone hydride:

After many stage rectification gives, pure trichloro silane by passing trichlorosilane through fixed bed columns filled with qualernary ammonium ion exchange resins containg acting catlyst.

$$2HSiCl_3 \longrightarrow H_2SiCl_2 + SiCl_4$$

$$3H_2SiCl_2 \longrightarrow SiH_4 + 2HSiCl_3$$

· The products are separated by distillation. tetra chlorosilane and trichlorosilane are recycled to hydrogenation reactor and the ion exchange resins respectively.

Silicon hydride is further purified by distillation and passed in to reactor containing heated silicon rods.
silane get pyrolysed to ~~to~~ form silicon

$$SiH_4 \longrightarrow Si + H_4$$

Photo voltaic cell

PV cell or Solar cells are often referred to as semiconductor devices that convert sunlight into direct current electricity.

Principle: It is based on photoelectric effect.

i) A photo cell needs to be only two function i. photo generation of charge carriers (positive and negative charges) in light absorbing material.

Seperation of positive and negative charges by a potential gradient within the material.

1) photogeneration of charge carriers:

The energy associated with photon (E) is given by $E = h\nu = hc/\lambda$

when the solar radiation are incident on the solar cell normal to the plane, those photons which possess energy greater than eg (energy gap] are absorbed and electron hole-pairs are formed. Electrons are driven out into the external circuit.

2) Seperation of charges carriers:

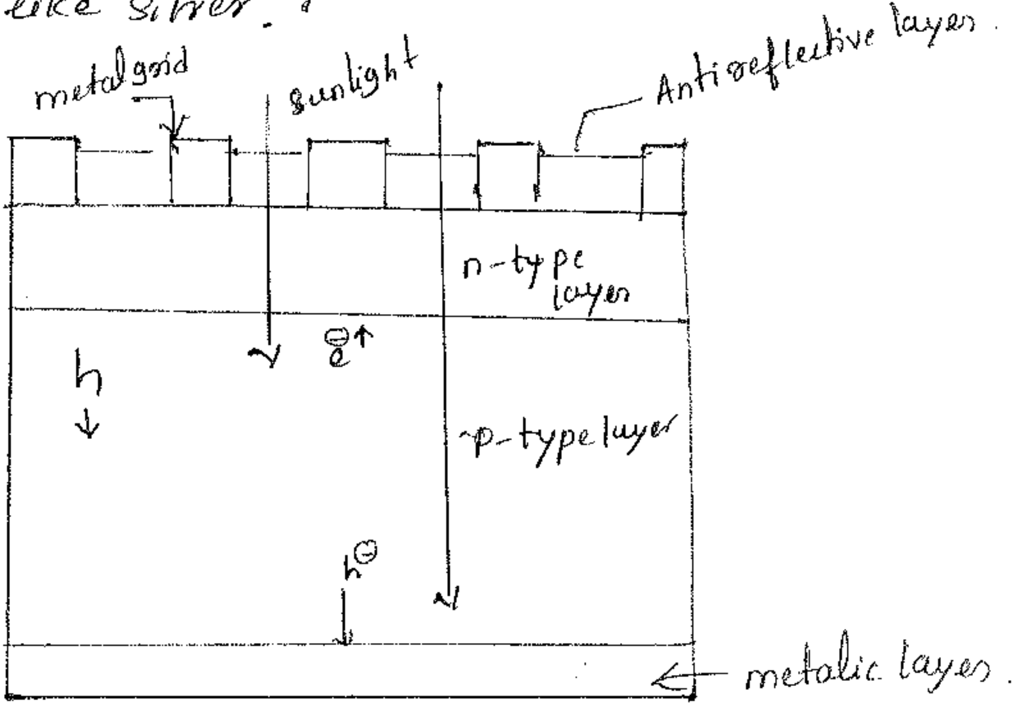
The electron holes can be made to flow through an external circuit (there-by accounting for current) if a potential gradient exists within the cell. In case of silicon, the potential gradient is established by keeping a layer of n-type silicon directly in contact with p-type silicon ie by p-n junctions.

The energy levels of Valence band and conduction band in p-types semiconductors are slightly higher than the energy levels in n-type semiconductors. when p and n-type are in contact, jump in energy level occurs at the interface. A potential gradient

~~agri~~ arises across the junction and this enough to separate the electrons and holes.

construction :

pv cell consists of a front contact ~~with~~ which is made up of metalic grids. Below the front contain a p-n junction (semiconductor diode) of silicon is placed. Bottom of p-n junction is in contact with nobel metal like silver.



Working.

1) The solar radiation is allowed to fall on front contact of solar cell, which consists of n-type region at the top.

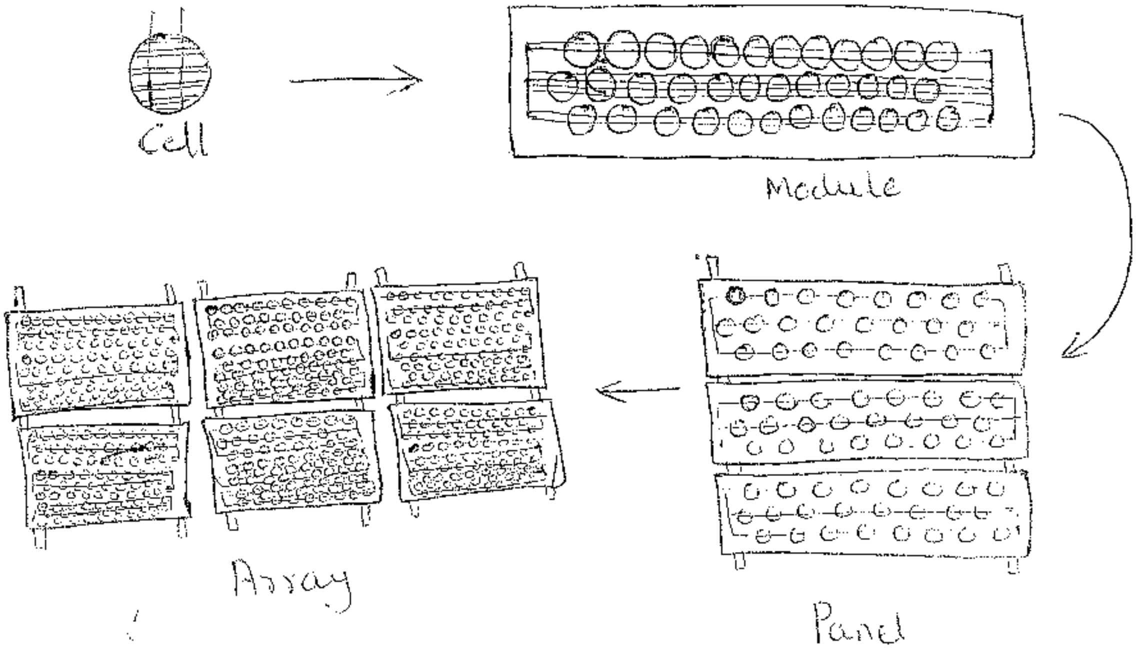
2) The ~~electron~~ photon of solar radiations knock the electrone from the ntype region of the material.

3) The free electron so formed will diffuse from n-type region to p-type region of semiconductor diode and complete the circuit.

4) In this way electrical energy is produced from solar cell or photovoltaic cell and is used for various applicatn

Design: Photovoltaic cells modules, panels and arrays.

Photovoltaic cells are connected electrically in series and/or parallel circuits to produce higher voltages, currents and power levels. Photovoltaic modules consist of PV cell circuits seald in an environmentally protective laminate, and are the fundamental building blocks of PV systems. Photovoltaic panels include one or more PV modules assembled as a pre-wired, field-installable unit. A photovoltaic array is the complete power-generating unit, consisting of any number of PV modules & panels.



Cell: The basic photovoltaic device that is the building block for PV modules. One silicon solar cell produces 0.5 V to 1 V

Module: A group of PV cells connected in series and/or parallel and Encapsulated in an environmentally protective laminate.

Panel: A group of modules that is the basic building block of a PV array.

Advantages of P V cells.

1) Solar source is vast and infinite.
2) No emission no combustion or radio active residues for disposal
3) Low operating costs.
4) No moving parts and no wear or tear.
5) Quick installation.
6) High public acceptance & excellent safety
7) These provide energy in remote areas.

Disadvantages of solar cells.

1) Solar source is a diffuse source i.e. relatively low energy density.
2) High installation costs.
3) Energy can be produced only during day

Nanomaterials

Introduction:

Nanoscience:

Nanoscience deals with the scientific study of objects with sizes in the 1 – 100 nm range in at least one dimension.

Nanotechnology:

Nanotechnology is the creation of functional materials, devices, and systems through control of product on the nanometer (1 to 100 nm) length with possible practical application.

It is a field of science whose goal is to control individual atoms and molecules to create devices that are thousands of times smaller than present technologies permit. An important idea of nanotechnology is that by controlling composition, size, and structure at the nanoscale one can engineer almost any desired properties.

Nano size: 1 nm = 10^{-6} millimeter (mm) = 10^{-9} meter (m)

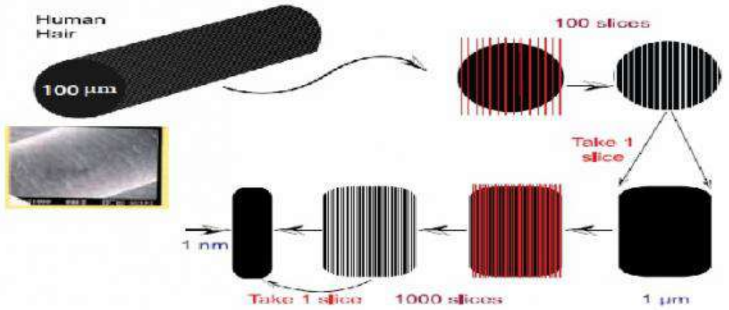
Combination of atoms or molecules to form objects of nanometer scale

Nanomaterials are foundation stone of nanoscience and nanotechnology. Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years.

What are nanomaterials?

The materials which are created from blocks of nanoparticles or they are defined as **a set of substances where at least one dimension is less than approximately 100 nanometers.**

- A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair.

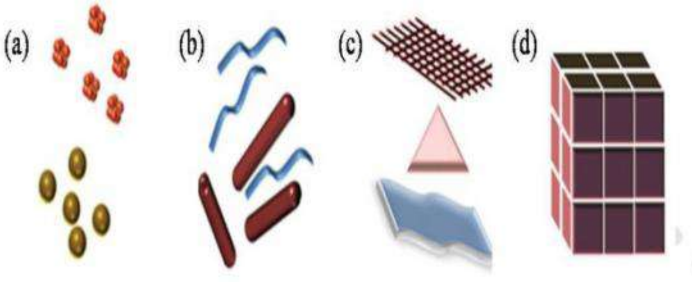


- Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and biological system other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields. Nano carbons such as fullerenes and carbon nanotubes are excellent examples of nanomaterials.

Classification of Nanomaterials:

According to Siegel **Nanostructured** materials are classified, (dimensions of the nanomaterials) are the ordered system of one dimension, two dimensions or three dimensions of nanomaterials, assembled with nanometer scale in certain pattern. Nanomaterials have extremely small size which having at least one dimension 100 nm or less. Nanomaterials can be nanoscale in **a) zero dimension** (eg. **spheres and clusters**), **b) One dimension** (**eg. nanofibers, wires, and rods**),

c) **two dimensions** (**eg. plates, and networks**), and d) three dimensions (eg. particles).. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. Nanomaterials have applications in the field of nano technology, and displays different physical chemical characteristics from normal chemicals (i.e., silver nano, carbon nanotube, fullerene, photocatalyst, carbon nano, silica)



Classification of Nanomaterials **(a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.**

Properties of Nanomaterials:

- Properties depends on size, composition and structure
- Nano size increases the surface area
- Change in surface energy (higher)
- Change in the electronic properties
- Change in optical band gap.
- Change in electrical conductivity.
- Higher and specific catalytic activity
- Change thermal and mechanical stabilities
- Different melting and phase transition temperatures
- Change in catalytic and chemical reactivities.

Nanomaterials have properties that are different from those of bulk materials. Most nanostructure materials are crystalline in nature and they have unique properties. Filling polymers with nanoparticles or nanorods and nanotubes, respectively, leads to significant improvements in their mechanical properties.

Physical Properties: Crystal structure of nanoparticles is same as bulk structure with different lattice parameters. The inter-atomic spacing decreases with size and this is due to long range electrostatic forces and the short range core-core repulsion. The melting point of nanoparticles decreases with size.

Chemical Properties: A large fraction of the atoms are located at the surface of the nanomaterial which increase its reactivity and catalytic activity. The large surface area to volume ratio, the variations in geometry and the electronic structure of nano particles have a strong effect on catalytic properties.

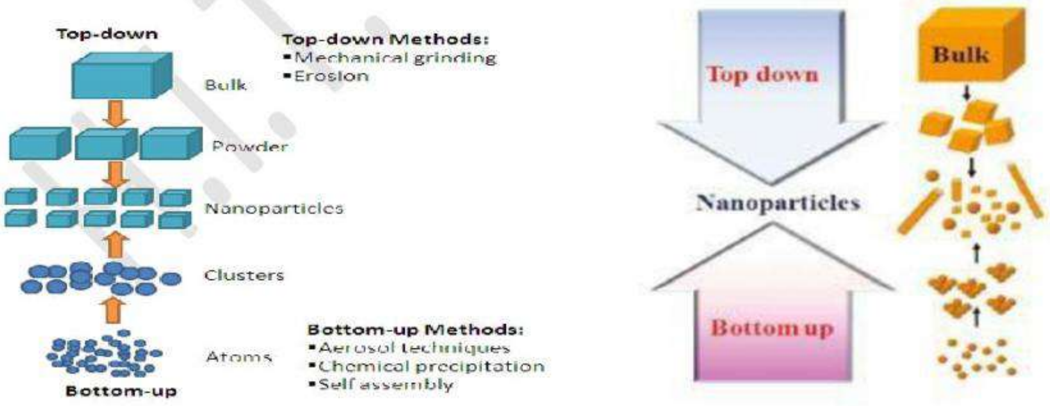
Electrical properties: The energy band structure and charge carrier density in the materials can be modified quite differently from their bulk and in turn will modify the electronic properties of the materials. Nanoparticles made of semiconducting materials like Germanium, Silicon and Cadmium are not semiconductor. Nanoclusters of different sizes will have different electronic structures and different energy level separations. So they show diverse electronic properties which depend on its size.

Magnetic Properties:

The magnetic moment of nano particles is found to be very when compared them with its bulk size**.** Actually, it should be possible that non-ferromagnetic bulk exhibit ferromagnetic-like behavior when prepared in nano range. Bulk gold and Pt are non-magnetic, but at the nano size they are magnetic. This phenomenon opens the possibility to modify the physical properties of the nanoparticles by capping them with appropriate molecules. Actually, it should be possible that non-ferromagnetic bulk materials exhibit ferromagnetic-like behavior when prepared in nano range. One can obtain magnetic nanoparticles of Pd, Pt and the surprising case of Au (that is diamagnetic in bulk) from non-magnetic bulk materials. In the case of Pt and Pd, the ferromagnetism arises from the structural changes associated with size effects. However, gold nanoparticles become ferromagnetic when they are capped with appropriate molecules: the charge localized at the particle surface gives rise to ferromagnetic-like behavior.

Optical properties: One of the most fascinating and useful aspects of nanomaterials is their optical properties. Applications based on optical properties of nanomaterials include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photocatalysis, photoelectrochemistry and biomedicine. The optical properties of nanomaterials depend on parameters such as feature size, shape, surface characteristics, and other variables including doping and interaction with the surrounding environment or other nanostructures.

. Synthesis of Nanomaterials:



Schematic of Bottom-up and Top-down approaches

The goal of any synthetic method for nanomaterials is to yield a material that exhibits properties that are a result of their characteristic length scale being in the nanometer range (~1 – 100 nm). Accordingly, the synthetic method should exhibit control of size in this range so that one property or another can be attained. Often the methods are divided into two main types "Bottom Up approach" and "Top Down approach."

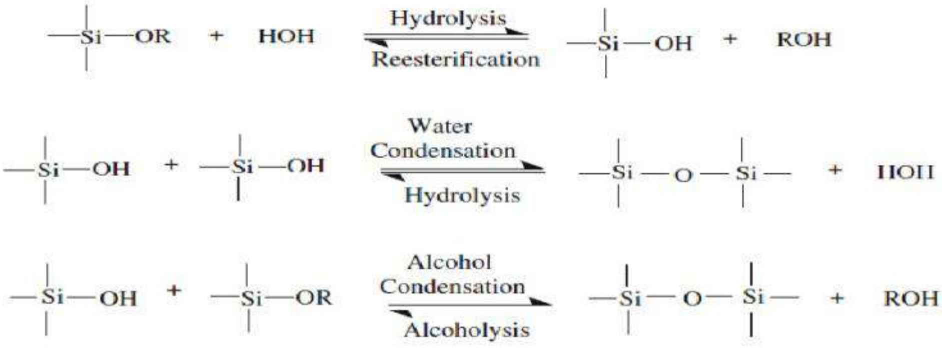
In **Top-down** approach (shape away atoms), one considers the evolution of the properties of a sample as its size is shape down from macroscopic toward nanometric lengths.

In **Bottom-up** approach (or **Atom-Atom Assembly**), Bottom up methods involve the assembly of atoms or molecules into nano structured arrays. In these methods the raw material sources can be in the form of gases, liquids or solids. The latter requiring some sort of disassembly prior to their incorporation onto a nanostructure. Example: Precipitation synthesis techniques.
One assembles atoms and molecules into objects whose properties vary discretely with the number of constituent entities, and then increases the size of the object until this discretisation gives way in the limit to continuous variation. The relevant parameter becomes the size rather than the exact number of atoms contained in the object.

The latter approach is far more popular in the synthesis of nanoparticles owing to several advantages associated with it. Figure shows the general overview of the two approaches. There are many bottom up methods of synthesizing metal oxide nanomaterials, such as hydrothermal, combustion synthesis, gas-phase methods, microwave synthesis and sol-gel processing

1. Sol-gel method:

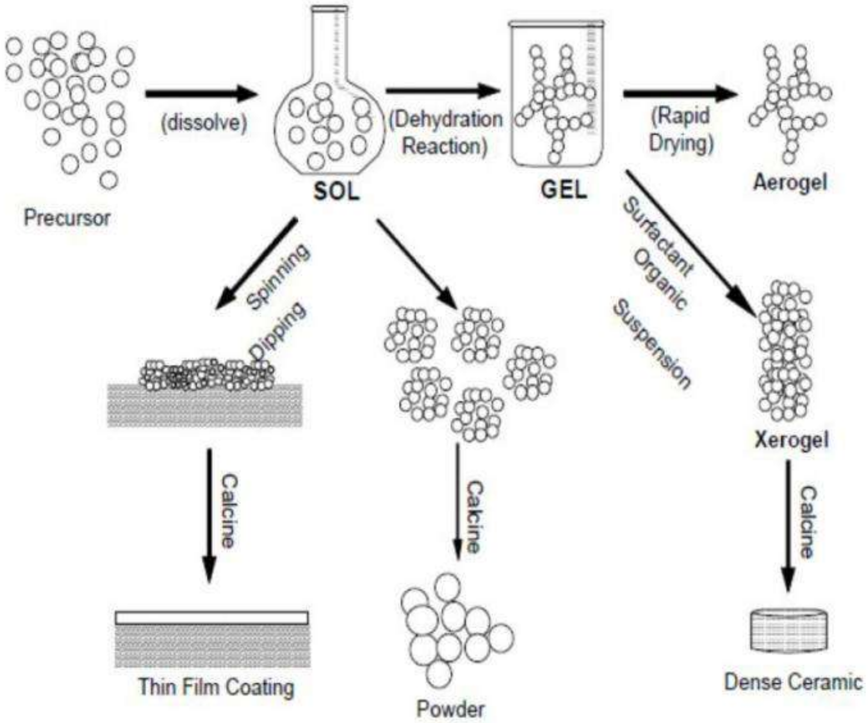
- Sol-gel processing refers to the hydrolysis and condensation of alkoxide-based
- precursors such as $Si(OEt)_4$ (tetraethyl orthosilicate, or TEOS).
- The reactions involved in the sol-gel chemistry based on the hydrolysis and
- condensation of metal alkoxides can be described as follows:



$$\equiv Si-OR + HOH \underset{\text{Reesterification}}{\overset{\text{Hydrolysis}}{\rightleftharpoons}} \equiv Si-OH + ROH$$

$$\equiv Si-OH + \equiv Si-OH \underset{\text{Hydrolysis}}{\overset{\text{Water Condensation}}{\rightleftharpoons}} \equiv Si-O-Si\equiv + HOH$$

$$\equiv Si-OH + \equiv Si-OR \underset{\text{Alcoholysis}}{\overset{\text{Alcohol Condensation}}{\rightleftharpoons}} \equiv Si-O-Si\equiv + ROH$$



Schematic representation of sol-gel process of synthesis of nanomaterials.

Over all Steps:

Step 1: Formation of different stable solutions of the alkoxide (the sol).

Step 2: Gelation resulting from the formation of an oxide- or alcohol- bridged network (the gel) by a polycondensation or polyesterification reaction

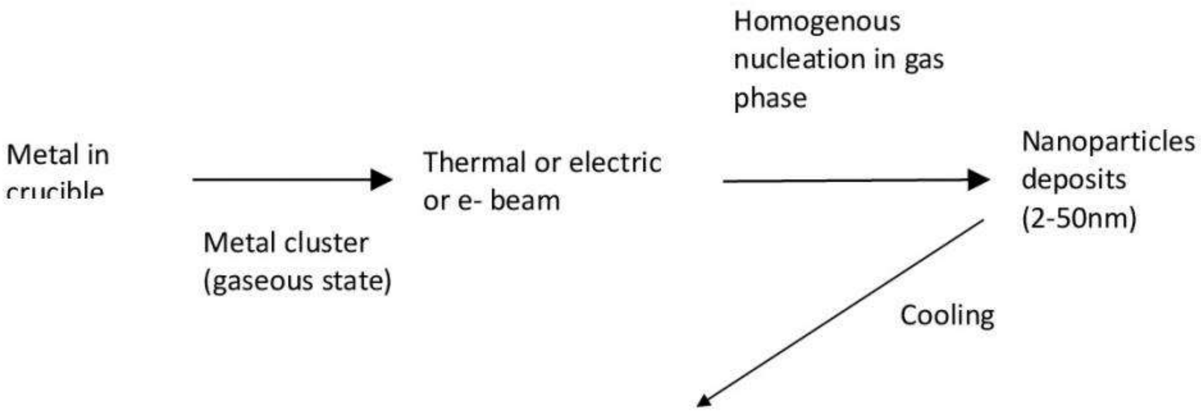
Step 3: Aging of the gel, during which the polycondensation reactions continue until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores.

Step 4: Drying of the gel, when water and other volatile liquids are removed from the gel network.If isolated by thermal evaporation, the resulting monolith is termed a *xerogel*. If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an *aerogel*.

Step 5: Dehydration, during which surface- bound M-OH groups are removed, there by stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperatures up to 800^0C.

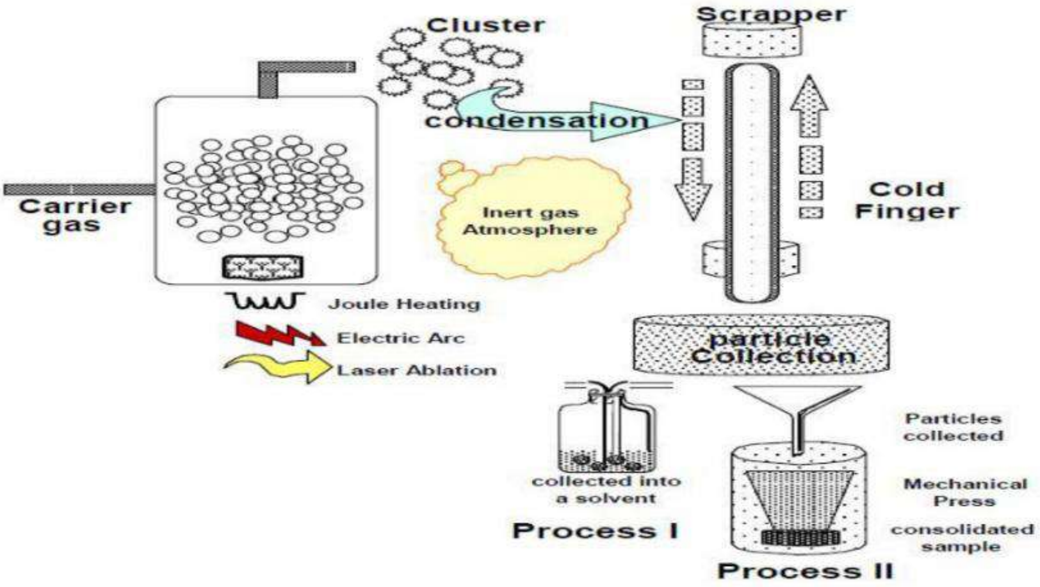
Step 6: Densification and decomposition of the gels at high temperatures ($T>800^0$C). The pores of the gel network are collapsed, and remaining organic species are volatilized. The typical steps that are involved in sol-gel processing are shown in the schematic diagram.

2. Gas Condensation Processing (GCP)-Bottom-up approach:



Method:

- In this technique, a metallic or inorganic material, e.g. a suboxide, is vaporized using thermal evaporation sources such as crucibles, electron beam evaporation devices or sputtering sources in an atmosphere of 1-50 mbar He (or another inert gas like Ar, Ne, Kr).
- The cluster or particle size depends critically on the residence time of the particles in the growth system and can be influenced by the gas pressure, the kind of inert gas, i.e. He, Ar or Kr, and on the evaporation rate/vapour pressure of the evaporating material.
- The synthesis of nanocrystalline pure metals is relatively straightforward as long as evaporation can be done from refractory metal crucibles (W, Ta or Mo).



Schematic representation of typical set-up for gas condensation synthesis of nano materials

- If metals with high melting points or metals which react with the crucibles, are to be prepared, sputtering, i.e. for W and Zr, or laser or electron beam evaporation has to be used.
- Composite materials such as Cu/Bi or W/Ga have been synthesised by simultaneous evaporation

from two separate crucibles onto a rotating collection device. It has been found that excellent intermixing on the scale of the particle size can be obtained.

•Nanocrystalline oxide powders are formed by controlled postoxidation of primary nanoparticles of a pure metal (e.g. Ti to TiO_2) or a suboxide (e.g. ZrO to ZrO_2). Although the gas condensation method including the variations have been widely employed to prepared a variety of metallic and ceramic materials, quantities have so far been limited to a laboratory scale.

• The quantities of metals are below 1 g/day, while quantities of oxides can be as high as 20 g/day for simple oxides such as CeO_2 or ZrO_2. These quantities are sufficient for materials testing but not for industrial production.

Advantages:

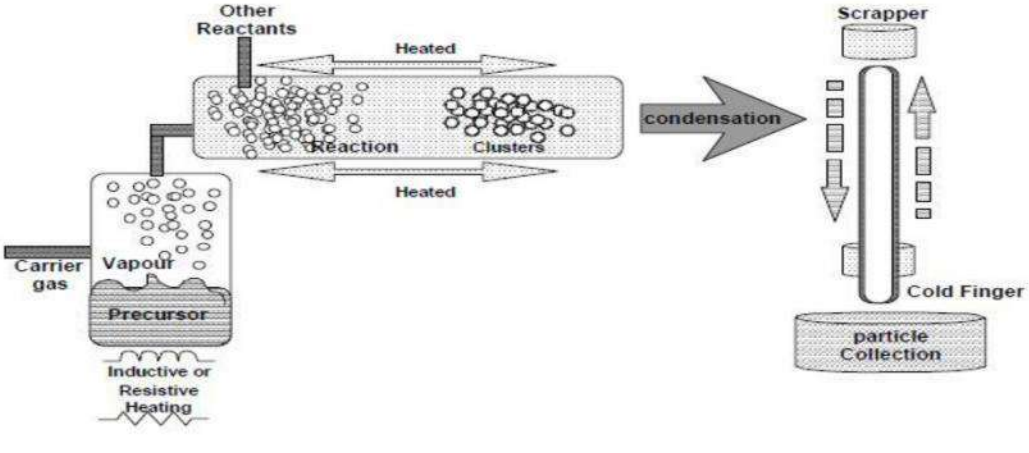
- Major advantage over conventional gas flow is the improved control of the particle sizes.
- These methods allow for the continuous operation of the collection device and are better suited for larger scale synthesis of nanopowders.
- However, these methods can only be used in a system designed for gas flow, i.e. a dynamic vacuum is generated by means of both continuous pumping and gas inlet via mass flow controller.

Limitation:-

1.Control of the composition of the elements has been difficult and reproducibility is poor.
2.Oxide impurities are often formed.
3. The method is extremely slow.

3. Chemical Vapour Condensation (CVC)

The schematic figure of Chemical Vapour Condensation or the CVC process shown is shown below.



- Involves pyrolysis (heat treatment) of vapors of metal organic precursors (starting materials) like Hexamethyldisilazane $(CH_3)_3Si\text{-}NH\text{-}Si\text{-}(CH_3)_3$ to produce $SiC_xN_yO_z$.
- Evaporate source in the GPC is replaced by a hot wall reactor in the CVC process.

•Precursor residence time is the key parameter to control the size of nanoparticle here (gas flow rate, pressure, heating temperature can be controlled).

•Adjusting the residence time of the precursor molecules by changing the gas flow rate, the pressure difference between the precursor delivery system and the main chamber occurs.

• Then the temperature of the hot wall reactor results in the fertile production of nano sized particles of metals and ceramics instead of thin films as in CVD processing.

• In the simplest form a metal organic precursor is introduced into the hot zone of the reactor using mass flow controller. In addition to the formation of single phase nanoparticles by CVC of a single precursor the reactor allows the synthesis of

1. Mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of the reactor, and
2. Coated nanoparticles, i.e., n-ZrO_2 coated with n-Al_2O_3 or vice versa, by supplying a second precursor at a second stage of the reactor. In this case nanoparticles which have been formed by homogeneous nucleation are coated by heterogeneous nucleation in a second stage of the reactor.

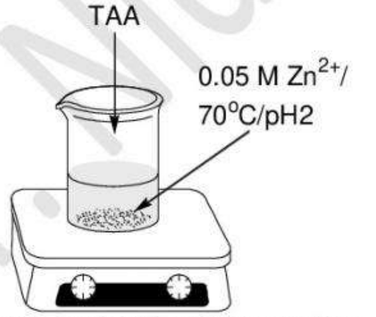
•Because CVC processing is continuous, the production capabilities are much larger than in Gas condensation processing.

• Quantities in excess of 20 g/hr have been readily produced with a small scale laboratory reactor. A further expansion can be envisaged by simply enlarging the diameter of the hot wall reactor and the mass flow through the reactor.

4. Precipitation method:

This method is more economical and wide range used for the synthesis of nonmaterials in the form of oxide may be of single component or more than one components.

Synthesis Method

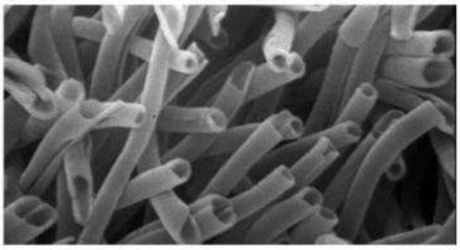


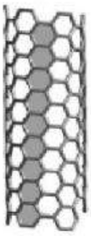
- Nanomaterials are produced by precipitation from a solution.
- In this method by the precipitation of inorganic metal salts like chloride, nitrate, acetate etc are dissolved in solvent like water
- The method involves high degree of homogenization and low processing temperature.
- ZnS powders were produced by reaction of aqueous zinc salt solutions with thioacetamide (TAA).
- Precursor zinc salts were chloride, nitric acid solutions, or zinc salts with ligands (i.e., acetylacetonate, trifluorocarbonsulfonate, and dithiocarbamate).
- The precipitate is then washed with distilled water, filtered and dried.
- The dried precipitate on calcined to obtain final metal oxide nano powder.

Nano scale materials-

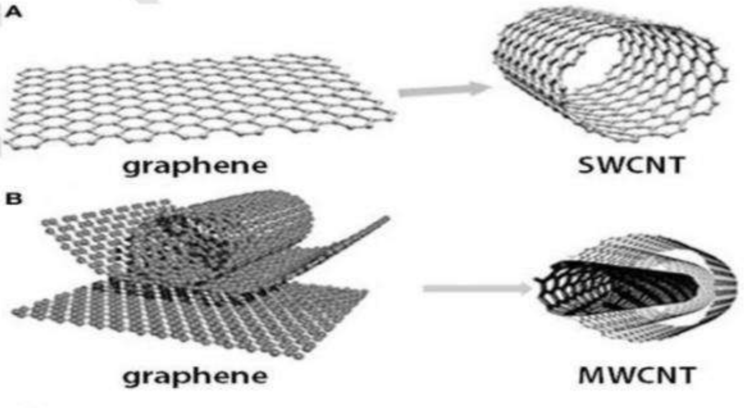
1. Carbon Nanotubes (CNT)

- **Carbon Nanotubes (CNTs)** are allotropes of carbon. These cylindrical carbon molecules have interesting properties that make them potentially useful in many applications in nanotechnology, electronics, optics and other fields of materials science, as well as potential uses in architectural fields. They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat. Their final usage, however, may be limited by their potential toxicity.





- CNTs are at least 100 times stronger than steel, but only one-sixth as dense. In addition, they conduct heat and electricity far better than copper. So, CNTs can be used in tiny, physically strong conducting devices.
- CNTs have been filled with potassium atoms, making them even better electrical conductors.
- CNTs may be synthesized, with sizes ranging from a few microns to a few nanometers and with thicknesses of many carbon layers down to single-walled structures. The unique structure of these nanotubes gives them advantageous behavior relative to properties such as electrical and thermal conductivity, strength, stiffness, and toughness.
- Types of Carbon Nanotubes: i) Single walled nanotubes (SWNTs) ii) Multi walled nanotubes (MWNTs).
- A single-walled carbon nanotube (SWNT) consists of a single graphene cylinder whereas a multi-walled carbon nanotube (MWNT) comprises of several concentric graphene cylinders.

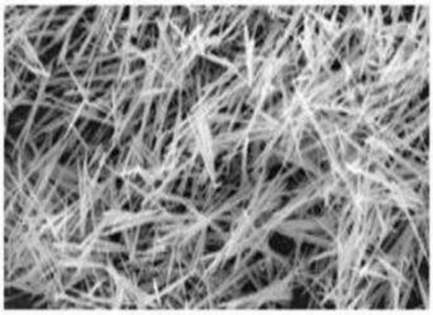


Application of Carbon Nano tubes:

- Bicycle components
- Wind turbines
- Flat panel displays
- Scanning probe microscopes
- Sensing machines

- The sports equipment like bats of baseball, hockey sticks, archery arrows and surf boards etc.
- Batteries with long lifetime
- Electronics
- Electrical Circuits:
- Paper Batteries:
- Solar Cells

2. **Nanowires:** Nanowires are microscopic wires that have a width measured in nanometers. **It is defined as the ratio of the length to width being greater than 1000 times.** A nanowire is a connecting structure that has a diameter of 10^{-9} meters, which is extremely small.



- Typically, the diameter of nanowires range from 40 to 50 nanometers, but their length is not so limited. Since they can be lengthened by simply attaching more wires end to end or just by growing them longer, they can be as long as desired.
- Nanowires are also known as ***Quantum Wires***, these connectors are used to connect tiny components together into very small circuits.
- **Four Different types of Nanowires:** They are (a) **Metal nanowires** are made from nickel, platinum or gold (b) **Semi-conducting** wires are comprised of silicon, indium phosphide or gallium nitride, (c) **Insulating** wires are made of silicon dioxide or titanium dioxide (d) To create a **Molecular** nanowire, the process involves repeating organic or inorganic molecular units in a particular format.
- **Some uses of nanowires include:** Nanowires are simply very small wires that will be able to greatly reduce the size of electronic devices while allowing us to increase the efficiency of those devices.
- The most apparent impact this will have on society would be the increase of storage space for MP3 players, computers, and phones without increasing size.

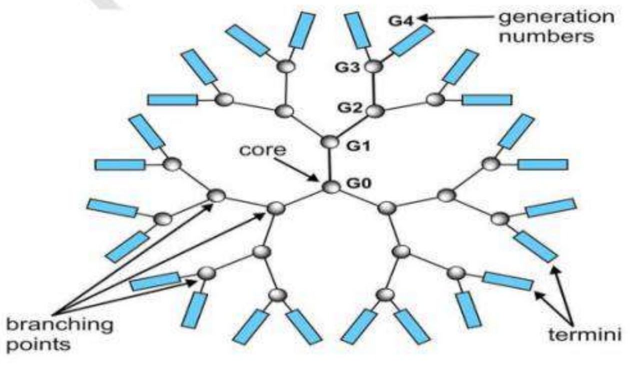
1. Data storage/transfer - transfer data up to 1,000 times faster, and store data for as long as 100,000 years without degradation
2. Batteries/generators - tiny, efficient solar panels, turning light into energy, able to hold 10 times the charge of existing batteries.
3. Transistors, LED's, Optoelectronic devices, Biochemical sensors and Heat-pumping thermoelectric devices.

3. **Fullerenes**

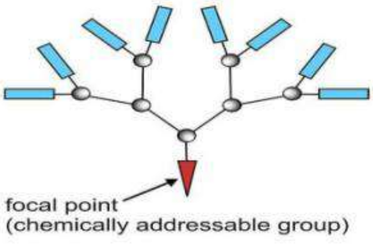
Structure of fullerenes.

- **Fullerenes** are made by the heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The sooty material formed by condensation of vapourized C_n small molecules consists of mainly C60 with smaller quantity of C70 and traces of fullerenes consisting of even number of carbon atoms up to 350 or above.
- Fullerenes can be of a different type C 60, C 70, C 76, C 78, C 80 etc. depending on the number of carbon atoms. The most important fullerene is a C60 containing 60carbon atom which is commonly known as Buckminster fullerene.
- Fullerenes are cage like molecules. C_{60} molecule has a shape like soccer ball and called ***Buckminsterfullerene*.** Spherical fullerenes are also called ***Bucky balls*** in short.
- Fullerenes are a class of cage-like carbon compounds that contained 60 carbon atoms, composed of fused pentagonal and hexagonal carbon rings, looking just like a soccer ball. It contains 20, six- membered rings and 12, five membered rings.
- A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. C-60 can be used as excellent microscopic ball bearings, lubricant and catalyst
- **Some uses of fullerenes include:**
  (1) Used for the conversion of diamonds.
  (2) For making carbon films, double layer capacitors and storage devices.
  (3) Used as lubricants, adhesives, cosmetics, catalysts etc.
  (4) In secondary battery, non-aqueous batteries and in fuel cells as electrodes.
  (5) As gas sensors, temperature sensors, particle sensors and detection of organic vapors.
  (6) Used for the conversion of diamond.

4. Dendrimers



DENDRIMER



DENDRON

- The word Dendrimer comes from the Greek word"DENDRON" meaning tree and "MEROS" meaning part.

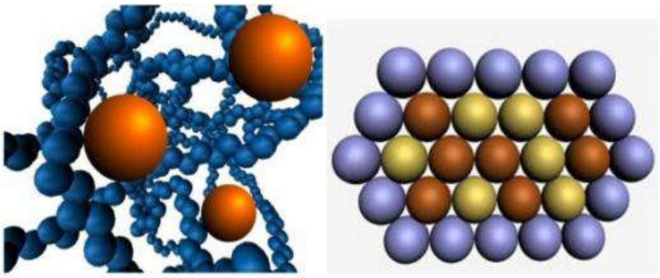
- A dendrimer is generally described as a macromolecule, which is characterized by its highly branched 3D structure that provides a high degree of surface functionality. Dendrimers have often been referred to as the "Polymers of the 21st century".
- Dendrimers are large and complex molecules with very well defined chemical structures.
- Each step of addition of branches to a dendrimer is called as a generation.
- A dendrimer can be grown up to 10-15 generations. Low generation dendrimers have a disc-like structure, while higher generations have a globular or spherical shape.
- Dendrimers are manmade, nanoscale compounds with unique properties that make them useful to the health and pharmaceutical industry as both enhancements to existing products and as entirely new products.
- Dendrimers are constructed by the successive addition of layers of branching groups. Each new layer is called a generation. The final generation incorporates the surface molecules that give the dendrimer the desired function for pharmaceutical, life science, chemical, electronic and materials applications.
- Because they are built up layer by layer and the properties of any individual layer can be controlled through selection of the monomer, they are ideal building blocks in nanochemistry for the creation of more complex three-dimensional structures.
-
- In addition, the chemical reactivity and properties of their periphery and core can be controlled easily and independently.

Some uses of dendrimers include:

- Targeted And Controlled Release Drug Delivery.
- Delivery of Anticancer Drugs
- Dendrimer As Solubility Enhancers
- Cellular Delivery Using Dendrimer Carriers
- Dendrimers As Nano-Drugs
- Dendrimers In Photodynamic Therapy
- Diagnostics-MRI
- Dendritic Catalysts / Enzymes
- Metallodendritic catalysts.
- Catalysis with phosphine-based dendrimers
- Catalysis with (metallo) dendrimers containing chiral ligands.
- Non-metal containing dendrimers.
- Industrial Processes.

5. Nanocomposites

- **Nanocomposite** is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material.

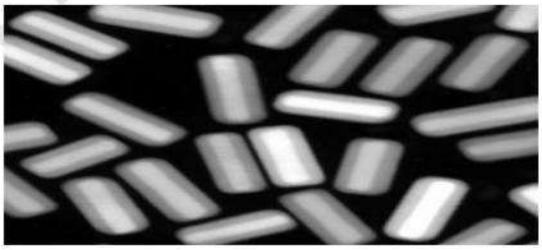


- **Nanocomposites encompass a large variety of systems composed of dissimilar components that are mixed at the nanometer scale.** These systems can be one-, two-, or three-dimensional; organic or inorganic; crystalline or amorphous.
- Nanocomposites can be classified into three types,
  1. Ceramic Matrix Nanocomcomposites (CMNCs)
  2. Metal Matrix Nanocomcomposites (MMNCs) and
  3. Polymer Matrix Nanocomcomposites (PMNCs)
- The behavior of nanocomposites is dependent on not only the properties of the components, but also morphology and interactions between the individual components, which can give rise to novel properties not exhibited by the parent materials.
- Most important, the size reduction from micro composites to nanocomposites yields an increase in surface area.

Some uses of nanocomposites include:

1. In producing batteries with greater power output.
2. In speeding up the healing process for broken bones.
3. In producing structural components with a high strength to weight ratio.
4. In making lightweight sensors with nanocomposities.
5. As light weight materials in vehicles for fuel economy.
6. It is economically beneficial for artificial joints.

6. Nanorods



- In nanotechnology, **nanorods** are one morphology of nanoscale objects. Each of their dimensions range from 1–100 nm.
- They may be synthesized from metals or semiconducting materials. Standard aspect ratios (length divided by width) are 3-5.
- Nanorods are produced by direct chemical synthesis. A combination of ligands act as shape control agents and bond to different facets of the nanorod with different strengths. This allows different faces of the nanorod to grow at different rates, producing an elongated object.

- **Some uses of nanorods include:**

1. One potential application of nanorods is in display technologies, because the reflectivity of the rods can be changed by changing their orientation with an applied electric field.
2. Another application is for microelectromechanical systems (MEMS). Nanorods, along with other noble metal nanoparticles, also function as theragnostic agents.
3. Nanorods absorb in the near IR, and generate heat when excited with IR light. This property has led to the use of nanorods as cancer therapeutics. Nanorods can be conjugated with tumor targeting motifs and ingested. When a patient is exposed to IR light (which passes through body tissue).
4. Nanorods selectively taken up by tumor cells are locally heated, destroying only the cancerous tissue while leaving healthy cells intact.
5. Nanorods based on semiconducting materials have also been investigated for application as energy harvesting and light emitting devices.

Nanocrystals and Clusters

Nanocrystals are crystals of nanometer dimensions, usually consisting of aggregates of a few hundred to tens of thousands of atoms combined into a cluster. Nanocrystals have typical dimensions of 1 to 50 nanometers (nm),

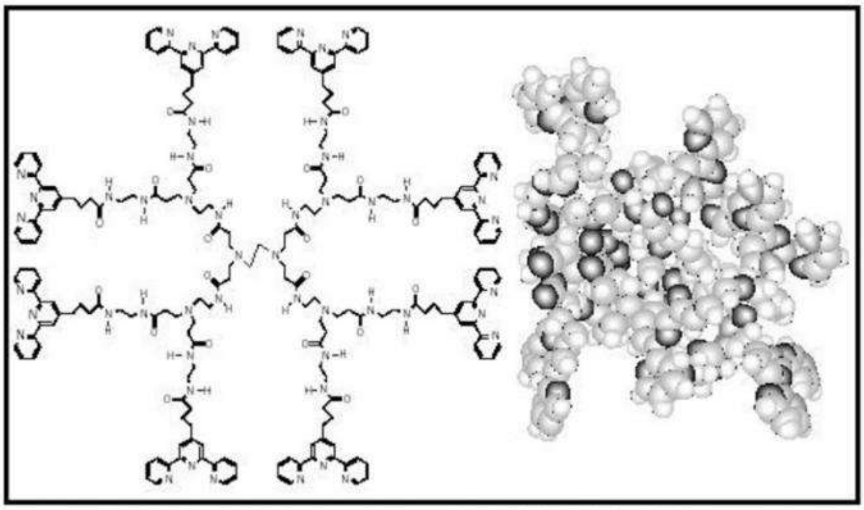


Figure 1. Molecular representation of a dendrimer (left) and a 3-D molecular model of the same dendrimer (right).

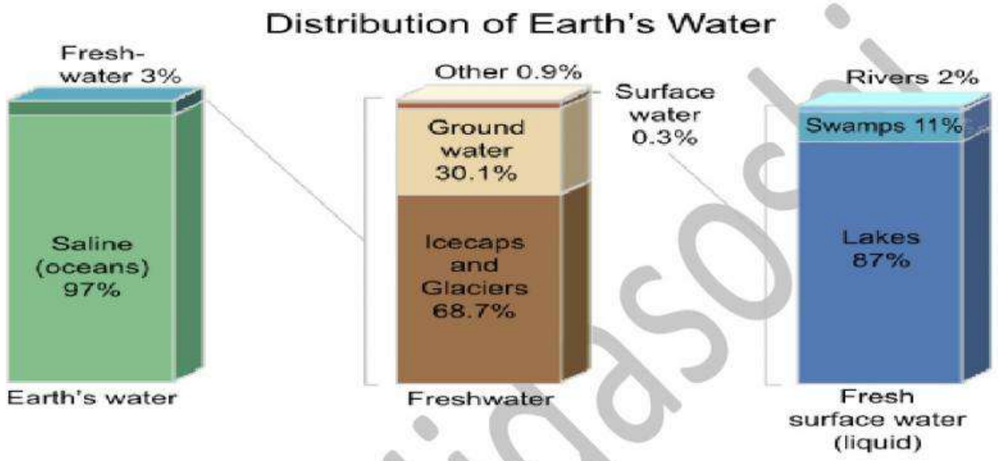
and thus they are intermediate in size between molecules and bulk materials and exhibit properties that are also **intermediate** . For example, the small size of semiconductor quantum "dots" leads to a shifted light emission spectrum through quantum confinement effects—with the magnitude of the shift being determined by the size of the nanocrystal. Nanocrystals are of great interest because of their promise in high density data storage and in optoelectronic applications, as they can be efficient light emitters. Nanocrystals have also found applications as biochemical tags, as laser and optical components, for the preparation of display devices, and for chemical**catalysis** .

Hydrothermal method:

Hydrothermal synthesis is typically carried out in a pressurized vessel called an autoclave with the reaction in aqueous solution . The temperature in the autoclave can be raised above the boiling point of water, reaching the pressure of vapour saturation. Hydrothermal synthesis is widely used for the preparation of metal

Water Technology

Water plays an important role in our daily life. 70% of the earth is covered by water, out of which 97% is in oceans and hence saline (not usable) 2% is locked in polar ice caps (not available for use) only 1% is available as surface and ground water (Usable) Though the ground water is clear, it contains dissolved salts, hence not pure. Surface water contains dissolved salts, dissolved gases, and suspended impurities. Water is an essential commodity for any engineering industry. The sources for water are of stationary or of flowing type. Depending on the source, water may consist of impurities insoluble or dispersed or suspended form. The impurities in water impart some undesirable properties to water and hence render water ineffective for the particular engineering application.



Importance of water

- Living things are indeed in need of water.
- It cleanses our body.
- It energises us every day.
- It keeps our body temperature at the right level.
- It is one of the essential resources for our health.

Uses of water: Domestic, Agriculture, Industry, Power generation: Hydroelectric power.

The chief sources of waterfall in two main groups,

1. Surface water
2. Underground water

Surface Water: Surface water exists as

i) Rainwater: It is the main source of water obtained as a result of evaporation of seawater. Rainwater may be the purest form of water. It is made impure by the polluted atmosphere. It contains a considerable amount of industrial gases (like CO_2, SO_2, NO_2 etc.) and suspended solid particles, both of organic and inorganic origin.

ii) River water: It is the water that flows over the surface of the land. River water starts from spring water and fed by rainwater. It flows through a different kind of terrain and dissolves the soluble minerals of the soil. Chlorides, sulphates, bicarbonates of sodium, calcium, magnesium and iron are some of the major mineral salts present in river water. River water also contains organic matter, produced by the decomposition of plants and small particles of sand and rock suspension.

iii) Sea water: Sea Water it is the most impure water. Continuous evaporation of water makes it continuously richer in dissolved impurities. About 3.5% of the seawater contains dissolved salts, out of which 2.6% contains sodium chloride. Sulphates of sodium, bicarbonates of potassium, calcium, magnesium and a number of other compounds.

iv) Lake water: It contains fewer amounts of dissolved materials and high quantity of organic impurities. Its chemical composition is constant.

Underground Water: Underground water shallow and deep springs and wells. About 9.86% of the total freshwater resources are in the form of ground water. A part of rain water which falls on earth surface percolates into the earth and continues its journey till it meets a hard rock where it may be stored or come in the form of spring. During its downward journey, it dissolves a number of salts.

Types of impurities:

1) Dissolved Impurities: -

a) **Dissolved salts:** Inorganic salts of Na, K, Ca, Mg, Al, Fe and traces of other metals as chlorides, sulphates, bicarbonates, etc. Dissolved impurities cause hardness, alkalinity etc.

b) **Dissolved gases –** Most of the water contains dissolved gases like oxygen, nitrogen, CO_2 and some water contains oxides of N and S, NH_3, or H_2S which gives the bad odour.

2) Suspended Impurities: -Mainly aluminium hydroxide, ferric hydroxide, insoluble minerals such as clay, sand etc. Because of these impurities, water gets turbidity, colour, and odour.

a)**Organic impurities:** - Oil, vegetable and animal matter. The presence of organic impurities colour and odour and alters the taste of water.

Inorganic impurities: - Clay and sand. Because of these impurities, water gets turbidity, colour, and odour. Because of these impurities, water gets turbidity, colour, and odour.

3) Colloidal Impurities: - Finely divided silica and clay, organic waste products, amino acids. Because of these impurities, water gets turbidity.

4) Microbial and biological impurities – Pathogenic microorganisms like fungi and bacteria, Spread various disease like typhoid, dysentery, hepatitis etc.

Boiler Feed Water:

In Industry, one of the chief uses of water is a generation of steam by boilers**. The water fed into the boiler for the production of steam is called boiler feed water.**

Requirements of boiler feed water

1. It should have zero hardness.
2. It must be free from dissolved gases like O_2, CO_2, etc.
3. It should be free from suspended impurities.
4. It should be free from dissolved salts and alkalinity
5. It should be free from turbidity and oil.
6. It should be free from hardness causing and scale-forming constituents like Ca and Mg salts.

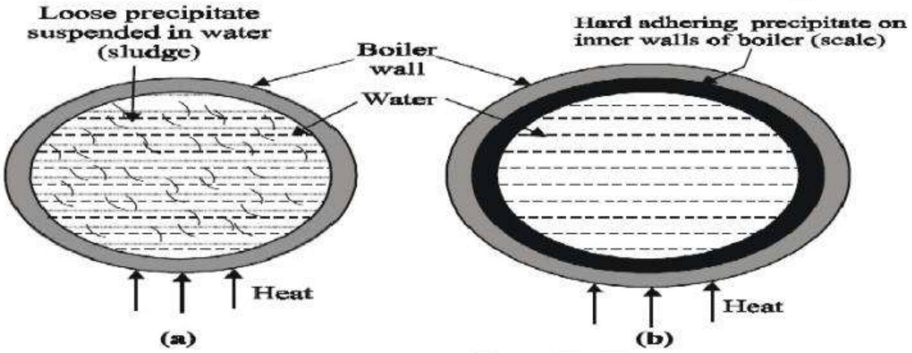
Boiler troubles (or) Disadvantages of using hard water in boilers

If the boiler feed water contains impurities (or) if the hard water obtained from natural sources is fed directly to the boilers, the following troubles may arise.

1. Formation of deposits (scales and sludges).
2. Priming and foaming (carry over).
3. Boiler corrosion.

1. Scale and Sludge Formation in Boilers

In boilers, water evaporates continuously and the concentration of the dissolved salts increases progressively. When the salts concentration reaches their saturation point, they are thrown out of water in the form of precipitates on the inner walls of the boiler.



Scale: If the precipitate forms hard and adherent coating on the inner walls of the boiler is known as scale. It is formed by the substances like $CaSO_4$, Mg $(OH)_2$ and Ca $(HCO_3)_2$.

1. Decomposition of calcium bicarbonate.
2. Deposition of calcium sulphate.
3. Hydrolysis of magnesium salts.
4. The presence of silica.

Scale Formation

i. The scale is a hard, adherent coating forms on the inner walls of the boiler during steam generation.

ii. In a low-pressure boiler, the main scale forming substances are $Ca(HCO_3)_2$ and $MgCl_2$.

iii. In high-pressure boiler, the scale forming substances are mainly $CaSO_4$ and Silica

Scales are difficult to remove even with the help of a hammer and cut in slices. Scales are the main sources of boiler troubles. Formation of scales may be due to

a) In Low-Pressure Boilers

1. Decomposition of Ca $(HCO_3)_2$

$$Ca(HCO_3)_2 \rightarrow \underset{\substack{\text{Soft Scale}\\ \text{(Insoluble)}}}{CaCO_3} + H_2O + CO_2$$

2. Hydrolysis of Magnesium Salts

Dissolved magnesium salts undergo hydrolysis forming magnesium hydroxide precipitate.

$$MgCl_2 + 2H_2O \rightarrow \underset{\substack{\text{Soft Scale}\\ \text{(Precipitate)}}}{Mg(OH)_2} + 2HCl$$

b) In High-Pressure Boilers

1. Deposition of $CaSO_4$

The solubility of calcium sulphate in water decreases with rising of temperature. $CaSO_4$ gets precipitate as hard scale on the heated portion of the boiler. $CaSO_4$ is quite adherent and difficult to remove.

2. Presence of SiO_2 (Silica)

SiO_2 present in water even in small quantities deposits as $CaSiO_3$ and $MgSiO_3$. These deposits stick very firmly to the inner side of the boiler surface and are very difficult to remove.

Disadvantages of Scale Formation

1. Wastage of Fuel

Scale acts thermal insulator in boilers. Because scale has low thermal conductivity. Scale deposit decreases the rate of heat transfer from the boiler to inside water. So, more amount of fuel is required in order to get a steady supply of heat to water. This causes an increase in fuel consumption.

2. Decrease in Efficiency

The scale may sometimes, deposit in the valves, condensers of the boiler and choke them partially. This results in a decrease in efficiency of the boiler.

3. Danger of Explosion

When a thick scale develops, any cracks due to uneven expansion, water comes suddenly in contact with the overheated surface of the iron plate. This causes the formation of a large amount of steam. So sudden high pressure is developed inside the boiler which may lead to an explosion in boilers.

Prevention of Scale Formation

Scale formation in boilers can be prevented by

1. External treatment

This method involves the removal of scale forming impurities from water before feeding to the boiler.

Example

- **Lime soda process:** Softening of water by using lime $Ca(OH)_2$ for to remove bicarbonate hardness and soda ash Na_2CO_3 for to remove non carbonate hardness.
- **Zeolite process:** Zeolite is a hydrated sodium alumino silicate (Na_2O, Al_2O3, $xSiO_2$, yH_2O),(where x=2-10 and y=2-6) is used to remove Ca^{2+} and Mg^{2+}
- **Demineralization process:** Ion exchange process is used to dematerialize the water.

2. Internal treatment

This method involves the addition of chemicals directly to the water in boilers to remove the scale forming substances which were not completely removed during external treatment.

Example

- **Colloidal Conditioning:** - spreading of organic compounds like tannin, agar gel-act as protective colloid-prevent precipitation of scale forming substances
- **Carbonate Conditioning:** Scale formation can be avoided by adding Na_2CO_3 to the boiler water. It is used only in low pressure boilers. The scale forming salt like $CaSO_4$ is converted into $CaCO_3$, Which can be removed easily.

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2\,SO_4$$

- **Calgon Conditioning: Calgon** is sodium hexa Meta phosphate $Na_2\,[Na_4\,(PO_3)_6]$. This substance interacts with calcium ions forming a highly soluble complex and thus prevents the precipitation of scale forming salt.

$$\underset{\text{Calogen-sodium hexa meta phosphate}}{Na_2\,[Na_4\,(PO_3)_6]} \rightarrow 2Na^+ + [Na_4\,(P_6O_{18})]^{2-}$$

- **Phosphate Conditioning:** Scale formation can be prevented by adding sodium phosphate to the boiler water which reacts with the hardness producing ions and forms easily removable phosphate salts of respective ions

$$3CaCl_2\text{ (Boiler water)} + 2\,Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6\,NaCl$$

Sludge: In a boiler, water contains the precipitate loose and slimy is known as sludge. It is formed by the substances like $CaCl_2$, $MgCl_2$, $MgSO_4$ and $MgCO_3$.

1. Sludge is a soft, loose and slimy precipitate forms inside the boiler during steam generation.
2. The main sludge forming substances in water are $MgCO_3$, $MgCl_2$, $MgSO_4$, $CaCl_2$ etc.,
3. Sludges are generally formed at cooler portions of the boiler.
4. Sludges can be easily scraped off with a wire brush.

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Disadvantages of Sludge Formation

1. Sludges are poor conductors of heat, so they waste a portion of the heat generated.
2. Excess of sludge formation decreases the efficiency of the boiler.
3. If sludges are formed along with scales, then both will be deposited on inner walls of the boiler as scales, and then it cannot be removed easily.

Prevention of Sludge Formation

Sludge formation in boilers can be prevented

1. By using well-softened water.
2. Blow-down operation should be carried out (Blow - down operation is a process in which a portion of concentrated water containing large amount of dissolved salts is replaced with fresh water frequently, during steam making).
3. It can be easily scraped off with a wire brush.

2. Priming and Foaming (Carry Over Process)

Steam sometimes may be associated with small droplets of water. Such steam containing liquid water is called wet steam. These droplets of water may carry with them some dissolved salts and sludge materials present in water. This phenomenon is called *Carry Over Process*. This occurs mainly due to Priming and Foaming.

Priming: Process in which some water droplets are carried along with the steam is called priming. The resulting process is called as wet steam or carry over. The process of formation of wet steam in boilers is called as priming.

Priming

Causes : Priming may be caused by

i) High steam velocity.

ii) The Very high water level in the boiler.

iii) Improper boiler design.

iv) Sudden boiling of water.

v) Presence of dissolved salts.

Prevention: Priming can be controlled by

i) Controlling the velocity of steam.

ii) Keeping the water level lower.

iii) Good boiler design.

Foaming: Formation of continuous foam or hard bubblers in boilers is called foaming. These bubbles are carried along with steam leading to excessive priming.

Foaming

Causes : Due to the presence of substance like oil & grease in boiling water., presence of sludge particles

Prevention: Foaming can be prevented by

i) Adding coagulants like sodium aluminate, aluminium hydroxide, ferrous sulphate etc.,

ii) Adding anti-foaming chemicals such as castor oil and synthetic polyamides.

3. Boiler corrosion: The decay of boiler material by its environment is termed as boiler corrosion.

Degradation or destruction of boiler materials (Fe) due to the chemical or electrochemical attack of dissolved gases or salts is called boiler corrosion.

Corrosion in boilers is due to the presence of

i) Dissolved oxygen

ii) Dissolved carbon dioxide

iii) Dissolved salts

i) Dissolved Oxygen: The presence of dissolved oxygen in water is the main cause of boiler corrosion. When water containing dissolved oxygen is heated in the boiler, the dissolved oxygen gets liberated and corrodes the boiler material as follows

$$2Fe + O_2 + 2H_2O \rightarrow 2\ Fe(OH)_2\downarrow$$

$$4\ Fe(OH)_2 + O_2 \rightarrow 2[Fe_2O_3.2H_2O]\downarrow$$

Ferrous hydroxide Rust

Removal of Dissolved Oxygen: Dissolved oxygen can be removed by chemical (or) mechanical methods.

Mechanical method: Dissolved oxygen can also be removed from water by mechanical de-aeration.

Chemical method: Sodium sulphite, hydrazine is some of the chemicals used for removing oxygen.

$$2\ Na_2SO_3 + O_2 \rightarrow 2\ Na_2SO_4$$

Sodium sulphite Sodium sulphate

$$N_2H_4 + O_2 \rightarrow N_2\uparrow + 2\ H_2O$$

Hydrazine

Hydrazine is found to be an ideal compound for removing dissolved oxygen in the water. It reacts with oxygen forming nitrogen and water. Nitrogen is harmless.

ii) Dissolved carbon dioxide: Dissolved carbon dioxide in water produces carbonic acid, which is acidic.

$$CO_2 + H_2O \rightarrow H_2CO_3 \text{ (Carbonic Acid)}$$

Carbon dioxide is also released inside the boiler, if water used for steam generation contains bicarbonates of Calcium and Magnesium.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \rightarrow MgCO_3 + H_2O + CO_2\uparrow$$

Removal of dissolved carbon dioxide

a) Carbon dioxide may be removed by adding calculated amount of NH_4OH into water.

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$

b) Carbon dioxide along with oxygen in water can be removed by mechanical de-aeration.

iii) Dissolved salts

If water used for steam-generation contains dissolved magnesium salts, they liberate acids on hydrolysis.

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

The liberated acid reacts with iron material of the boiler in a chain-like reaction producing HCl again and again.

$$Fe + 2HCl \rightarrow FeCl_2 + H_2$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$$

$$4\ Fe(OH)_2 + O_2 \rightarrow 2[Fe_2O_3.2H_2O]\downarrow$$

Ferrous hydroxide Rust

Thus presence of even a small amount of $MgCl_2$ will cause corrosion of iron to a large extent.

Removal of acids: Corrosion by acids can be avoided by the addition of alkali to the boiler water.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

DISSOLVED OXYGEN (DO):

It is the amount of free molecular oxygen dissolved in water. It is expressed in mg/litre of molecular oxygen. Dissolved oxygen (DO) is essential for the survival of aquatic animals. In a water sample containing biological organisms such as virus, bacteria. etc., the amount of dissolved oxygen (DO) would be less as they utilize it for their growth.

Dissolved oxygen (DO) determination measures the amount of dissolved (or free) oxygen present in water or wastewater. Aerobic bacteria and aquatic life such as fish need dissolved oxygen to survive. If the amount of free or DO present in the wastewater process is too low, the aerobic bacteria that normally treat the sewage will die.

The presence of oxygen in water is a good sign. Depletion of dissolved oxygen in water supplies can encourage the microbial reduction of nitrate to nitrite and sulfate to sulfide. Hence, analysis of dissolved oxygen is an important step in water pollution control and wastewater treatment process control.

In a healthy body of water such as a lake, river, or stream, the dissolved oxygen is about 8 parts per million. The minimum DO level of 4 to 5 mg/L or ppm is desirable for survival of aquatic life.

Determination of DO is by the Winkler's method:

Principle: 1. Dissolved molecular oxygen in water is not capable of reacting with KI, therefore an oxygen carrier such as manganese hydroxide is used. $Mn(OH)_2$ is produced by the action of KOH on $MnSO_4$.

2. $Mn(OH)_2$ so obtained reacts with dissolved molecular oxygen to form a brown precipitate of basic manganic oxide, $MnO(OH)_2$.

3. $MnO(OH)_2$ then reacts with concentrated sulphuric acid to liberate nascent oxygen.

4. Nascent oxygen results in oxidation of KI to I_2.

5. This liberated iodine is then titrated against standard sodium thiosulphate solution using starch as an indicator.

6. Thiosulphate reduces iodine to iodide ions and itself gets oxidized to tetrathionate ion.

Reactions

$$MnSO_4 + 2KOH \rightarrow Mn(OH)_2 + K_2SO_4 \quad ...(1)$$

$$2Mn(OH)_2 + O_2 \rightarrow 2MnO(OH)_2 \quad ... (2)$$

Oxygen carrier Basic Manganese oxide (Brown ppt)

$$MnO(OH)_2 + H_2SO_4 \rightarrow MnSO_4 + 2H_2O + [O] \quad ...(3)$$

$$2KI + H_2SO_4 + [O] \rightarrow K_2SO_4 + H_2O + I_2 \quad ... (4)$$

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI \quad ... (5)$$

$$2NaN_3 + H_2SO_4 \rightarrow 2NH_3 + Na_2SO_4 \quad ..... (6)$$

To destroy nitrates

$$HNO_2 + HN_3 \rightarrow N_2O + N_2 + H_2O \quad .... (7)$$

Procedure:

1. 250 cm^3 of water sample is pipette out into a clean Winkler's flask, 2cm^3 of manganous suphate and 2cm^3alkaline KI containing sodium azide are added.
2. The Winkler's flask was stoppered and shaken well, brown ppt. was formed and it is allowed to settle down for 10 to 15 minutes.

3. Then add 1 cm^3 of concentrated H_2SO_4 is added slowly and mixed well to dissolve the precipitate.
4. Pipette out 100 cm^3 of solution into a clean conical flask and titrate with standard sodium thiosulphate solution till it turns to pale yellow.
5. Then add 2 to 3 drops of starch indicator, titrate against standard sodium thiosulphate solution till the blue colour disappears. Note down the volume of standard sodium thiosulphate solution as V_1 cm^3.

Calculation:

1. Normality of $Na_2S_2O_3$ solution=N_1
2. Volume of $Na_2S_2O_3$ solution=V_1
3. Normality of dissolved oxygen= $\frac{N1 \times V_1}{100}$
4. Amount of dissolved oxygen in terms of equivalent of oxygen=$\frac{N_1 \times V_1 \times 8}{100}\ gm/litre$

$$=\frac{N_1 \times V_1 \times 8 \times 10^6}{100 \times 1000}\ ppm$$

Biochemical oxygen demand or biological oxygen demand: (BOD)

Biochemical oxygen demand is also called biological oxygen demand) is the quantity of dissolved oxygen needed (i.e., demanded) by micro organisms to break down organic material present in one litre(1000cm^3) water sample at 20 °C temperature and for a time period of 5 days.

It represents the quantity of oxygen which is consumed in the course of aerobic processes of decomposition of organic materials, caused by microorganisms. The BOD therefore provides information on the biologically-convertible proportion of the organic content of a sample of water. BOD is stated in mg/l of oxygen and is usually measured within a period of 5 days (BOD_5).

Determining BOD values after five days (BOD_5) has been adopted as a compromise between a short test-period and the detection of a practically complete biological breakdown of organic materials. With domestic effluents, at 20 °C a complete degradation (= 100 % BOD) is achieved only after 20 days (BOD_{20}); however, after only 5 days, 70 % of the biologically convertible substances are broken down.

Measurement of biochemical oxygen demand (BOD):

Two bottles are filled with water sample and dissolved oxygen of the first bottle is determined immediately by the Winkler's method. The second bottle is incubated under 20 $^\circ$C (adjusted to pH between 6.5 and 8.5 in the dark under standard conditions) for 5 days and the dissolved oxygen is once more measured. The difference between the two DO values is the amount of oxygen that is consumed by microorganisms during the 5 days and is reported as BOD_5 (5-day BOD) value of the sample.

Blank Titration:

1. DO in one bottle is determined immediately by taking 250 cm^3 of water sample is pipette out into a clean Winkler's flask 2cm^3 of manganous suphate and 2cm^{3}alkaline KI containing sodium azide are added.

2. The Winkler's flask was stoppered and shaken well, brown ppt. was formed and it is allowed to settle down for 10 to 15 minutes.
3. Then add 1 cm^3 of concentrated H_2SO_4 is added slowly and mixed well to dissolve the precipitate.
4. Pipette out 100 cm^3 of solution into a clean conical flask and titrate with standard sodium thiosulphate solution till it turns to pale yellow.
5. Then add 2 to 3 drops of starch indicator, titrate against standard sodium thiosulphate solution till the blue colour disappears. Note down the volume of standard sodium thiosulphate solution consumed.
6. DO is calculated by Winkler's method and represented as D_1.

Sample Titration:

1. The second bottle is incubated for 5 days at 20^{o}C. After 5 days unconsumed DO is measured as above procedure.
2. Calculated DO content is represented as D_2.

Calculation: The BOD of a sample is given by

$$BOD_5 = \frac{D_1 - D_2}{A} \times B \text{ mg/L}$$

Chemical oxygen demand (COD):

It is a measure of both biologically oxidizable and inorganic matters in a water sample.

It is the amount of oxygen required by organic and inorganic matters in a 1000 ml of waste water using a strong chemical oxidizing agent like acidified $K_2Cr_2O_7$ for refluxing two hours.

Measurement of chemical oxygen demand (COD):

Principle: A known volume of waste water is refluxed with known concentration with known volume of $K_2Cr_2O_7$ solution with dilute H_2SO_4 medium. Add 1gm of $HgSO_4$ (catalyst) and 1gm Ag_2SO_4 (Avoids interference of Cl- ions). The reaction mixture was refluxed about two hours for complete oxidation. Part of $K_2Cr_2O_7$ used is used for the oxidation of impurities. The remaining unreacted $K_2Cr_2O_7$ is determined by titration with standard FAS solution using ferroin indicator till the colour changes from blue green to reddish brown.

Sample Titration:

i) A known volume (Vcm^3) of waste water is pipetted out into a round bottom flask and add known concentration with known volume of $K_2Cr_2O_7$ solution with dilute H_2SO_4. Add 1gm of $HgSO_4$ (catalyst) and 1gm Ag_2SO_4 (Avoids interference of Cl- ions).
ii) The flask is refluxed with reflux condenser and the mixture is refluxed for 2 hours.
iii) The contents are cooled and transferred into a clean conical flask, add 5 drops of ferroin indicator and titrated against standard FAS solution till the colour changes from blue green to reddish brown.
iv) Note down volume of FAS used as A cm^3.

Blank Titration:

i) The above procedure is repeated by taking same volume of distilled water in place of waste water.

ii) Note down volume of FAS used as B cm^3.

Calculation: The COD of the waste water sample is given by

$$\text{COD}=\frac{N(B-A)}{V}\times 8\times 1000\ \text{mg/L}$$

N= Normality of FAS

V= Volume of the waste water sample

A= Volume of FAS used for sample titration

B= Volume of FAS used for Blank titration

Sewage and its treatment: Sewage treatment is the process of removing contaminants from wastewater, primarily from household sewage. It includes physical, chemical, and biological processes to remove these contaminants and produce environmentally safe treated wastewater (or treated effluent).

Treatment Objectives:

i. **Sources: Lakes and rivers-** do not meet all the required specifications of drinking water-contain suspended inorganic and org particles and micro-organics.

ii. Render water free from these disease producing organisms and toxic substances.

iii. Make it free from color, turbidity, taste, odors

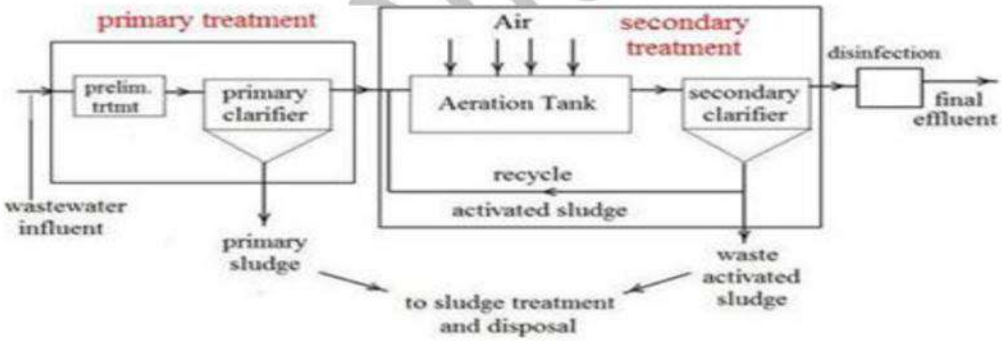
iv. Does not aim at removing all dissolved salt: Does not supply softened water.

When effluent discharged into a river body such as lake, river or sea a number of process occur like physical, chemical and biological characteristics of water change which cause loss of organism. Large quantity of biodegradable waste can affect living organism in the water bodies in which waste are discharged. It is necessary to treat effluent or waste water before discharging in water body.

Sewage is the water containing domestic, industrial, agriculture wastes etc., which is unfit for using.

It is more than 99% water, but the remainder contains some ions, suspended solids and harmful bacteria that must be removed before the water is released into the water streams.

The treatment of domestic sewage is carried out in 3 stages. a) Primary treatment. b) Secondary treatment. c) Tertiary treatment.



Primary and Secondary Wastewater Treatment

1. **Primary Treatment:** In primary treatment Oil, fatty acids and suspended solid and floating material is removed by the use of the following techniques:

Physical Treatment: Physical chemical waste water treatment techniques are techniques to remove the coarse fraction.

a) Screen chamber: Effluent is passes through a screen which is used to remove certain material like wood pieces, plastic, paper, floating debris. Screen chamber remove dead animals, branches of tree, logs of wood and other coarse floating material. The effluent is passed through the bar screens for rag removal. In this section, two automatic bar screen cleaners remove large solids (rags, plastics, etc.) from the raw sewage.

b) Grit Chamber: Grit include sand, ash, egg shell etc . Of diameter less than 0.2 mm. Next, the effluent moves to the grit tanks. These tanks reduce the velocity of the effluent so that heavy particles may fall to the bottom. The solids are pumped to an auger pump which separates the water from the grit while the water moves onward. The grit (mostly inorganic solids) goes to a dumpster which is taken to a landfill.

c) **Floatation or skimming tank :** Fats, waxes, fatty acid, soap, minerals and vegetable oil present in waste water are collectively called as oil and grease. As oil and grease are lighter than water they are normally separated by natural flotation. The air bubbles are passed on the bottom of the tank and floating matter rises and remain on the surface of waste water which can be separated easily.

Pysical chemical Treatment: Physical chemical treatment is normally used to prepare the waste water for the next treatment technique, in many cases biological treatment.

a) Sedimentation:- Coagulation In plain sedimentation, the heavier particles settle down. However fine particles take many hours or sometimes days to settle down. - Colloidal particles which are fine particles of size finer than 0.0001 mm. The water possesses colour which is mainly due to colloidal matter and dissolve organic matter in water. The turbidity in water is mainly due to the presence of very fine particles of clay, silt and organic matter. Sedimentation alone is not sufficient o remove all the suspended matter.

b) Coagulation: The process of coagulation is used to remove colloidal particles from water.- Coagulation is the process in which certain chemical agent is mixed with water then colloidal and suspended particles are agglomerated and form insoluble metal hydroxide known as flocks.

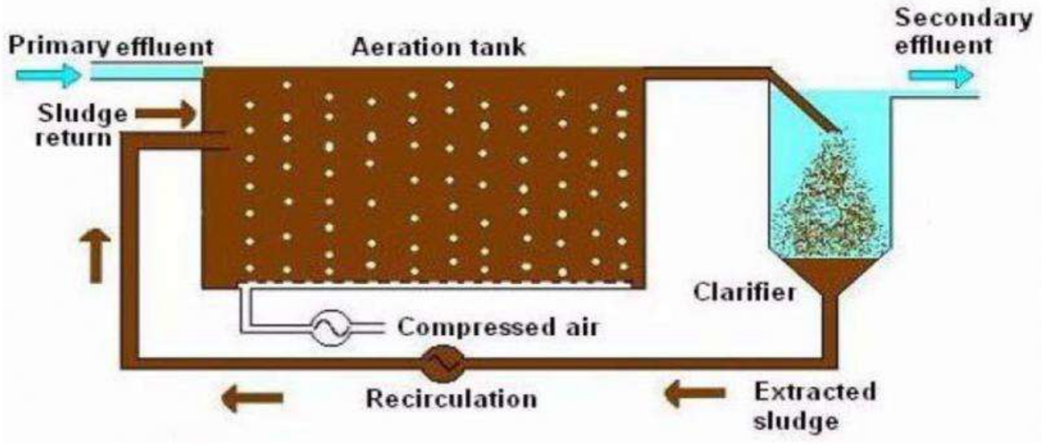
The most common coagulant are aluminum sulfhate, chlorinated copper, ferrous sulpahte, lime, magnesium carbonate, polyelectrolyte and sodium aluminates. Aluminum sulphate, $(Al_2 (SO_4)_3. 18 H_2O$ is also known as potash alum. It is most common coagulant that is available and used in the form of flakes.

c) Flocculation:- Flocculation is the agglomeration of destabilized particles into micro-floc and after into bulky floccules which can be settled called floc. The addition of another reagent called flocculants or a flocculants aid may promote the formation of the floc.

d)Filteration: - The filtering medium in a sand filter consists of three layers. The top layer is thick and is made of fine sand. The middle layer consists of coarse sand, while the bottom layer consists of gravels. The filter is provided with an inlet for water and an under drain channel at the bottom for the exit of the filtered water.

2. Secondary Treatment or Biological Treatment:

It is the process in which microorganism play a very important role for the treatment of effluent. Microorganism like bacteria, fungi decomposes the organic waste and converts into simpler form. The sewage is mixed with activated sludge composed of bacteria into a tank. Air is passed vigorously from bottom of the tank in order to bring about good contact between the organic waste and bacteria under aerobic conditions; oxidation occurs of the organic matters. The effluent along with sludge is sent to a settling tank, where sludge settles down. A part of sludge is reused for purification of fresh batch of sewage and rest is used as fertilizer.



2. Tertiary treatment:

i. **Removal of phosphate:** It is carried out by treating waste water with lime at pH 10.

$$3Ca(OH)_2 + 2PO_4^{2-} \rightarrow Ca_3(PO_4)_2 + 6OH^-$$

ii. **Removal of Heavy metals:** By treating waste water with S^{2-}, heavy metal ions can be removed as insoluble sulphides.

iii. **Degasification:** Dissolved gases can be removed by passing water through a degasifier. In this dissolved gases like H_2S, NH_3 and CO_2 can be removed. Activated charcoal can be used to adsorb any dissolved organic compounds.

iv. **Disinfection:** Destruction of harmful (pathogenic) microorganisms, i.e. disease causing germs. The chemicals used for deactivating or killing micro-organisms **are called disinfectants.**

Some of the important disinfectants are i) Chlorination ii) Ozone iii) UV treatment iv)Hydrogen peroxide.

Chlorination: By adding chlorine compounds like bleaching powder, chlorine gas, chloramines and sodium hypochlorite:

$$Cl_2 + H_2O \rightarrow \underset{\text{Hypochlorous acid}}{HOCl} + H^+ + Cl^-$$

$$NaOCl + H_2O \rightarrow Na^+ + HOCl + OH^-$$

This **produces nascent oxygen** which is a powerful oxidizing agent.

$$HOCl \rightarrow HCl + \underset{\text{Nascent oxygen}}{[O]}$$

The nascent oxygen oxidizes undesirable organic and inorganic compounds, thus removing offensive taste and odour as well as potential toxicity.

Desalination of Brackish Saline Water:

What is Desalination?

A desalination plants turns salt water (brackish or seawater) into fresh water (potable or distillate water).

The process of removing dissolved salts from sea water to make it potable for drinking and suitable for agriculture purpose is called as desalination.

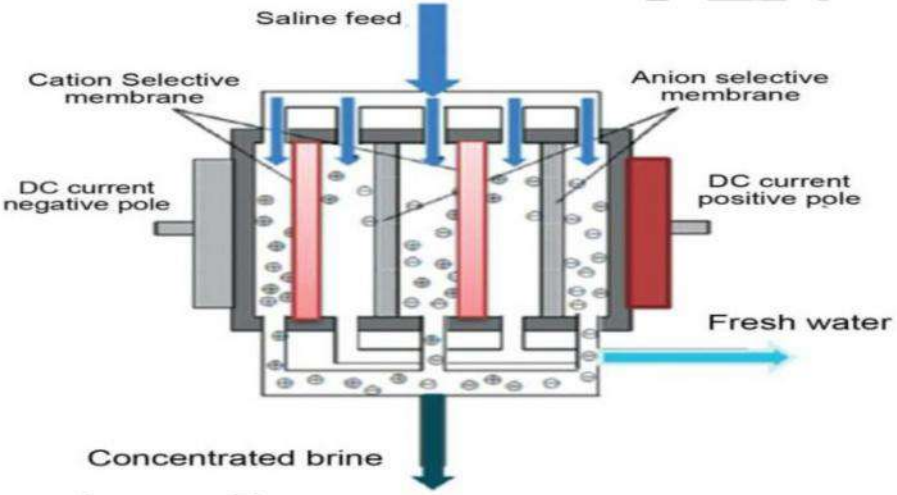
1. Electro dialysis:

The process of removing dissolved ionic impurities (salt, organic dyes) from water by using membranes and electric field is known as electro dialysis.

1. The basic principles of the electro-dialysis (ED) treatment process is dissolved ions present in water have either a positive or negative charge and are attracted to electrodes with an opposite electric charge.
2. Both cation and anion selective membranes to segregate charged ions extracted from a saline water.

Method:

- An electro-dialysis cell consists of a large number of paired sets of polymer membranes. The membranes are ion-selective.
- The cation selective membrane will allow only cations to pass through it, as it consist of functional groups like $-COO^-$, $-SO_3^{--}$ etc (which repel and do not allow anion to pass through it).
- The anion selective membrane will allow only anions to pass through it, as it consists of functional groups like $-NR^{3+}$ (which repel and do not allow cation to pass through it).
- It can be applicable for removing ionic pollutant, salts from sea water. The drinking water can be obtained by this technique.



In a typical ED cell, a series of anion and cation exchange membranes are arranged in an alternating pattern between an anode and a cathode to form individual cells. When a DC potential is applied between two electrodes, positively charged cations move toward the cathode, pass through the negatively charged cation exchange membrane and are retained by the positively charged anion exchange membrane. On the other hand, negatively charged anions move toward the anode, pass through the positively charged anion exchange membrane and are retained by the negatively charged cation exchange membrane. At the end, ion concentration increases in alternate compartments with a simultaneous decrease of ion concentration in other compartments. A schematic view of an ED cell is presented in Figure.

2. Reverse Osmosis

If two solutions of different concentration are separated by a semi-permeable membrane which is permeable to the smaller solvent molecules but not to the larger solute molecules, then the **Solvent will tend to diffuse across the membrane from the less concentrated to the more concentrated solution. This process is called osmosis.**

• When a semi permeable membrane separates a dilute solution from a concentrated solution, solvent crosses from the dilute to the concentrated side of the membrane in an attempt to equalize concentrations.

Reverse osmosis: Reverse osmosis is a membrane separation process for removing solvent from a solution in which solvent will flow from the concentrated to the dilute solution.

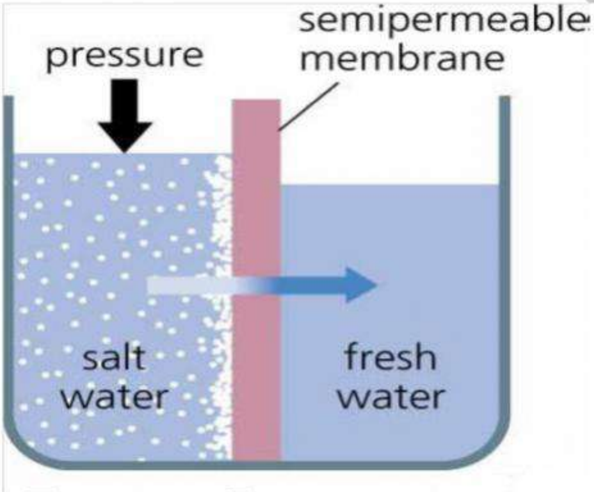
Pure solvent is separated from its contaminates rather than contaminates from the water

• It is done by applying an opposing hydrostatic pressure to the concentrated solution.

• The magnitude of the pressure required to completely slow down the flow of solvent due to osmosis is defined as the "osmotic pressure".

• If the applied hydrostatic pressure exceeds the osmotic pressure flow of solvent will be reversed, that is, solvent will flow from the concentrated to the dilute solution.

• Also called **'Super filtration'** or **'Hyper filtration'**.



- Water is pressurized (15-40kg/cm^2) on one side of a semi permeable membrane.
- The pressure must be high enough to exceed the osmotic pressure to cause reverse osmotic flow of water.
- The membrane is highly permeable to water, but essentially impermeable to dissolved solutes, pure water crosses the membrane.
- Membrane consists of very thin films of cellulose acetate, metha acrylate or polyamide polymers.
- As pure water crosses the membrane, the concentration of dissolved impurities increases in the remaining sea water and, as a consequence, the osmotic pressure increases.
- A point is reached at which the applied pressure is no longer able to overcome the osmotic pressure and no further flow of product water occurs. The membrane becomes stained by precipitated

Softening of water by ion exchange process:

In this method ion exchange resins are used as softening material. In this process cations like Ca^{2+}, Mg^{2+} and anions like Cl^-, SO_4^{2-} which are responsible for hardness are removed respectively by cation exchange resins and anion exchange resins.

Ion exchange resins are insoluble, cross linked, long chain organic polymers with a micro porous structure. The functional groups attached to the chains are responsible for the ion-exchanging properties.

Cation exchange resins (RH^+)

Resin containing acidic functional groups (-COOH, $-SO_3H$) are capable of exchanging their H^+ ions with cations of hard water.

Example: (i) Sulphonated coals.

(ii) Sulphonated polystyrene.

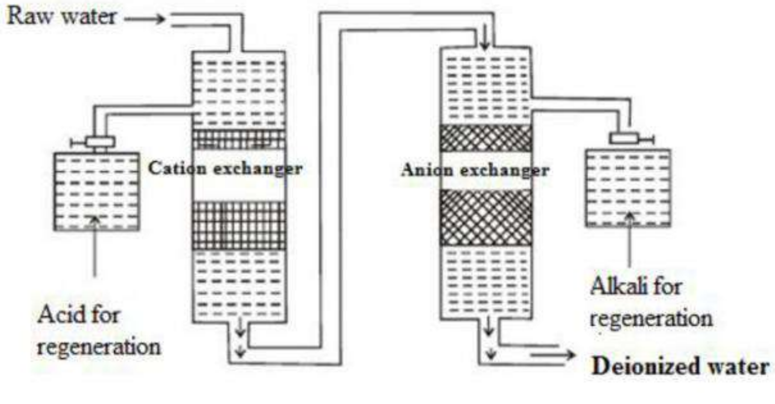
$$R\text{-}SO_3H;\quad R\text{-}COOH \equiv RH2$$

Anion exchange resins (ROH^-): Resins containing basic functional groups ($-NH_2$, -OH) are capable of exchanging their OH- ions with the anions of hard water.

Example: (i) Cross-linked quaternary ammonium salts.

(ii) Urea-formaldehyde resin

$$R\text{-}NR_3OH;\ R\text{-}OH;\ R\text{-}NH_2 \equiv R(OH)_2$$



Process

The hard water first passed through a cation exchange column which absorbs all the cations like Ca^{2+}, Mg^{2+}, Na^+, K^+ etc., present in the hard water.

$$2RH^+ + CaCl_2 \rightarrow R_2Ca + 2HCl$$

$$2RH+ + MgSO_4 \rightarrow R_2Mg + H_2SO_4$$

$$RH^+ + NaCl \rightarrow RNa + HCl$$

The cation free water is then passed through an anion exchange column, which absorbs all the anions like Cl^-, SO_4^{2-} etc., present in the water.

$$2ROH^- + 2HCl \rightarrow 2RCl + 2H_2O$$

$$2ROH^- + H_2SO_4 \rightarrow R_2SO_4 + 2H_2O$$

Thus the water coming out from the anion exchange is free from both cations and anions. This water is known as ion-free water (or) deionised (or) demineralised water.

Regeneration

When the cation exchange column is exhausted, it can be regenerated by passing a solution of dil. HCl (or) dil.H_2SO_4.

$$R_2Ca + 2HCl \rightarrow 2RH^+ + CaCl_2$$

$$R_2Mg + H_2SO_4 \rightarrow 2RH^+ + MgSO_4$$

$$RNa + HCl \rightarrow RH^+ + NaCl$$

When the anion exchange column is exhausted, it can be regenerated by passing a solution of dil. NaOH.

$$2RCl + 2NaOH \rightarrow 2ROH^- + 2NaCl$$

$$R_2SO4 + 2NaOH \rightarrow 2ROH^- + Na_2SO_4$$

Advantages

1. The process can be used to soften highly acidic (or) alkaline water.
2. It produces water of very low hardness (2ppm).

Disadvantages:

1. The equipment is costly and more expensive chemicals are needed.
2. If the water contains turbidity, the output is low due to clogging.