MALLA REDDY COLLEGE OF ENGINEERING & TECHNOLOGY

(An Autonomous Institution – UGC, Govt.of India)

Recognizes under 2(f) and 12(B) of UGC ACT 1956

(Affiliated to JNTUH, Hyderabad, Approved by AICTE –Accredited by NBA & NAAC-"A" Grade-ISO 9001:2015 Certified)

ENGINEERING CHEMISTRY

B.Tech – I Year – II Semester

DEPARTMENT OF HUMANITIES AND SCIENCES

Unit 1: Electrochemistry

Introduction:

Electrochemistry is the branch of chemistry which deals with the transformation of electrical energy to chemical energy and vice versa. In brief it deals with the chemical applications of electricity.

Electrical Energy $\rightleftharpoons$ Chemical Energy

Electric current is a flow of electrons generated by a battery, when the circuit is completed. Electrolysis is one process where electrical energy causes chemical changes. It is carried out in an apparatus called electrolytic cell. The cell contains electrolyte and electrodes. The electrode connected to the positive pole of the current source is called anode. The electrode connected to the negative pole of the current source is called cathode. When an electric current is passed through the electrolytic solution, cations move towards cathode (-ve electrode and anions move towards anode (+ve electrode)

Ex: Electrolysis of water yields H_2 and O_2

In other process, certain chemical reactions takes place in a vessel and produce electric energy. The device is called electrochemical cell. Eg. Galvanic cell, batteries and fuel cells Broadly we can classify the cells as electrolytic cells and electrochemical cells.

Electrolytic cell: A device which converts electrical energy to chemical energy
Electrochemical cell: A device which converts chemical energy to electrical energy

Types of Conductors:

Electrical Conductors: Substances which allow electric current to pass through them are known as electrical conductors. Eg. All metals, graphite, fused salts, aqueous solutions of acids and bases and salts.

Semi conductors: The substances which partially conduct electricity are called semi-conductors. The conducting properties of semi-conducting properties are increased by the addition of certain impurities called "dopping".

Ex: 'Si' and Ge on addition of V group elements like P produces n-type semi-conductor. On addition of III group element like B, Al, produces p-type of semi-conductor.

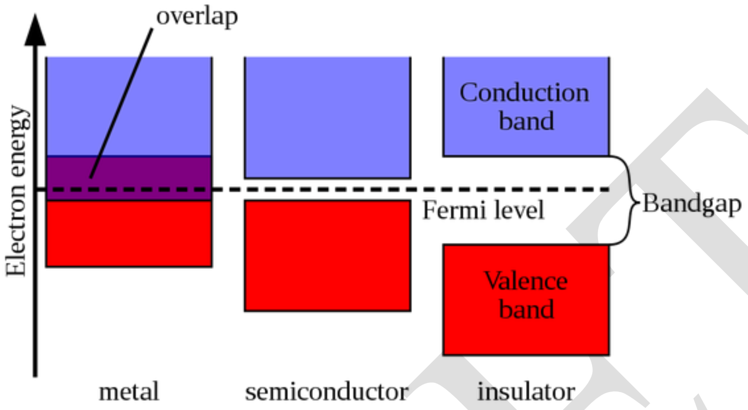
Non-conductors or Insulators: The substances which do not allow electricity are called non-conductors. . Eg. Rubber, wood, paper, all non-metals except carbon.

Conductance: The capacity of a conductor to allow the passage of current through it called conductance. It is a property of conductor which facilitates flow of electricity through it.

$$\boxed{\text{Conductance (C)} = \frac{1}{R}}$$

i.e. The reciprocal of resistance is called conductance. **Units:** Ohm.$^{-1}$

Conductor: The substance which allows the passage of electric current through it is called conductors. **E.g.:-** all metals, graphite, aqueous solution of acids and bases.



Band Theory of Electrical Conductivity

Electric conductors are two types

1. Metallic conductors: They conduct electricity by free electrons, mobile, valance electrons and involve flow of electrons. There is no chemical decomposition during conductance. E.g.; metals, alloys, certain solid salts and oxides.

2. Electrolytic conductors: The substance which allows the electricity to pass-through them in their molten state or in their aqueous solution are called electrolytic conductors or electrolytes. They undergo chemical decomposition.

Eg: Acids and bases.

Non-Electrolytes: Non-Electrolytes do not dissociate into ions even at low dilutions.
Eg: Glucose, Sugar.

Electrolytes are classified into two types:
Strong electrolytes: The electrolytes which completely dissociates in solution at all concentrations. Their conductance is very high**.** Eg. NaCl, HCl, NaOH.

Weak Electrolytes: The electrolyte which partially dissociates at moderate concentration. Their conductance is low as they dissociate only to a small extent even at very high dilutions. Eg: CH_3COOH, NH_4OH, sparingly soluble salts like AgCl, AgBr, AgI, $BaSO_4$, $PbSO_4$ etc

Differences between metallic conductors and electrolytic conductors:

Metallic conductor	Electrolytic conductors
Conductance due to the migration of electrons. **E.g.**: metals, graphite.	Conductance due to the migration of ions in a solution of fused electrolyte. **E.g.:** Acids and bases
Passage of current due to electron flow. No chemical reaction takes place.	Passage of current due to movement of ions. Some chemical reaction takes place.
Free electrons are responsible for electrical conduction.	Free ions are responsible for electrical conduction.
Mass is not transferred	Mass is transferred.
With increase of temp resistance increases and conductance decreases	With increase of temperature resistance decreases and conductance increases.

CONDUCTANCE:

Ohm's Law: Ohm's law states that the current (I) flowing through a conductor is directly proportional to potential difference (E) applied across the conductor and is inversely proportional to the resistance of conductor.

Thus,

$$\boxed{E \alpha I}$$

Where I is the current in amperes, and E is potential difference applied across the conductor in volts.

Thus

$$\boxed{E = IR}$$

or

$$\boxed{R = \frac{E}{I}}$$

Where R is the proportionality constant and is known as the resistance of conductor in ohms. Thus, the resistance of a conductor is directly proportional to the potential difference applied across the conductor and inversely proportional to the current carried by the conductor.

SPECIFIC RESISTANCE: The resistance of a uniform conductor is directly proportional to its length (l) and inversely proportional to the area of the cross- section (a). Thus

$$\boxed{R \alpha l/a}$$

$$\boxed{R = \rho\ l/a}$$

The proportionality constant (ρ) is called as the specific resistance of an electrolytic solution of 1cm in length and 1cm^2 area of cross section. i.e. resistance of 1cm^3 of the electrolytic solution.

UNITS: specific resistance units: Ohm cm

Specific conductance: The reciprocal of specific resistance (ρ) is called as specific conductance. This may be defined as the conductance of 1cm^3 of a material and denoted by K (kappa). Thus

$$\boxed{K = \frac{1}{\rho}}$$

But $\rho = \frac{R \times a}{l}$ $(\because R = \rho \times \frac{l}{a})$ $\therefore$ $\boxed{K = \frac{1}{R} \times \frac{l}{a}}$

Units: Ohms^{-1} Cm.$^{-1}$

Equivalence Conductance:

If one gram equivalent weight of an electrolyte is dissolved in Vml of the solvent, the conductivity of all ions produced from one gram equivalent of an electrolyte at the dilution V is known as equivalent conductance. This is denoted by the symbol λeq.

$$\boxed{\lambda_{eq} = K \times V}$$

V = volume of electrolytic solution in milliliters containing 1g equivalent wt of an electrolyte

$$\boxed{V = \frac{1000}{C} = \frac{1000}{\textit{Normality of the electrolyte solution.}}}$$

Let C be the concentration of a solution containing gm equivalent of electrolyte per liter and the volume V of the solution will be 1000/C.

$$\boxed{\lambda_{eq} = \frac{K \times 1000}{N}}$$

Units: ohm^{-1}cm^{2}eq^{-1} or Scm^{2}eq^{-1}

Molar conductance: Molar conductance is defined as the conductance of an electrolyte solution containing 1 mol of an electrolyte. It is denoted by λm. If Vml is the volume of solution containing 1 g mol of the electrolyte,

$$\boxed{\mu_m = K \times V_m}$$

$$\boxed{V = \frac{1000}{M} = \frac{1000}{\textit{Molarity of the electrolyte solution.}}}$$

$$\boxed{\mu_m = \frac{K \times 1000}{M}}$$

UNITS: $ohm^{-1}\ cm^{2}\ mol^{-1}$

Cell constant:

It is a constant, characteristic of the cell in which the electrolyte is taken and its value depends on the distance between the electrodes and area of cross-section of the electrodes.

$$\text{Cell constant} = \frac{\text{Distance between the electrodes}}{\text{Area of cross} - \text{section of each electrode}}$$

$$\boxed{x = \frac{l}{a}}$$

And specific conductance, $K = \frac{1}{R} \times \frac{l}{a}$

$$\therefore \text{Specific conductance} = \frac{\text{Cell constant}}{R}$$

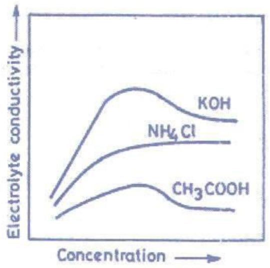
$$\boxed{\text{or } x = K \times R; \quad \text{or } x = \frac{K}{c} \ (\because c = 1/R)}$$

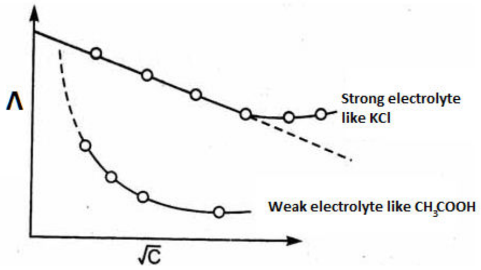
If area of cross-section is in cm^2 and distance between the electrodes is in cm, the unit of cell constant is cm^{-1}.

Effect of dilution on conductance:

Since conductivity of a solution is due to the presence of ions in solution, greater the number of ions in a solution greater will be its conductivity. As the dilution increases more and more, the electrolyte ionizes more and more i.e ionization increase, the conductivity of the solution also increases on dilution. Hence dilution of solution is directly proportional to its conductivity. *Dilution* $\propto$ *conductance*

Effect of dilution on Specific conductance: On dilution, the volume of electrolyte solution increases. Thus, the number of ions present in one centimeter cube of the solution is decreased. Hence, the specific conductance decreases on progressive dilution. Hence, dilution is inversely proportional to specific conductance. *Dilution* $\propto$ *1/K*





Effect of dilution on Equivalent conductance and molar conductance:

- Equivalent and molar conductance of an electrolyte increases on dilution because ionization increases on dilution
- On dilution, the concentration of electrolyte decreases and the retarding influence of charged ions decreases. So speed of ions increases and hence equivalent and molar conductance increases.
- The equivalent and molar conductance increases with dilution because these are the products of specific conductance and volume of the solution containing 1 g equivalent of the electrolyte. (λ_{eq}= K x V). Hence they are directly proportional to volume. On dilution volume of electrolytic solution increase and therefore equivalent and molar conductance increases with dilution.

FACTORS INFLUENCING THE MAGNITUDE OF CONDUCTANCE OF AN ELECTROLYTIC SOLUTION:

1. **Nature of electrolyte:** A strong electrolyte which ionizes completely has a large conductance while a weak electrolyte which partially ionises has low conductance.
2. **Concentration of electrolyte:** If an electrolyte is diluted, the extent of ionization increases and large number of ions are produced and hence equivalent conductance increases with dilution.
3. **Temperature:** Conductance increases with increase in temperature. At higher temperature the mobility of ions is increased and hence the conductivity increases.
4. **Size of ions:** Increase in the size of ions increases ionic interaction due to solvation and decreases the conductance.
5. **Inter-ionic forces:** Increase in interionic forces will inhibit the movement of ions and the conductance of the electrolyte decreases.
6. **Nature of solvent:** Viscous medium restricts the movement of ions and hence the conductivity is reduced.

APPLICATIONS OF CONDUCTANCE:

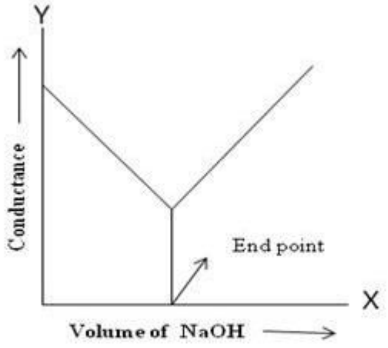
CONDUTOMETRIC TITRATIONS: Titrations involving conductivity measurements of electrolytes to get endpoint are called conductometric titrations. The end point is generally found out by plotting the conductance values on y-axis against the volume of electrolyte on x-axis. The electrical conductance of an aqueous solution depends up on:

1. The number of free ions in the solution containing an electrolyte.
2. The charge on the free ions.
3. The mobility of the ions.

1. Strong acid Vs Strong base titrations:

In an acid–base titration, acid is taken in the conical flask and base is added through the burette. Consider the titration of strong acid (HCl) with strong base (NaOH). Before the addition of NaOH, the conductivity is mainly due to the H^+ ions; hence the conductivity is high. On the gradual addition of NaOH from the burette, the fast moving H^+ ions of acid are replaced by OH^- ions. The conductivity of the solution decreases progressively by the addition of NaOH till the equivalence point is reached. The conductance again increases after the equivalence point.

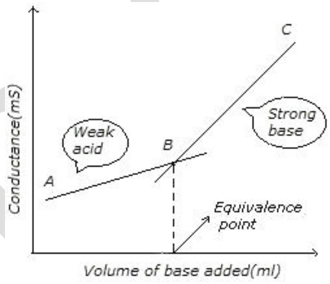
$$HCl + NaOH \rightarrow NaCl + H_2O$$



2. Weak acid Vs Strong base titration:

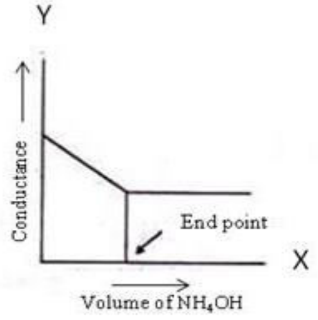
When weak acid is titrated with strong base, the conductance of the solution is low in the beginning, since the dissociation of weak acid is very low. On addition of base, highly dissociated sodium acetate is formed. Due to the common ion effect, the acetate ion tends to suppress the ionization of acetic acid. Later the conductivity begins to increase due to the conductivity power of the highly ionized salt exceeds that of weak acid. After end point, the addition of NaOH contributes sharp increase in the conductivity of the solution. The point of intersection of the two cures gives the end point of the titration.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$



3. Strong acid Vs weak base titrations: When strong acid is titrated against a weak base, the conductance of the solution first decrease due to the replacement of fast moving H^+ ions with slow moving NH_4^+ ions. After the end point, the addition of excess of NH_4OH will not result in any appreciable change in the conductivity.

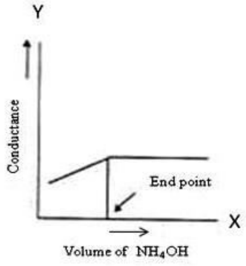
$$HCl + NH_4OH \rightarrow NH_4Cl + H_2O$$



4. Weak acid Vs weak base Titration:

Consider the titration of acetic acid against ammonium hydroxide. The titration of weak acid with weak base does not give sharp end point by volumetric titrations. The initial conductance of the solution is low due to the poor dissociation of weak acid, but starts raising as CH_3COONH_4 is formed. After the equivalent point, the conductivity remains almost constant because the free base NH_4OH is weak electrolyte. The end point is quite sharp by conductometric titrations

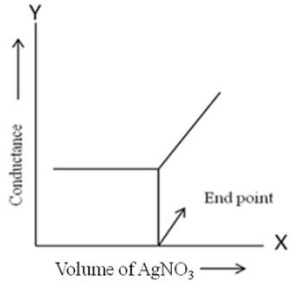
$$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$$



5. Precipitation titrations:

In precipitation titrations, sharp endpoint is obtained, e.g. The titration of KCl against $AgNO_3$. There is no sharp increase in conductance after the addition of $AgNO_3$, because the mobility of K^+ and Ag^+ is one and the same. After the end point, there is a sharp increase in conductance due to an increase in the number of free ions in the solution.

$$KCl + AgNO_3 \rightarrow KNO_3 + AgCl\ (ppt)$$



Advantages of conductometric titrations:

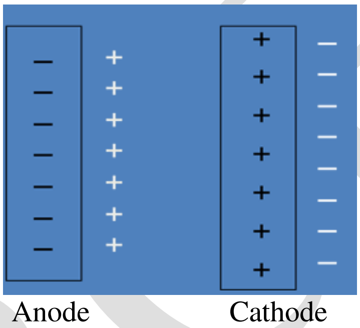
1. The results obtained by conductometric titrations are more accurate because the end point is obtained graphically.
2. The titrations of a weak acid with a weak base do not give a sharp end point with indicator in volumetric titrations. Accurate results are obtained in conductometric titrations.
3. Colored solutions where no indicator is found to work satisfactorily can be successfully titrated.
4. Conductometric titrations can be used even in case of polybasic acids.

Precautions:

1. The temperature must be kept constant throughout the experiment.
2. In acid–base titration, the titrant should be about 10 times stronger than the solution to be titrated so that the volume change is as little as possible.

ELECTRODE POTENTIAL:

- When a metal rod is dipped in its salt solution (electrolyte), the metal atom tends either to lose electrons (oxidation) or to accept electrons (reduction).
- The process of oxidation or reduction depends on the nature of metal.
- In this process, there develops a potential between the metal atom and its corresponding ion called the electrode potential.
- It is a measure of tendency of a metallic electrode to lose or gain electrons when it is in contact with its own ions in solution.
- **Reduction potential:** The tendency of an electrode to gain electrons and to get reduced is called *reduction potential, i*ts value is +x volts.
- **Oxidation potential:** Similarly the tendency of an electrode to lose electrons and to get oxidized is called *oxidation potential,* its value is –x volts
- The potential develop between electrode and electrolyte by the formation of charges and these charges are formed Helmholtz electrical double layer, through which potential develop between electrode and electrolyte.



Helmholtz Electrical Double Layer

Single electrode potential:

Each electrochemical cell is made up of two electrodes, at one electrode electrons are evolved and at other electrode electrodes used up. Each electrode which is dipped in its salt solution is called Half Cell. The potential of half-cell i.e. the potential difference between the metal and its salt solution in which it is dipped is called single electrode potential. It cannot be measured directly.

$Zn/ZnSO_4//CuSO_4/Cu$

←Half-cell→ ←half cell→

← Single electrode→ ← single electrode→

The total cell E.M.F is equal to the sum of the single electrode potentials. Each electrode is affixed with a symbol corresponding to the reaction that takes place near the electrode.

$$\boxed{E_{cell} = E_{(anode)} + E_{(Cathode)}}$$

The half-cell reactions are as follows; the half-cell reaction which corresponds oxidation is

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

The electrode is called oxidation electrode and potential of the electrode is oxidation potential or the potential of left hand electrode which is represented as E_{OX} or E_L . The cell reaction of the electrode where reduction takes place is given below

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

The electrode is called reduction electrode or right hand electrode and the potential of this electrode is reduction potential and represented as $E_{(Red)}$ or $E_{(R)}$.

The total cell reaction is $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$.

$$E_{(cell)} = E_{(OX)} + E_{(Red)}$$

E.M.F of the cell is equal to the sum of the oxidation potential and reduction potential, also expressed as the reduction potential of the right hand electrode minus reduction potential of the left hand electrode.

GALVANIC CELL: A galvanic cell is a system in which a spontaneous oxidation and reduction reaction occurs and generates electrical energy. Eg. Daniel cell

Construction of Galvanic Cell

A galvanic cell is made up of two half cells. One is oxidation or anodic half- cell and other one is reduction or cathodic half cell. Daniel cell is an example of galvanic cell having zinc and copper electrodes. The first half cell consists of zinc electrode dipped in $ZnSO_4$ solution and the second half is made of copper electrode dipped in copper sulphate solution. Both half cells are connected externally by metallic conductor and internally by a bent glass tube having saturated solution of a strong electrolyte (KCl) called salt bridge. It acts as a bridge between the two half cells.

Working of Galvanic cell:

When two half cells are connected externally by a wire through a voltmeter, spontaneous redox reaction takes place at the electrode.

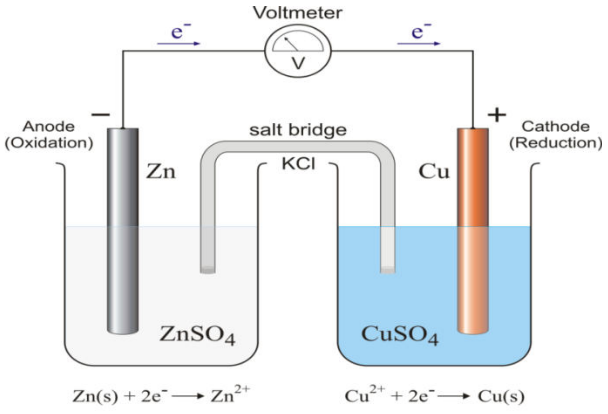
At anode: Oxidation takes place with the liberation of two electrons.

$$Zn \rightarrow Zn^{+2} + 2e^- \text{ (oxidation or de-electronation)}$$

At cathode: Reduction occurs and cuprous ion is reduced to metallic copper.

$$Cu^{+2} + 2e^- \rightarrow Cu \text{ (reduction or electronation)}$$

The overall reaction is $Zn + Cu^{+2} \rightleftharpoons Zn^{+2} + Cu$



$Zn(s) \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu(s)$

As the connection is complete, the flow of electrons will be externally from anode to cathode and internally from cathode to anode through the salt bridge. The flow of current is due to the difference in electrode potentials of both the electrodes. The potential difference in the cell is called the EMF and is measured in volts. It can be measured by the potentiometer. The flow of current becomes slow after using the electrodes for a long time because of the polarization of the electrodes.

At this stage, the salt bridge comes to the aid and restores the electrical neutrality of the solution in the two half cells. When the concentration of Zn^{2+} ions around the anode increases, sufficient number of Cl^- ions migrate from the salt bridge to the anode half cell. Similarly, sufficient number of K^+ ions migrate from the salt bridge to cathode half cell for neutralizing excess negative charge due to the additional SO_4^{2-} ions in the cathodic half cell. Thus it maintans the electrical neutrality of the two solutions in the half cells.

Representation of a galvanic cell:

1. The electrode showing oxidation reaction is anode and the other electrode where reduction occurs is cathode.
2. As per IUPAC convention, the anode is always represented on the left and cathode always represented on the right side of the cell.

Anode Half-Cell ‖ Cathode Half-Cell

Electrode | Anode Soln ‖ Cathode Soln | Electrode

$Zn(s) \mid Zn^{2+} (1\ M) \parallel Cu^{2+} (1\ M) \mid Cu(s)$

3. The electrode on left (i.e, anode) is written by writing the metal first and then the electrolyte. The two are separated by a vertical line or a semicolon. The electrolyte may be represented by the formula of the whole compound or by ionic species and concentration may also be mentioned in bracket.

Examples of representing anode half-cell as:

Eg: Zn/Zn^{2+} or $Zn;Zn^{2+}$ or $Zn/ZnSO_4(1M)$.

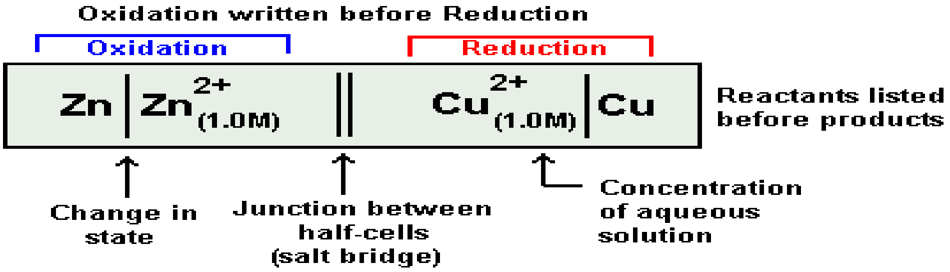
4. The cathode of the cell (at which reduction takes place) is written on the right hand side. In this case, the electrolyte is represented first and then the metal. The two are separated by a vertical line or a semicolon.

Examples of representing cathode half-cell as:

Cu^{2+}/Cu or $Cu^{2+}; Cu$ or $CuSO_4(1M)/Cu$.

5. A salt bridge is indicated by two vertical lines, separating the two half-cells.

$Zn;Zn^{2+}(1M) // Cu^{2+}(1M); Cu$.



Electromotive Force or Cell Potential (EMF):

The flow of electricity from one electrode to another electrode in a galvanic cell indicates that the two electrodes have different potentials. The difference of potentials between the electrodes of a cell which causes flow of current from an electrode at higher potential to other electrode at lower potential is known as electromotive force or cell potential.

The EMF of the cell depends on (a) temperature (b) nature of reactants and (c) concentration of solutions in two half cells.

Mathematically:

$$\boxed{\begin{array}{c}\textbf{EMF or Ecell} = E_{cathode} - E_{anode} \textbf{ or} \\ E(cell) = E(right) - E(left)\end{array}}$$

Where

E(cell) = e.m.f of cell
E(right) = reduction potential of right hand side electrode (cathode)
E(left) = reduction potential of left hand side electrode (anode)

$$E_{cell} = E_{ox}\,(\text{anode}) + E_{Red}\,(\text{cathode})$$

$$E_{cell} = E_R - E_L \text{ (both are reduction potentials)}$$

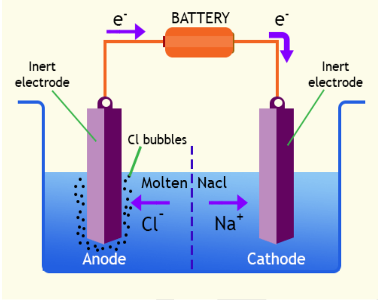
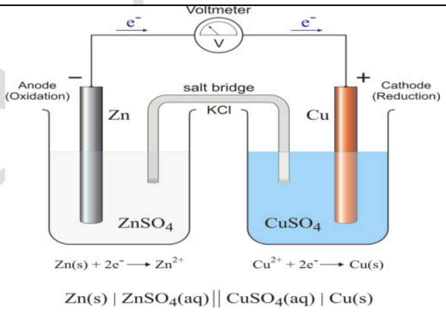
$$E_{cell} = E_L\,(\text{anode}) - E_R\,(\text{cathode}) \text{ (both are oxidation potentials)}$$

Salt bridge: Salt bridge is a U shaped glass tube containing concentrated solution of an inert electrolyte such as KCl, KNO_3 and K_2SO_4 or paste of inert electrolyte (whose ions do not take part in redox reaction and do not react with the electrolyte) in agar–agar medium or gelatin.

Functions of salt bridge:

1. Salt bridge helps to complete the circuit by allowing the ions to flow from one solution to the other without mixing the two solutions.
2. It helps to maintain electrical neutrality of the solution in the half cells.

Differences between electrolytic and electrochemical cells

S.No	Electrolytic Cell	Electrochemical Cell
1	Electrical energy is converted into chemical energy	Chemical energy is converted into electrical energy
2	Electrical energy brings about a redox reaction	Electrical energy is generated by a redox reaction
3	Anode is positive while cathode is negative	Cathode is positive while anode is negative
4	Redox reaction takes place in a same container	Oxidation and reduction reactions are carried out separately.
5	No salt bridge is required	Salt bridge is generally required
6	Ions are discharged at both the electrodes	Ions are discharged at the cathode while anode is consumed
7	Eg. Charging of lead storage battery, electrolytic purification of metals, electroplating	Eg. Batteries (lead storage battery)
8		

Derivation of Nernst equation: Nernst found that the single electrode potential varies with the change in concentration of ions and temperature and hence the EMF of the cell also varies. He derived a mathematical relationship between the standard electrode potential, temperature and the concentration of ions. This relationship is known as the Nernst equation.

Consider the redox reaction: $M^{n+} + ne^{-} \rightleftarrows M$

In the above reversible reaction the free energy change (G) and its equilibrium constant (K) are related by the following equation which is popularly known as Van't Hoff reaction isotherm.

$$\Delta G = RT \ln K + RT\ln \frac{\text{product}}{\text{reactant}}$$

$$\Delta G = \Delta G^0 + RT\ln \frac{\text{product}}{\text{reactant}}$$

When ΔG^0 is the standard free energy change

The free energy change is equivalent to the electrical energy –nFE

Where n = valency

F = Faraday (96500 coloumbs)

E = Electrode potential

R = 8.314 Joules K^{-1} $mole^{-1}$(Gas constant)

T = Temperature (K)

$-nFE = -nFE^0 + RT\ln([M])/([M^{n+}])$ (Concentration of M is unity)

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

$= -nFE^0 - RT2.303 \log_{10} [M^{n+}]$

Dividing the equation by – nF

$$E = E^{0+} + \frac{2.303RT}{nF} \log_{10} [M^{n+}]$$

$$\frac{2.303RT}{nF} = \frac{0.0591}{n}$$

$$\boxed{E = E^0 + \frac{0.0591}{n} \log_{10} [M^{n+}]}$$

Reference electrodes:

The electrode of standard potential, with which we can compare the potentials of an other electrode is called a reference electrode. The best reference electrode used is standard hydrogen electrodes. Its electrode potential at all temperatures is taken as zero.

The different types of electrodes are:
1) Metal-Metal ion electrode
2) Metal-Metal insoluble electrode
3) Gas -ion electrode
4) Redox electrode
5) Glass electrode

1) Metal-Metal ion electrode: An electrode of this type consists of a metal rod dipped in to a solution of its own salt.

E.g.: Zn rod dipped in a solution of $ZnSO_4$ ($Zn/ZnSO_4$)

2) Metal -Metal insoluble electrode: These electrodes consist of a metal in contact with a sparingly soluble salt of the same metal dipped in a solution containing anion of the salt.

E.g.: Calomel electrode ($Hg/Hg_2Cl_2/Cl^-$)

3) Gas-ion electrode: It consists of an inert metal dipped in a solution containing ions to which the gas is reversible

E.g.: Hydrogen electrode

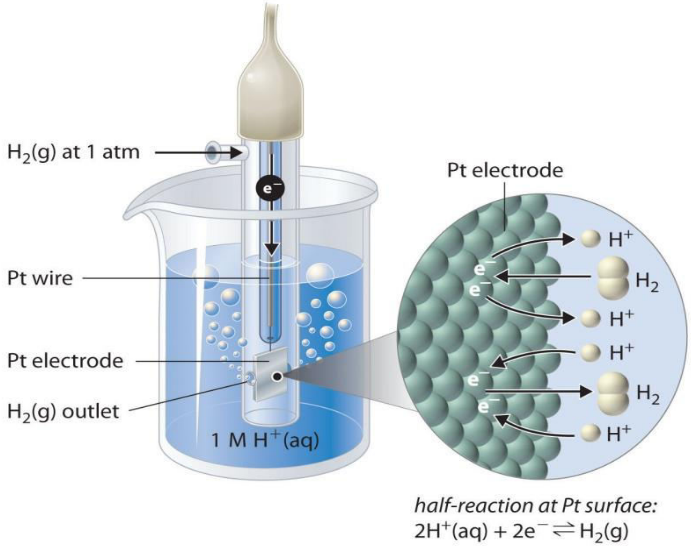
4) Redox electrode: It consists of an inert metal dipped in a solution containing ions in two oxidation states of the substance.

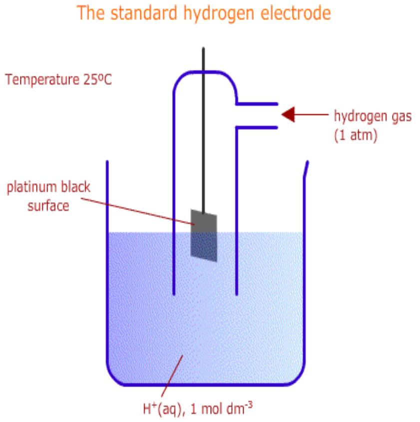
E.g: Quinhydrone electrode ($Pt/Q/H_2Q$)

5) Glass electrode: **E.g:** Ag/AgCl(s), HCl (0.1M)/ Glass+

Standard Hydrogen Electrode (or) Gas electrode:

It is a redox electrode which is widely used as reference electrode. It can be used as either anode or cathode depending upon the nature of the half-cell for which it is used. The standard hydrogen electrode consists of a platinum electrode immersed in a solution with a hydrogen ion concentration of 1.0 M. The platinum electrode is made up of a small square of platinum foil which is platinized and known as platinum black. A stream of pure hydrogen is bubbled around the platinum foil at a constant pressure of one atmosphere.





The SHE may be represented as

$$H_2\ (1atm);\ Pt/H^+\ (C = 1)$$

The electrode potential of SHE = Zero. Depending on half-cell to which it attached hydrogen electrode can act as a cathode or anode.

At oxidation reactions act as anode: $\frac{1}{2}H_2\ (g)\ (1atm) \rightarrow H^+\ (1M) + e^-$

At reduction reaction act as cathode: $H^+ (1M) + e^- \rightarrow \frac{1}{2} H_2 (g) (1atm)$

Nernst equation:

The concentration effect i.e. when H^+ concentration is not 1M the EMF of the electrode alters. To calculate the potential of the standard electrode, Nernst equation is used as given below.

$$E = E^o - 2.303RT/nF \log_{10} [H^+]$$

Substituting all the values we get the potential of the electrode at 25°C as

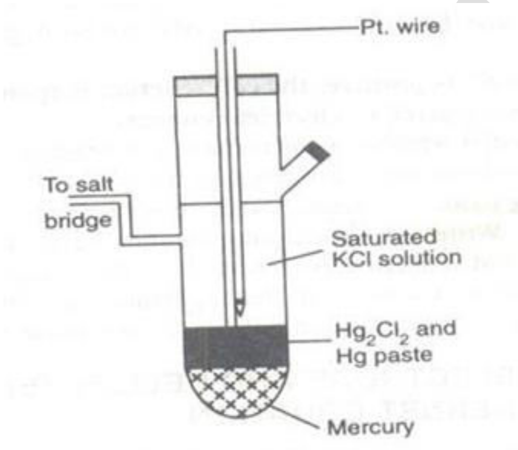
$$E = E^o - \frac{2.303 \times 8.313 \times 298}{1 \times 96500} log_{10}[H^+]$$

$$E = E^o - 0.0591 \log_{10} [H^+]$$

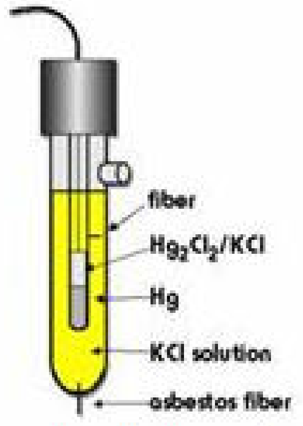
$$E = E^0 - 0.0591 P^H$$

$$E_{(red)} = -E_{(ox)} = -E^o + \frac{0.0591}{n} Log_{10}[H^+]$$

Saturated Calomel Electrode:



Calomel electrode



Calomel Electrode

Calomel electrode is a metal-metal salt ion electrode. It consists of mercury, mercuous chloride and a solution of KCl. Mercury is placed at the bottom of a glass tube having a side tube on each side. Mercury is covered by a paste of mercurous chloride (calomel) with mercury & KCl.

A solution of KCl is introduced above the paste through the side tube. A platinum wire sealed in a glass tube is dipped into mercury and used to provide the external electrical contact. The concentration of KCl used is either decinormal, normal (or) saturated. The electrode is known as decinormal, normal, saturated calomel electrode.

The electrode whose potential is to be determined is connected to this electrode through salt bridge. The potential of electrode depends upon the concentration of KCl solution.

The net reversible electrode reaction is;

$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg\ (l)\ + 2Cl^-$$

NERNST EQUATION:

$$E\ = E^0{}_{Hg2Cl2} - \frac{2303RT}{2F}\ \log[Cl^-]^2$$

$$= E^0 - \frac{2.303RT}{F} \log\ [Cl^-]$$

$$= E^0 - 0.0591\log[Cl^-]$$

The electrode potential depends up on the conc. of KCl solution (i.e. chloride ions)

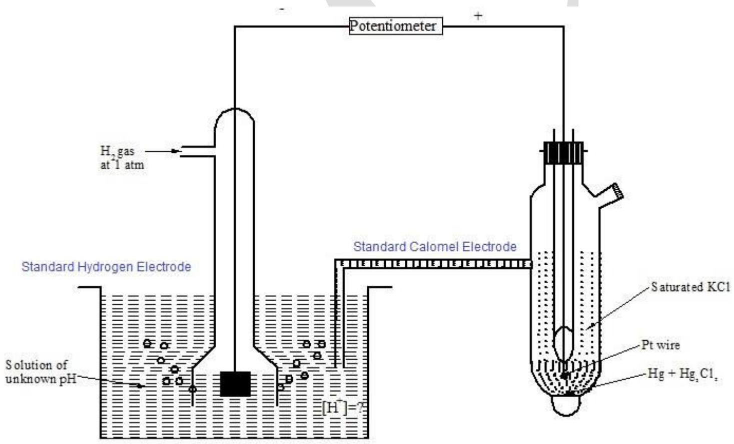
At 25^0C For Saturated KCl solution electrode potential is 0.2415 volts.

For 1N KCl solution standard reduction potential is 0.281 volts.

For 0.1N KCl solution the reduction potential is 0.3338 volts.

The electrode can be coupled with hydrogen electrode containing solution of unknown concentration.

$^-$Pt, H_2 (1atm)// H^+ =? //Hg_2Cl_2 (s)/Hg^+



Finding Unknown pH USING Standard Calomel Electrode

The e.m.f. of the cell,

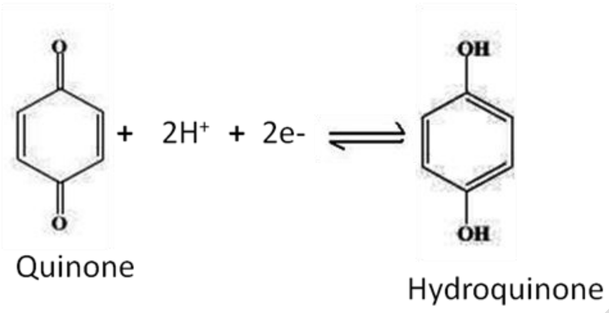
$$Ecell = E_{right} - E_{left} = 0.2422V + 0.0592VP^H$$

$$P^H = \frac{Ecell - 0.02422V}{0.0592V}$$

USES:

1. It is used as a secondary reference electrode in the measurement of single electrode potential.
2. It is the most commonly used reference electrode in all potentiometric determinations.

Quinhydrone Electrode:



$$C_6H_4O_2 + 2H^+ + 2e^- \rightleftharpoons C_6H_4(OH)_2$$

Quinone (Q) Hydroquinone (QH_2)

Quinone and hydroquinone form a reversible redox system in the presence of hydrogen ions. The potential E developed when an inert electrode, e.**g.** platinum is immersed in this system is given by the Nernst reduction equation.

$$E_Q = E_Q^0 - \frac{2.303RT}{nF}\log\frac{[QH2]}{[Q][\,H+]2}$$

Where E^o_Q is the standard potential of the electrode.

Since $[Q] = [QH_2]$, Concentration of quinine and hydroquinone are equal. Thus,

$$E_Q = E^0_Q - \frac{2.303RT}{2F}\log\frac{1}{[H^+]^2}$$

$$E_Q = E_Q^0 - \frac{2.303RT}{F}\log\frac{1}{[H^+]}$$

$$E_Q = E^0_Q + \frac{2.303RT}{F}\log[H^+]$$

$$E_Q = E_Q^0 + 0.05915\,P^H$$

$$= 0.6994v - 0.0592vP^H$$

CONSTRUCTION:

Quinhydrone electrode can very easily be set up by adding a pinch of quinhydrone powder (a sparingly soluble solid) to the experimental solution with stirring, until the solution is saturated and a slight excess of its remains undissolved. The indicator electrode usually of bright platinum is inserted it. For determining the P^H values, this half-cell is combined with any other reference electrode, usually saturated calomel electrode and the EMF of cell so formed is determined potentiometrically.

The cell may be represented as

Pt/ H2Q, Q, H^+ (unknown) // KCl(sat), Hg_2Cl_2(s) / Hg^+

$$E_{cell} = E_{Calomel} - E_{\text{ Quinhydrone}}$$

$$E_{cell} = 0.2422V\text{- }(0.6994V\text{-}0.0592V\ P^{H})$$

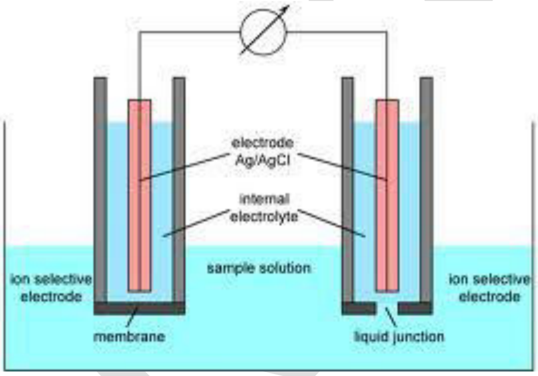
$$\boxed{P^{H} = \frac{0.6994V - 0.2422V + Ecell}{0.0592V}}$$

Advantages and limitations of Quinhydrone:

1. The electrode is very easy to set up.
2. The pH values obtained are very accurate.
3. Very small quantities of the solution are sufficient for the measurement. The electrode cannot be used for more alkaline (pH ≥8.5) solutions and the solutions which react with quinhydrone or quinone. (**E.g.:** Fe^{2+}, MnO_2).

Ion selective electrode (ISE):

An ion selective electrode (ISE) is a sensor which converts the activities of a specific ion dissolved in a solution into an electrical potential which can be measured by a voltmeter, E.g. Glass electrode.

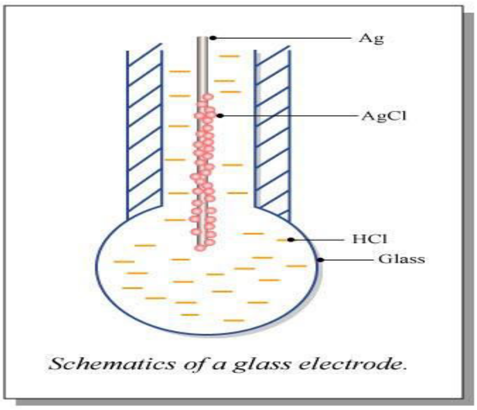


Glass Electrode:

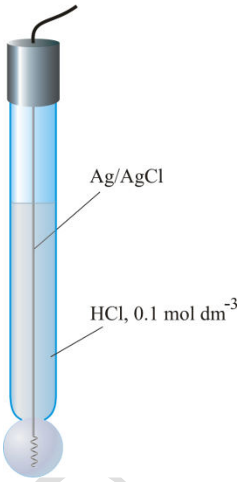
A glass electrode is a type of ion- selective electrode and consists of a thin- walled glass bulb attached to a glass tube. A very low melting point and high electrical conductivity glass are used for the construction of this bulb. The glass tube contains a dilute solution of constant pH of HCl (0.1N) solution. A silver–silver chloride electrode or platinum wire is immersed as reference electrode in the HCl solution. The working of glass electrode is based upon the observation that when a glass surface is in contact with a solution, there exists a potential difference between the glass surface and the solution, the magnitude of which depends upon the H^+ ion concentration of the solution and the nature of glass. The glass electrode may be represented as

Ag, AgCl (s) /0.1 N HCl / glass /H+ = unknown

The electrode potential of the glass electrode depends up on the concentration of H^+ ions contained in the experimental solution and are given by.



Schematics of a glass electrode.



$$E_G = E^o_G + \frac{2.303RT}{F}\log H^+$$

$$= E^o_G - 0.0591\log H^+$$

$$= E^o_G + 0.0591pH$$

E^o_G is the standard electrode potential, i.e. the potential of the glass electrode when the solution contains unit concentration of H^+ ions. The value of E^o_G depends on the nature of the glass used in the construction of the bulb.

The pH of the solution can be determined if the potential of the glass electrode is known. To determine the value of glass electrode potential (E_G), the glass electrode is combined with a reference electrode such as calomel electrode. The EMF of this cell will be given by

$$E_{cell} = E_{(calomel)} - E_{(glass)}$$
$$= E_c - E_g{}^0 - 0.0591P^H$$

$$P^H = \frac{Ec - Eg - Ecell}{0.0591}$$

Advantages of glass electrode:

1. Glass electrode is easy to operate and equilibrium is rapidly reached.
2. The P^H value obtained is very accurate.

Limitations of glass electrode:

1. Glass electrode can be used in solutions with pH range 0-10, because electrodes are composed of special glass that can be used up to pH 12.

2. The resistance is extremely high in the order of 10 to 100 million ohms, which cannot be measured by ordinary potentiometers and special electronic potentiometers have to be used.

APPLICATIONS OF NERNST EQUATION:

1. It can be used to study the effect of electrolyte concentration on electrode potential.
   $E = E^o - RT/nF \ln[1/M^{n+}]$
2. It can also be used for the calculation of the potential of a cell under non-standard conditions.

For example,

$Cu(s)/Cu^{2+}(aq)(0.50M)//H^{+}(0.01)/H_2(0.95atm)$

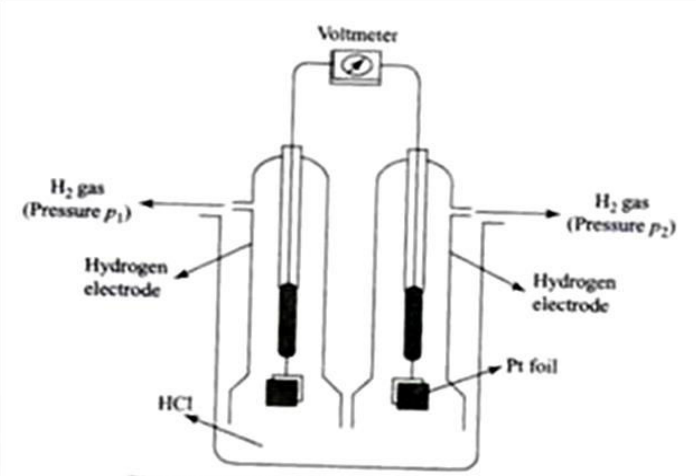
$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{2}\log(Cu^{2+})P_{H2}/[H^{+}]^{2}$$

3. Determination of unknown concentration of one of the ionic species in a cell is possible with the help of Nernst equation, provided E_{cell} and concentration of other ionic species are known.
4. The pH of a solution can be calculated from the measurement of EMF and Nernst equation.
5. Nernst equation can also used for finding the valence of an ion or the number of electrons involved in the electrode reaction.

Concentration cells:

In the concentration cell, the EMF is produced due to the difference in the concentration of the electrodes or in the concentration of electrolyte, i.e., a concentration cell is an electrochemical cell which produces electrical energy by the transfer of a material from a system at higher concentration to a system at lower concentration. The difference in concentration may be due to the difference in concentration of electrodes or electrolyte. Based on this concentration, cells are classified into groups:

(i) Electrode Concentration Cells



Electrode concentration cell (H_2 gas electrodes)

In these cells, the potential difference is developed between two like electrodes at different concentrations dipped in the same solution of the electrolyte. For example, two hydrogen electrodes at different gas pressure dipped in the same solution of hydrogen ions constitute a cell of this type.

Pt/H_2 (pressure P_1) / H+ (a) / (H_2 (pressure P_2) /Pt

If $P_1>P_2$ oxidation occurs at L.H.S. electrode and reduction occurs at R.H.S .electrode

$H_2 (P_1) = 2H^{+} + 2e^{-}$

$2H^{+}+ 2e^{-} = H_2 (P_2)$

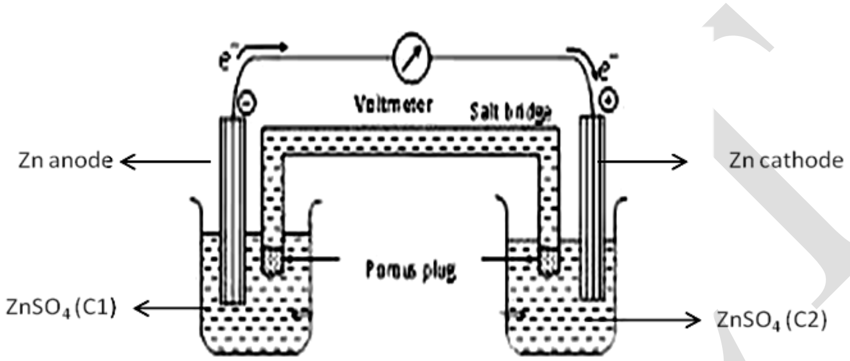
$H_2 (P_1) = H_2 (P_2)$

$$Ecell = \frac{0.0591}{2} \log \frac{P1}{P2}$$

ELECTROLYTE CONCENTRATION CELLS:

A concentration cell consists of two half cells having identical electrodes and electrolytes at different concentrations. The electrical energy in a concentration cell arises due to the transfer of a substance from the solution of high concentration to solution of low concentration. The concentration cell can represented as

$$Zn/ ZnSO_4 (C_1) // ZnSO_4 (C_2)/ Zn$$



The electrolytes are connected by a salt bridge of ammonium nitrate.

Theory:

When a metal electrode is dipped in a solution of its own ions with concentration (C) then a potential E is developed at the electrode in accordance with the Nernst equation.

$$E = E^0 + \frac{2.303RT}{nF} \log C$$

$$E = E^0 + \frac{0.0591}{n} \log C$$

Concentration cell represented as $M / M^{n+} (C_1) // M^{n+} (C_2) / M^+$

Where C_1 and C_2 are the concentration of the active metal ions (M^{n+}) in contact with the same two metal electrodes and $C_2 > C_1$.

Emf of the cell (E) = E^0 right - E^0 left.

$$\left(E^0 + \frac{0.0591}{n} \log C_2\right) - \left(E^0 + \frac{0.0591}{n} \log C_1\right)$$

$$E = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

$$[or]$$

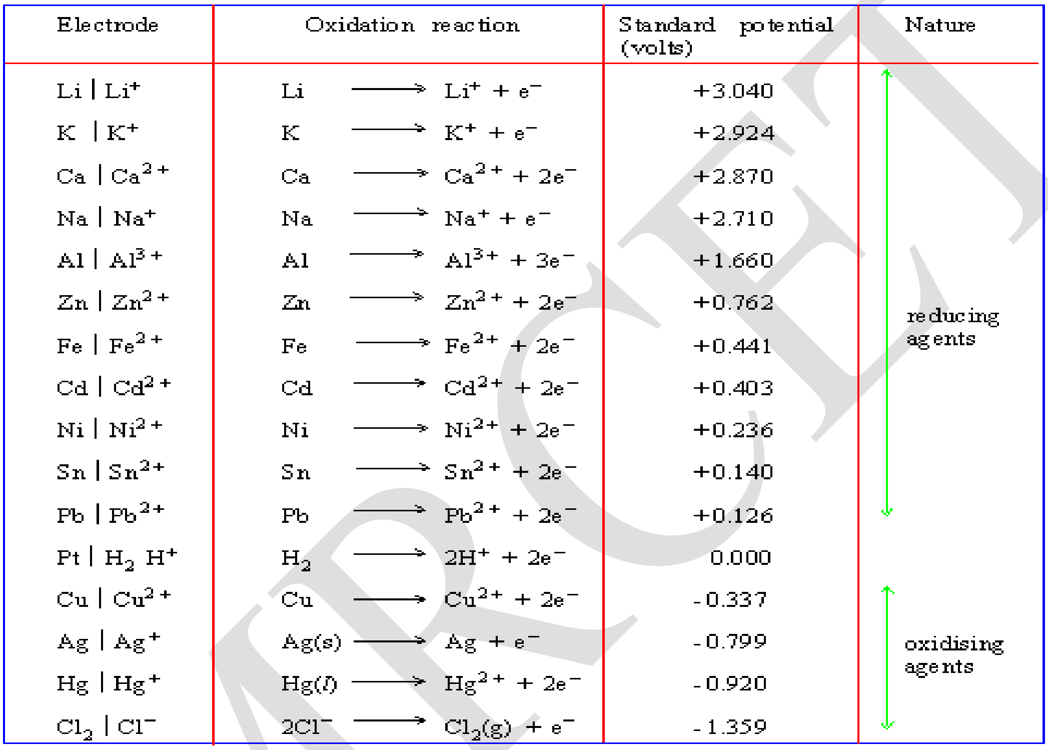
$$E = \frac{2.303RT}{nF} \log \frac{C_2}{C_1}$$

Applications of concentration cell:

1. To determine the solubility of a sparingly soluble salt.
2. To calculate the valency of cations.
3. To determine the transition point.
4. To calculate the extent of corrosion in metals.

ELECTROCHEMICAL SERIES:

Metals arranged in the increasing order of standard electrode reduction potential or decreasing order of standard oxidation potential as compared to that of standard hydrogen electrode is called electrochemical series. These standard electrode potentials are measured at 25^0C



Electrode	Oxidation reaction	Standard potential (volts)	Nature
$Li \mid Li^+$	$Li \longrightarrow Li^+ + e^-$	+3.040	reducing agents
$K \mid K^+$	$K \longrightarrow K^+ + e^-$	+2.924	
$Ca \mid Ca^{2+}$	$Ca \longrightarrow Ca^{2+} + 2e^-$	+2.870	
$Na \mid Na^+$	$Na \longrightarrow Na^+ + e^-$	+2.710	
$Al \mid Al^{3+}$	$Al \longrightarrow Al^{3+} + 3e^-$	+1.660	
$Zn \mid Zn^{2+}$	$Zn \longrightarrow Zn^{2+} + 2e^-$	+0.762	
$Fe \mid Fe^{2+}$	$Fe \longrightarrow Fe^{2+} + 2e^-$	+0.441	
$Cd \mid Cd^{2+}$	$Cd \longrightarrow Cd^{2+} + 2e^-$	+0.403	
$Ni \mid Ni^{2+}$	$Ni \longrightarrow Ni^{2+} + 2e^-$	+0.236	
$Sn \mid Sn^{2+}$	$Sn \longrightarrow Sn^{2+} + 2e^-$	+0.140	
$Pb \mid Pb^{2+}$	$Pb \longrightarrow Pb^{2+} + 2e^-$	+0.126	
$Pt \mid H_2\ H^+$	$H_2 \longrightarrow 2H^+ + 2e^-$	0.000	
$Cu \mid Cu^{2+}$	$Cu \longrightarrow Cu^{2+} + 2e^-$	-0.337	oxidising agents
$Ag \mid Ag^+$	$Ag(s) \longrightarrow Ag + e^-$	-0.799	
$Hg \mid Hg^+$	$Hg(l) \longrightarrow Hg^{2+} + 2e^-$	-0.920	
$Cl_2 \mid Cl^-$	$2Cl^- \longrightarrow Cl_2(g) + e^-$	-1.359	

In this series, iron lies above hydrogen and copper lies below it. Hence, if an iron rod is dipped in $CuSO_4$ solution a layer of copper metal will get deposited on the surface of the iron rod.

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

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

$Fe + Cu^{++} \rightarrow Fe^{++} + Cu$.

The reverse of this reaction is not possible, i.e. a copper rod dipped in $FeSO_4$ solution will not show redox reaction.

Applications of Electrochemical Series:

1. Comparison of oxidizing and reducing power: It gives information about the relative ease with which oxidation and reduction of metal occurs. Based on the electrochemical series the element with higher reduction potential have a greater tendency to get reduced and act as good oxidizing agents. Whereas the elements with lower reduction potential have a tendency to get oxidized and act as good reducing agents.

Ex: F_2 can be reduced easily than Li^+ ions. So it is a good oxidizing agent

2. Relative activities of metal: Provides information about the replacement tendencies of metals. The greater the O.P of a metal, more easily it can lose electrons and greater is its reactivity, i.e. the metal with higher O.P can displace the metal with lower O.P. in their salt solution.

Ex: Mg > Zn > Fe > Cu > Ag. Zn has lower reduction potential than Cu. Hence Zn can displace copper from $CuSO_4$ solution

3. Any metal above hydrogen will displace hydrogen from dil. acid solution. For example, Na reacts with water to liberate hydrogen because

E^0 (Na^+/Na) = -2.714 V is less than E^0(H^+ / H_2 = 0).

$$2Na + H_2SO_4 \rightarrow Na_2SO_4 + H_2$$

$$2K + H_2SO_4 \rightarrow K_2SO_4 + H_2$$

$$Ca + H_2SO_4 \rightarrow CaSO_4 + H_2$$

4. Provides information about the relative corrosion tendencies of metals.
5. Predicts spontaneity of redox reaction. If EMF of a cell is –ve, the reaction is non spontaneous and if EMF is +ve then the reaction is spontaneous.
6. This series is also helpful in direct calculation of the EMF of cell formed between electrodes.

E^0= -0.76V (reduction potential)

E^0= 0.34V (reduction potential)

$E^0 = E_R - E_L$

$= 0.34 - (0.76) = 1.10V$

Potentiometric titrations:

The potential of electrode depends upon the concentration of the ions to which it is reversible in accordance with Nernst equation. Thus in a titration, the potential of an electrode is measured by the change in ionic concentration.

The potentiometric titrations are those titrations which involve the measurement of electrode potentials with the addition of the titrant. The end point is detected by measuring the changes in the potential of a suitable electrode during the course of reaction. No indicator is used in this titrations. The end point of the reaction is indicated by a sharp change in the potential of the system.

(i) ACID BASE TITRATIONS:

The acid solution whose strength has to be determined is taken in a beaker and the hydrogen electrode and calomel electrode were dipped in the solution. The electrodes were connected to the potentiometer and the E.M.F is measured. A known volume of standard alkali solution is added from a burette and stirred and the EMF of the cell is recorded. Like this 10-15 readings are recorded by repeating the procedure of the addition of standard alkali.

On adding alkali solution (NaOH) from the burette, the H^+ concentration goes on decreases, i.e. pH of the solution goes on increases and hence the EMF of the cell goes on increases gradually, but at the end point the rate of change of potential will be suddenly quite large. After the end point, further addition of NaOH produces very little change in the H^+ ion concentration and hence there is very little change in the EMF of the cell.

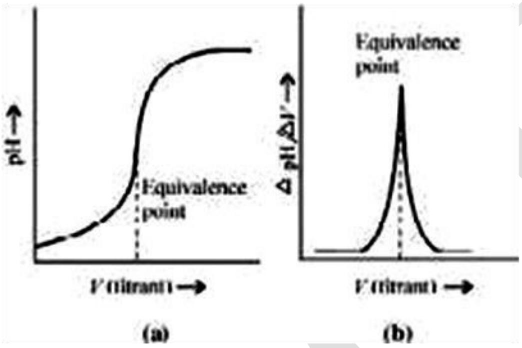
The complete cell may be represented as

Pt, H_2 (1atm) / H^+ (unknown) //KCl (sat. sol^n) / Hg_2Cl_2.Hg

The emf of the indicator electrode (hydrogen electrode) is given as

$$E_{H2/H+} = E^o_{H2/H+} + 0.0591 \log_{10} [H^+]$$

A graph is plotted by taking volume of alkali added against EMF observed. A sigmoid curve is obtained and the steepest portion of the curve indicates the equivalence point of the titration



From the graph, we draw the conclusion that the EMF increases with the decrease in concentration of hydrogen ions because electrode potential of indicator electrode depends on the concentration of H^+ ions.

(ii) OXIDATION- REDUCTION TITRATIONS:

The procedure adopted for oxidation titration is the same as in acid-base titration; the only difference is that the electrode reversible to hydrogen ions is replaced by a bright platinum electrode. The EMF of the electrode is determined by the activity of ratio of the substance being oxidized or reduced. For E.g.; Fe^{2+} titrated against $K_2Cr_2O_7$. The Fe^{2+} solution is taken in the beaker, treated with dil.H_2SO_4 and Pt electrode and calomel electrodes are dipped. The electrodes are connected to the potentiometer and EMF of the solution after the addition of $K_2Cr_2O_7$ is recorded. On addition of $K_2Cr_2O_7$ from the burette, EMF of the cell increase first slowly, but at the equivalence point there will be sudden jump in potential, since change in ratio of Fe^{2+}/Fe^{3+} ion concentration. A graph is plotted with EMF and volume of $K_2Cr_2O_7$. A sigmoid curve is obtained and the steepest portion of the curve indicates the end point of the titration.

(iii) PRECIPITATION REACTION:

In precipitation reaction also an electrode reversible to one of the ions involved is made use of, for **E.g:** titration of $AgNO_3$ with NaCl, where AgCl precipitates out, Ag-electrode is used along with calomel electrode. The silver nitrate is placed in the micro burette and added to sodium chloride taken in the beaker, containing electrodes. The EMF of the cell is measured and plotted against volume of silver nitrate added. The steep rise in the curve shows the end point of the titration.

DETERMINATION OF P^H BY EMF METHOD:

The EMF of a solution depends on the concentration of H^+ ions or pH of the solution. A hydrogen electrode containing solution of unknown P^H is paired with a standard calomel electrode.

The complete cell may be represented as

$$\text{Pt, } H_2 \text{ (1atm) / } H^+ \text{ (unknown) //KCl (sat. sol}^n\text{) / } Hg_2Cl_2\text{.Hg}$$

The EMF of the above cell is measured by potentiometer, and the P^H of the unknown solution can be calculated as follows.

The EMF of the cell will be given by the expression

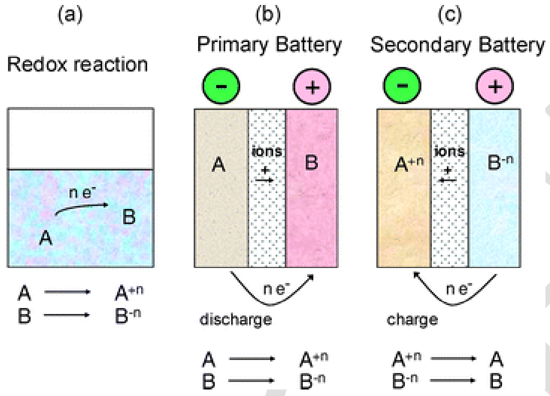
$$E_{cell} = E_{right} - E_{left}$$

$$E_{cell} = 0.2415 - (- 0.0591\, P^H)$$

$$E_{cell} = 0.2415 + 0.0591\, P^H$$

BATTERIES AND FUEL CELL

Battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at constant voltages. A device which converts chemical energy to electrical energy is called battery cells, connected together electrically in series. Batteries are commercial electrochemical cells.



ADVANTAGES OF BATTERIES:

(1) Batteries act as a portable source of electrochemical energy.

(2) The portability of electronic equipment in the form of handsets has been made possible by batteries.

(3) A variety of electronic gadgets have been made more useful and popular with the introduction of rechargeable storage batteries having reliability, better shelf life and tolerance to service.

(4) For all commercial applications, batteries are constructed for their service. For example batteries for automotives and aircrafts, stand by batteries etc.

The following requirements should be possessed by the batteries.

(1) High capacity, which is very small variation of voltage during discharge.

(2) High energy efficiency, which is calculated as

% of efficiency = energy released on discharge/energy required for charge x100

(3) High cycle life is required which is the number of charging and discharging cycles before failure.

(4) Long shelf-life is required.

(5) Tolerance to different service conditions such as variation in temperature, vibration shock etc.

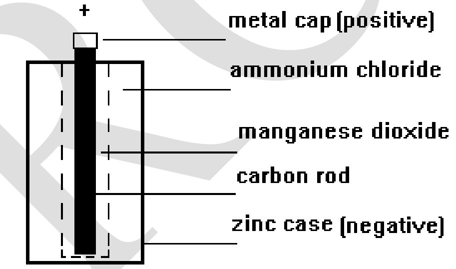
(6) Reliability is another important criteria.

Differences between Primary, Secondary and Fuel cells:

Primary cell	**Secondary cells**	**Fuel Cell**
It acts as a simple galvanic cell.	It acts as a galvanic cell while discharging and electrolytic cell while charging.	It acts as a simple galvanic cell.
Cell reaction is not reversible.	Cell reaction can be reversed.	Cell reaction is not reversible
Cannot be recharged.	Can be recharged	Do not store energy
Can be used as long as the materials are active in their composition. **E.g:** Leclanche or dry cell. Zn/NH_4Cl (20%), $ZnCl_2$/ MnO_2/C. emf =1.5V. Applications: Radios, torches, transistors, hearing aids.	Can be used again and again by recharging the cell **E.g:** 1. Lead storage cell 2. Nicol or Nickel cadmium battery emf =1.4 Applications: Electronic calculators, electronic flash units & cordless electronic shavers etc.	Energy can be withdrawn indefinitely as long as outside supply of fuel is maintained **E.g:** H_2-O_2, CH_3OH-O_2 Applications: Space vehicles due to their light weight and the bi product H_2O produced is a valuable source of fresh water for astronauts.

PRIMARY CELLS:

Dry Cell: (Leclanche Cell)



Dry cell (Leclanche)

It consists of cylindrical zinc container that acts as an anode. A graphite rod placed in the center (but not touching the base) acts as a cathode. The space between the anode cathode is packed with the paste of NH_4Cl and $ZnCl_2$, and the graphite rod is surround by powdered MnO_2 and carbon. The cell is called dry cell because of the absence of any liquid phase, even the electrolyte consists of NH_4Cl, $ZnCl_2$and MnO_2 to which starch is added to make a thick paste which prevents leakage. The graphite rod is fitted with a metal cap and the cylinder is sealed at the top with a pitch.

Cell representation: $Zn^- / NH_4Cl // MnO_2^+ C / C^+$

At Anode: (oxidation) $Zn \rightarrow Zn^{2+} + 2e^-$

At cathode: (reduction) $2MnO_2 + 2H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$

The net reaction is: $Zn + 2MnO_2 + H_2O \rightarrow Zn^{2+} + Mn_2O_3 + 2OH^-$

The resulting OH- ions react with NH_4Cl to produce NH_3 which is not liberated as gas but immediately combines with the Zn^{2+} and Cl^- ions to from a complex salt $[Zn(NH_3)_2]Cl_2$.

$$2NH_4Cl + 2OH^- \rightarrow 2NH_3 + 2Cl^- + 2H_2O$$

$$Zn^{2+} + 2NH_3 + 2Cl^- \rightarrow [Zn(NH_3)_2]Cl_2$$

Net reaction:

$$Zn(s) + 2NH_4Cl + 2MnO_2(s) \rightarrow Mn_2O_3(s) + [Zn(NH_3)_2]Cl_2(s) + 2H_2O.$$

Applications

1. These cells have voltage ranging from 1.25V to 1.50V.
2. Primary cells are used in torches, radios, transistors, hearing aids, pacemakers, watches.
3. Price is low.

Disadvantages:

1. These cells do not have a long life, because the acidic NH_4Cl corrodes the container even when the cell is not in use.
2. When current is rapidly drawn from the cell, voltage drop takes place due to the building up of production on the electrodes.

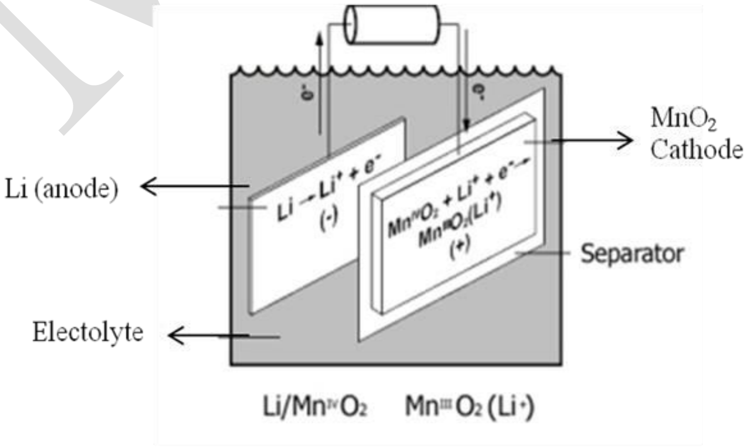
Lithium cells:

Lithium cells are primary cells in which lithium acts as anode and the cathode may differ. Lithium metal **is** used as anode because of its light weight, high standard oxidation potential (≥3V) and good conductivity. As the reactivity of lithium in aqueous solution is more, lithium cells use non-aqueous solvents as electrolyte.

Lithium cells are classified into two categories:

(a) Lithium cells with solid cathode:

The electrolyte in this system is a solid electrolyte. The most widely used cell is lithium – manganese dioxide cell (3V). MnO_2 should be heated to over 300^0C to remove water before keeping it in the cathode, thereby increasing the efficiency of the cell.



Anode: Lithium Metal,

Cathode: MnO_2 as an active material.

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

Reactions:

At anode: $Li \longrightarrow Li^+ + e^-$

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

Net reaction: $Li + MnO_2 \longrightarrow LiMnO_2$

Applications:

1. The coin type cells are used in watches and calculators.
2. Cylindrical cells are used in fully automatic cameras.

(b) Lithium cells with liquid cathode: Lithium–sulphur dioxide cell is an example of liquid cathode. The co-solvents used are acrylonitrile or propylene carbonate (or) mixture of the two with SO_2 in 50% by volume.

Cell reaction: $2Li + 2SO_2 \longrightarrow Li_2S_2O_4$.

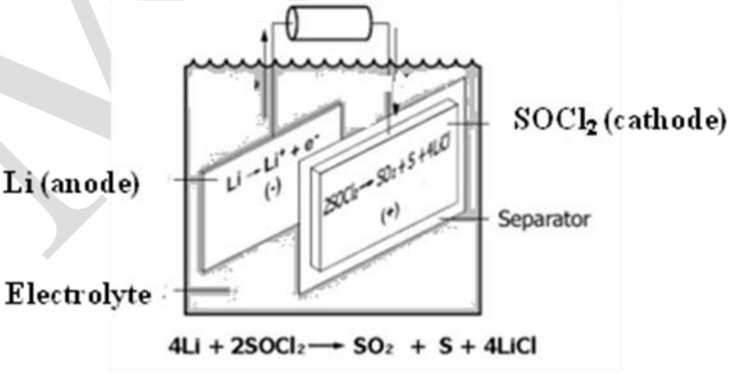
Lithium thionyl chloride cell is another example of liquid cathode. It consists of high surface area carbon cathode, a non – woven glass separator. Thionyl chloride acts as an electrolyte and as a cathode.

Cell reaction:

At anode: $Li \longrightarrow Li^+ + e^-$

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

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



In this cell no co-solvent is required as $SOCl_2$ is a liquid with moderate vapor pressure. The discharging voltage is 3.3 -3.5V.

USES:

1. They are used for military and space applications.

2. In medicinal devices such as neuro-stimulators, drugdelivery system, lithium batteries are widely used.
3. They are also used in electric circuit boards for supplying fixed voltage for memory protection and standby functions.

Advantages:

1. The energy output of a lithium cell is 2-4 times better than that of conventional zinc anode batteries.
2. Lithium batteries can work over temperature range of 40-70^{0}C.
3. They have higher voltages of about 4V when compared to other primary cells with 1.5 V only.

Secondary cell: E.g.: Lead – Acid cell:

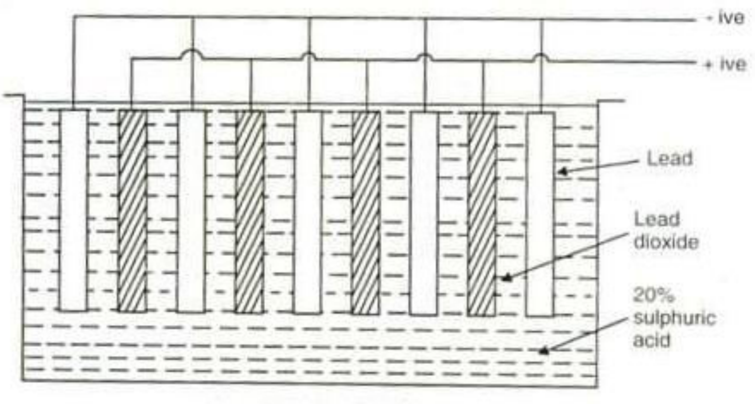
If a number of cells are connected in series, the arrangement is called a battery. The lead storage battery is one of the most common batteries that are used in the automobiles. A 12 V lead storage battery is generally used, which consists of six cells, each providing 2V. Each cell consists of a lead anode and a grid of lead packed with lead oxide as the cathode. These electrodes are arranged alternately, separated by a thin wooden piece and suspended in dil. H_2SO_4 (38%), which acts as an electrolyte. Hence, it is called lead acid battery.

Anode: Pb

Cathode: PbO_2

Electrolyte: H_2SO_4 (20-22%)

EMF = 2 V



Lead Acid storage cell

Lead storage cells: To increase the current output of each cell, the cathode and the anode plates are joined together, keeping them in alternate positions. The cells are connected parallel to each other.

The cell is represented as

$$Pb/PbSO_4(s), H_2SO_4/PbSO_4(s),Pb$$

In the process of discharging, i.e., when the battery produces current, the reactions at the electrodes are as follows:

Discharging reactions:

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

$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4\downarrow$

At cathode: $PbO_2(s) + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$

$Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$

Therefore, the overall reaction is:

$$\boxed{Pb(s) + PbO_2 + 4H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O + \text{Energy}}$$

During discharging the battery, H_2SO_4 is consumed, and as a result, the density of H_2SO_4 falls. When it falls below 1.20 g/cm^3, the battery needs recharging. In discharging, the cell acts as a voltaic cell where oxidation of lead occurs.

Recharging:

During recharging, the cell is operated like an electrolytic cell, i.e. electrical energy is supplied to it from an external source. The electrode reactions are the reverse of those that occur during discharge.

$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ (Reaction at cathode)

$PbSO_4 + 2H_2O \rightarrow PbO_2 + 2H_2SO_4 + 2e^-$ (Reaction at anode)

$2PbSO_4 + 2H_2O + \text{Energy} \rightarrow Pb + PbO_2 + 2H_2SO_4$

During this process, lead is deposited at the cathode, PbO_2 is formed at the anode and H_2SO_4 is regenerated in the cell.

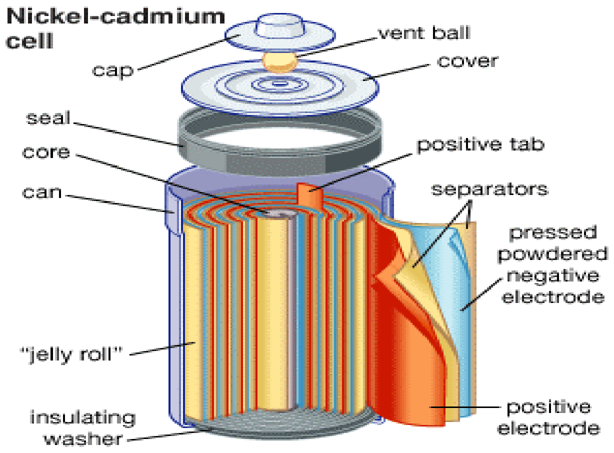
Advantages:

Lead-acid batteries are used for supplying current to railways, mines, laboratories, hospitals, automobiles, power stations, telephone exchange, gas engine ignition, UPS. Other advantages are its recharge ability, portability, and relatively constant potential and low cost.

Disadvantages: Use of conc. H_2SO_4 is dangerous. Use of lead battery is fragile.

Nickel – Cadmium Cell:

It is a rechargeable secondary cell. It consists of cadmium as the negative electrode (anode) and NiO_2 as the positive electrode (cathode). Potassium hydroxide (KOH) is used as an electrolyte. The cell reaction during charging and discharging are as follows.



Anode: Cd

Cathode: NiO(OH)

Electrolyte: KOH

EMF = 1.4 V

At anode: $Cd + 2OH \rightleftharpoons Cd(OH)_2(s) + 2e^-$

At cathode: $NiO_2 + 2H_2O + 2e^- \rightleftharpoons 2\ Ni(OH)_2 + 2OH^-$

Overall reaction:

$$Cd + 2NiO(OH) + 2H_2O \rightleftharpoons Cd(OH)_2 + 2Ni(OH)_2$$

Uses:

1. The nickel-cadmium cell has small size and high rate of charge/discharge capacity, which makes it very useful.
2. It also has very low internal resistance and wide temperature range (up to 70^0C).
3. It produces a potential of about 1.4 V and has a longer life than lead storage cell.
4. These cells are used in electronic calculators, electronic flash units, electrical shavers, transistors, etc.
5. Ni–Cd cells are widely used in medical instrumentation and in emergency lighting, toys, etc.
6. It is also used in aircraft and space satellite power system.

Advantages:

1. Ni-Cd batteries last longer, in terms of number of charge/discharge cycles, than other rechargeable batteries.
2. Ni-Cd batteries have much higher energy efficiency.

FUEL CELLS

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

Principle: The basic principle of fuel cell is as same as that of an electrochemical cell. The fuel cell operates like a galvanic cell. The only difference is that the fuel and the oxidant are stored outside the cell. Fuel and oxidant are supplied continuously and separately to the electrodes at which they undergo redox reaction. Fuel cells are capable of supplying current as long as reactants are replenished.

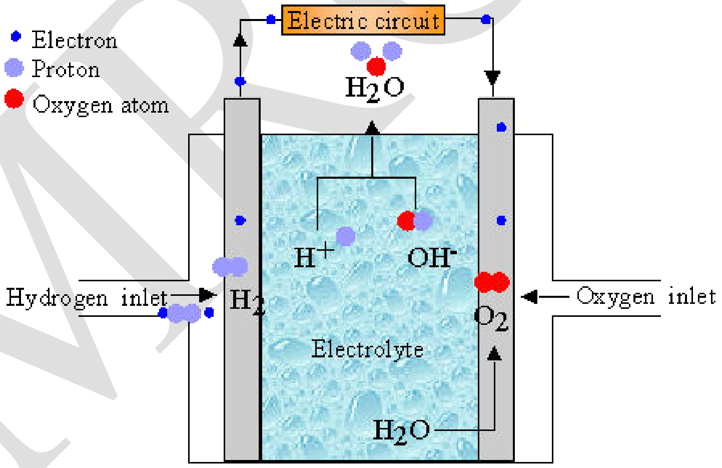
Fuel + Oxidant → Oxidation products + Electric Energy

Examples: 1. H_2-O_2 fuel cell

2. CH_3OH-O_2 fuel cell

Hydrogen oxygen fuel cell:

This cell is a common type of fuel cell. Similar to a galvanic cell, fuel cell also have two half cells. Both half cells have porous graphite electrode with a catalyst (platinum, silver or a metal oxide). The electrodes are placed in the aqueous solution of NaOH or KOH which acts as an electrolyte. Hydrogen and oxygen are supplied at anode and cathode respectively at about 50 atmospheric pressure, the gases diffuse at respective electrodes. The two half-cell reactions are as follows;



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

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

The net reaction: $2H_2\ (g) + O_2\ (g) \rightarrow 2H_2O\ (l)$

The EMF of this cell is measured to be 1.23V. A number of such fuel cell are stacked together in series to make a battery.

Advantages:

1. The energy conversion is very high (75-82%).
2. Fuel cell minimizes expensive transmission lines and transmission losses.
3. It has high reliability in electricity generation.
4. The byproducts are environmentally acceptable.
5. Maintenance cost is low for these fuels.
6. They save fossil fuels.
7. Noise and thermal pollution are very low.
8. They have low maintenance cost.
9. They have quick start system.

Disadvantages:

1. The major disadvantage of the fuel cell is the high cost and the problems of durability and storage of large amount of hydrogen.
2. The accurate life time is also not known.

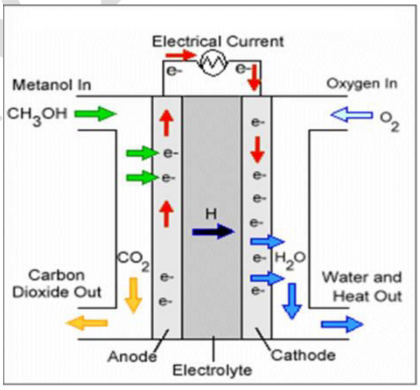
APPLICATIONS:

1. The most important application of a fuel cell is its use in space vehicles, submarine or military vehicles.
2. The product H_2O is valuable source of fresh water by the astronauts.
3. It is hoped that fuel cell technology will bring a revolution in the area of energy production.
4. Fuel cell batteries for automotive will be a great boom for the future.

Limitations:

1. The life time of fuel cells is not accurately known
2. It cannot store electricity
3. Electrodes are expensive ad short lived.
4. Storage and handling of H_2 gas is dangerous because it is inflammable.

Methyl Alcohol- Oxygen (Alkaline Fuel Cell):



In this fuel cell, CH_3OH is used as a fuel and O_2 as oxidant to generate electrical energy. The methyl alcohol–oxygen fuel cell has two electrodes. The anode consists of porous nickel electrode impregnated with Pt/Pd catalyst. Porous nickel electrode coated with silver catalyst constitutes a cathode of the cell. The electrolyte, KOH, is taken in between the two electrodes. CH_3OH and O_2 are sent continuously into their respective electrodes as shown in Fig. and the electrical energy is produced with the continuous replenishment of the fuel, CH_3OH at the anode.

At anode: $CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^-$

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

Overall reaction: $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$

Advantages of methyl alcohol-oxygen fuel cell:

1. Methanol fuel cells are reasonably stable at all environmental conditions.
2. Easy to transport
3. Do not require complex steam reforming operation.
4. These fuel cells are targeted to portable applications.
5. Because of high hydrogen concentration in methanol. it is an excellent fuel.
6. Methanol poses less risk to aquatic plants, animals and human beings than gasoline
7. Because methanol possess lower inflammability limit than gasoline it poses less fire risk than gasoline.
8. There is zero emission by the cells hence the fuel cells are eco friendly.

Application of alcohol-oxygen fuel cell:

1. The major application of methyl alcohol oxygen fuel cells is a fuel for fuel cell motor vehicles like NECAR-5 in Japan, USA etc.

Numerical Problems:

1. A solution of salt (1.0 N) surrounding platinum electrodes 2.1cm apart and 4.2 cm^2 in area was found to offer a resistance of 50 Ω. Calculate the equivalent conductivity of the solution.

Solution: $l = 2.1$ cm, C = 1.0N

$a = 4.2cm^2$

R= 50

Specific conductance (K) = $\frac{1}{R} . \frac{l}{a}$

$$= \frac{1}{50} \times \frac{2.1}{4.2} = 0.01\Omega^{-1}\text{cm-1}$$

$$Equivalent\ \ conductance\ \ (\lambda\ eq) = K \times \frac{1000}{C}$$

$$= 0.01 \times \frac{1000}{1} = 10\Omega^{-1}cm^2equiv^{-1}.$$

2. Specific conductance of a decinormal solution of KCl is 0.0112 ohm^{-1} cm^{-1}. The resistance of a cell containing the solution was found to be 56 Ohms. What is the cell constant.

Solution: $K = 0.0112\Omega^{-1}cm^{-1}$

$R = 56\Omega$

Cell constant = Specific conductance ×Resistance

$= K\times R = 0.0112\times 56 = 0.6272 cm^{-1}$.

3. The specific conductivity of a N/50 solution of a NaCl at 30^0C is 0.00368 $ohm^{-1}cm^{-1}$. If the resistance offered by the solution when placed in a cell is 1,500 ohms, Calculate cell constant and equivalent conductance of solution.

Solution: $K = 0.00368 Ohm^{-1}cm^{-1}$

C= N/50 = 0.02

R = 1,500 ohms.

Equivalent conductance $(\lambda\ eq) = K \times \frac{1000}{C}$

$K = \frac{l}{a} \cdot \frac{1}{R}$

Cell constant $(\frac{l}{a}) = K.R$

$= 5.52\ cm^{-1}$

Equivalent conductance $(\lambda\ eq) = K \times \frac{1000}{C}$

$= 0.00368 \times \frac{1000}{0.02}$

$= 184\ ohm^{-}cm^{-1}$

4. Calculate the Emf for the cell,

Zn/Zn^+ // Ag^+ /Ag given $E^0_{Zn+/Zn}{}^{+2}$ / Zn = 0.762v and $E^0_{Ag+/Ag}$ = 0.8 v

Solution: Given cell is Zn/Zn^{+2} //Ag^+/Ag.

$E^0_{Zn+2/Zn} = 0.762$ v

$E^0_{Ag+/Ag} = 0.8$ v

$E^0_{cell} = E^0_{right} - E^0_{left}$

$= 0.8 - (-0.762)$

$= 1.562$v

5. Calculate the E^0Cu^{+2}/Cu, given $E^- Cu^{+2}/Cu = 0.296$ v and $[Cu^{+2}] = 0.015M$.

Solution: Cell reaction is $Cu \rightarrow Cu^{+2} + 2e^-$

$E = E^0 + \frac{0.0591}{n} \log [cu^{+2}]$

$0.296 = E^0 + \frac{0.0591}{2} \log [cu^{+2}]$

$E^0 = 0.296 - \frac{0.0591}{2} \log (0.015)$

$= 0.296 - 0.2955\ (-1.8239)$

$= 0.296 + 0.0538$

$= 0.3498V$

6. Write the half cell and net cell reactions for the following cell,

$Zn / ZnSO_4$ (aq) // $CuSO_4$ (aq) / Cu. Calculate the standard emf of the cell given,

$E^0Zn^{+2}/Zn = 0.76$ v and $E^0Cu^{+2}/Cu = + 0.34V$.

Solution: Half cell reactions

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

At cathode: $Cu^{+2} + 2e^- \rightarrow Cu$.

Net cell reaction = $Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$.

$$E^0_{cell} = E^0_{Cathode} - E^0_{Anode.}$$

$$= E^0_{cu^{+2}/cu} - E^0_{Zn^{+2}/Zn}$$

$$= 0.34 - (-0.76)$$

$$= 1.1\ V$$

UNIT II: CORROSION AND ITS CONTROL

Introduction:

Metals and alloys are used as fabrication or construction materials in engineering. If the metals or alloy structures are not properly maintained, they deteriorate slowly by the action of atmospheric gases, moisture and other chemicals. This phenomenon of destruction of metals and alloys is known as corrosion.

The surface of almost all the metals begin to decay more or less rapidly when exposed to atmospheric gases, water or other reactive liquid medium.

Corrosion

- *The process of decay of metal by environmental attack is known as corrosion.*
- Metals undergo corrosion and convert to their oxides, hydroxides, carbonates, sulphides, etc.
- Examples:-
- i) Rusting of iron – when iron is exposed to the atmospheric conditions, a layer of reddish scale and powder of Fe_3O_4 is formed.

- ii) Formation of green film of basic carbonate- $[CuCO_3 + Cu(OH)_2]$ on the surface of copper when exposed to moist air containing CO_2.
- The corrosion of metals is measured in the units of *milli/inches/year or mm/year.*

$$\textbf{Metal} \underset{\text{Metallurgy-Reduction}}{\overset{\text{Corrosion-Oxidation}}{\rightleftharpoons}} \textbf{Metallic Compound} + \textbf{Energy}$$

Corrosion is an oxidation process and it is reverse of metal extraction.

Causes of corrosion:

1. The metals exist in nature in the form of their minerals or ores in the stable combined forms as oxides, chlorides, silicates, carbonates and sulphides.
2. During the extraction of metals, these ores are reduced to metallic state by supplying considerable amount of energy.
3. Hence the isolated pure metals are in excited states than their corresponding ores.
4. So metals have natural tendency to go back to their combined state (minerals/ores).
5. When metal is exposed to atmospheric gases, moisture, liquids etc, the metal surface reacts and forms more thermodynamically stable compounds.

Effects of corrosion:

1. Wastage of metal in the form of its compounds.
2. The valuable metallic properties like conductivity, malleability, ductility etc. are lost due to corrosion.
3. Life span and efficiency of metallic parts of machinery and fabrications is reduced

Theories of corrosion:

1. Dry corrosion
2. Wet corrosion

Dry corrosion or Chemical corrosion: The direct chemical action of environment on the surface of metal in absence of moisture is known as dry corrosion.

This type of corrosion occurs mainly through the direct chemical action of atmospheric gases like O_2, halogens, H_2S, SO_2, N_2 or anhydrous inorganic liquid with the metal surface.

Example: (i) Silver materials undergo chemical corrosion by Atmospheric H_2S gas .
(ii) Iron metal undergo chemical corrosion by HCl gas.

There are three types of chemical Corrosion:

1. Oxidation corrosion
2. Corrosion due to other gases
3. Liquid metal corrosion

Oxidation Corrosion:

Direct action of oxygen at low or high temperatures on surface of metals in absence of moisture is known as oxidation corrosion. Alkali metals and Alkaline earth metals are rapidly oxidized at lower temperatures. At high temperature all metals are oxidized (except Ag, Au, Pt).

Mechanism:

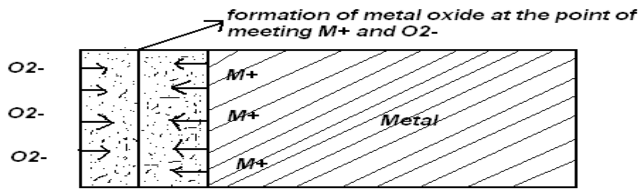
1) Oxidation takes place at the surface of the metal forming metal ions M^{2+}
2) Oxygen is converted to oxide ion (O^{2-}) due to the transfer of electrons from metal.
3) The overall reaction is of oxide ion reacts with the metal ions to form metal oxide film.

Reactions in oxidation corrosion

$$M \longrightarrow M^{2+} + 2e^- \quad \text{(Oxidation)}$$

$$1/2O_2 + 2e^- \longrightarrow O^{2-} \quad \text{(Reduction)}$$

$$M + O_2 \longrightarrow M^{2+} + O^{2-} \quad \text{(Metal oxide)}$$



Oxidation mechanism of metals

Mechanism:

Initially the surface of metal undergoes oxidation and the resulting metal oxide scale forms a barrier which restricts further oxidation. The extent of corrosion depends upon the nature of metal oxide.

Nature of the oxide formed: - It plays an important role in further oxidation corrosion process.

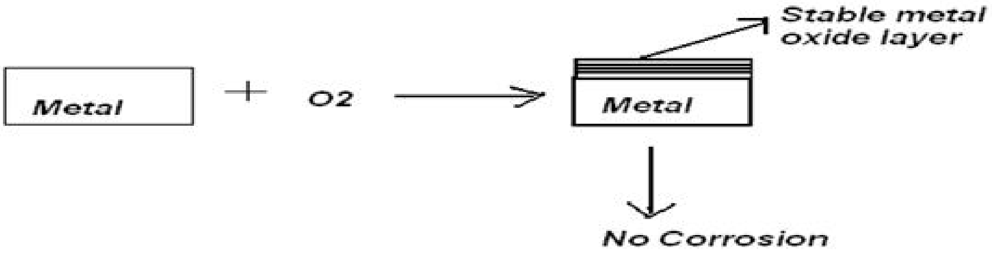
Metal + oxygen ⟶ metal oxide (corrosion product)

When the oxide film formed is:

(a) Stable metal oxide layer

A stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Such a layer will be impervious in nature and hence behaves as protective coating, thereby shielding the metal surface. Consequently further oxidation corrosion is prevented.

E.g.: Al, Sn. Pb, Cu, etc. form stable oxide layers on surface thus preventing further oxidation.



(b) Unstable metal oxide layer

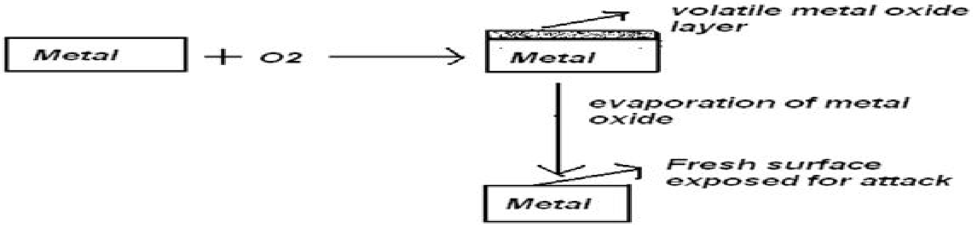
The oxide layer formed decomposes back into metal and oxygen. Consequently oxidation corrosion is not possible in such cases.

Eg: Ag, Au and Pt do not undergo oxidation corrosion.

Metal oxide ⟶ Metal + oxygen

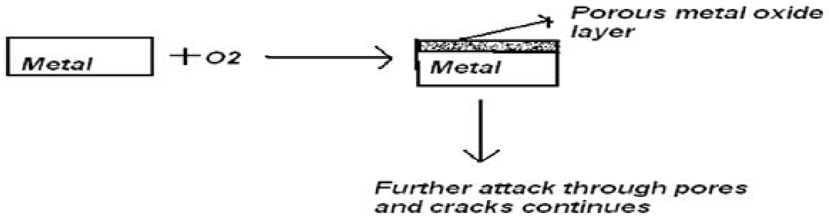
(c) Volatile Metal oxide layer

The oxide layer formed is volatile in nature and evaporates as soon as it is formed. There by leaving the under lying metal surface exposed for further attack. This causes rapid continuous corrosion, leading to excessive corrosion eg: Mo- molybdenum forms volatile MoO_3 layer.



(d) Porous Metal oxide layer

If the metal oxide layer is porous, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrode the underlying metal surface. This cause continuous corrosion till conversion of metal into its oxide is completed. **Eg:** Alkali and alkaline earth metals (Li, Na, K, Mg etc.)



Pilling Bedworth rule:

- To express the extent of protection given by the corrosion layer to the underlying metal Pilling Bedworth rule was postulated.
- It is expressed in terms of specific volume ratio.
- **Specific Volume ratio** $= \frac{\text{Volume of metal oxide layer}}{\text{Volume of parent metal}}$
- Smaller the specific volume ratio, greater is the oxidation corrosion
- Eg. The specific volume ratio of W, Cr, and Ni are 3.6, 2.0 and 1.6 respectively. Consequently the rate of corrosion is least in Tungsten(W)

- If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent, non-porous and does not allow the penetration of corrosive gases. No further corrosion.
- If the volume of the corrosion film formed is less than the underlying metal, it forms pores/cracks and allow the penetration of corrosive gases leading to corrosion of the underlying metal.

Wet Corrosion or Electrochemical Corrosion

- The direct chemical action of environment on the surface of metal in presence of conducting liquid with the formation of electrochemical cells.
- It a common type of corrosion which occurs usually in aqueous corrosive environment
- Occurs when metal comes in contact with a conducting liquid.
- Formation of galvanic cell on the surface of metal generating anodic and cathodic areas
- At anode oxidation takes place liberating electrons.
- Electrons at anode are transported to cathodic area where H^+ or O_2 and H_2O consumes the electrons generating non-metallic ions like OH^- or O^{2-}
- Metallic (M^+) and non metallic (OH^- or O^{2-}) diffuse towards each other and results in the formation of corrosion product in between the anodic and cathodic area.

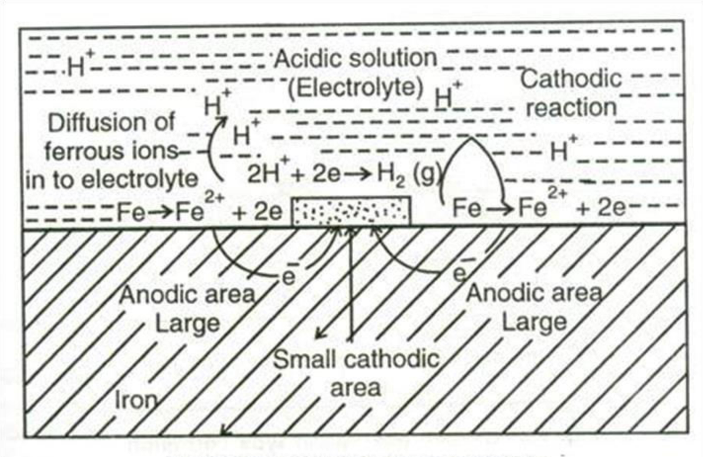
Mechanism*:* Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.

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

The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

Wet corrosion takes place in two ways.
1. Evolution of Hydrogen
2. Absorption of Oxygen

Evolution of Hydrogen:
This type of corrosion occurs in acidic medium.
Eg: Rusting of iron metal in acidic environment takes place in the following way:



Hydrogen evolution type corrosion

At Anode dissolution of iron to ferrous ion takes place with the liberation of electrons

Anode: $Fe \longrightarrow Fe^{2+} + 2e^-$ (Oxidation)

The electrons released at anode flow through the metal from anode to cathode, where as H+ ions of acidic solution take up these electrons and eliminated as hydrogen gas.

Cathode: $2H^+ + 2e^- \longrightarrow H_2\uparrow$ (Reduction)

The overall reaction is: $Fe + 2H^+ \longrightarrow Fe^{2+} + H_2\uparrow$

This type of corrosion causes “displacement of hydrogen ions from the acidic solution by metal ions.
In hydrogen evolution type corrosion, the anodic areas are large and cathodic areas are small.

Absorption of Oxygen:
- This type of corrosion takes place in basic or neutral medium in presence of oxygen.
- For example, rusting of iron in neutral or basic aqueous solution of electrolyte in presence of atmospheric oxygen.
- Usually the surface of iron is coated with a thin film of iron oxide.

- If the film develops cracks, anodic areas are created on the surface and the rest of the metal surface acts as cathodes.
- It shows that anodic areas are small and the cathodic areas are large.

Anode: $Fe \longrightarrow Fe^{2+} + 2e^-$ (Oxidation)

The released electrons flow from anode to cathode through iron metal.

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

Overall reaction: $Fe_2^+ + 2OH^- \longrightarrow Fe(OH)_2$

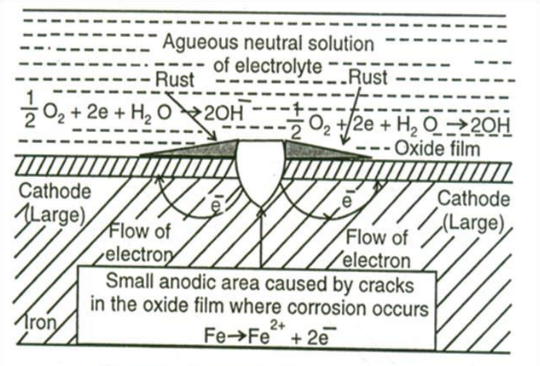
If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide and then to hydrated ferric oxide which is known as rust.

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$

$$4Fe(OH)_2 + O_2 + 2H_2O \xrightarrow{oxidation} 4Fe(OH)_3 \xrightarrow{oxidation} Fe_2O_3.3H_2O$$

Rust (hydrated ferric oxide)

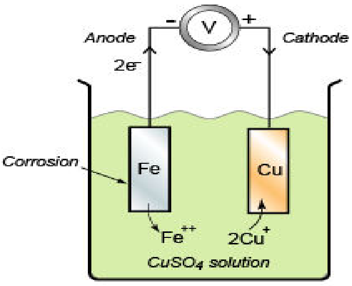
The product called rust corresponds to **$Fe_2O_3.3H_2O$.**



Oxygen absorption type corrosion

Types of Corrosion:

Galvanic Corrosion:



- When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series (low reduction potential) undergoes corrosion and the metal lower in electrochemical series (high reduction potential) is protected. This type of corrosion is called galvanic corrosion.

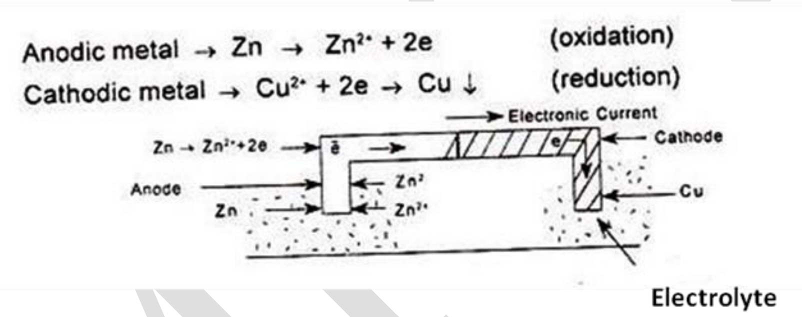
- **Eg:** When Zn an Cu are connected and exposed to corroding environment, Zinc higher in electrochemical series forms anode, undergoes oxidation and gets corroded. Cu lower inelectrochemical series acts as cathode, undergoes reduction and protected as the electrons released by Zn flow towards Cu.

Examples of Galvanic corrosion

- Steel pipe connected to copper plumbing
- A steel propeller shaft in bronze bearing
- Lead antimony solder around copper wire
- Steel screws in a brass marine hardware

Galvanic corrosion can be minimized:

- By avoiding galvanic couple (contact of two dissimilar metals must be avoided
- Buy providing an insulating material between the two metals


Anodic metal $\rightarrow$ Zn $\rightarrow Zn^{2+} + 2e$ (oxidation)

Cathodic metal $\rightarrow Cu^{2+} + 2e \rightarrow Cu \downarrow$ (reduction)

Galvanic Series:

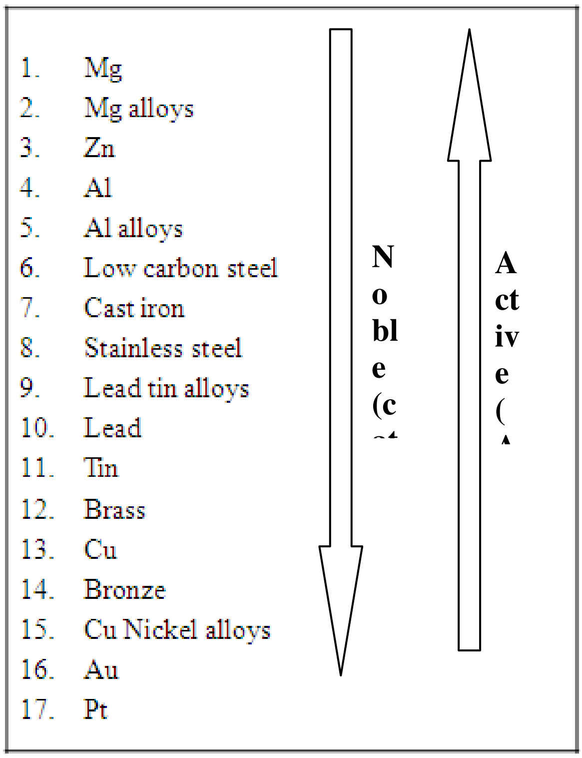
Although electrochemical series give very useful information regarding chemical reactivity of metals, it did not provide sufficient information in predicting the corrosion behavior under a particular set of environmental conditions.

Hence electrode potentials of various metals and their alloys in common use are measured by immersing them partially in sea water,and the values have been arranged in decreasing order of activity and is called as galvanic series.

In galvanic series,oxidation potentials are arranged in the decreasing order of activity of a series of metals.Thus galvanic series give real and useful information for studying the corrosion tendency of metals and alloys.

Electrochemical Series	Galvanic series
1. This series consists of metal and non-metals 2. The position of metal in this series is permanently fixed 3. It predicts relative displacement tendencies 4. Electrode potentials are measured by dipping the pure metal in their salt solution of 1M concentration	1. This series consists of metals and alloys 2. The position of metal is different from that of the position of its alloy 3. It predicts the relative corrosion tendencies 4. Electrode potentials of metals and alloys are measured by immersing in sea water

Galvanic Series



1. Mg
2. Mg alloys
3. Zn
4. Al
5. Al alloys
6. Low carbon steel
7. Cast iron
8. Stainless steel
9. Lead tin alloys
10. Lead
11. Tin
12. Brass
13. Cu
14. Bronze
15. Cu Nickel alloys
16. Au
17. Pt

Passivity or Passivation:

- ➢ The phenomenon in which a metal or an alloy exhibits a much higher corrosion resistance than expected from its position in the electrochemical series is called Passivity.
- ➢ It is due to formation of a highly protective, but very thin film on the surface of metal or an alloy and makes it more noble
- ➢ The film is insoluble, non porous and of self–healing nature that when broken, it will repair itself on re-exposure to oxidizing conditions
- ➢ Eg 1. Passive metals and alloys are Ti, Al, Cr and a wide variety of stain less steel alloys containing Cr. These exhibit outstanding corrosion resistance in oxidizing environments, but in reducing environments, they become chemically active
- ➢ Eg 2.The action of more conc. Nitric acid on active metals (Fe and Al) produces a thin protective oxide film, thereby shifting the anodic reaction and making them passive.

Factors effecting corrosion:

The rate and extent of corrosion depends on

1. Nature of Metal
2. Nature of Environment

Nature of metal:

1. Purity of the metal:

If impurities are present in a metal the corrosion rate is increased due to formation of tiny electrochemical cells at the exposed parts and the anodic parts get corroded. A pure metal is more corrosion resistant than impure metal. By increasing its purity the corrosion resistance of a metal can be improved

Ex: Zn metal containing impurity undergoes corrosion of zinc, due to the formation of electrochemical cells. The rate and extent of corrosion increases with the increasing exposure and extent of the impurities.

2. Position of metal in galvanic series: Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily.

Metals which possess high reduction potentials and occupy lower end of galvanic series do not undergo corrosion and they get protected.

- When two metals are in electrical contact in presence of an electrolyte, then the metal which is more active undergoes corrosion.
- The rate of corrosion depends on the difference in their position in galvanic series. Greater the difference more will be the extent of corrosion at anode.

Eg: The potential difference between Fe and Cu is 0.78V which is more than that between Fe and Sn (0.30V). Therefore, Fe corrodes faster when in contact with Cu than that with Sn. On this account, the use of dissimilar metals should be avoided wherever possible (Eg. Bolt & nuts, screw & washer).

3. **Relative areas of anodic and cathodic parts**:If the metal has small anodic and large cathodic area, the rate of corrosion is very high. This is because the more electrons are liberated at smaller anodic area, which are consumed at cathode. If the cathodic area is larger, the liberated electrons are rapidly consumed at cathode. This further enhances the anodic reaction leading to increase in the rate of corrosion.

   When two dissimilar metals or alloys are in contact,

   corrosion at anodic area $\propto \frac{\text{Areaofcathodicpart}}{\text{Areaofanodicpart}}$

4. Hydrogen over voltage:

The difference between the potential of the electrode at which the electrolysis actually proceeds continuously (actual decomposition potential) and the theoretical decomposition potential for the same solution is called overvoltage.

When a metal which is at a high position in galvanic series (eg. Zn) is placed in 1N H_2SO_4, it undergoes corrosion with deposition of a film on its surface and evolution of hydrogen gas.So the initial rate of corrosion is high, but decreases after a while due to salt film and H_2 film surrounding the metal which causes high over voltage and reduces the corrosion rate. However, if few drops of $CuSO_4$ are added, the corrosion rate of Zn is accelerated because some copper gets deposited on the Zn metal, forming minute cathodes, where the hydrogen overvoltage is reduced. Hence reduction in overvoltage of the corroding metal/alloy accelerates the corrosion. So higher the over voltage, lesser is the corrosion

$$Rate\ of\ corrosion\ \alpha\ \frac{1}{over\ voltage}$$

5. **Physical state of metal**: Metals with small grain size have more tendencies to undergo corrosion. Metal with more stress/strain also undergoes corrosion easily.

Nature of Environment:

1. Temperature: The rate of corrosion increases with increase in temperature due to increase in diffusion rate.

$$Rate\ of\ corrosion\ \alpha\ temperature$$

2. Humidity in air: The rate of corrosion increases with the presence of moisture in atmosphere because the moisture or humidity present in atmosphere furnishes water to the electrolyte which is essential for setting up of an electrochemical cell. The oxide film formed has the tendency to absorb moisture which creates another electrochemical cell.

$$Rate\ of\ corrosion\ \alpha\ Humidity$$

3. Effect of P^H: pH value of the medium has the greater effect on corrosion. Generally acidic medium (i.e. pH < 7) is more corrosive than basic medium. Acidic pH increases the rate of corrosion. However some metals like Al, Pbetc dissolve in alkaline solutions as complex ions. Consequently, corrosion of metals, readily attacked by acid can be reduced by increasing the P^H of the attacking environment.

Acidic medium: $P^H < 7$- Corrosion is more

Basic medium: $P^H > 7$- Corrosion is less

Eg: Zn which is readily corroded in acidic solutions suffers very less corrosion in alkaline medium, i.e P^H=11. Al has less corrosion at pH=5.5 which corrodes rapidly at P^H= 8.5.

$$Rate\ of\ corrosion\ \propto \frac{1}{PH}$$

Corrosion control methods:

1. Proper designing
2. Using Pure metals
3. Using metal alloys
4. Use of inhibitors

5. Modifying Environment
6. Cathodic protection
7. Application of protective coatings

Cathodic Protection:

The method of protecting the base metal by forcibly making it to behave like a cathode there by corrosion does not occur is called as cathodic protection.

There are two types of cathodic protection

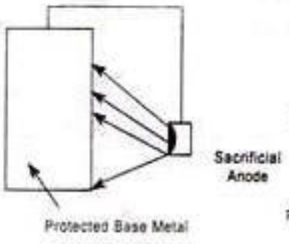
(a) Sacrificial anodic protection
(b) Impressed current cathodic protection

Sacrificial anodic protection

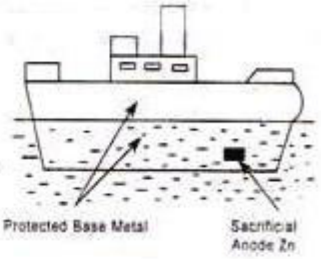
- In this protection method, the metallic structure to be protected (base metal) is connected by a conducting wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal.
- The more anodic metal itself gets corroded slowly, while the parent structure (cathodic) is protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode is replaced by a fresh one, when consumed completely.
- The artificially made anode thus gets corroded gradually protecting the original metallic structure. Hence the process is known as sacrificial anodic protection.
- Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys which possess low reduction potential and occupies higher end in electrochemical series.

Eg: A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

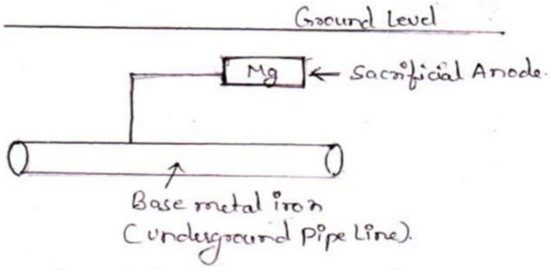
Unprotected base metal



(b) Sacrificial anodic protection



(c) Protection of ship-hull below water line by



(d) Buried Pipeline protected by connecting to Mg block.

Figure1. Sacrificial anode method: Ship hull and underground water pipeline

Applications of Sacrificial anodic protection:

By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.

1. To protect underground pipelines- Buried pipe line protected by connecting to Mg block
2. Protection of ship hulls and other marine devices
3. Protection of water tank- by suspending Zn or Mg rods, body of the tank made cathode and protected

Advantages:

1. It is a simple method.
2. It does not require external power.
3. It has low maintenance and installation cost
4. Cathodic interferences are minimum.

Disadvantages:

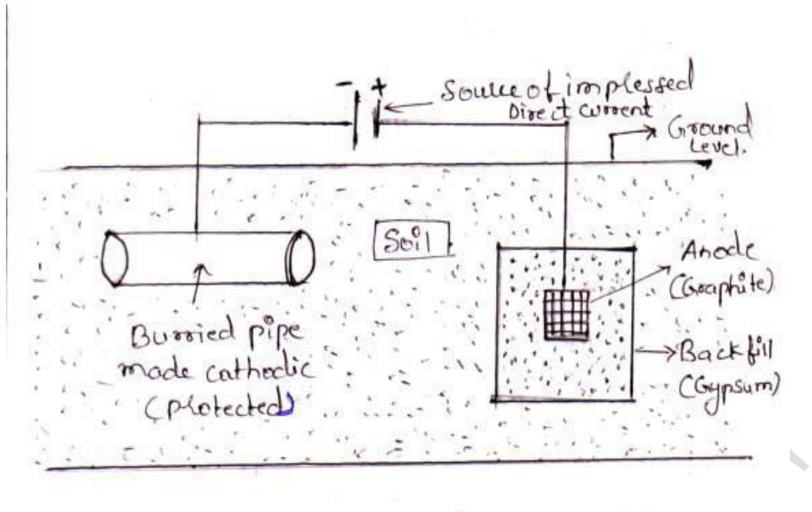
1. More than one anode is required some times.
2. It does not work properly in high corrosive environment.
3. Sacrificial anode must be replaced periodically as and when it is consumed

Impressed current cathodic protection:

- In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.
- The impressed current is slightly higher than the corrosion current. Thus the anodic corroding metal becomes cathodic and protected from corrosion.
- The impressed current is taken from a battery or rectifier on A.C. line.
- The metal to be protected is made cathode by connecting to an external battery (-ve terminal)
- The anode is usually insoluble anode like graphite, stainless steel, or platinum connected to +ve terminal of the battery. Usually a sufficient D.C current is passed on to the insoluble anode kept in a black fill composed of coke or gypsum, so as to increase the electrical contact with the surrounding soil.
- In impressed current cathodic protection, electrons are supplied from an external cell, so that the object itself becomes cathodic and does not get oxidized.

Applications:

- The impressed current cathodic protection is used for the protection of water tanks, water & oil pipe lines, transmission line towers etc.



Advantages

The method is mainly employed to protect large structures for long term operations.

Disadvantages

1. The method is expensive as it requires high current
2. Capital investment and maintenance costs are more
3. It is difficult to maintain uniform current over the entire metal surface as a result localized corrosion may occur.
4. The metal should not be over protected, ie, use of much high potential is avoided otherwise problems related to cathodic reactions like evolution of H_2 and formation of OH^- Ions talks place leading to corrosion of base metal

Metallic coatings:

The surface of the base metal coated with another metal (coating metal)is called metallic coatings. Metallic coatings are broadly classified into anodic and cathodic coatings.

1. Anodic coating:

- The metal used for the surface coating is more anodic than the base metal which is to be protected.
- For example, coating of Al, Cd and Zn on steel surface are anodic because their electrode potentials are lower than that of the base metal iron. Therefore, anodic coatings protect the underlying base metal sacrificially.
- The formation of pores and cracks over the metallic coating exposes the base metal and a galvanic cell is formed between the base metal and coating metal. The coating metal dissolves anodically and the base metal is protected.

2. Cathodic coating:

- Cathodic coatings are obtained by coating a more noble metal (i.e. metals having higher electrode potential like Sn, Au, Ag, Pt etc.) than the base metal. They protect the base metal as they have higher corrosion resistance than the base metal due to cathodic nature.
- Cathodic coating protects the base metal only when the coating is uniform and free from pores.
- The formation of pores over the cathodic coating exposes the base metal (anode) to environment and a galvanic cell is set up. This causes more damage to the base metal.

Methods of application of metallic coatings:

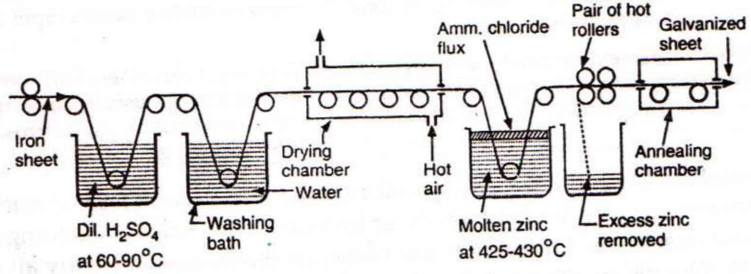
1. Hot dipping:

- Hot dipping process is applicable to the metals having higher melting point than the coating metal.
- It is carried out by immersing a well cleaned base metal in a bath containing molten coating metal and a flux layer.
- The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal. **Eg:** Coating of Zn, Pb, Al on iron and steel surfaces.
  The most widely used hot dipping processes are
  (a) Galvanizing
  (b) Tinning

Galvanizing:

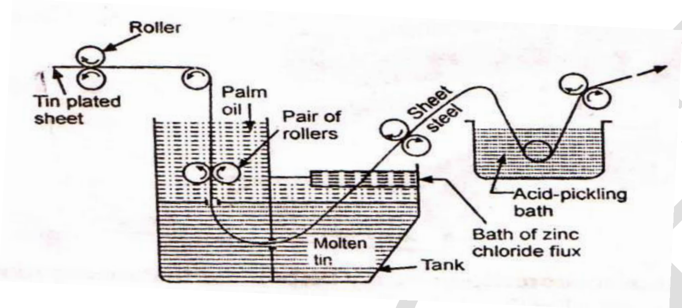
- Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc.
- It is the anodic protection offered by the zinc.
- In this process, at first iron or steel is cleaned by pickling with dil H2SO4 solution for 15-20 minutes at 60-90^{0}C. In pickling any scale, dirt, oil, grease or rust and any other impurities are removed from the metal surface.
- The article is washed well and then dried.
- It is then dipped in bath of molten zinc maintained at 425-430^{o}C.
- The surface of bath is kept covered with ammonium chloride – flux to prevent oxide formation. The article is covered with a thin layer of zinc when it is taken out of bath.
- It is then passed through a pair of hot rollers, which removes any excess of zinc and produces a thin film of uniform thickness
- Then it is annealed and finally cooled slowly.

Applications: Galvanizing is widely used for protecting iron exposed to the atmosphere (roofs, wire fences, pipes etc.) Galvanized metallic sheets are not used for keeping eatables because of the solubility of zinc.



Tinning

- The process of coating tin over the iron or steel articles to protect them from undergoing corrosion is known as tinning.
- Tin is a noble metal and therefore it possess more resistance to chemical attack. It is the cathodic protection offered by the tin. In this process, iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film, if present.
- A cleaned iron sheet is passed through a bath of $ZnCl_2$ molten flux followed by molten tin and finally through a suitable vegetable oil. The $ZnCl_2$ flux helps the molten metal to adhere to the base metallic surface.
- Palm oil protects the tin coated surface against oxidation.
- Finally the sheet is passed through rollers to remove excess of tin and produce thin coat of tin of uniform thickness



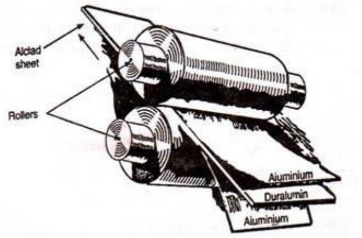
Applications:

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

Metal Cladding:

The surface of the base metal to be protected is sandwiched between two thin layers of coat metal and pressed between rollers.

- Coating of a thin homogeneous layer of a coating metal on a base metal such that it strongly binds permanently either on one side or on both sides under heat and pressure.
- The finished product may be welded at the edges. The coat metal has to be anodic to the base metal and only plain surfaces can be cladded.
- This method is used for coating Al, Cr, Ni, Duralumin, etc. All corrosion-resistant metals like Ni, Cu, Ag, Au & Pt and alloys like steel/nickel alloys can be used as cladding materials.



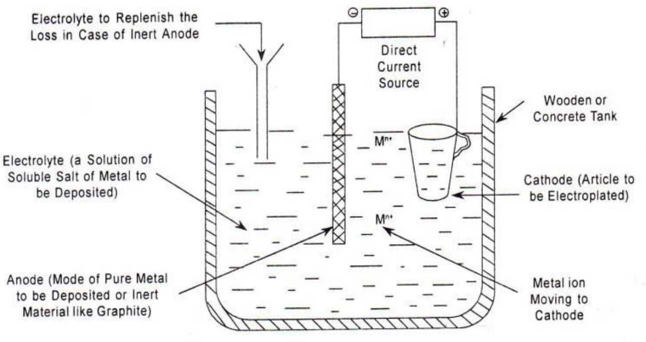
Cladding of Duralumin

Applications:

1. This method is widely used in aircraft industry and automobile industry.
2. Copper clad steel is used in electrical industry because of its good electrical conductivity and high strength aluminum clad steel is used in air craft fuel gauges and in gasoline water tanks.
3. A 99.5% pure Al is subjected to cladding to protect Duraluminium to produce Alclad – used in air craft industry.

Electroplating:

- It is a process in which coating metal is deposited on the base metal by passing direct current through an electrolytic solution containing the soluble salt of the coating metal.
- The base metal is first subjected to acid pickling to remove any scales, oxides etc. The base metal is made as cathode of the electrolytic cell and the coating metal is made as anode.
- The two electrolytes are dipped in the electrolyte solution which contains the metal ions to be deposited on the base metal.
- When a direct current is passed from an external source, the coating metal ions migrate towards cathode and get deposited over the surface of base metal in the form of a thin layer.
- Low temperature, medium current density, low metal ion concentration conditions are maintained for better electro-plating.



Objectives of Electroplating

1. To increase resistance to corrosion, chemical attack and wear resistance of the plated metal
2. To improve physical appearance and hardness
3. To increase the decorative and commercial values of metals
4. To increase the strength of non-metals like plastics, wood and glass etc.
5. To make surface conductive by using light weight non-metallic materials like wood and plastics

Electroplating-Copper plating:

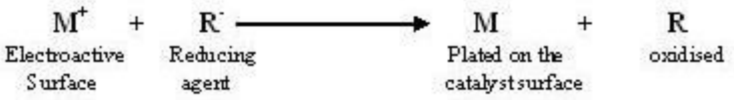
For example, for electroplating of copper on iron article the following are maintained
Electrolytic bath solution: $CuSO_4$
Anode: Pure copper
Cathode: Base metal article
Temperature: 20-40°C (low temp for brighter and smooth surface)
Current density: 20-30 mA/cm^2
When direct current is passed, the Cu^{2+} ions migrate to the cathode and deposit on the base metal article.

Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Electroless plating

- The method of deposition of a metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electrical energy is called electroless plating.
- This process is also called chemical plating or autocatalytic plating.
- The metallic ions (M^+) are reduced to the metal with the help of reducing agents(R^{-1}). When the metal(M) is formed, it gets plated over a catalytic surface.



$$M^+ + R^- \longrightarrow M + R$$

Pretreatment and activation of the surface:
The surface to be plated is first degreased by using organic solvents or alkali, followed by acid treatment.

1. The surface of the stainless steel is activated by dipping in hot solution of 50 % dilute sulphuric acid.
2. The surface of magnesium alloy is activated by thin coating of zinc or copper over it.
3. Metals (Al, Cu, Fe) and alloys like brass can be directly nickel plated without activation.
4. Non metallic articles like plastics, glass are activated by dipping them in the solution containing $SnCl_2$+HCl, followed by dipping in palladium chloride solution. On drying, a thin layer of palladium is formed on the surface.

The following are the requirements of electroless plating.

1. Soluble electro active metal in the form of metal chloride or sulphate
2. The reducing agents like formaldehyde hypophospites
3. Complexing agents like citrate, tartrate and succinate
4. Exaltants like succinates, glycinates and fluorides to improve the rate of plating
5. To control P^H of the bath, buffer solution is added

Electroless-Ni plating:

It is an auto-catalytic chemical technique used to deposit a layer of nickel-phosphorus or nickel-boron alloy on a solid work piece, such as metal or plastic. The process relies on the presence of a reducing agent

It involve the following features

Pretreatment and activation of the surface: The surface to be plated is activated by treatment with organic solvents or alkali, followed by acid treatment

Composition of Bath:

Coating solution- $NiCl_2$ solution
Reducing agent- Sodium hypophosphite ($NaH_2PO_2.H_2O$)
Buffer- Sodium acetate
Complexing agent- Sodium succinate
Optimum P^H- 4.5
Optimum temperature - 93°C

Reactions:

$$Ni^{2+} + 2e^- \longrightarrow Ni \quad \text{(Cathode)}$$

$$H_2PO_2^- + H_2O \longrightarrow H_2PO_3^- + 2H^+ + 2e^- \text{ (Anode)}$$

Net Rexn: $Ni^{2+} + H_2PO_2^- + H_2O \longrightarrow Ni + H_2PO_3^- + 2H^+$

Advantages of Electroless plating:

1. Electrical energy is not required.
2. Even intricate parts (of irregular shapes) can be plated uniformly
3. There is flexibility in plating volume and thickness.
5. The process can plate recesses and blind holes with stable thickness.
6. Chemical replenishment can be monitored automatically.
7. Matte, semi bright or bright finishes can be obtained.
8. Plating on articles made of insulators (like plastics) and semiconductors can easily be carried out.
9. Electroless plated Ni objects has better corrosion resistance, deposits are pore free, hard and wear resistant.

Applications:

1) It is used extensively in electronic appliances.
2) It is used in domestic as well as automotive fields (eg. jewellery, tops of perfume bottles).
3) Its polymers are used in decorative and functional works.
4) Its plastic cabinets are used in digital as well as electronic instruments.

UNIT 3: ENGINEERING MATERIALS

Polymers

Introduction:

Polymers form very important components in our daily life. The polymers are highly useful in domestic, industrial & medical fields. The following are the reasons for the extensive use of polymers.

1) Most of the polymers are non-toxic & safe to use
2) They have low densities (light in weight), so transportation of polymers will be easy
3) They possess good mechanical strength
4) They are resistant to corrosion and will not absorb moisture when exposed to the atmosphere
5) They can function as good thermal & electrical insulators
6) They can be moulded and fabricated easily
7) They possess esthetic colors

But the limitations for the use of polymers are:

- Some polymers are combustible.
- The properties of polymers are time dependent
- Some of them cannot withstand high temperatures.
- It is also interesting to note that many carbohydrates, proteins & enzymes, DNA & RNA are natural polymers.

Polymer:

Polymers can be defined as the large molecules (macro molecules) formed by the linking together of large number of smaller molecules called monomers. (In Greek language ‘poly’ means “*many”* & ‘mer’ means “*units”*)

E.g.:- polyethylene is a polymer formed by linking together of a large number of ethylene molecules

$$nCH_2=CH_2 \xrightarrow{\text{Polymerisation}} -\!\left(CH_2-CH_2\right)_n\!-$$

Thus the repeated unit of polymer is called monomer. The number of repeating units in a polymer chain is called degree of polymerization. For e.g. if 100 molecules of ethylene polymerize to give the polymer chain, the degree of polymerization is 100.

Depending on the degree of polymerization, there are two types of polymers.

1. Oligo Polymers: Those polymers whose degree of polymerization is less than 600 are called oligo polymers.

2. High Polymers: When the degree of polymerization of a polymer is more than 600, it is called high polymer.

Important terms:

Homo Polymer: Polymer made up of only one type of monomer. $-\left(M_1-M_1-M_1\right)_n-$

Ex: Polyethylene, PVC.

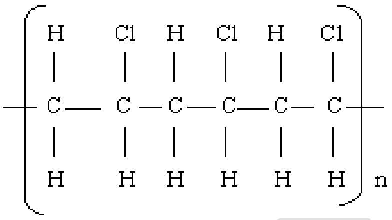
Copolymer: Polymer formed by the reaction between different monomers.

Ex: Buna-s rubber. $-\left(M_1-M_2-M_1-M_2\right)_n-$

Tacticity:

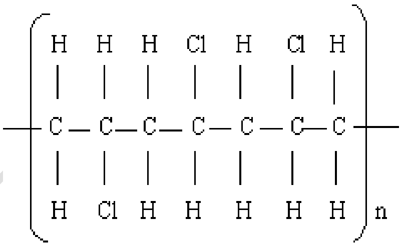
The arrangement of functional groups on carbon backbone of the polymer is called tacticity. It is manly divided into 3 types.

1) **Isotactic polymers:** Those polymers in which the functional groups are arranged on the same side of polymer back bone are called isotactic polymers. Ex: PVC



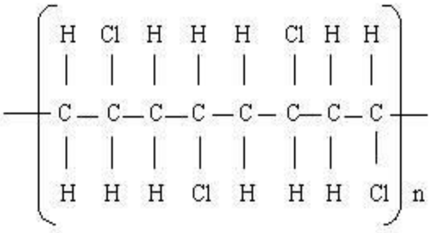
$$-\left[\begin{array}{cccccc} \mathrm{H} & \mathrm{Cl} & \mathrm{H} & \mathrm{Cl} & \mathrm{H} & \mathrm{Cl} \\ | & | & | & | & | & | \\ \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C} \\ | & | & | & | & | & | \\ \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} \end{array}\right]_n-$$

2) **Atactic polymers**: When there is no regular arrangement of functional groups on the back bone of the polymer chain, those polymers are called atactic polymers. Ex: PVC



$$-\left[\begin{array}{ccccccc} \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{Cl} & \mathrm{H} & \mathrm{Cl} & \mathrm{H} \\ | & | & | & | & | & | & | \\ \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C} \\ | & | & | & | & | & | & | \\ \mathrm{H} & \mathrm{Cl} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{H} \end{array}\right]_n-$$

3) **Syndiotactic Polymers:** The polymers with alternate arrangement of functional groups are called syndiotactic polymers for e.g. PVC



$$-\left[\begin{array}{cccccccc} \mathrm{H} & \mathrm{Cl} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{Cl} & \mathrm{H} & \mathrm{H} \\ | & | & | & | & | & | & | & | \\ \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C}- & \mathrm{C} \\ | & | & | & | & | & | & | & | \\ \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{Cl} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \mathrm{Cl} \end{array}\right]_n-$$

Functionality:

- For a substance to act as a monomer, it must have at least two reactive sites or bonding sites.
- The number of reactive sites or bonding sites in a monomer is called functionality of the monomer.
- If two reactive sites are there in a monomer then it is called bi-functional and forms linear or straight chain polymers
- A tri-functional monomer has three reactive sites and forms branched chain polymers.

- A poly-functional monomer has more than three reactive sites and forms three dimensional network polymers.

Classification of polymers:

1. Classification on the basis of source:
a) Natural polymers, which are found in nature. For example, starch, cellulose, proteins etc..
b) Synthetic polymers, which are man-made. For example, PVC, Teflon, Bakelite etc…

2. Classification on the basis of structure:
a) Linear polymer, in which monomeric units are joined in the form of long straight chains. For example, Nylon, polyester, HDPE, etc. These polymers possess high melting point, density and tensile strength, due to close packing of polymer chains.
b) Branched chain polymers, are mainly linear in nature, but also possess some branches along the main chain. For example, Glycogen, LDPE, etc. These polymers possess low melting point, density and tensile strength, due to poor packing of polymer chains.
c) Cross-linked polymers, in which one linear polymeric chain links to another polymer chain. They can be covalent bonds. For example, Bakelite, urea-formaldehyde resin, etc. These polymers possess hard, rigid, and brittle and do not melt.

3. **Classification on the basis of polymerization:**
a) Addition polymers, which are obtained by addition polymerization method. For example, polyethylene, PVC, etc…
b) **Co polymers,** which are obtained by co polymerization method. For example Buna-S rubber, Buna-N rubber, etc…
c) Condensation polymer, which are obtained by condensation polymerization method. For example, Bakelite, urea-formaldehyde resin, nylon6, etc…

4. Classification based on intermolecular force:
a) Thermoplastic polymers, are linear, long chain polymers, which can be softened on heating and hardened on cooling. For example PVC, polystyrene, Teflon, etc…
b) Thermosetting polymers, are three dimensional, cross linked polymers, which cannot be softened on heating and hardened on cooling. For example, Bakelite, urea-formaldehyde resin, etc…
c) Fibres, are those polymers whose chains are held by strong intermolecular forces like hydrogen bonding. For example, nylon, polyester etc…
d) Elastomer, are rubber like elastic polymer, which can be stretched to at least thrice its length, but it returns to its original shape and dimensions as soon as stretching force is released. For example, Buna-S, Buna-N etc…

S.No	Type	Division		
1.	Structure/shape	Linear	Branched	Cross linked
2.	Tacticity	Isotactic	Syndiotactic	Atactic
3.	Physical state	Amorphous		Crystalline

4.	Heat	Thermoplastic	Thermosetting
5.	Conductance	Insulators	Conductors
6.	Origin	Natural	Synthetic
7.	Environment	Biodegradable	Durable
8.	Monomer	Polar	Non-polar
9.	Number of monomers	Homo-polymer	Co-polymer
10.	Polymer chain	Homo – chain	Hetero – chain
11.	Polymerization	Addition	Condensation

Types of polymerization:

There are three types of polymerization.

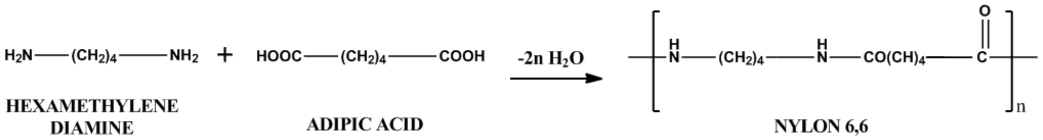
Step Polymerization (Condensation Polymerization)

Step polymerisation takes place by condensation reaction of the functional groups of the monomer, with the elimination of bi-products like H_2O, HCl etc, hence known as condensation polymerisation. The following are the characteristics of step polymerisation.

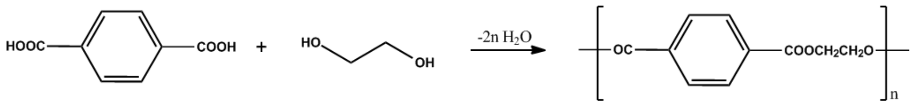
1) The monomers contain functional groups like –OH, -COOH, NH_2, $RCOOR^1$, halides etc.
2) The functionality of the monomer must be two or more than two. The monomers must be dibasic acids, diols, diamines or triols etc.
3) The polymer is built up by a slow step wise condensation reaction of the functional groups of the monomer.
4) The polymerisation reaction is accompanied by the elimination of biproducts like HCl, CH_3OH, H_2O etc.
5) The reaction is not exothermic.
6) The molecular weight of the polymer is not the sum of the molecular weights of the monomers.
7) The polymers produced are living polymers containing functional groups at the end of the chain.
8) It is not three step mechanism of initiation, propagation and termination.
9) The reactions are catalyzed by catalysts.

Examples:

1) Nylon 6,6



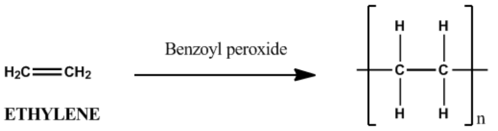
2) Polyester (Terylene (or) Dacron)



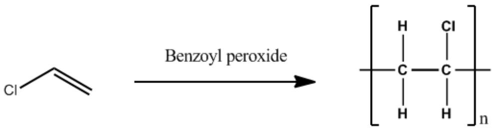
Chain Growth Polymerization: (Addition Polymerization)

A chain polymerisation is a reaction that yields a polymer product which is the exact multiple of monomers. Thus the mechanism is also called addition polymerisation. The following are the characteristics.

1) The functionality of the monomer is a double bond and it is bi-functional.
2) The polymerisation takes place by self-addition of the monomer molecules to each other through a chain reaction.
3) No bi-products like H_2O, CH_3OH etc. are produced.
4) The polymer has the same chemical composition as that of monomer.
5) The mechanism is carried out in three steps, i.e. initiation, propagation and termination.
6) The mechanism is rapid.
7) The conversion of Π bond to σ bond takes place during the polymerisation, liberating 20 k.cal/mole of energy. Hence highly exothermic reaction.
8) An initiator is required to start the polymerisation reaction.



POLYETHYLENE



VINYL CHLORIDE

POLY VINYL CHLORIDE

Coordination polymerization (or) Zeigler – Natta polymerization:

Zeigler (1953) and Natta (1955) discovered that in the presence of a combination of transition metal halides like $TiCl_4$, $ZnBr_2$ etc., with an organometallic compound like triethyl aluminium or trimethyl aluminium, stereospecific polymerization can be carried out. Combination of metal halides and organometallic compounds are called Zeigler Natta catalysts. Here the mechanism is same as anionic addition polymerization.

Significance of Zeigler-Natta polymerization:

The Ziegler–Natta initiators are the only initiators that polymerize α-olefins such as 1-propene and 1-butene which cannot be polymerized by either radical or ionic initiators.

Difference between condensation and addition polymerization:

Condensation polymerisation	Addition polymerisation
(1) It is also known as step growth polymerization	(1) It is also known as chain growth polymerization
(2) It takes place in monomers having	(2) It takes place only in monomers

reactive functional groups	having multiple bonds.
(3) It takes place with elimination of simple molecule like H_2O, NH_3, HCl etc.	(3) It takes place without elimination of simple molecule.
(4) Repeating units of monomers are different	(4) Repeating units & monomers are same
(5) The polymer is formed in gradual steps	(5) Reaction is fast and polymer is formed at once
(6) The molecular mass of polymer increases throughout the reaction	(6) There is very little change in the molecular mass throughout the reaction
(7) Product obtained may be thermosetting/thermoplastic	(7) Products obtained are thermoplastic
(8) E.g.: Bakelite, polyester, polyamides etc.	(8) E.g: Polyethylene, PVC, polystyrene

Plastics:

Plastics are the polymers characterized by the property of plasticity (permanent deformation in structure on applying some stress/force). They can be moulded to desired shape when subjected to heat and pressure in the presence of catalyst.

Plastics as engineering materials:

Advantages of plastics over other engineering materials

1. Low fabrication cost, low thermal & electrical conductivities, high resistance to corrosion & solvents.
2. The stress – strain relationship of plastics is similar to that of the metals.
3. Plastics reduce noise & vibration in machines.
4. Plastics are bad conductors of heat and are used to make handles for hot objects, most plastics are inflammable.
5. Plastics are electrical insulators & find large scale use in the electrical industry.
6. Plastics are resistance to chemicals.
7. Plastics are clear & transparent so they can be given beautiful colours.

Types of Plastic:
1) Thermoplastics
2) Thermosetting plastics

Difference between Thermoplastic & Thermosetting resins:

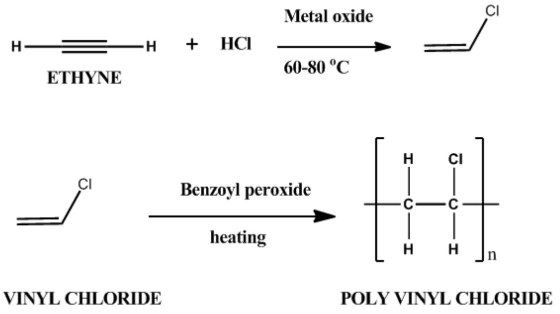
Thermoplastic Resins	Thermosetting Resins
1. These resins become soft on heating and rigid on cooling by regaining original properties. These can be reshaped and used.	1. They do not soften on heating and become hard. On prolonged heating they decompose and cannot get back its structure. Hence cannot be reshaped and used.
2. The heating and cooling do not alter the chemical nature of these resins but involves changes in physical nature.	2. These resins are permanent setting resins.
3.They are formed by addition polymerization	3. They are formed by condensation polymerization.

4. Small molecular weight compounds with linear structures.	4. Large molecular weight compounds with three dimensional networks.
5. They consist of long chain linear polymer with weak secondary vandarwaal's forces of attraction in between them.	5. Highly cross-linked structure strong covalent bonds are responsible for strength.
6. They soften on heating readily because the secondary force of attraction between the individual chain can break easily by heat, pressure or both	6.The bonds retain their strength on heating, hence do not soften on heating
7. These plastic can be reclaimed from waste	7. Cannot be reclaimed from waste
8. They are soft, weak and less brittle	8. They are hard, strong and more brittle
9.These resins are usually soluble in organic solvents	9. Due to strong bonds and cross links, they are insoluble in all organic solvents.
10. Curing by cooling Ex: PE, PS, PVC, Teflon	10. By applying heat and pressure Ex: Bakelite, Polyester and silicones

Chemistry of some important thermoplastic & thermosetting resins:

(1) Polyvinyl chloride (PVC):

Preparation: The monomer used for the manufacture of PVC is vinyl chloride. Vinyl chloride is prepared by treating acetylene with HCl at 60-80^{0}C and in presence of a metal oxide catalyst. Polyvinyl chloride is produced by heating vinyl chloride in presence of benzyl peroxide or H_2O_2.



Properties:

- PVC is a colorless, non-inflammable and chemically inert powder
- It has specific gravity 1.33 and melting point 148°C
- Resistant to atmospheric conditions like O_2, CO_2 and moisture
- They are rigid and flexible
- It has resistance to light

Applications:

There are two kinds of PVC plastics

Rigid PVC (Unplasticized PVC):

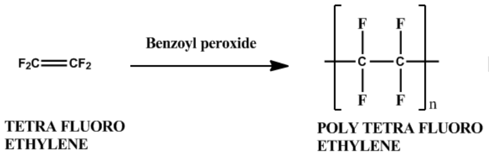
- It is chemically inert & non-inflammable powder having a high softening temperature of 148^0C.
- This PVC is used for making safety helmets, refrigerator components, tyres, cycle & motor cycle mud guards.

Plasticized PVC:

- It is produced by mixing plasticizers like dibutyl phthalate with PVC resin uniformly.
- It is used for making rain coats, table-cloths, handbags, curtains & electrical insulators, radio, T.V components. All PVC shoes for beach wear.

2) Teflon (polytetrafluoro ethylene):

Preparation: Teflon is obtained by polymerization of tetrafluoro ethylene under pressure in presence of benzoyl peroxide as catalyst.



Properties:

Teflon is also known as Fluon. Due to the presence of highly electronegative fluorine atoms, Teflon has got:

- High melting point (350^oC)
- The strong attractive force is responsible for high toughness & high chemical resistance towards all chemicals except hot alkali metal & hot fluorine.
- High density 2.1-2.3gm/cc
- It is a very good electrical insulator
- It possess very good abrasion resistance

Engineering applications:

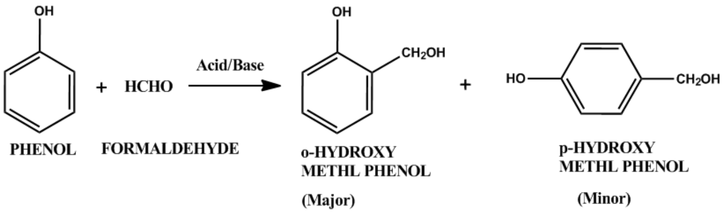
- It is used in making seals & gaskets, which have to withstand high temperature.
- It is also used for insulation of electrical items and for making non-sticky surface coating, particularly for cooking utensils.
- Teflon used as insulating material for motors, transformers, cables, wires, fitting etc.,

Some examples for Thermosetting Resins:

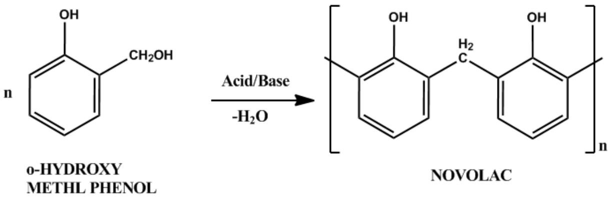
Bakelite (or) Phenol Formaldehyde Resin:

Bakelite is an important thermosetting resin named after the scientist Bakeland, who synthesized this resin in the year 1909. The condensation reaction of phenol & formaldehyde in the presence of acid or alkali catalyst and at proper temperature produces the phenol formaldehyde resin or Bakelite resin.

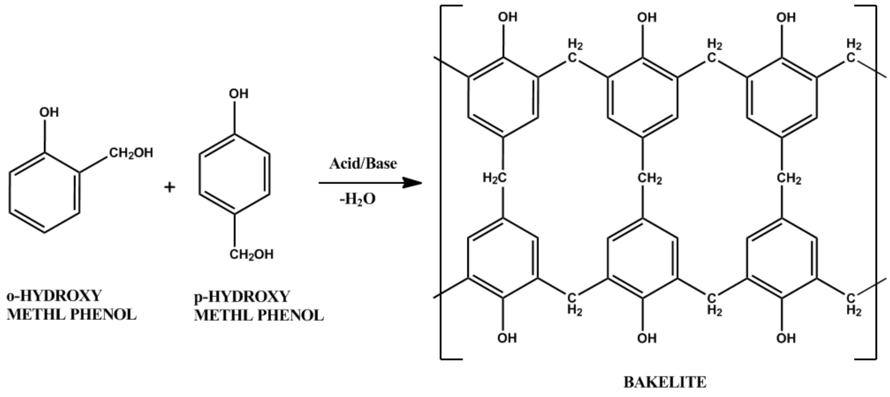
Stage-I: The initial reaction of phenol & formaldehyde in presence of acid or alkali produces *o*-hydroxy methyl phenol and *p*-hydroxy methyl phenol.



Stage-II: *o*-hydroxy methyl phenol undergoes self condensation in presence of acid or alkali and forms a linear polymeric chain called novolac.



Stage-III: On further heating, in the presence of hexamethylenetetramine both o-hydroxy methyl phenol and p-hydroxy methyl phenol undergoes self condensation and forms a 3D-cross linked thermosetting polymer which is known as "Bakelite"**.**



Properties:

(1) Bakelites are hard, rigid and withstand very high temperatures.
(2) They have excellent heat and moisture resistance.
(3) They have good chemical resistance, resistance to acids, salts and many organic solvents, but it is attached by alkalis due the presence of –OH group.
(4) They have good abrasion resistance.
(5) They have electrical insulation characteristics.
(6) It is a good anionic exchanging resin, exchange –OH group with other anion.
(7) Low molecular weight grades have excellent bonding strength and adhesive properties.

Engineering Applications:

(1) It is used for making electric insulator parts like switches, plugs, switch boards etc.
(2) For making moulded articles like telephone parts cabinet of radio and television.
(3) As an anion exchanger in water purification by ion exchange method in boilers.
(4) As an adhesive (binder) for grinding wheels etc.,
(5) In paints and varnishes.

(6) For making bearings used in propeller shafts, paper industry and rolling mills.

Conducting polymers:

Most polymeric materials are poor conductors of electricity because of the non-availability of large number of free electrons for the conduction process. Thus most of the polymers are used as insulators. However some polymers have electrical conductivity and can be used in place of metals due to their light weight and low cost, Polymeric materials which possess electrical conductivities on par with the metallic conductors are called conducting polymers. Special polymers with conductivities as high as 1.5 x 10^7 ohm^{-1} m^{-1} have been made their conductivity may be due to unsaturation or due to the presence of externally added ingredients to polymers.

Those polymers which conduct electricity are called conducting polymer. The conduction of polymers is due to unsaturation or due to the presence of externally added ingredients to them. Conducting polymers are classified into two types.

a) Intrinsic conducting polymers:

These are characterized by intensive conjugation of π-bonds in their structure. This is a polymer whose back bones or associated groups consisting of delocalized electron pair or residual charge, which increases their conductivity to a large extent. The conduction process is due to the overlapping of orbitals containing conjugated π-electrons, resulting in the formation of valence bands as well as conduction bands separated by significant Fermi energy gap. The electrical conductivity is due to thermal or photolytic activation of the electrons, which gives them sufficient energy to cross the Fermi gap and cause conduction. Important commercially produced intrinsic conducting polymers are polyacetylene, polythiophene, polyaniline.

Doped conducting polymers:

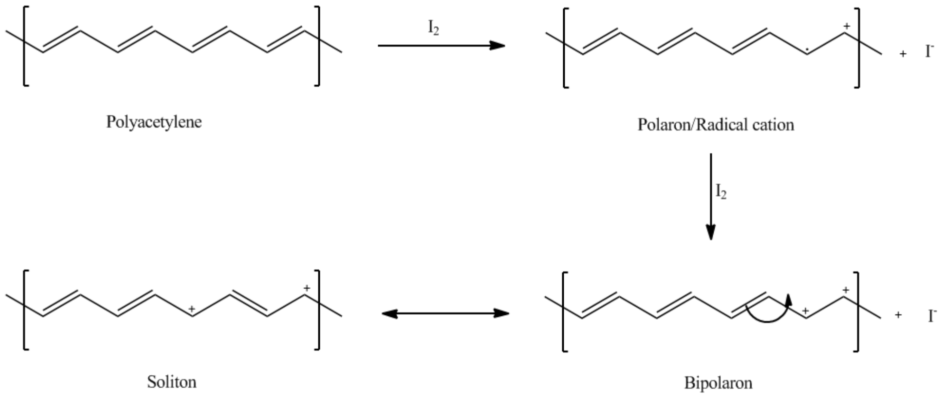
The conducting polymers having πe^-s in their backbone can easily be oxidized or reduced because they possess low ionization potential and high electron affinities. Hence their conductance can be increased by introducing a positive charge or negative charge on polymer backbone by oxidation or reduction. This process is similar to semiconductor technology and is called doping. Doping is again two types.

(1) Creating a positive site on the polymer backbone called p-doping.
(2) Creating a negative site on the polymer backbone called n-doping.

P-doping:

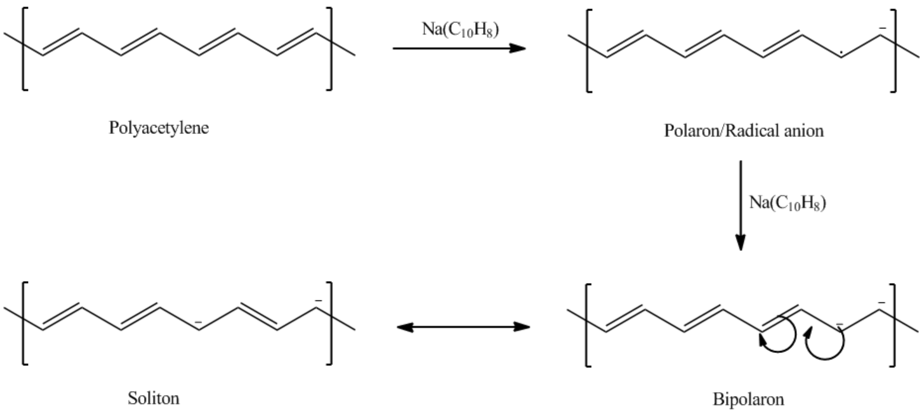
P-doping is carried out by oxidation process by the removal of an electron from conducting polymer like polyacetylene with a Lewis acid or iodine. This is called oxidative doping.

During oxidation process the removal of π electrons from polymer back bone lead to the formation of a delocalized radical ion called polaron. The second oxidation of the polaron leads to the formation of bipolaron, which are mobile because of delocalization. These delocalized charge carriers (holes) are responsible for conductance when placed in electric field.



N-doping:

N-doping is carried out by reduction process by the addition of an electron to conducting polymer like polyacetylene with reducing agents like sodium napthalide Na($C_{10}H_8$). Formation of polaron, bipolaron takes place in two steps, which yields two negative charge carriers on the polyacetylene chain. These delocalized charge carriers (electrons) are responsible for conductance when placed in electric field.



Applications of conducting polymers:

(1) The conducting polymers are used in rechargeable batteries, small in size (bottom size), producing current density up to 50mA/cm^2

(2) Conducting polymers are also used for making analytical sensors for P^H, O_2, NO_x,SO_2, NH_3 and glucose

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

(4) The conducting polymers are used for making electronic displays and optical fibres

(5) They are used for cancer chemotherapy

(6) The conducting polymers are applicable in photovoltaic devices, LED's and data storage.

Rubbers:

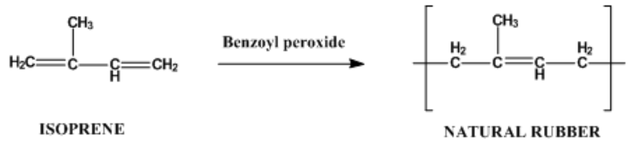
Those polymers which posses the property of elasticity is called rubber. Temporary deformation in structure on applying some stress is more than 600e.u.When stress is applied polymers chains get partially aligned with respect to another, thereby causing crystallization, temporary deformation which makes the polymer stiff. On releasing the stress the chains get reverted back to their original coiled state. The elasticity of rubber is due to its coiled helix structure.

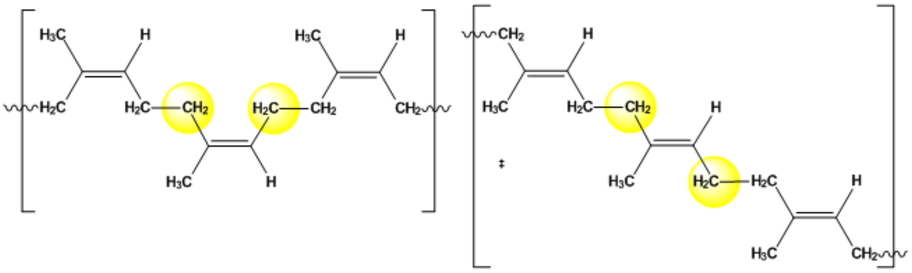
Natural Rubber:

Natural Rubber is a high molecular weight hydrocarbon polymer represented by the formula $(C_5H_8)_x$. It is obtained from a milk emulsion called latex by tapping the bark of the tree "Hevea brasiliensis." The main composition of natural rubber is polyisoprene which is in the form of long coiled chains. The isoprene units polymerise to form rubber. Isoprene in natural rubber exits in two geometrical isomeric forms, cis and trans.

cis-polyisoprene is present in Natural rubber

trans-polyisoprene is present in Gutta percha rubber





CIS POLYISOPRENE/HEVEA RUBBER TRANS POLYISOPRENE/ GUTTAPERCHA RUBBER

Processing of Natural Rubber:

By cutting the bark of rubber tree the milky colloidal rubber milk is obtained. The main constituent of rubber latex is 25-45% of rubber and the remaining are water, protein & resinous materials. The rubber latex is coagulated by using 5% acetic acid and made in to sheets. The rubber sheets are cured under mild heat and then subjected to further processing.

Crepe rubber:

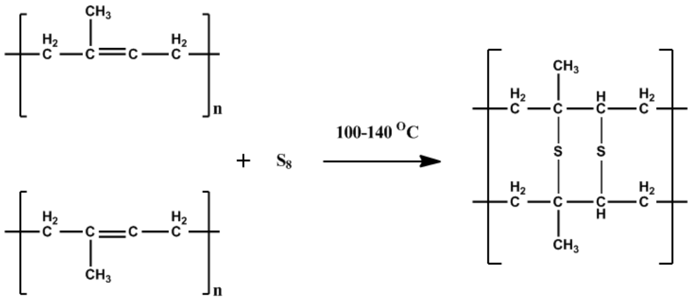
To the rubber latex a small amount of sodium bisulphate is added to bleach the colour and feed in to roller which produce 1mm or more thickness sheets which are dried in air at about 40-50^{0}C. The dried thin sheet of rubber is known as "smoked crepe rubber".

Vulcanization of Rubber:

The raw or crude rubber is very little useful because it has very undesirable properties, such as low tensile strength, possesses elasticity only over a limited range of temperature. To improve the properties of rubber**,** Charles Good in 1839 compounded the raw rubber with some chemicals and heated to 100-140^{o}C

In order to give more strength and more elasticity, natural rubber is heated with sulphur or sulphur compounds at 100-140^{0}C for few hours. The sulphur combines chemically at the double bonds of different rubber spring and provides cross-linking between the chains. This cross linking during vulcanization brings about a stiffening of the rubber by anchoring and consequently preventing intermolecular movement of rubber springs. This process is known as vulcanization of rubber.

The amount of sulphur added determines the extent of stiffness of vulcanized rubber. For eg, ordinary rubber (say for battery case) may contain as much as 30% sulphur.



Advantages of vulcanization:

1. Vulcanized rubber has good tensile strength and load bearing capacity.
2. Vulcanized rubber has excellent resilience.
3. It has better resistance to moisture, oxidation & abrasion.
4. It is resistance to organic solvents like CCl_4, benzene, petrol etc.
5. It has good elasticity.
6. It is a good electrical insulator.

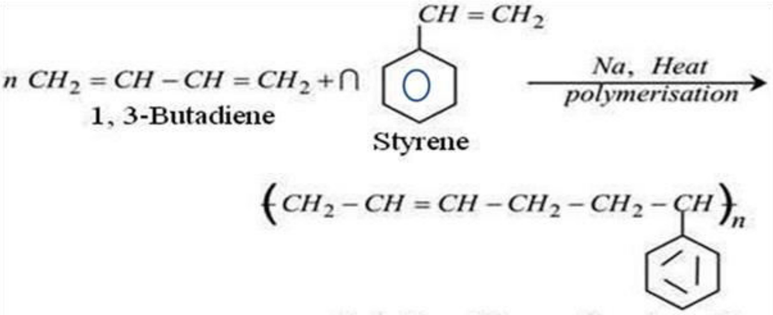
Applications

1. The major application of natural rubber is in the manufacture of tyres.
2. In heavy duty tyres, the major portion of the rubber used is natural rubber.
3. The tank linings in chemical plants where corrosive chemicals are stored are prepared from rubber.
4. To reduce machine vibrations, rubber is used for sandwiching between two metal surfaces.
5. Foam rubber is used for making cushions', matrices, padding etc. toys and sports items are manufactured from natural rubber.
6. Gutta percha is used for making submarine cables, golf ball covers, tissue or adhesive etc.

Synthetic Rubbers or Elastomers

(1) Styrene Rubber or Buna-S-Rubber (SBR)

It is a copolymer of butadiene (75%) and styrene (24%). It is prepared by the copolymerization of butadiene & styrene in the presence of sodium catalyst. In Buna-S, 'Bu' stands for butadiene, 'na'(symbol Na for sodium) and S for styrene. It is also called GRS (government rubber styrene) or SBR (styrene butadiene rubber).



(Butadiene-Styrene Copolymer)
(SBR or BUNA-S)

Properties:

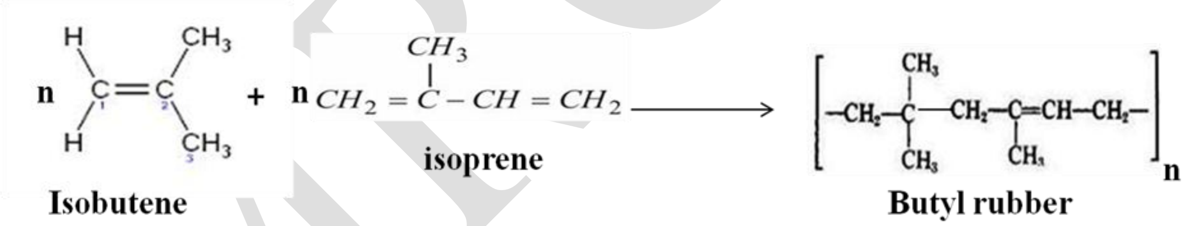
(1) It is a strong & tough polymer.
(2) The rubber can be vulcanized similar to natural rubber using either sulphur or sulphur monochloride.
(3) It is a good electrical insulator.
(4) It possess excellent abrasion resistance.
(5) It is resistance to chemicals but swells in oils and attacked by even traces of ozone present in the atmosphere.
(6) It possess high load bearing capacity and resilience.

Applications:

(1) Major application of styrene rubber is in manufacture of tyres.
(2) It is used in foot wear industry for making shoe soles and footwear components.
(3) It is also used for making wires and cable, insulators.
(4) It is also used for the production of floor files, tank linings in chemical industries.

(2) Butyl rubber (GR–I or Polyisobutylene rubber):

Butyl rubber is also is also known as GR-I (Government Rubber Isobutene) produced by copolymerization of isobutene (98%) with butadiene (2%) or isoprene in presence of anhydrous $AlCl_3$.



Properties:

1. The rubber shows extremely low permeability to air and other gases.
2. It also possesses resistance to heat, mineral acids, polar solvents etc.
3. It can be vulcanized with S, but it possesses low hardness due to less number of double bonds.

Applications:

1. Butyl rubber is used for making cycle and automobile tubes.
2. It is also used for making hoses, conveyor belts, insulating cable, tank linings etc.

Fibers:

Fibers are a class of materials that are continuous filaments or discrete elongated pieces. They are crystalline, present in both plants & animals.

They are used for making textiles, ropes, utilities, strings etc.

These are of two types

(1) Natural Fibers

(2) Synthetic fibers

1. Natural fibers: Produced by plants, animals & geological materials.

a. Vegetable fibers: Cellulosic material

Ex: cotton, jute etc. used for making textiles, ropes, mats, paper, bags etc.

b. Wood fiber: The strength of a plant is due to presence of wood fiber. Wood pulp is used in making paper and wood fibers like jute are used for making bags.

c. Animal fibers: They are largely made of protein. E.g. Pure silk, wool, hair are animal fibers. Spider silk is used for making special bullet proof jackets.

d. Mineral fibers: Asbestos is a typical example of mineral fiber. Mica & other minerals are used as fibers.

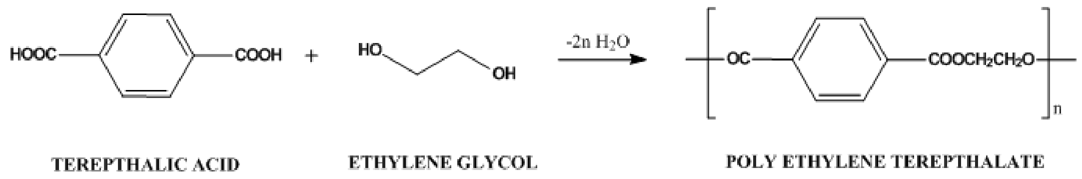
2. Synthetic fibers: This type fiber can be produced in large quantities and are cheaper than some of the natural fibers like pure silk. Polyamide nylons, polyesters, PVC, phenol-formaldehyde resin, polyethylene are often used for making textiles.

Polyester (or) Terylene (or) Polyethylene terephthalate:

This category of polymers has ester linkages in the main chain. It takes 18% of market share of synthetic polymers.

Preparation:

Terylene is a polyester fiber made from ethylene glycol and terephthalic acid. Terephthalic acid required for the manufacture of terylene is produced by the catalytic atmospheric oxidation of p-xylene.



Properties:

1. This occurs as a colorless rigid substance.
2. This is highly resistant to mineral & organic acids but is less resistant to alkalis.
3. This is hydrophobic in nature.
4. This has high melting point due to presence of aromatic ring.

Uses:

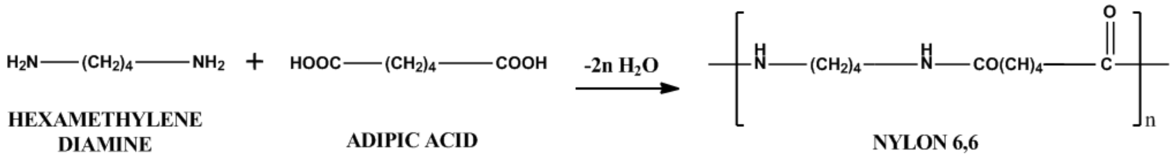
1. It is mostly used for making synthetic fiber.
2. It can be blended with wool, cotton for better use and wrinkle resistance.
3. Other application of polyethylene terephthalate film is in electrical insulation.

Nylon (Polyamide resin):

Nylon is a polyamide resin containing recurring amide groups in its structure produced by copolymerization of di-amine with di-acid. Depending on the number of C atoms in di-amine & di-acid there are different types of nylons like nylon 6,6, nylon 6,10 etc., where the first number indicates number of carbon atoms in di-amine & the second number indicates the number of 'C' atoms in di-acid.

Nylon 6,6:

Preparation: It is prepared by condensation polymerization of adipic acid and hexamethylene diamine in the absence of air.



Properties:

(1) They are translucent, whitish, horny, high melting polymer.

(2) They possess high temperature stability and good abrasion-resistance.

(3) They have good strength.

(4) They are insoluble in common organic solvents.

Applications:

(1) The major application is in textile industry.

(2) Because of its high thermal & abrasion resistance nylons are used in mechanical engineering applications like gears, bearings, machine parts where greater friction is there.

(3) Flexible tubing's for conveying petrol etc are made from nylons

(4) Nylons are used as electrical insulators.

(5) Nylon 6 is used for making tire cords.

(6) Nylons are used in automobile industry and telecommunication industry for making radiator parts and coil formers respectively.

Fiber Reinforced Plastics (FRP):

- Combination of plastic material & solid fillers give hard plastic with mechanical strength & impact resistant is known as reinforced plastic.
- The fiber polymers with solid/fillers to impart mechanical strength & hardness without losing plasticity are known as fiber reinforced plastics (FRP).
- Fillers like carborandum, quartz & mica – impart hardness & strength.
- Barium salt impervious to x-rays.
- Asbestos provide heat & corrosion resistant for FRP.

Nature of polymers used for FRP:

Composition of FRP – 50% of the mouldable mixture contain fillers.

- Addition of carbon black to natural rubber increase the 40% strength of rubber & used in the manufacture of tyres.
- China clay improves the insulation property of PVC, Teflon.
- When $CaCO_3$ is added to PVC, then they are used for insulation of tubing, seat covers, wires & cables.
- Asbestos filled FRP → for electrical appliances'.

- FRP has good shock & thermal resistances, mouldability, dimensional stability & reparability.

Applications:

- Fiber reinforced plastics find extensive use in space crafts, aeroplanes, boat nulls, acid storage tanks, motor cars and building materials.
- Melamine FRP is used for insulation & making baskets.

Advantages of FRP:

(a) Low efficient of thermal expansion
(b) High dimensional stability
(c) Low cost of production
(d) Good tensile strength
(e) Low dielectric constant
(f) Non inflammable & non-corrode and chemical resistance

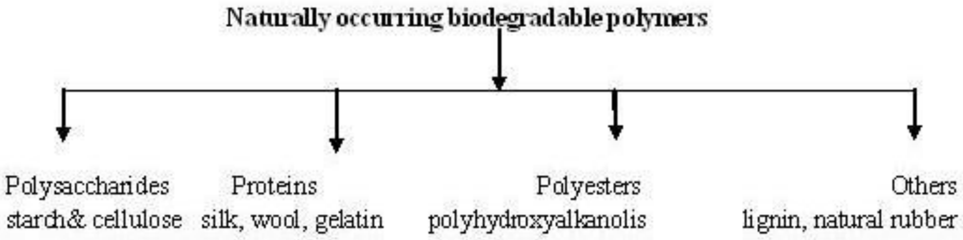
Biodegradable Polymers

Generally polymers are not affected by the environment. To some extent polymers and plastics are degraded slowly by oxidation, UV radiations, extreme temperature etc. Natural polymers are biodegradable, but synthetic polymers and plastics are not prone to biodegradation and cause pollution of environment. The growing awareness on the hazards caused by the disposal of plastics has resulted in the search for plastics which are biodegradable

Biodegradable polymers are defined as the degradable polymers in which degradation is caused by the action of naturally occurring micro organisms such as bacteria, fungi and algae. During compositing they yield CO_2, H_2O, inorganic compounds and biomass without leaving toxic residue

The biodegradable polymers may be naturally occurring or may be synthesized by chemical means. In addition feed stocks to synthesis these biodegradable polymers may come from the processing of crops grown for the purpose or the byproducts of other crops, along with chemical and biochemical process.

Naturally occurring biodegradable polymers: A wide variety of naturally occurring polymers are available, the fact that these substances were polymers was not known. In many quarters this ignorance persists. The naturally biodegradable polymers classified in to four groups as given below.



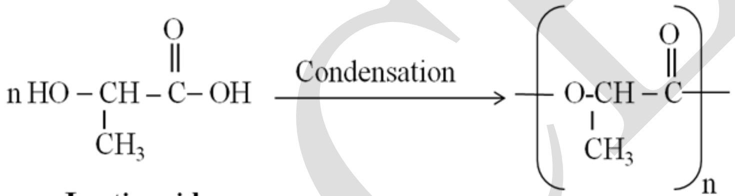
Synthesized biodegradable polymers:

There are many polymers produced from derived from petrochemical or biological sources that are biodegradable. There are a number of biodegradable synthetic resins that are:

1) Poly-lactic acid
2) Polyvinyl acetate
3) Polyvinyl alcohol
4) Polyamide esters

Polylactic acid or **Polylactide** (**PLA**):

- Polylactic acid is a biodegradable aliphatic thermoplastic polyester
- It is derived from renewable resources, such as corn starch (in the United States), tapioca roots, chips or starch (mostly in Asia), or sugarcane (in the rest of the world).
- Lactic acid is obtained by the bacterial fermentation of sugarcane or from the starch obtained from corn.
- Oligomerisation and catalytic dimerisation of lactic acid results in the formation of lactide monomer
- Polylactic acid is obtained by the condensation polymerization of lactic acid in the presence of acid or base catalyst.



$$n\,HO-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}}-OH \xrightarrow{\text{Condensation}} \left[O-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{\|}{C}} \right]_n$$

Lactic acid **Polylactic acid (PLA)**

Properties:

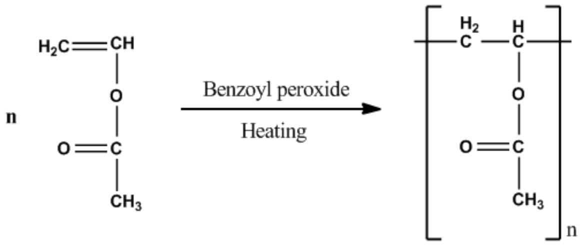
1. Due to the chiral nature of lactic acid, several distinct forms of polylactide exist: poly-L-lactide (**PLLA**) is the product resulting from polymerization of L-lactide
2. PLLA has a crystallinity of around 37%, a glass transition temperature between 60-65°C, a melting temperature between 173-178 °C
3. However, heat resistant PLA can withstand temperatures of 110°C
4. PLA is soluble in chlorinated solvents, hot benzene, tetrahydrofuran, and dioxane.

Applications

1. It is used in biomedical applications such as sutures, drug delivery devices and dialysis media.
2. It is useful for producing loose-fill packaging, compost bags, food packaging, and disposable tableware.
3. In the form of fibers and non-woven textiles, PLA also has many potential uses, for example as disposable garments, awnings, feminine hygiene products, and diapers.
4. PLA is also used as a feedstock material in 3D printers such as Reprap and Makerbot.

2) **Polyvinyl acetate**:

Preparation: Polyvinyl acetate is obtained by the addition polymerization of vinyl acetate in the presence of benzoyl peroxide.



Properties:

- PVAc is a rubbery synthetic polymer with the formula $(C_4H_6O_2)_n$.
- It belongs to the polyvinyl esters family.
- It is water soluble, colorless and transparent.
- It possess excellent mechanical properties and has good heat resistance
- It is harmless if taken orally

Applications and uses:

1. As an emulsion in water, a PVAc emulsions are used as adhesives for porous materials, particularly for wood, paper, and cloth, and as a consolidant for porous building stone, in particular sandstone.
2. As wood glue PVAc is known as "white glue" and the yellow "carpenter's glue" or PVA glue.
3. As paper adhesive during paper packaging converting in bookbinding and book arts, due to its flexible strong bond and non-acidic nature (unlike many other polymers) in handcrafts
4. It is used for making of chewing gums, paint emulsions etc…
5. It can also be used as coating to protect cheese from fungi and humidity
6. Polyvinyl acetate is also the raw material to make other polymers like polyvinyl alcohol.

MATERIAL CHEMISTRY

LUBRICANTS

Introduction:

- When one solid surface is sliding past over another solid surface, friction and wear is developed due to relative motion of two contacting surfaces which results in loss of energy as heat. As the equipment gets heated up it is damaged and some times results in welding or seizure.
- Lubricant or lube is a substance introduced between the two moving surfaces to reduce friction between them, improving efficiency and reducing wear. It functions in dissolving (or) transporting foreign particle s & distributing heat.
- One of the single largest application for lube in the form of motor oil is protecting the internal combustion engine in motor vehicles & powered equipment.
- Typically lubes contain 90% base oil (i.e. petroleum fractions called mineral oils) and less than 10% additives, sometimes vegetable oils (or) synthetic liquids such as hydrogenated polyolefins, esters, silicones, fluorocarbons & many others are also used as base oils.

- A lubricant may thus be defined as a substance which reduces the friction when introduced between two surfaces.

Functions of Lubricants:

1. Lubricants help in reducing frictional forces between two sliding surfaces.
2. Generally lubricant to surface friction is much less than surface-to-surface friction in a system without any lubrication. It reduces heat generation and reduces formation of wear particles and improves efficiency.
3. It reduces wear and tear and surface deformation.
4. Both gas and liquid lubricants can transfer heat. Liquid lubricants are much more effective on account of their high specific heat capacity.
5. It reduces the loss of energy in the form of heat that is it acts as a coolant.
6. It prevents loss of heat energy produced by frictional forces between two sliding surfaces.
7. In a machine, frictional heat is produced at the point of contact between the rubbing parts. Cool oil which is flowing on a heated surface carries away the heat.
8. It reduces running cost and maintenance cost of machines and tools.
9. A lubricant prevents corrosion and rusting of machine parts.
10. In internal combustion engines, lubricant is used as a seal between the wall of the cylinder and piston and prevents the leakage of gases under high pressure from the cylinder.
11. It carries away contaminants and debris and prevents accumulation of dirt, foreign matter entering the bearing.
12. It prevents welding or seizure of moving surfaces.
13. Lubricant minimizes the liberation of frictional heat and avoids welding or seizure of moving surfaces and expansion of metal.
14. It also reduces loss of heat energy there by increasing the efficiency of the machine.
15. In chemical labs: lubricants are used in burettes, vacuum pumps, condensers etc.
16. It keeps moving parts apart.

Classification of Lubricants:

Lubricants are classified on the basis of their physical state as follows

1. Liquid Lubricants or Lubricating Oils
2. Semi-Solid Lubricants or Greases
3. Solid Lubricants.

1. Liquid Lubricants or Lubricating Oils:

Lubricating oils reduce friction and wear between two moving metallic surfaces by providing a continuous fluid film in between the surfaces. A good lubricant must have the following characteristics.

- It must have high boiling point or low vapour pressure.
- Thermal stability and oxidation resistance must be high.
- It must also have adequate viscosity for particular operating conditions.
- The freezing point must be low.
- It must also have non-corrosive property

Lubricating oils are further sub-classified as:

1. Animal and Vegetable oils

2. Petroleum oils or Mineral oils
3. Blended oils or Additives for lubricating oils
4. Synthetic lubricants

Animal and Vegetable oils: Animal and vegetable oils are glycosides of higher fatty acids. They have very good oiliness. However, they are costly, undergo oxidation very easily, and have a tendency to hydrolyze when it contact with moist air or water. They are used as additives to improve the oiliness of petroleum oils.

Petroleum oils or Mineral oils: They are obtained by fractional distillation of crude oil. They are cheap and quite stable under operating conditions. They possess poor oiliness, the oiliness of which can be improved by the addition of high molecular weight vegetable or animal oils. Crude liquid petroleum oil cannot be used as such, because they contain lot of impurities like wax, asphalt, colored substances and other oxidisable impurities

Blended oils or Additives for lubricating oils: No single oil serves as the most suitable lubricant for many of the modern machineries. Specific additives are incorporated into these oils and are called "blended oils" and give desired lubricating properties, required for particular machinery.

Synthetic lubricants: Mineral oils cannot be used effectively as they tend to get oxidized at very high temperature while wax separation will occur at very low temperature. So, synthetic lubricants have been developed, which can meet the severe operating conditions such as in aircraft engines. The same lubricants may have to be in the temperature range of -50^0C to 250^0C. Polyglycol ethers, fluoro and chloro hydrocarbons, organophosphates and silicones are currently used as synthetic lubricants.

2. Semi-Solid Lubricants or greases:

When liquid lube oil cannot be maintained, lubrication is done by a semi-solid lube. Greases are very good semisolid lubricant. A semi solid lubricant is obtained by combining lubrication oil with thickening agent. They are special soaps of sodium, calcium, barium etc. They have resistance to friction than oils and can support heavier loads at low speeds.

Semi-solid lubricants are used a) where oil is not suitable for machines b) when machines are working with heavy load at low speed.

3. Solid Lubricants:

- In certain aero space devices and some other environments liquid and semi-solid lubes can't be used.
- Solid lubricates like. MoS_2, mica, chalk, wax, soap, graphite which can with stand very heavy load and low speed can be made use of.
- They consist of a number of layers. In these layers atoms are held together by weak Vanderwalls forces which make them soft and smooth to act as lube. Because of its slippery touch, non-inflammability, resistance to oxidation, graphite is widely used solid lube. It can be used as powder or as colloidal dispersion in water (aqua dag) oil (oil dag)
- Graphite is used in IC engines, lathes, air compression engines, but is ineffective in vacuum conditions and above 370ºC. MoS_2 can be used up to 800ºC.

- It possesses very low coefficient of friction. Hence it can be used in air frame lubrication and wire drawing.

Properties of Lubricants:

Lubricants have several properties. Some important properties are

Viscosity:

It is the property of a liquid or fluid by virtue of which it offers resistance to its own flow. A liquid flowing under steady state conditions may flow in a series of parallel layers moving one above the other with different velocities.

Due to internal friction i.e., drag the bottom layer moves slower than next upper layer. If the two layers of a liquid separated by distance‘d’ and moving with a velocity difference, V, then the frictional force per unit area (F) required to maintain their difference of velocity is given as

$$F = \frac{\eta v}{d}$$

where η = coefficient of viscosity.

If $d = 1$ cm and $v = 1$ cm/sec. then $F = \eta$

Viscosity of lubricating oil determines the operating characteristics of oil. If the viscosity of oil is too high, friction will not results, but if the viscosity of oil is too low, lubricating film cannot be maintained, excessive friction develops.

Viscosity measurement is made by determining the time taken for a given volume of oil to flow from a given height of a standard capillary under its own weight at a given temperature. This viscosity is called kinematic viscosity. It is equal to absolute viscosity divided by density of the oil and is expressed in centistokes.

Redwood Viscometer is used to determine the viscosity of lubricating oils. A schematic diagram of Redwood viscometer is shown in the figure.

Viscometer consists of the following parts

1. **Oil cup:** It is a brass cylinder, open at the upper end. The bottom of the cylinder is fitted with agate jet with a bore of 1.62 mm. For thin film lubricates a jet of a bore of 1.60 mm and 10 mm length and for thick lubricants a jet of 3.8 mm and length 15 mm. is used. There is a valve rod to open and close the jet. A pointer in the oil cup indicates the level of oil in the cup. A thermometer is fitted in the lid of the cup for measuring the temperature of oil.

2. **Heating bath:** Oil cup is surrounded by a cylindrical copper bath filled with water. A thermometer is inserted in to the bath to measure the temperature of water. Heating bath is also provided with a stirrer to maintain uniform temperature of bath and oil cup.

3. **Leveling screws:** There are three leveling screws to level the apparatus.

4. **Kolrausch’s flask:** A flask of 50 ml capacity is placed below the jet to receive the oil from the jet out let.

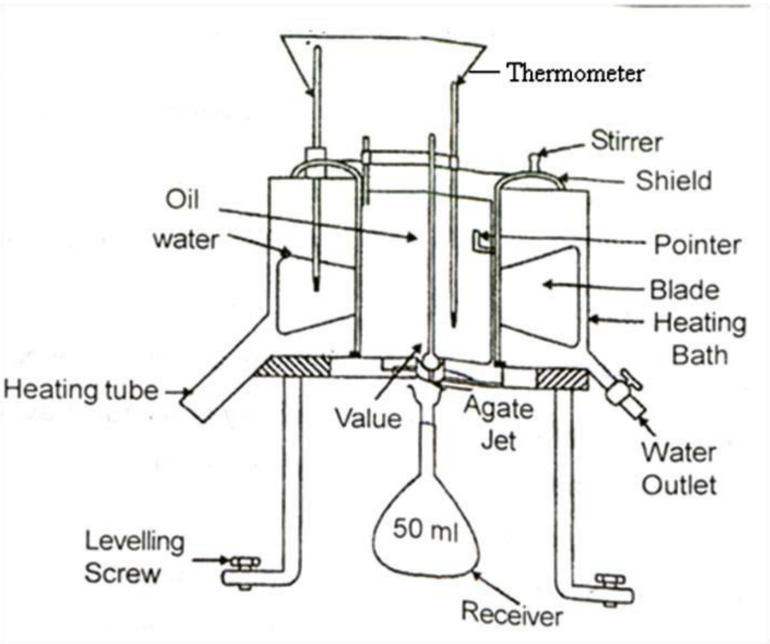


Fig: Redwood Viscometer

Working:

The apparatus is leveled with leveling screws. Water bath is filled with water and a thermometer is inserted into it. Oil cup is thoroughly cleaned and the jet is closed with ball valve. The oil is filled in the cup upto the point, and a thermometer is inserted into the cup to note the temperature of oil. Water bath is heated to a certain temperature with constant stirring to maintain uniform temperature of water. When the oil acquires desired temperature, heating is stopped and the ball valve in lifted. The time taken to fill the Kohlrausch flask of 50 ml capacity is noted. The valve is immediately closed to prevent the overflow of oil. The experiment is repeated and the mean value of time of flow for 50 ml oil sample is reported and the result is expressed in "Redwood No 1 seconds" at a particular temperature. Viscosity of liquids decreases with increases in temperature. A good lubricating oil should not undergo change in viscosity with temperature.

Viscosity Index:

- To indicate the change in viscosity with temp. an arbitrary scale, known as "viscosity index" is used.
- Viscosity index is a scale based on arbitrarily fixing a value of 100 for pennsylvanian oils containing paraffin's.
- The viscosity of paraffin oil (VH) is little affected by increasing temperature.
- At lower end of scale viscosity index is fixed as '0' for Gulf coast oil (VL) which contains naphthalene's, whose viscosity decrease drastically with increasing temperature.
- A high value of viscosity index for an oil indicates that its viscosity is slightly affected by increase in temperature and a low value of V.I. indicate that its viscosity appreciably changes with temperature rise.

The mathematical expression for viscosity index (VI) is:

$$\mathbf{VI = L - U/L - H\ x100}$$

Where, U = viscosity of test oil at $38^{o}C$

L = viscosity of the standard oil at $38^{o}C$ having a VI of zero

H = viscosity of the standard oil at $38^{o}C$ having a VI of 100

Flash Point and Fire Point:

- Flash point is defined as the minimum temperature at which the lubricating oil gives off its vapours that ignite for a moment, when a flame is brought near to it.
- Fire point is the lowest temperature at which the vapours of the oil burn continuously for at least five seconds, when a flame is brought near to it.
- The flash point of the lubricating oil is above the operating temperature, because good lubricating oil should not volatalize under the working conditions usually.
- The fire points are 5 to 40°F higher than flash points.
- They indicate the occurrence of fire accident.
- The flash occurs before a fire accident.

DETERMINATION OF FLASH AND FIRE POINT:

The flash and fire points of a lubricating oil are determined experimentally by Pensky - Marten's apparatus. The apparatus consists of a small cup of 5 cm diameter and 5.5 cm. height. The cup is closed at the top with a lid containing three openings for inserting a thermometer, stirrer and for introducing test flame. A shutter which can be moved on the top of the container by lever mechanism is used to open the lid for introducing the test flame.

Working

The container is filled up to the standard mark with the lubricating oil. The cup is gradually heated using a burner. Stirrer is worked and oil is exposed to the flame for every 1ºC rise in temperature of lubricating oil. The temperature at which the introduced test flame produces a flash is noted as the flash point. Similarly the temperature at which the oil ignites and continues to burn for at least 5 seconds is noted as the fire point of the oil.

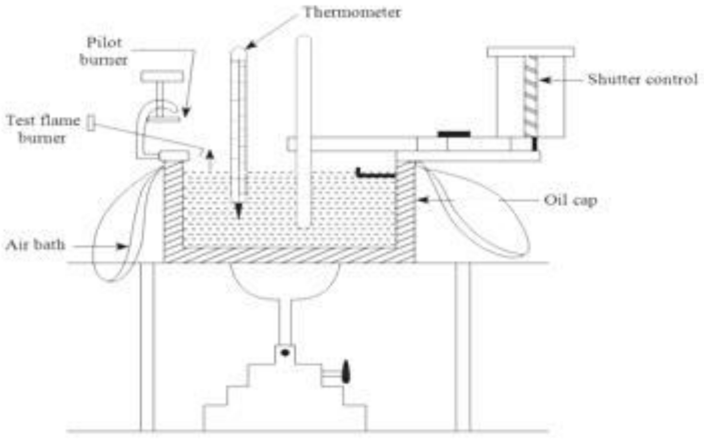


Fig: **PENSKYMARTEN'S APPARATUS**

CLOUD AND POUR POINTS

- The lubricating oil is derived from petroleum. It contains dissolved paraffin wax and other resinous impurities. These impurities tend to separate out of oil at lower temperatures.
- The temperature at which the impurities begin to separate out from the solution and lubricating oil becomes cloudy or hazy in appearance is called cloud point.
- The temperature at which the oil ceases to flow or pour is called pour point.
- Cloud point and pour points indicate the suitability of lubricants in cold conditions.
- Machines working with low temperatures like refrigerator plants, aircraft engines, lubricants with low cloud and pour points are preferred

DETERMINATION OF CLOUD AND POUR POINTS:

The cloud and pour points are determined experimentally using pour point apparatus. The apparatus consists of flat bottomed glass tube filled with lubricating oil of standard height enclosed in an air jacket. The jacket is surrounded by freezing mixture (ice + $CaCl_2$). A thermometer is introduced in the oil. As the cooling proceeds slowly, the temperature falls continuously. For every 1℃ fall of temperature, the tube is withdrawn from air jacket for a moment and observed for cloudiness.

The temperature at which cloudiness is noticed is recorded as cloud point. Similarly after sometime the temperature at which the lubricating oil solidifies and resists to flow is recorded as the pour point.

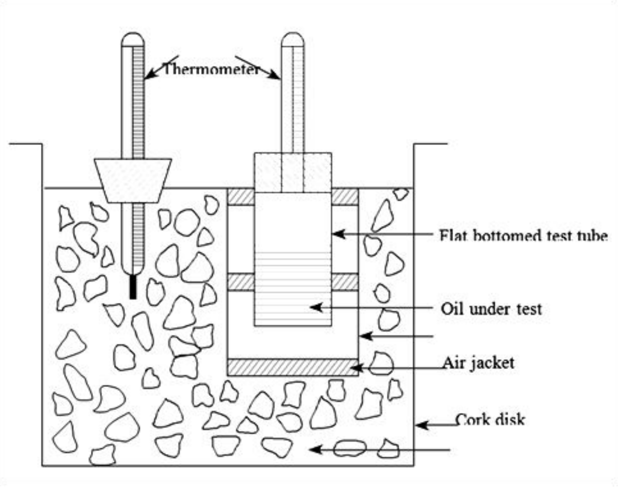


Fig: Pour point apparatus

REFRACTORIES:

Refractories are inorganic materials which can withstand very high temperatures without softening or suffering deformation. They are used for the construction of kilns, oven crucibles, retorts, furnaces, The main function of refractories varies depending on the purpose to which they are subjected like confining heat within the furnace, transmitting or storing heat in regenerators. The selection of a refractory for a particular purpose depends on the service conditions, like working temperature to which it is exposed, the nature of the materials which come into contact with it, temperature fluctuations, load applied and the nature of chemical reactions which occur.

Classification of Refractories:

Refractories are broadly classified into three categories.

1. On the basis of their chemical nature:

a) Acidic refractories: They are made from acidic materials such as alumina (Al_2O_3) and silica (SiO_2). They are resistant to acid, but attacked by basic materials such as CaO, MgO.

Examples: Silica, Alumina and (fireclay refractories contain silicate mineral kaolinite. Silicate refractories which rank next to fireclay refractories are produced from quartzite and quartz pebbles).

b) Basic refractories: Basic refractories are those which consist of basic materials. They are not attacked by basic materials, but attacked by acidic materials

Examples: Magnetite, dolomite, chrome magnetite refractories.

c) Neutral refractories; they are not completely neutral in chemical since. They consists of weakly basic/acidic materials such as carbon, zirconia (ZrO_2), Chromite ($FeOCrO_2$), graphite and silicon carbide.

2. On the basis of fusion temperature:

a) Normal refractory: Fusion temperature is 1580-1780 °C

Examples: fire clay refractory.

b) High refractory: Fusion temperature is 1780-2000 °C

Examples: chromite refractory

a) Super refractory: Fusion temperature is above 2000 °C

Examples: zirconia

3. On the basis of oxide content:

a) Single oxide refractory.

Examples: Alumina, magnesia and zirconia refractory.

b) Mixed oxide refractory.

Example: Spinel and mullite.

c) Non–oxide refractory.

Examples: Borides, carbides and silicates.

Characteristics of a Refractory:

A good refractory material should possess:

1. High temperature resistance under working conditions.
2. Good abrasion resistance by dusty gases and molten metals.
3. Low permeability or ability to contain heat.
4. High mechanical strength, structural strength and crack resistance to withstand overlying load
5. Thermal strength to withstand thermal shock due to rapid and repeated temperature fluctuations.
6. High resistance to change in physical, chemical and mechanical properties.

Applications of Refractories:

1. The main objective of a refractory is to resist heat losses and also to resist the abrasive and corrosive action of molten metals, slags and gases at higher temperatures, without softening or deformation in shape.
2. Refractories are mostly used for the construction of the lining of the furnaces, tanks, converters, kilns crucibles, ladles, etc. They are employed for the manufacture of cement, glass, ceramics, paper, metals (both ferrous and non-ferrous), etc.

Ex. Alumina bricks or fire clay refractories.

- It is used in lining of cement rotary kilns soaking pita, reheating furnaces, hearts and walls, etc., which are subjected to high abrasion.
- It is used in hottest zone of cement rotary kilns, lower parts of soaking pits, brass melting reverberatories, aluminium melting furnaces, etc.,

Ex. Fireclay refractories

- They are used where high temperature is required to be maintained, together with great resistance to basic materials.
- They are used in steel industry for the lining of basic converters and open–hearth furnaces.
- They are also used in hot mixer linings, copper converters and reverberatory furnaces.

Ex. Zirconia bricks

- They are used only where very high temperature is maintained, e.g., high – frequency electric furnaces.

Nanomaterials

Introduction:

- Nanomaterials are the materials of nano-metre (10^{-9}m) dimension.
- The properties of nano materials significantly differ from bulk materials.
- For e.g.: The electronic structure of metals and semi conductor crystals greatly differs from those of isolated atoms and bulk materials.
- Some of the nano materials like gold particles of 1-2nm size exhibit unusual catalytic properties. Large pieces of gold and silver show inert (noble) behavior.
- Silver is widely used in jewellery because of its inert nature, but it shows anti-bacterial activity at nano scale.
- Now-a-days nano particles of silver are used in wound dressing.
- The uniqueness of nano particles is due to two factors.
- Smaller particles have a relative large surface area than their volume,
- Below 100nm size, quantum effects can change the magnetic and electronic properties.
- Nano particle reinforced polymeric materials could replace structural metallic components in the automobile industry.
- Wide spread use of the nano composites could reduce the consumption of 1.5 billion liters of gasoline by the vehicles in 1 year thereby reducing CO_2 emission by about 5 billion Kg annually.

Nanotechnology is the latest technology in which the materials are used in nano size, i.e. atoms are in the order of 1 to 100nm.

Nanoscale: 1nm = 10^{-9}m = 10^{-7}cm

Nano means 10^{-9}m i.e. a billionth part of a meter. Atoms are extremely small & the diameter of a single atom can vary from 0.1 to 0.5nm depending on the type of the element.

Ex: Carbon atom – 0.15 in diameter, water molecule – 0.3nm

Red blood cell – 7,000nm, Human hair-80,000nm wide

White blood cell-10,000nm, Virus – 100nm, Hydrogen atom - 0.1nm

Bacteria range – 1,000 to 10,000nm, proteins – 5 to 50nm

DNA – 2nm Width, Quantum dots – 8nm

Nano particles – 1 to 100nm, Fullerenes – 1nm

Nanomaterials: The materials in which the atoms are in the order of 1 to 100nm and these atoms will not move away from each other, called as nanomaterials.

Ex: C, ZnO, Cu – Fe alloys, Ni, Pd, Pt etc.

1. Materials that are nanoscale in one dimension called as nano layers [Thin films, surface coatings].
2. Two dimensional nanomaterials are called as nano tubes and nanowires.
3. Three dimensional nanomaterials are called as nanoparticles.
   Ex: Precipitates, Colloids & quantum dots, tiny particles of semi-conductor materials.

Classification of Nanomaterials:

Generally, nanomaterials are categorized into two types. They are

1. Fullerenes
2. Inorganic nanoparticles

1) **Fullerenes:** The fullerenes are class of allotropes of carbon which are graphene sheets rolled into tubes or hollow spheres. Fullerenes are again divided into two types
   a) Bucky balls
   b) Carbon nano-tubes or bucky tubes.

a) **Buckyballs:** Spherical fullerenes are called as buckyballs. The first fullerene “buckminister fullenrene C_{60}” was discovered by “Richard Buckminister Fuller”, a famous arichetectural modeller in 1985.

b) **Carbon nano tubes or bucky tubes:**
Cylindrical fullerenes are called as carbon nano tubes or bucky tubes. Fullerenes are similar to graphite structure, but they contain pentagonal rings.
Carbon nano tubes are of two types,
   i) Single walled nano tubes (SWNT)
   ii) Multi Walled nano tubes (MWNT)

1) **Nanoparticles:** Nanoparticles sized 1 & 100 nm are available in different forms such as clusters, metal nano particles, Colloids, nanocrystals, quantum dots etc.

- Nanoclusters have dimension between 1 & 100nm
- Nanopowders are agglomerates of nanoparticles (or) clusters.
- Nano sized single crystals are called as nanocrystals.
- When nanoparticles are in suspended form in liquid phase, it is called as nanocolloids.
- Quantum dots are tiny particles of semiconductor materials.

Nanomaterials exhibit different properties when compared to bulk materials. For example, opaque substances become transparent (copper), inert materials become catalysts (Platinum), Solids change into liquids at room temperature (gold), semiconductors become conductors (silicon).

Basic principles /properties of Nanomaterials:

Two principal factors can cause the properties of nanomaterials to differ significantly from bulk materials. They are

(i) Increase in surface area to volume ratio

(ii) Quantum confinement

Applications of Nanomaterials:

Nanochemistry undertakes the synthesis of precisely defined nanoparticles to achieve novel materials for specific applications in the field of medicine, advanced catalysis, control pollution, storage devices, optical and electronic devices.

In Electronic Devices:

- The potential application of nano particles is in the design of new super computers, includes zero dimensional quantum dots, one dimensional quantum dot, nano scale circuits etc.
- In communication technology, nano wires 20 times thinner and longer than conventional wires are used

In Solar Cells:

- Nanotechnology improves energy efficiency, storage and production of solar cells.
- Solar cells are expensive and nano-meter sized solar cells provide more energy at a cheaper price.
- This would reduce the usage of fossil and nuclear fuels.

In Food:

- Silver nanoparticles embedded in plastic for storage bins to kill bacteria, minimizing health risks from harmful bacterial
- Clay nanoparticles used in bottles, cartons and films to act as barrier to the passage of gasses and odours
- A combination of nanomaterials with enzymes improves the durability of enzymes, creates localized high concentration of proteins and reduces cost by minimizing losses.

In Automobiles:

- Nylon nanocomposites containing small amount of clay are capable of withstanding high temperature environments and used in automobile air intake covers.
- High power switches in ignition devices.
- On-line sensors for the measurement of wear and abrasion
- Create more efficient ultra-thin hydrocarbon membranes which allow to build light-weight fuel cells.

To Control Pollution:

- Nanotechnology helps in reducing chemical pollution.
- Nanoparticles as catalysts to transform vapours escaping from cars or industrial plants into harmless gases
- Nanostructures menbranes to separate CO_2 from industrial plant exhaust streams
- Eg. TiO_2 nanocrystals for air purification, manganeseoxide nanoparticles containing catalysts for removal of volatile organic compounds in indudtrial air emissions.

Water Pollution

- Nanotechnology helps in reducing water pollution
- Iron nanoparticles convert the contaminating chemicals to harmless compound
- Usage of electrodes composed of nano-sized filters to remove salts or metals
- Usage of filters of few nanometer in diameter to remove virus cells from water. Eg. Nanofibres.

As Catalyst:

- Catalyst are stable at high temperatures and can be used in smaller possible amount have been discovered.
- Eg: Rhodium hydrosols are the effective catalysts for the hydrogenation of olefins in organic phase.
- The complex oxide barium hexaaluminate BaO_3 Al_2O_3 retains its catalytic activity at high temperature.
- Nano chemical routes catalyze the chemical reactions at much lower temperature, pressure and in a very short period of time.

In Medical field:

- In the field of medicine and surgery nano technology possesses several potential applications
- Mutations in DNA could be repaired and cancer cells, toxic chemicals, viruses could be destroyed with the help of nano devices.
- Sensor systems which detect the emerging diseases in the body would shift the focus from the treatment of disease to early detection and prevention.
- eg: Nano scale devices smaller than 50nm can easily enter most cells and those smaller than 20nm can move through the walls of the blood vessels. As a result, a nano-scale device can interact with molecules on both the cell surface and within the cell.
- Eg. Nanocrystalline silver as antimicrobial agent in the treatment of wounds
- Biomarkers to disease identification, for targeted delivery of drugs to tumors

- Nanoparticles that target tumor cells such as iron and gold
- Aluminosilicate nanoparticles in medical gauze which help blood clot fater in open wounds

Consumer products:

- Increasing the strength of tennis rackets by adding nanotubes to the frame which increases control and power
- Using nao-sized material to fill any voids in golf shafts
- Cleaning products:
- TiO2 nanoparticles spary on film that uses energy fromlight to kill bacteria onn surfaces
- Silver manoparticles used in household appliances such as refrigerator or washing machines for cloths to kill bacteria and reduce odour.

In Space

- Nanotechnology helps in creating lighter, stronger and thermally stable materials for aircrafts, rockets and exploratory platforms
- Employing materials made from CNTs to reduce the weight of space ships while even increasing the structural strength.

In Defence:

Nanotechnology has tremendous potential in defence applications. Nanosensors are used in aircrafts for vibration damping, noise reduction and life monitoring of missiles

Fullerenes:

- Fullerenes, carbon nano materials were under study for potential medicinal use.
- Fullerenes are classes of allotropes of carbon which conceptually are graphene sheets rolled into tubes or spheres.
- Fullerenes are the classic three-dimensional carbon nano materials.
- This is made of 60 carbon atoms arranged in a soccer ball like shape and is less than 1nm in diameter.
- It has a hollow interior. There are now thirty or more forms of fullerenes up to and beyond C_{120}. The important fact for nanotechnology is that atoms can be placed inside the fullerene.
- Eg: The hollow structure can fit a molecule of a particular drug inside, while outside buckyball is resistant to interaction with other molecules in the body.
- So, they can be safe functional drug ‘containers’ that can enter cancer cells without reacting with them.

Buckminster fullerene C_{60}, also known as **buckyball,** the smallest member of the fullerene family.

- Buckminster fullerene was prepared in 1985 by Richard Smalley, Robert Curl, James Health, Sean O’ Brien and Harold Kroto.
- This is a football like structure made of carbon atoms.
- It contains 12 pentagons and 20 hexagon rings joined together to produce C_{60}.

- It contains 60 carbon atoms in 32 rings. It is hollow in side. The average bond length is $1.4A^0$.
- Medicinal use of fullerenes are binding specific antibiotics to the structure of resistant bacteria and even certain types of cancer cells such as melanoma.
- A common method used to produce fullerenes is to send a large current between two nearby graphite electrodes in an inert atmosphere.
- The resulting carbon plasma are between the electrodes cools into sooty residue from which many fullerenes can be isolated.
- The applications include catalysts, drug delivery systems, optical devices, chemical sensors and chemical separation devices.
- The molecule can absorb hydrogen with enhanced absorption when transition metals are bound to the fullerenes, leading to potential use in hydrogen storage.
- To replace steel in suspension bridges.
- To produce nano wires of gold and zinc oxide.
- To replace indium-tin oxide in LCDs, touch screens.
- As artificial muscles.
- To be used in cancer therapy.
- These are some other applications of fullerenes.

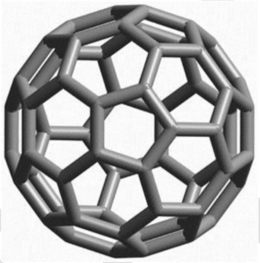


Fig: Fullerene/buckyball

Quantum Dots:

- Quantum dots are referred as artificial atoms.
- Quantum dot is a semiconductor that exhibits quantum confinement properties in all three dimensions.
- The size is in the range of 1-10nm.
- E.g.: cadmium selenide, lead selenide etc.
- They display any chosen colour in UV-region.
- Because of this property multi colour lasers are developed.
- Quantum dots absorb photons from solar radiation and release electrons to generate electricity.
- Used to manufacture extremely efficient thin-film photo voltaic cells
- Used in transistors, LEDs and diode layers as agents for medical imaging.
- In communication technology, nano wires 20-times thinner and longer than conventional wires are used.
- The magnetic nano metal particles are widely used in magnetic separation, magnetic drug transport and magneto-optical data storage.

UNIT 4: WATER AND ITS TREATMENT

.

Introduction:

Like air water is one of the few basic materials which is of prime importance for the preservation of life on this earth .All are aware of the uses of water for drinking,cooking ,bathing and farming etc., but few know the importance of water as an engineering material. For the existence of all living beings (humans, animals and plants) water is very crucial. Without water we cannot survive and almost all human activities–domestic, agricultural and industrial demand use of water. Although water is nature's most wonderful and abundant compound but only less than 1% of the world's water resources are available for the ready use. As engineering material water is used for producing steam in boilers to generate hydroelectric power, furnishing steam for engines, for refrigeration and air conditioning, for construction of concrete structures for manufacturing purposes and as a solvent in the chemical process.

Hardness:

Hardness of water is defined as the property which prevents the lathering of soap. This is due to presence of certain salts of Ca^{+2}, Mg^{+2} and other heavy metals dissolved in it. Soaps are sodium or potassium salts of higher fatty acids like oleic acid or palmitic acid or stearic acids ($C_{17}H_{35}COONa$). Hard water does not give lather with soap while soft water gives lather readily with soap.

Soap with hard water reactions:

When soap comes in contact with soft water lather is produced due to sodium stearate.

$$\underset{\text{(Sodium stearate)}}{C_{17}H_{35}COONa} + H_2O \rightarrow \underset{\text{(Stearic acid)}}{C_{17}H_{35}COOH} + NaOH$$

When soap comes in contact with hard water, sodium stearate will react with dissolved calcium and magnesium salts and produce calcium stearate or magnesium stearate which is white precipitate. This insoluble white precipitate prevents lathering of soap.

$$\underset{\text{(Sodium stearate)}}{2C_{17}H_{35}COONa} + CaCl_2 \rightarrow \underset{\text{(insoluble scum)}}{(C_{17}H_{35}COO)_2\,Ca} + 2NaCl$$

$$\underset{\text{(Sodium stearate)}}{2C_{17}H_{35}COONa} + MgSO_4 \rightarrow \underset{\text{(insoluble scum)}}{(C_{17}H_{35}COO)_2\,Mg} + Na_2SO_4$$

Different types of water have different degrees of hardness. The different types of water are commercially classified on the basis of degree of hardness as follows:

Hardness	**Name of water**
0-70mg/liter	Soft water
70-150mg/liter	Moderate hard water
150-300mg/liter	Hard water

300mg/liter and above	Very hard water

Degree of hardness:

The total hardness of water is caused by eight different dissolved salts of calcium and magnesium, [$Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $Ca(NO_3)_2$ and $Mg(NO_3)_2$]. Hence the hardness of water is expressed in terms of calcium carbonate equivalents. The weight of different hardness salts causing hardness are converted to weight equivalent to that of calcium carbonate. $CaCO_3$ is selected for expression of hardness because the molecular weight of $CaCO_3$ is 100, which is easy for calculation and it is the most insoluble salt and all the dissolved salts of calcium are precipitated as $CaCO_3$.

Name of the salt	**Molecular weight**
$Ca(HCO_3)_2$	162
$Mg(HCO_3)_2$	146
$CaCl_2$	111
$MgCl_2$	95
$CaSO_4$	136
$MgSo_4$	120
$CaCO_3$	100

The method for calculating degree of hardness will be clear from the following formula:
Hardness of water in terms of calcium carbonate equivalents

$$= \frac{\text{Amount of hardness causing salts}}{\text{Molecular weight of hardness causing salts}} \times 100$$

Causes of hardness:

The natural water is usually contaminated by different types of impurities.
They are mainly 3 types

1. Physical impurities
2. Chemical impurities
3. Biological impurities
4. Collodial impurities

Expression of hardness – Units

Units of Hardness:

1Parts Per Million: Parts of $CaCO_3$ equivalent hardness per 10^6 parts of water.

1 ppm = 1 part of $CaCO_3$ equivalent hardness present in 10^6 parts of water.

Milligram per liter: Number of milligrams of calcium carbonate equivalent hardness present in 1 liter of water.

1mg / L = 1 mg of $CaCO_3$ equivalent hardness present in 1 liter of water.
1 L = 1 Kg = 1000 g = 1000 x 1000 mg = 10^6 mg.
1mg /L= 1 mg of $CaCO_3$eq per 10^6 mg of H_2O = 1ppm

Degree Clark: (°Cl): It is the number of grains (1/7000 lb) of $CaCO_3$ equivalent hardness per 70,000 parts of water.

1Clark = 1 grain of $CaCO_3$ equivalent hardness per gallon of water.
= 1 part of $CaCO_3$ of hardness per 70,000 parts of water.

Degree French (°Fr): It is the parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.
1^0French =1 part of $CaCO_3$ per 10^5 parts of hard water

Milliequivalents per litre : - No of milliequivalents of hardness present per liter of water.
1m eq/L= 1 m eq of $CaCO_3$ per / liter of water = 50 mg /L of $CaCO_3$eq = 50ppm

Relation between various units of hardness:

$$\boxed{1\text{ ppm} = 1\text{mg /L} = 0.1^{0}\text{Fr} = 0.07\ ^{0}\text{Cl} = 0.02\text{ meq /L}}$$

Total hardness of the sample water=121ppm=121mg/L
121x0.07=8.47°cl and 121x0.1=12.1°Fr
Permanent hardness=101mg/l,101ppm,7.07°cl,10.1°Fr
Temporary hardness=20mg/l,20ppm,1.4°cl and 2^0Fr

Types of Hardness:

Hardness of water is mainly two types
1. Temporary Hardness
2. Permanent Hardness

1. Temporary Hardness:

It is caused mainly due to the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals. The salts mainly responsible for temporary hardness of water are Calcium bicarbonate $Ca(HCO_3)_2$ and Magnesium bicarbonate $Mg(HCO_3)_2$.
When bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, which gets deposited as a crust at the bottom of vessel. Temporary hardness can be largely removed by mere boiling of water. On boiling bicarbonates converts into corresponding carbonates which are insoluble. They can be removed by filtration.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$
(Calcium bicarbonate)

$$Mg(HCO_3)_2 \rightarrow Mg(OH)_2 + 2CO_2$$
(Magnesium bicarbonate)

2. Permanent Hardness:

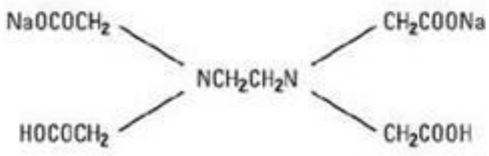
It is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other metals. The salts responsible for permanent hardness are $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $FeSO_4$, $Al_2(SO_4)_3$. Permanent hardness cannot be removed by boiling but it can be removed by the use of chemical agents.

Total hardness of water =Temporary hardness+Permanent hardness

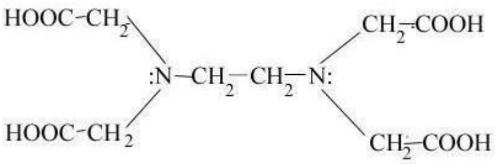
Estimation of temporary & permanent hardness of water:

Estimation of Hardness of Water by EDTA method (Complexometric titration)

This is a complexometric titration(method) where ethylene diamine tetra acetic acid [EDTA] is used as a complexing agent. EDTA form complexes with different metal ions at different P^H 9-10. To maintain the P^H 9-10 ammonical buffer is used. An alcoholic solution of Eriochrome black –T is used as an indicator. The disodium salt of EDTA is used for complexation since solubility of EDTA is very low.



Di-sodium salt of EDTA



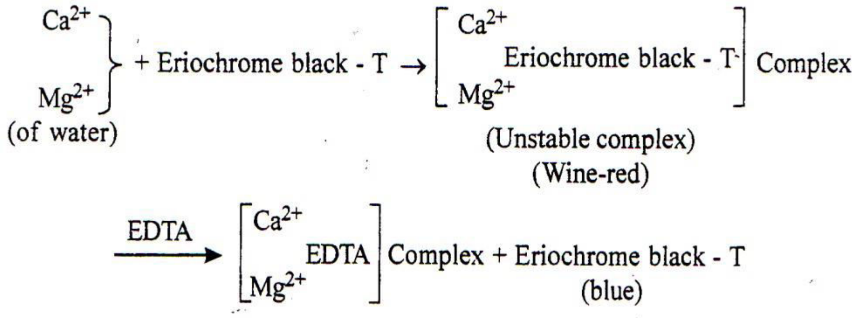
structure of EDTA

Basic Principle:

In this complexometric titration, the water sample is titrated with standard solution of Di-sodium salt of EDTA using EBT indicator. First EDTA solution is standardized with a standard solution of calcium carbonate, prepared by dissolving a known weight of cacium carbonate in dil.HCl and then making up the solution to a known volume with distilled water .The permanent hardness of water can be determined by titrating the water after boiling well to remove the temporary hardness as carbonates of calcium and magnesium against EDTA by adding EBT and buffer solution. Temporary hardness can be determined by subtracting total hardness of water from permanent hardness of water.

Reactions involved:

EBT indicator when added to hard water at pH = 10, forms weak complexes with calcium and magnesium present in hard water. It results in the formation of unstable wine red Ca-EBT or Mg-EBT complexes. During titration with EDTA, calcium first reacts to form relatively stable complex followed by magnesium to give Mg^{+2}-EDTA complex releasing the free indicator(blue).The colour changes from wine-red to blue at the endpoint.



Various steps involved in this method are…

1. **Preparation of standard hard water:** Dissolve 1g of pure, dry $CaCO_3$ in minimum quantity of dil. HCl and then evaporate the solution to dryness on a water bath. Dissolve the residue in distilled water to make 1 liter solution. Each mL of this solution thus contains 1mg of $CaCO_3$ equivalent hardness.
1 mL hard water solution = 1mg of $CaCO_3$ equivalent hardness.
2. **Standardization of EDTA solution:** Rinse and fill the burette with EDTA solution. Pipette out 50mL of standard hard water in a conical flask. Add 10-15mL of buffer solution and 4 to5 drops indicator. Titrate with EDTA solution till wine-red colour changes to clear blue.
3. **Titration of unknown hard water:** Rinse and fill the burette with EDTA solution. Pipette out 50 ml of unknown sample hard water in a conical flask. Add 10-15mL of buffer solution and 4 to 5 drops of indicator. Titrate with EDTA solution till wine-red colour changes to clear blue. Let volume used is V1mL.
4. **Titration of Permanent hardness:** Take 250mL of the water sample in a large beaker. Boil it till the volume is reduced to about 50mL, filter it, wash the precipitate with distilled water, collect filtrate and washing in a 250mL measuring flask. Finally make up the volume to 250mL with distilled water. Then, titrate 50mL of boiled water sample just as in Step (2). Let volume used is V2mL.

Experimental Procedure:

To a known volume of the sample of hard water (Vml) 10ml of a buffer solution and 5 drops of Eriochrome –Black T indicator are added. This solution is then titrated against the standard EDTA solution. The end point is the colour change from wine-red to blue.

Let the volume of EDTA consumed =V_1ml
1ml of EDTA=1mg of $CaCO_3$
V_1 ml of EDTA=V_1mg of $CaCO_3$
This hardness is present in V_1ml of hard water
Total hardness of the sample=$\frac{V_1 x1000}{V}$ ppm of $CaCO_3$

A known volume of (Vml) of sample water is taken in a beaker and boiled for 15 minutes. After cooling it is filtered and the filtrate is collected and make upto a known volume (Vml).This solution is titrated against EDTA. Hence the volume of EDTA consumed is V_2ml.

Permanent hardness of the sample = $\frac{V_2 x1000}{V}$ ppm of $CaCO_3$ equivalents

Hence temporary hardness = (Total hardness- Permanent hardness)

Hardness-Numerical Problems:

1) One liter of water from an underground reservoir in Nalgonda town in Andhra Pradesh found to have the fallowing dissolved salts. $Mg(HCO_3)_2$=14.6mg, NaCl=11.7mg. $MgCl_2$=48mg, $CaSO_4$=13.6mg, $Ca(HCo_3)_2$=32.4mg. Find the total hardness temporary &permanent hardness of water in degree French.

Solution:

S.No	Salt	Amount (mg)	Multiplication factor	$CaCO_3$ equivalents
1	$Mg(HCO_3)_2$	14.6	100/146	14.6x100/146 =10
2	NaCl	11.7	------	----------------
3	$MgCl_2$	48	100/95	48x100/95 =50
4	$CaSO_4$	13.6	100/136	13.6x100/136 =10
5	$Ca(HCO_3)_2$	32.4	100/162	32.4x100/162 =20

Temporary hardness = $Mg(HCO_3)_2$+ $Ca(HCO_3)_2$

= 10 + 20 = 30 ppm

Permanent hardness = $CaSO_4$ + $MgCl_2$

= 10 + 50 = 60 ppm

Total Hardness = Temporary hardness + Permanent hardness = 30 + 60 = 90 ppm

In degree French = 90×0.07 = 6.3^{o}Fr

2) One liter of water from Khammam Dist. in Andhra Pradesh showed the following analysis: $Mg(HCO_3)_2$ = 0.0256gms, $Ca(HCO_3)_2$ = 0.0156gms, NaCl = 0.0167gms, $CaSO_4$ = 0.0065gms, and $MgSO_4$ = 0.0054gms. Calculate temporary, permanent and total hardness.

Solution:

S.No	Salt	Amount (mgs)	Multiplication factor	$CaCO_3$ equivalents
1	$Mg(HCO_3)_2$	25.6	100/146	25.6x100/146=17.5
2	$Ca(HCO_3)_2$	15.6	100/162	15.6x100/162 =9.6

3	NaCl	16.7	-------------	--------------
4	$CaSO_4$	6.5	100/136	6.5x100/136 =4.77
5	$MgSO_4$	5.4	100/120	5.4x100/120 =4.5

Temporary hardness = $Mg(HCO_3)_2 + Ca(HCO_3)_2$
= 17.5 + 9.6 = 27.1ppm
Permanent hardness = $CaSO_4 + MgSO_4$
= 4.77 + 4.5 = 9.27ppm
Total Hardness = Temporary hardness + Permanent hardness
= 27.1 + 9.27 =36.37ppm

Boiler Troubles:

Water finds a great use in various industries for generation of steam in boilers. When water is continuously evaporated to generate steam, the concentration of the dissolved salts increase progressively causing bad effects for steam boilers. The boiler troubles that arise are

1. Carryover – Priming and Foaming
2. Scale formation
3. Caustic embrittlement

Carryover - priming & foaming

Priming:

It may be defined as the violent or rapid boiling of water occurring in the boiler which results in carrying out of water with steam in the form of a spray. When a boiler is producing steam rapidly, some particles of liquid water are carried along with the steam. The steam carrying water droplets is called wet steam. This process of wet steam formation is called priming.

Reasons:

(i) Priming is mainly due to very high water level.
(ii) Presence of large amount of dissolved solids, high steam velocities, sudden increase in steam production rate.
(iii) Sudden steam demand which leads to sudden boiling, presence of excessive foam filling the foam spare, and due to faulty boiler design.

Priming can be controlled by

1. Proper boiler design,
2. Fitting mechanical steam purifier
3. Avoiding rapid change in steam-rate.
4. Proper evaporation and adequate heating surfaces,
5. Uniform distribution of fuel and providing anti priming pipes, keeping the water level low and avoid sudden steam demands.

Foaming:

Foaming is the formation of small but stable bubbles above the surface of water.

Reasons:

(i) The main reason for foaming is being presence of fatty acids and other impurities.

(ii)The presence of large quantity of suspended impurities and the oils lowers the surface tension of boiler water producing foam.

Foaming can be controlled by

1. Using anti-foaming chemicals like castor oil. The amount of castor oil to be added varies with the boiler. Excess of castor oil can cause foaming.
2. Removal of concentrated boiler water and replacing it by fresh feed water.
3. Removing oil from boiler water by adding compounds like sodium aluminate.
4. Blowdown of the boiler can prevent foaming.

Disadvantages of priming and foaming:

Priming and foaming may cause the following boiler troubles:

1) The actual height of the water in boiler cannot be judged.

2) Wastage of heat with the result that it becomes difficult to keep up steam pressure and efficiency of the boiler is lowered.

3) Water concentrated with dissolved salts may deposit on parts of the machinery, which cause corrosion due to the formation of concentration cell in that part resulting the decay of metal on that spot.

Scale and Sludge formation in boilers:

Boilers are employed for the generation of steam in power plants ,where water is continuosly heated to produce steam.As more and more water is removed from water in the form of steam,the boiler warer gets concentrated with dissolved salts progressively reaches the saturation point.At this point the dissolved salts are precipitated out and slowly settle on the inner walls of the boiler plate.The precipitation takes place two ways

i) Sludge ii) Scale

Sludge:

Sludges are soft, loose and slimy precipitate formed with in the boiler. It is formed at comparatively colder portions of the boiler and collects in the area where flow rate is slow.

Reasons:

The dissolved salts whose solubility is more in hot water and less in cold water produce sludges Eg. $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$. The sludges were formed at comparatively colder portions of the boiler and get collected where rate of flow of water is low.

Dis-advantages:

a.Excessive sludge formation leads to settling of sludge in slow circulation area such as pipe connections ,plug openings, guage-glass connections leading to the choking of the pipes .

b. As the sludges are poor conductor of heat they cause loss of heat.

c. The working of the boiler is disturbed because of chocking of pipes by the sludge.

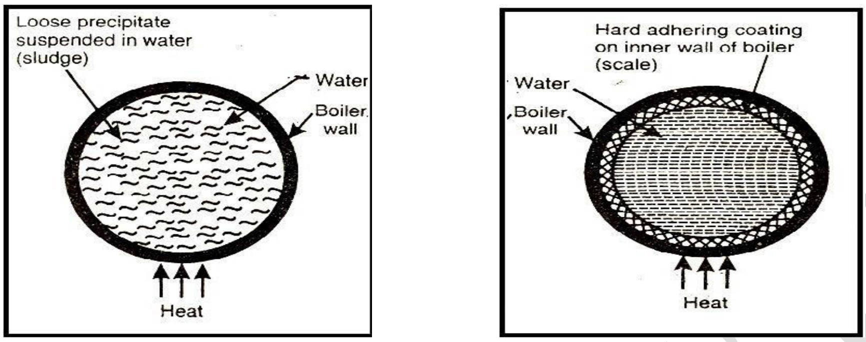
Prevention:

a. By using well softened water.

b. By blow down operation i.e. by drawing off a portion of concentrated water frequently.

Scales:

Scales are hard, adhering precipitates formed on the inner walls of the boilers. They stick very firmly on to the inner wall surface.



Sludges and Scales in boilers

Causes of scale formation:

Following are the causes:

a. Decomposition of calcium bicarbonate:

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

In low pressure boilers, $CaCO_3$ causes scale formation.

In high pressure boilers, $CaCO_3$ becomes soluble.

$$CaCO_3 + H_2O \rightarrow Ca(OH)_2 + CO_2$$

b. Decomposition of calcium sulphate:

$Caso_4$ is more soluble in cold water,hence its solubility decreases as the temperature of the boiler increases and precipitates out to produce hard scale on the surface of the bolier.The solubility of $Caso_4$ is 3200ppm at $15^{O}c$,reduces to 27ppm at $320^{O}c$ and completely insoluble in super heated water in high pressure boilers.This is the main reason for the formation of scales in high pressure boilers.$Caso_4$ scale is very hard ,highly adherent and difficult to remove

c. Hydrolysis of Magnesium salts:

Dissolved Magnesium salts undergo hydrolysis forming $Mg(OH)_2$ precipitate causing scales.

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

d. Presence of Silica: Silica present in small quantities deposits as silicates like $CaSiO_3$ and $MgSiO_3$. These are very difficult to remove.

Disadvantages:

a. **Wastage of fuel:**

The scale formation causes decreases of heat transfer. As a result over heating is required this causes consumption of fuel.

b. **Lowering of boiler safety**:

The hot scale cracks because of expansion and water suddenly comes in contact with overheated iron plates. This causes in formation of large amount of steam suddenly. This results in high pressure, causing boiler to burst.

c. **Decrease in efficiency**:

Deposition of scales in the valves and condensers of the boiler, choke them partially. This results in decrease in efficiency of boiler.

d.**Danger of explosion:**

Because of the formation of the scales .the boiler plate faces higher temperature outside and lesser temperature inside due to uneven heat transfer resulting the development cracks in the layers of scales.Water passes through the crack and comes in contact with boiler plate having high temperature.This causes formation of large amount of steam suddenly developing sudden high pressure which causes explosion of the boiler.

Removal of scales:

1. Scales can be removed by applying thermal shocks
2. Using scrapers, wire brush etc. scales can be removed.
3. Using certain chemicals scales can be removed. For example using 5-10% HCl. Calcium carbonate scales can be removed. Calcium sulphate scales can be removed using EDTA solution.
4. By blow down operation the scale formation can be avoided.

Prevention of scales or softening of hard water:

a. **External treatment:** Efficient softening of water is to be carried out by

i) Lime-soda process (ii) Zeolite process (iii) ion-exchange process

b. **Internal treatment**: Suitable chemicals are added to the boiler water either to precipitate or to convert the scale into sludge.

1. Colloidal conditioning
2. Phosphate conditioning
3. Carbonate conditioning
4. Aluminates conditioning
5. Calgon conditioning

S.No	**Sludges**	**Scales**
1	Sludges are soft, loose and slimmy precipitate	Scales are hard deposits.
2	Sludges are non-adherent deposits and can be removed easily	Scales stick firmly to the inner surface of boiler and are very difficult.

3	Sludges are formed by substances like $CaCl_2$ $MgCl_2$, $MgSO_4$, $MgCO_3$	Scales are formed by substances, like $CaSO_4$, $Mg(OH)_2$ etc.
4	Formed at comparatively colder portions of the boiler.	Generally formed at heated portions of the boiler.
5	Decrease the efficiency of boiler but are less dangerous	Decrease the efficiency of boiler and chances of explosions are also there.
6	Can be removed by blow-down	Cannot be removed by blow- down

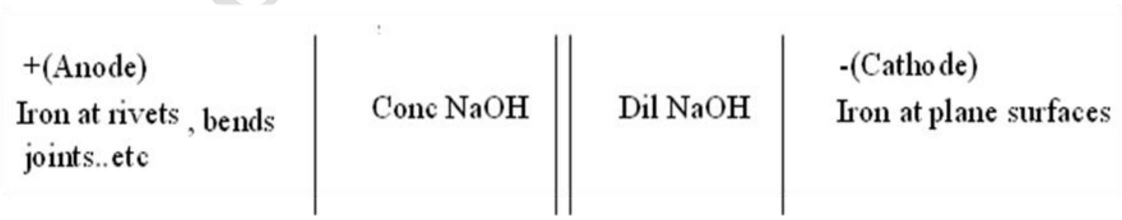
Caustic embrittlement:

Caustic embrittlement is a term used for the appearance of cracks inside the boilers particularly at those places which are under stress such as riveted joints due to the high concentration of alkali leading to failure of the boiler.

Reasons: It is a type of boiler corrosion caused due to the presence of alkali-metal carbonates and bicarbonates in feed water and also the presence of sodium carbonate.

$$Na_2CO_3 + H_2O \rightarrow NaOH + CO_2$$

This caustic water flows inside the boiler and causes some minute hair-cracks, by capillary action. On evaporation of water, the dissolved caustic soda increases its concentration which attacks the surrounding area, thereby dissolving iron of boiler as sodium ferroate (Na_2FeO_2). This causes embrittlement of boiler parts such as bends, joints, rivets etc, due to which the boiler gets fail.Caustic cracking can be explained by considering the following concentration cell. The iron at plane surfaces surrounded by dilute NaOH becomes cathodic and the iron at bends, joints and rivets surrounded by highly concentrated NaOH becomes anodic which consequently gets corroded



Prevention:

- By maintaining the pH of water and neutralization of alkali.
- By using sodium phosphate as softening reagents instead of sodium carbonate in the external treatment of boiler feed water.

- Caustic embrittlement can also be prevented by adding tannin or lignin or Sodium sulphate which prevents the infiltration of caustic-soda solution blocking the hair-cracks.

Treatment of water:

Internal treatment:

Internal treatment of boiler water is carried out by adding proper chemicals to precipitate the scale forming impurities in the form of sludge and to convert the scale forming chemicals into compounds which will stay in dissolved form in water.

1. Colloidal conditioning
2. Phosphate conditioning
3. Calgon conditioning

Colloidal conditioning: The addition of organic substances such as kerosene, tannin, gel etc., to the surface in low pressure boilers may prevent the scale formation. These substances gets coated over the scale forming precipitates and gives a loose and non-sticky precipitates which can be removed by blow-down operation.

Phosphate conditioning: The addition of sodium phosphate in hard water reacts with the hardness causing agents and gives calcium and magnesium phosphates which are soft and non-adhere and can be removed easily by blow-down operation. In this way, scale formation is removed in high-pressure boilers.

$$3CaCl_2 + 2\,Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6NaCl$$

$$3MgCl_2 + 2Na_3PO_4 \rightarrow Mg_3(PO_4)_2 + 6NaCl$$

The calcium phosphate and magnesium phosphate complexes were removed by blow down operation.

The three phosphates employed for conditioning are

1. NaH_2PO_4 –sodium dihydrogen phosphate (acidic)
2. Na_2HPO4 –Di sodium hydrogen phosphate (weakly alkaline)
3. Na_3PO_4-Trisodium phosphate (alkaline)

Trisodium phosphate is the most preferred reagent because it not only form complex with Ca^{+2} and Mg^{+2} ions, but also maintains the p^H of water between 9-10, where the calcium and magnesium ions undergo complexation.

Calgon conditioning: Involves in adding calgon to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$.

$$\text{Calgon} = \text{Sodium hexametaphosphate} = Na_2\,[Na_4\,(PO_3)_6]$$

$$Na_2[Na_4\,(PO_3)_6] \rightleftarrows 2Na^+ + [Na_4\,(PO_3)_6]$$

$$2CaSO_4 + [Na_4\,(PO_3)_6] \rightarrow [Ca_2\,(PO_3)_6\,]^{-2} + 2Na_2SO_4$$

External treatment:

The treatment given to water for the removal of hardness causing salts before it is taken into the boiler is called external treatment or softening of water. In industry three main external treatment methods employed for softening of water are.

1. Zeolite process

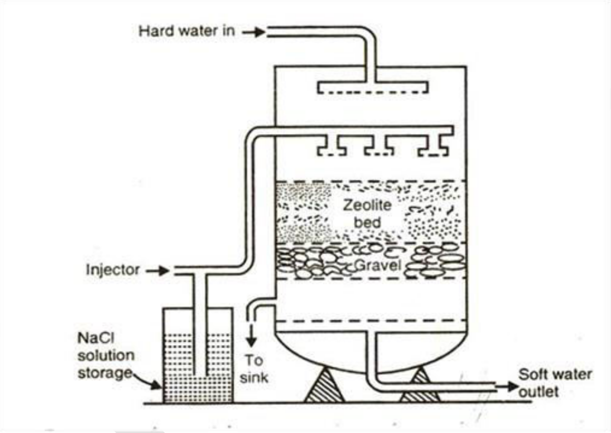
2. Ion-Exchange process

ZEOLITE PROCESS (Permutit Process)

The term zeolite stands for boiling stones(zeo=boiling,olite=stone).Zeolites are porous ,when water passes through it, it gives the appearance as through water is boiling hence the name zeolite which was discovered and named by a geologist.Zeolite is a 3D silicate. The chemical composition of zeolites is hydrated sodium aluminium silicate, represented as $Na_2O.Al_2O_3.xSiO_2.yH_2O$ where x = 2-10 and y = 2-6. Zeolites are capable of exchanging reversibly its sodium ions for hardness causing Ca^{2+} and Mg^{2+} in water. Hence zeolites are cation exchangers.

Zeolites are of two types

1. Natural zeolites are natural and non-porous having the composition
Natural zeolite: $Na_2O\ Al_2O_3\ .4SiO_2\ .2H_2O$.
2. Synthetic zeolites are porous and posses gel structure and are prepared from china clay, feldspar and a soda ash. Synthetic zeolites posses higher exchange capacity. Zeolites have cage like structure. It is derived from SiO_4.



Zeolite Process

Process: The hard water is passed through a zeolite bed fixed in a cylinder at a specific rate.The hardness causing ions Ca^{2+}, Mg^{2+} etc are retained by the zeolite as CaZe and MgZe respectively

The reactions taking place during softening process are

$$Na_2Ze + Ca(HCO_3)_2 \rightarrow CaZe + 2NaHCO_3$$

$$Na_2Ze + Mg(HCO_3)_2 \rightarrow MgZe + 2NaHCO_3$$

$$Na_2Ze + CaCl_2 \rightarrow 2NaCl + CaZe$$

$$Na_2Ze + MgCl_2 \rightarrow 2NaCl + MgZe$$

After the use of this process for certain time zeolite is exhausted i.e. all Na^+ ions of the zeolite are replaced by Ca^{+2} and Mg^{+2} ions and hard water will not be further softened.

Regeneration: Exhausted zeolite can be regenerated by heating it with brine solution (10% NaCl)

$$CaZe + 2NaCl \rightarrow Na_2Ze + CaCl_2$$

$$MgZe + 2NaCl \rightarrow Na_2Ze + MgCl_2$$

Limitations of Zeolite process:

1. Raw water should not contain turbidity. Turbidity will clog the pores of zeolite bed and makes it inactive. Turbidity of water must be removed by coagulation, filtration etc.
2. Mineral acids if present in the water will destroy the zeolite bed permanently. Water must be neutralized with soda before it is fed into zeolite bed.
3. Raw water must be not contain any coloured ions like Mn^2+ and Fe^2+,because they form manganese zeolite and ferrous zeolite which cannot be regenerated.

Advantages of Zeolite process:
1) It removes hardness almost completely and treated water contains hardness upto 10ppm.
2) No precipitation of the product takes place. Hence no disposal of sludge is required.
3) The equipment is compact and requires less skilled assistance.
4) The process adjusts itself for variation of hardness of incoming water.

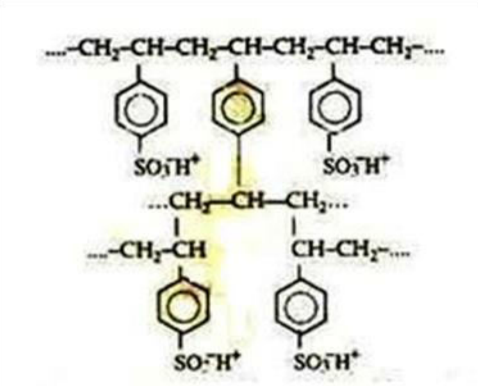
Disadvantages of zeolite process:
1) The treated water contains more sodium salts than in lime-soda process.
2) This method replaces only Ca^{2+} and Mg^{+2} ions by Na^+ ions, leaves acidic ions like HCO_3^- and CO_3^{2-} as $NaHCO_3$ and Na_2CO_3.
3) These $NaHCO_3$ salt decompose and liberate CO_2 which cause corrosion.
4)The Na_2CO_3 salt produced in water decomposed due to the high temperature maintained in the boiler to NaoH ,which causes caustic embrittlement.

Ion exchange process or deionization process or demineralization process

Ion-exchange process includes the exchange of the cations and anions of the dissolved salts with H^+ and OH^- respectively. For this two types of ion-exchangers are used, which are insoluble, cross–linked long chain organic polymers with microporous structure. In de-ionization process all the ions present in water are eliminated by using ion-exchange resins.
Basically resins with acidic functional group are capable of exchanging H^+ ions with other cations. Resins with basic functional groups are capable of exchanging OH^- ions with other anions.
Resins are classified as
1. Cation Exchange Resins
2. Anion Exchange Resins

1. Cation Exchange Resins:

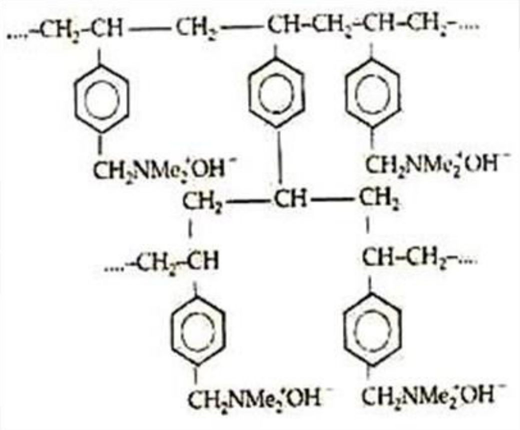
These are mainly styrene divinyl benzene co-polymers, which contains sulphonic or carboxylic functional groups. They are capable of exchanging their hydrogen ions with cations present in water.



Sulphonated styrene co-polymer –cationic resin

2. **Anion Exchange Resins:**

Anion exchange resins are styrene-divinyl benzene or amine-formaldehyde copolymers, which contains amino, quaternary ammonium or quaternary phosphonium or tertiary sulphonium groups as an internal parts of the resin matrix. These after treatment with dilute NaOH solution become capable of exchanging their OH^- ions with anions present in water.



N-methyl ammonium hydroxyl styrene co-polymer –anionic resin

Cation Exchange Resins

$2RH^+ + Ca^{+2} \longrightarrow R_2Ca^{+2} + 2H^+$

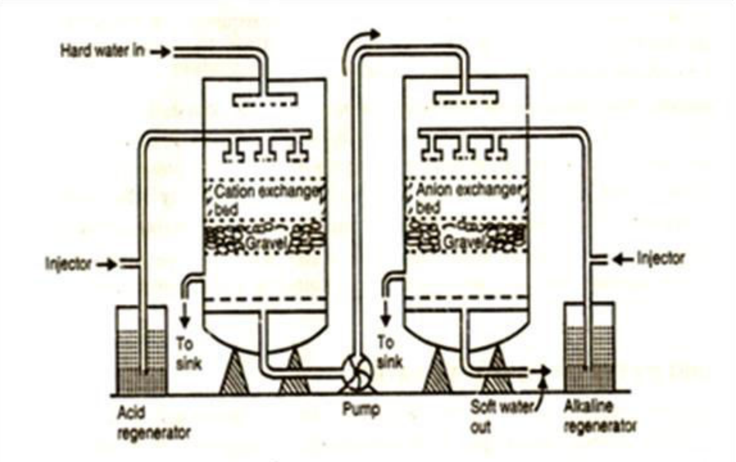
$2RH^+ + Mg^{+2} \longrightarrow R_2Mg^{+2} + 2H^+$ (RH^+ = cation exchange resin)

Anion Exchange Resins

$2R^1OH + Cl^{-2} \longrightarrow 2R^1Cl + 2OH^-$

$2R^1OH^- + SO_4^{-2} \longrightarrow R^1{}_2SO_4^{-2} + 2OH^-$

$2R^1OH + CO_3^{-2} \longrightarrow R^1{}_2CO_3^{-2} + 2OH^-$



De-ionization of water

Regeneration:

When cation exchanger losses capacity of producing H^+ ions and anion exchanger losses capacity of producing OH^- ions, they are said to be exhausted. The exhausted cation exchanger is regenerated by passing it through dilute sulphuric acid.

$$R_2Ca^{+2} + 2H^+ \rightarrow 2RH^+ + Ca^{+2}$$

The exhausted anion exchanger is regenerated by passing a dilute solution of NaOH.

$$R_2^1SO_4^{-2} + 2OH^- \rightarrow 2R^1OH^- + SO_4^{-2}$$

Merits of Ion-exchange process:

1. This process can be used to soften highly acidic or alkaline water.
2. It produces water of very low hardness (2ppm). So it is very good for treating water for use in high-pressure boilers.

Demerits of Ion-exchange process:

1. The equipment is costly and more expensive chemicals are needed.
2. If water contains turbidity, the output of the process is reduced. The turbidity must be below 10 ppm; else it has to be removed by coagulation and filtration.

POTABLE WATER:

Drinking water or potable water is safe enough to be consumed by humans or used with low risk of immediate or long term harm. In most developed countries the water supplied to households, commercial and industry needs drinking water standards, even though only a very small proportion is actually consumed or used in food preparation. As water flows over the surface of earth it picks up a number of impurities in the form of dissolved particles of soil, garbage, pesticides and other human, animal or chemical wastes. Some of these impurities may make water more useful and potable and some of these render it harmful and unfit.

Drinking or potable water, fit for human consumption, should satisfy the following essential requirements:

1. It should be sparkling clear and odour less.
2. It should be pleasant in taste.

3. It should be perfectly cool.
4. Its turbidity should not exceed 10ppm.
5. It should be free from objectionable dissolved gases like hydrogen sulphide.
6. It should be free from minerals such as lead, arsenic, chromium and manganese salts.
7. Its alkalinity should not be high.
8. Its pH should be about 8.0.
9. It should be reasonably soft.
10. Its total dissolved solids should be less than 500 ppm.
11. It should be free from disease-producing micro-organisms.
12. Chloride, fluoride and sulphide contents should be less than 250ppm, 1.5ppm and 250ppm respectively.

Steps involved in treatment of potable water:

Disinfection of surface water / Removal of micro-organisms in water:

Disinfection:

The process of destroying/killing the disease producing Bacteria, microorganisms, etc. from the water and making it safe for use, is called disinfection.

Disinfectants:

The chemicals or substances which are added to water for killing the bacteria are called disinfectants.

The disinfection of water can be carried out by following methods:

a). **Boiling**:

When water is boiled for 10-15 minutes, all the disease-producing bacteria are killed and water becomes safe for use.

b) **Bleaching power:**

Bleaching powder contains 80% chlorine. When bleaching powder is mixed with water, the result of chemical reaction produces a powerful germicide called hypochlorous acid. The presence of chlorine in the bleaching powder produces disinfecting action, kills germs and purifies the drinking water effectively.

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$H_2O + Cl_2 \longrightarrow HCl + HOCl$$

c) **Chlorine:**

Chlorination is the process of purifying the drinking water by producing a powerful germicide like hypochlorous acid. When this chlorine is mixed with water it produces hypochlorous acid which kills the germs present in water.

$$H_2O + Cl_2 \longrightarrow HOCl + HCl$$

Chlorine is basic (means pH value is more than 7) disinfectant and is much effective over the germs. Hence chlorine is widely used all over the world as a powerful disinfectant. Chlorinator is an apparatus, which is used to purify the water by chlorination process.

d) **Ozonisation:**

Ozone is a powerful disinfectant and is readily dissolved in water. Ozone being unstable decomposes by giving nascent oxygen which is capable of destroying the bacteria. This nascent oxygen removes the colour and taste of water and oxidizes the organic matter present in water.

$$O_3 \longrightarrow O_2 + [O]$$

(Nascent Oxygen-disinfectant)

The nascent oxygen is very powerful oxidizing agent and kills all the bacteria's as well as oxidizes the organic matter present in water. For carrying out the disinfection by ozone, ozone is released/injected into the water and the two are allowed to come in contact in sterilizing tank. The disinfected water is removed from the top. The contact period is about minutes and the usual dose strength is 2-3 ppm.

Advantages:

Disinfection by ozone is costlier than chlorine, but it simultaneously removes colour, odour and taste without giving any residue. Its excess is not harmful, since it is unstable and decomposes into oxygen.

Disadvantages:

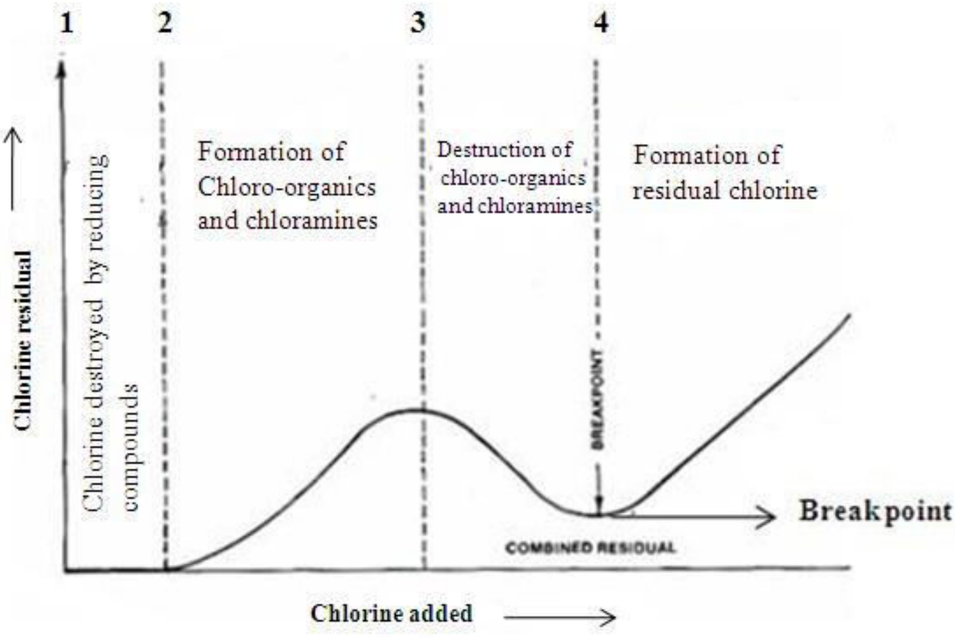
This method is quite expensive and hence, not employed for disinfection of municipal water supply.

Break point chlorination:

The amount of chlorine required to kill bacteria and to remove organic matter is called break point chlorination.

A typical relationship between the amount of chlorine added to water and the experimentally determined free residual chlorine is shown in the graph below which explains the break point chlorination.

(i) First (between points 1 and 2), the water reacts with reducing compounds in the water, such as hydrogen sulfide. These compounds use up the chlorine, producing no chlorine residual.



(ii) Between points 2 and 3, the chlorine reacts with organics and ammonia naturally found in the water and forms chloro-organics and chloramines.

(iii) Between points 3 and 4, the added chlorine will break down most of the chloramines in the water, leaving behind free chlorine which destroys pathogenic bacteria, actually lowering the chlorine residual.

(iv) Finally, the water reaches the breakpoint, at point 4 (minima). The breakpoint is the point at which the chlorine demand has been totally satisfied - the chlorine has reacted with all reducing agents, organics, ammonia and pathogenic bacteria in the water. After minima when more chlorine is added, it is not used in any reaction. Thus, the residual chlorine keeps on increasing in proportion to added chlorine. Hence for effective killing of microorganisms, sufficient amount of chlorine has to be added. Addition of chlorine in such dosages is known as break point chlorination.

Advantages of breakpoint chlorination:

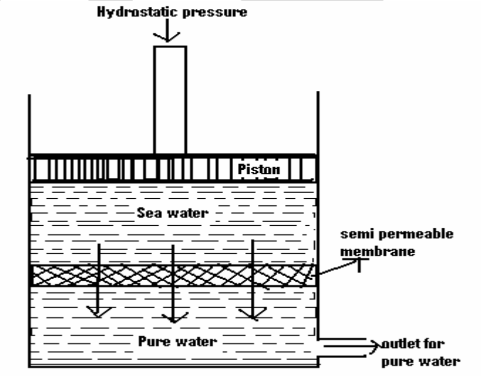
1. It ensures complete destruction of organic compounds which imparts colour, bad odour and unpleasant taste to water.
2. It completely destroys all the disease producing bacteria.
3. It prevents the growth of any weeds in water.

Desalination of Brackish water:

The process of removing common salt from the water, is known as desalination. Water containing high concentration of dissolved solids with peculiar salty or brackish taste is called brackish water. Sea water is an example for brackish water as it contains about 3.5% of dissolved salts.

Commonly used methods for the desalination of brackish water is:

1. Reverse Osmosis 2. Electrodialysis



Reverse Osmosis:

When two solutions of unequal concentrations are separated by a semi permeable membrane, flow of solvent takes place from dilute to concentrated sides, due to osmosis. If, however, a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow is reversed, i.e. solvent is forced to move from concentrated side to dilute side across the membrane. This is the principle of reverse osmosis. This membrane filtration is also called 'super-filtration' or 'hyper – filtration. The membrane consists of very thin films of cellulose acetate, affixed to either side of a perforated tube. However, more recently superior membranes made of polymethacrylate and polyamide polymers have come into use.

Method of purification: The reverse osmosis cell consists of a chamber fitted with a semi permeable membrane, above which sea water / impure water is taken and a pressure of 15 to

40 kg/cm^2 is applied on the sea water / impure water. The pure water is forced through the semi-permeable membrane which is made of very thin films of cellulose acetate.

Advantages:

1. Reverse osmosis possesses a distinct advantage of removing ionic as well as non-ionic, colloidal and high molecular weight organic matter.
2. It removes colloidal silica, which is not removed by demineralization.
3. The maintenance cost is almost entirely on the replacement of the semi permeable membrane.
4. The life time of membrane is quite high, about 2 years.
5. The membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.
6. Due to low capital cost, simplicity, low operating cost and high reliability, the reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high pressure boilers.

UNIT 5: FUELS

Introduction:

In recent years the dependency on energy by mankind has tremendously increased because of increase in standard of living and rapid technological advances. The energy needed today is derived from fossil fuels such as petroleum, coal and natural gas. Owing to the growing demands of these fuels, a proper knowledge of various fuels, their utilization and conservation is necessary.

Fuel:

A fuel can be defined as a combustible substance containing carbon as the major constituent which is capable of releasing a large amount of heat that can be used for domestic and industrial needs. The main sources of fuel are coal and petroleum oils. For example, coal is used in locomotives and as reducing agent in blast furnaces. Petrol is used in internal combustion engines and for doing mechanical work.

Combustion is the process of chemical reaction between fuel and oxygen. During combustion heat and products of combustion are released. The combustion process is an exothermic chemical reaction.

$$\textbf{Fuel} \longrightarrow \textbf{Heat energy + Light + Combustion products}$$

Heating value of a fuel is the amount of energy or heat released per unit mass during combustion of that fuel. The main elements of combustion are carbon, hydrogen, sulphur, oxygen and nitrogen.

CLASSIFICATION OF FUELS:

Fuels can be classified into 2 types

a) On the basis of their occurrence

b) On the basis of physical state of aggregation

On the basis of occurrence:

1) **Natural or primary fuels,** which are found in nature such as e.g., wood, peat, coal, petroleum, natural gas etc.

2). **Artificial or secondary fuels** are those which are prepared from the primary fuels. For example, charcoal, coke, kerosene, diesel, petrol, coal gas, oil gas, producer gas, blast furnace gas, etc.

On the basis of physical state of aggregation:

a) Solid fuels; b) Liquid fuels, and c) Gaseous fuel

Type of fuel	Natural or primary	Artificial or secondary
Solid	Wood, peat, lignite, dung, bituminous coal and anthracite coal	Charcoal, coke etc.
Liquid	Crude oil	Petrol, diesel and various other fractions of petroleum

Gaseous	Natural gas	Coal gas, oil gas, bio gas, water gas etc.

Comparison of solid, liquid and gaseous fuels

S.NO	Characteristic property of a fuel	Solid fuels	Liquid fuels	Gaseous fuels
1	Example	Coal	Crude oil	Coal gas
2	Cost	Cheap	Costlier than solid fuels	Costly
3	Storage	Easy to store	Closed containers should be used for storing	Storage space required is huge and should be leak proof.
4	Risk towards fire hazards	Less	More	Very high, since these fuels are highly inflammable
5	Combustion rate	It is a slow process	Fast process	Very rapid and efficient
6	Combustion control	Cannot be controlled	Cannot be controlled or stopped when necessary	Controlled by regulating the supply of air
7	Handling cost	High since labour is required in their storage & transport.	Low, since the fuel can be transported through pipes	Low, similar to liquid fuels, these can be transported through pipes
8	Ash	Ash is produced and its disposal also possess problems	No problem of ash	No problem of ash
9	Smoke	Produce smoke invariably	Clean, but liquids associated with high carbon and aromatic fuels produce smoke	Smoke is not produced
10	Thermal efficiency	Least	High	Highest
11	Calorific value	Least	High	Highest

12	Use in internal combustion engine	Cannot be used	Can be used	Can be used

Characteristics of a good fuel: A good fuel should satisfy the following requirements:

- It should have a high calorific value per unit weight i.e. it should evolve a large amount of heat when a unit weight of it is burnt under the conditions in which it is to be used as a fuel.
- Its moisture content should be low, so that its heating value should be high.
- It should not produce harmful products like CO_2, SO_2, H_2S and other poisonous gases on burning since they pollute the atmosphere.
- A fuel should have low content of non-combustible matter in the form of ash or clinker. The presence of non-combustible matter will enhance the cost of storage, handling and disposal of the waste.
- In case of solid fuel, the fire should be controllable so that it can be started or stopped.
- It should be economical and easily available.
- It should not give any offensive odour.
- An ideal fuel should have moderate ignition temperature. Normally low ignition temperature during storage and transport of fuel leads to fire hazards on the other hand, fuel with high ignition temperature is safe for storage, handling and transport.

SOLID FUELS:

Coal:

It is highly carbonaceous matter and is regarded as a fossil fuel produced from large accumulations of vegetable debris and alternation of vegetable matter like plants etc. under certain favorable conditions by the action of heat and pressure over millions of years. Coal is mainly composed of carbon, oxygen, hydrogen and nitrogen.

Its formation can be explained by the following theories.

i) In-situ theory: This theory states that the coal formation took place at the same area where vegetation grew and accumulated originally. The great purity of coal can be explained on the basis of this theory.

ii) Drift theory: According to this theory, the organic matter, vegetables, trees tec. when uprooted due to climatic conditions are transported by rivers to lakes and get deposited in the deeper parts of the soil. During a period of time they undergo gradual decomposition due to high temperature, pressure, absence of oxygen and presence of bacteria and transformed into highly carbonaceous matter

Coal has been classified in several ways. The most common method of classification is on the basis of rank. From the origin of coal it is clear the wood, after a long interval of time and under certain conditions was converted into coal. The successive stages in the transformation of vegetable matter into coal are wood, peat, lignite, bituminous coal and anthracite coal.

Coal is classified based on the carbon content. The following is sequence of conversion.

Peat → Lignite → Bituminous → Anthracite
← Moisture content, H, O, S, N, Volatile matter
Carbon content, calorific value, hardness →

Peat: Peat is regarded as the first stage in the transformation of wood into coal. Brown, fibrous, jelly like mass. Un-economical fuel. Contains 80-90% of H_2O. Composition C = 57%, H= 6%, O = 35%, ash 2.5 to 6%. Calorific value = 5400 kcal/kg.

Lignite: (Brown coal) soft, brown, colored, lowest rank coal and moisture content is 20 to 60%. Composition: C = 60%, O = 20%, Calorific value = 6,500 to 7,100 k.cal/kg

Bituminous coal:

Bituminous coal (common coal) Black to dark colored. This coal is largely used in industries for making metallurgical coke, coal gas and for domestic heating. It has laminated structure it is sub classified based on carbon content.

Composition is % of C = 78 to 90%, VM = 20 to 45%, CV = 8000 to 8500 kcal/kg.

Anthracite:

It is highest rank coal. These coals have very low volatile matter, ash & moisture. This coal is very hard, dense and lustrous in appearance.

% of C = 98 %. CV = 8650 to 8700 k.cal/kg.

Fuel	**% of Carbon**	**Calorific Value (k.cal/kg)**	**Main application**
WOOD	50	4000-4500	Domestic fuels
PEAT	57	4125-5400	Used if high rank coal is deficient
LIGNITE	67	6500-7100	Used for steam generation in thermal power plants and for the production of producer gas
BITUMINOUS	83	8000-8500	Used in making coal gas and metallurgical coke. Also used for steam generation in thermal plants and for domestic heating.
ANTHRACITE	93	8650-8700	Used in household and for steam raising. Also used in metallurgical purposes, where no smoke and high local heat is desired.

Analysis of Coal:

The composition of coal varies widely and hence it is necessary to analyze the coal samples so that types of coal can be selected for a particular industrial use. The following methods of analysis can be utilized for the selection of coal.

1. Proximate analysis:

This analysis records moisture, volatile matter, ash and fixed carbon as percentages of the original weight of the coal sample. Proximate analysis is of significance in commercial classification and industrial utilization of coal.

2. Ultimate analysis:
   This consists of determination of C, H, S, N and O. The ultimate analysis is essential for calculating heat balances in any process for which coal is employed as a fuel.

1. **Proximate analysis**: It is a quantitative analysis of the following parameters.

1. Moisture
2. Volatile matter
3. Ash
4. Fixed carbon

Moisture:

About 1 gram of finely powdered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105 to 110^{0}C. The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in a desiccator and weighed. Loss in weight is reported as moisture.

$$\%\text{ of Moisture} = \frac{\text{Loss in weight due to removal of moisture}}{\text{Weight of coal sample taken}} \times 100$$

Volatile Matter:

The dried sample is taken in a crucible and then covered with a lid and placed in an electric furnace or muffle furnace, maintained at 925^{0}C. The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then inside desiccator and weighed again. Loss in weight is reported as volatile matter on percentage-basis.

$$\%\text{ Volatile matter} = \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Weight of coal sample taken}} \times 100$$

Ash:

The residual coal sample taken in a crucible and then heated without lid in a muffle furnace at 750^{o}C for half an hour. The crucible is then taken out, cooled first in air, then in desiccator and weighed. Heating, cooling and weighing is repeated, till a constant weight is obtained. The residue is reported as ash on percentage-basis.

$$\%\text{ of Ash} = \frac{\text{Weight of ash left}}{\text{Weight of coal taken}} \times 100$$

Fixed carbon:

After the determination of moisture, volatile matter and ash contents, the remaining material is known as fixed carbon. It is determined indirectly by deducting the sum of the percentages of moisture, volatile matter and ash from 100

% of Fixed carbon = 100 - % of (Moisture + Volatile matter + ash)

Significance of Proximate Analysis: Proximate analysis provides following valuable information in assessing the quality of coal.

1. **Moisture**:

Moisture in coal evaporates during the burning of coal and it takes some of the liberated heat in the form of latent heat of evaporation. Therefore, moisture lowers the effective calorific value of coal. Moreover, it quenches the fire in the furnace, hence, lesser the moisture content, better the quality of coal as a fuel.

2. **Volatile matter**:

High volatile matter content means that a high proportion of fuel will distil over as gas or vapour, a large proportion of which escapes un-burnt, So, higher volatile content in coal is undesirable. A high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Hence, lesser the volatile matter, better the rank of the coal.

3. Ash: Ash is a useless, non-combustible matter, which reduces the calorific value of coal.. Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. It also involves additional cost in ash disposal.

4. **Fixed carbon**: Higher the percentage of fixed carbon, greater is its calorific value and better is the quality of coal.

Ultimate analysis: This is the elemental analysis and often called as qualitative analysis of coal. This analysis involves the determination of carbon and hydrogen, nitrogen, sulphur and oxygen.

Carbon and Hydrogen:

About 1 to 2 grams of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO_2 and H_2O respectively. The gaseous products of combustion are absorbed respectively in KOH and $CaCl_2$ tubes of known weights. The increase in weights of these are then determined.

$$C + O_2 \rightarrow CO_2$$

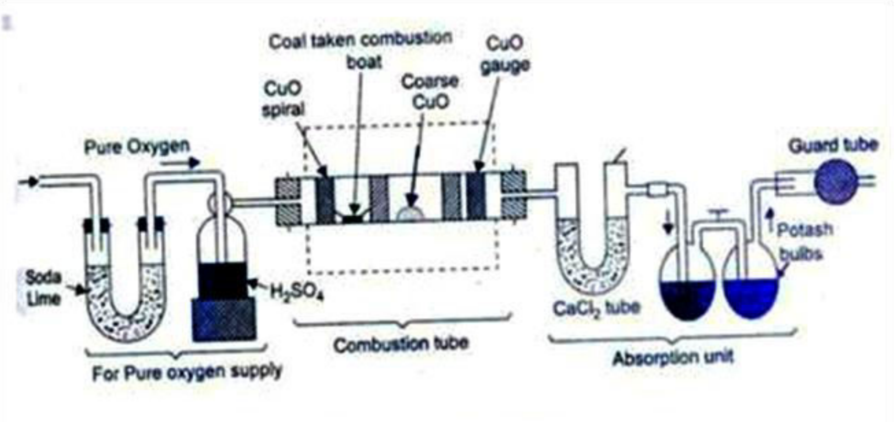
$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

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

$$CaCl_2 + 7\, H_2O \rightarrow CaCl_2.7H_2O$$

$$\%\text{ of Carbon} = \frac{\text{Increase in weight of KOH}}{\text{Weight of coal sample taken}} \times \frac{12}{44} \times 100$$

$$\%\ \text{of Hydrogen} = \frac{\text{Increase in weight of CaCl2 tube}}{\text{Weight of coal sample taken}} \times \frac{2}{18} \times 100$$



Carbon and hydrogen determination

Nitrogen:

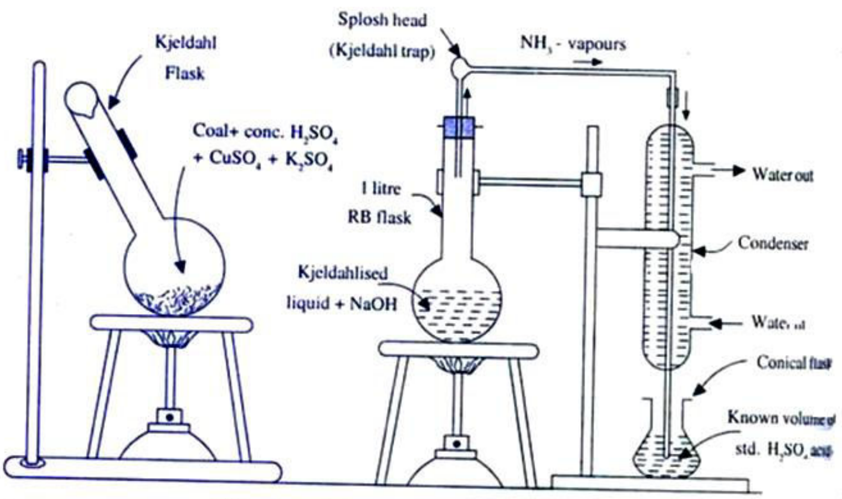
About 1 gram of accurately weighed powdered coal is heated with concentrated H_2SO_4 along with K_2SO_4 (catalyst) in a long-necked Kjeldahl's flask. After the solution becomes clear, i.e, when whole nitrogen is converted into ammonium sulphate, it is treated with excess of NaOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The unused acid is then determined by back titration with standard NaOH solution. From the volume of acid used by liberated ammonia, the percentage of N_2 in coal is calculated as follows:

$$N_2 + H_2SO_4 \xrightarrow{K_2SO_4} (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3\uparrow + 2Na_2SO_4 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$\%\ \text{of } N_2 = \frac{\text{Volume of acid} \times \text{Normality of acid} \times 1.4}{\text{Weight of coal taken}}$$



Estimation of nitrogen by Kjeldahl's method

Sulphur:

Sulphur is determined from the washings obtained from the known mass of coal, used in bomb calorimeter for determination of a calorific value. During this determination, S is converted into sulphates. The washings are treated with barium chloride solution, when barium-sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

$$S \xrightarrow{O_2} SO_4^{2-} \xrightarrow{BaCl_2} BaSO_4 + 2Cl^-$$

$$\%\text{ of Sulphur} = \frac{\text{Weight of BaSO4 obtained} \times 32}{\text{Weight of coal sample taken} \times 233} \times 100$$

Ash:

The residual coal is taken in a crucible and then heated without lid in a muffle furnace at 750^0C for ½ hour. The crucible is then taken out, cooled first in air, then in a desiccator and weighed. Heating, cooling and weighing is repeated, till a constant weight is obtained. The residue is reported as ash on percentage-basis.

Thus,

$$\%\text{ of Ash} = \frac{\text{Weight of ash left}}{\text{Weight of coal taken}} \text{ X } 100$$

Oxygen:

It is determined indirectly by deducting the combined percentage of carbon, hydrogen, nitrogen, sulphur and ash from 100.

% of Oxygen = 100 – % of (C + H + S + N + Ash)

Significance of Ultimate analysis:

- **Carbon and Hydrogen:** Greater the percentage of carbon and hydrogen, better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile mater and hence, it affects the use to which the coal is put.

- **Nitrogen:** Nitrogen has no calorific value and hence, its presence in coal is undesirable. Thus, a good quality coal should have very little nitrogen content.

- **Sulphur:** Sulphur, although contributes to the heating value of coal, yet on combustion produces acids like SO_2, SO_3, which have harmful effects of corroding the equipments and also cause atmospheric pollution.

- **Ash:** Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs.

- **Oxygen:** Oxygen content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value, and low coking power. Moreover, oxygen is a combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one. An increase in 1% oxygen content decreases the calorific value by about 1.7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen.

LIQUID FUELS:

Petroleum or Crude oil

- The crude oil or petroleum also known as rock oil or mineral oil is a dark colored liquid found well deep in the earth.
- It is mainly composed of hydrocarbons which may be solids, liquids or gases.
- Some optical active compounds having S and N also present.
- On average the composition of petroleum is

  C= 79.5-87.1% H= 11.5-14.8%

  S = 0.1-3.5% N and O = 0.1-0.5%

Origin of petroleum

The two theories which explain the formation of petroleum are

1. Carbide theory or Mendeleev's theory
2. Engler's theory or Organic theory

Carbide theory or Mendeleev's theory:

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

$$Ca+2C \longrightarrow CaC_2$$

$$4Al+3C \longrightarrow Al_4C_3$$
$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$
$$Al_4C_3+12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

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

$$C_2H_2 +H_2 \longrightarrow C_2H_4$$
$$C_2H_4 + H_2 \longrightarrow C_2H_6$$

The unsaturated hydrocarbons also get polymerized in the presence of metals.

$$3C_2H_2 \longrightarrow C_6H_6$$
$$C_2H_4 \longrightarrow C_6H_{12}$$

This theory was unable to explain the presence of nitrogen, sulphur and optical active compounds found in petroleum. This theory provides us a proof for the inorganic origin of petroleum

Engler's Theory or Organic Theory:

- Organic matter, animals, vegetation and marine animals died and get accumulated in sea. They were decomposed under high temperature and pressure by anaerobic bacteria to give a dark viscous liquid called petroleum.
- The existence of brine layer under petroleum and fossil remains of marine animals in that areas suggest the organic origin of the petroleum

Refining of Petroleum:

Crude oil obtained from the mines contains lot of soluble and insoluble impurities which must be removed. Refining can be defined as the process by which crude oil is separated into various useful fractions by fractional distillation and finally converted into desired specific products. The industry where the refining of crude oil takes place is called oil refinery.

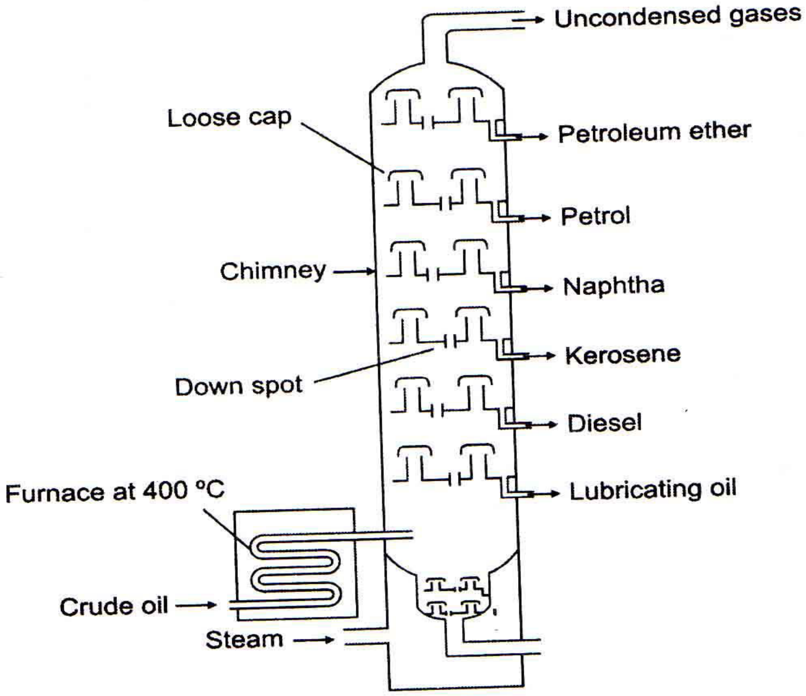
Refining of petroleum is done in different stages:

a. **Removal of solid impurities:** The crude oil is a mixture of solid, liquid and gaseous substances. This is allowed to stand undisturbed for some time, when the heavy solid particles settle down and gases evaporate. The supernant liquid is then centrifuged where in the solids get removed.

b. **Removal of water (Cottrell's process):** The crude oil obtained from the earth's crust is in the form of stable emulsion of oil and brine. This mixture when passed between two highly charged electrodes will destroy the emulsion films and the colloidal water droplets coalesce into bigger drops and get separated out from the oil.

c. **Removal of harmful impurities:** In order to remove sulphur compounds in the crude oil, it is treated with copper oxide. The sulphur compounds get converted to insoluble copper sulphide, which can be removed by filtration.

d. **Fractional distillation:** Heating of crude oil around 400^{0}C in an iron retort, produces hot vapours which is allowed to pass through fractionating column. It is a tall cylindrical tower containing a number of horizontal stainless trays at short distances and is provided with small chimney covered with loose cap. As the vapours go up they get cooled gradually and fractional condensation takes place. Higher boiling fractions condenses first later the lower boiling fractions



Name of Fraction	Boiling range	Approx- composition in terms of hydrocarbon 'C' atoms	Uses

(1) Uncondensed gas	Below 30^0C	C_1toC_4	A domestic or industrial fuel.
(2) Petroleum ether	30^0-70^0C	C_5-C_7	As a solvent.
(3)Gasoline or petrol	40^0-120^0C	C_5-C_9	As motor fuel, solvent, in dry cleaning
(4)Naphtha or solvent spirit	120-180°C	C_9-C_{10}	As solvent, in dry cleaning
(5) Kerosene	180^0C-250^0C	C_{10}-C_{16}	As an illuminant ,Engine fuel
(6) Diesel oil	250-320°C	C_{10}-C_{18}	Diesel engine fuel
(7)Heavy oil on refraction	320-400°C	C_{17}-C_{30}	Gasoline by cracking
(a) Lubricating oil	---	…….	As lubricant
(b) petroleum jelly	-----	…….	As lubricant and in cosmetics and ointments
c) Paraffin wax			In candles, boot polishes
d) Greases			As lubricant
8)Residue(asphalt, petroleum coke)			Used for making tar roads, water proof roofing

Synthetic petrol:

Because of increasing demand for petrol, the synthetic methods for preparation of petrol gain more importance. The important processes commonly used for synthesis of petrol are

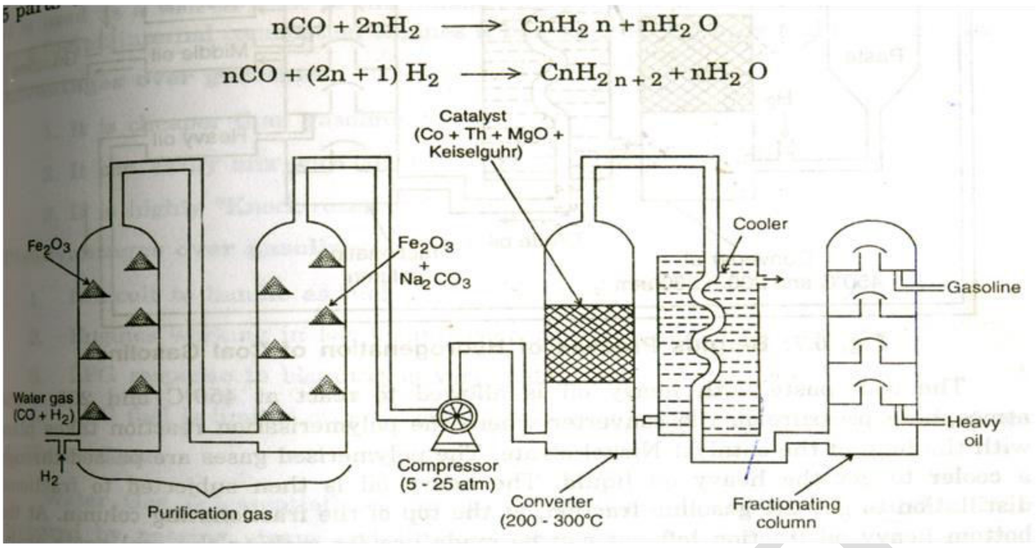
1. Fischer-Tropsch's method &
2. Bergius process.

Fischer-Tropsch's method:

This method was developed by Franz Fischer & Hans Tropsch (German scientists). The raw material is the hard coke which is converted into water gas ($CO + H_2$) by passing steam over red hot coke. In general, the mechanism of the reactions can be represented as

$$\mathbf{nCO + 2nH_2 \xrightarrow{\text{Ni or Co}} C_nH_{2n} + nH_2O}$$

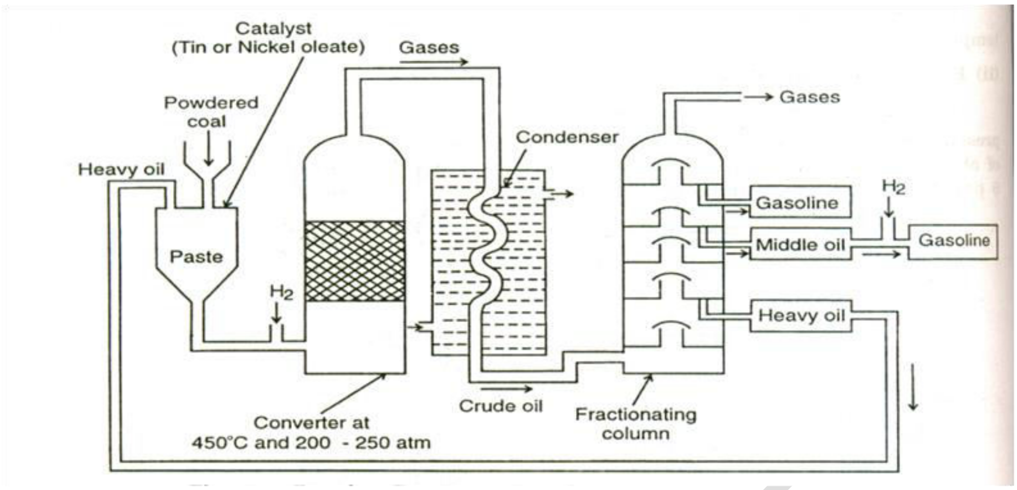
$$\mathbf{nCO + (2n+1)\,H_2 \longrightarrow C_nH_{2n+2} + nH_2O}$$



- Water gas ($CO + H_2$)s is mixed with hydrogen gas (H_2) in the presence of catalyst
- Catalyst consists of mixture of 100 parts of Co, 5 parts of Th, 8 parts of MgO and 200 parts of Kieselguhr earth
- Water gas and hydrogen gas mixture is purified by passing through Fe_2O_3 and Fe_2O_3 + Na_2CO_3
- Pressure is maintained to 5-25 atmosphere
- Passed through a convertor where the catalyst and temperature are maintained at 200-300°C.
- In the convertor polymerization takes place
- Hot gases are passed through a cooler where crude oil produced
- Crude oil is fractionated in a fractionating column and the gasoline fraction is produced in the top fraction
- The high boiling heavy oil is obtained at the bottom can be used for cracking to get more gasoline

Bergius Process:

- Low ash content coal is powdered and mixed with heavy oil to make paste along with a catalyst (Ni or Sn oleate)
- Paste is heated with H_2 at 450°C and 200-250 atmospheric pressure in the convertor
- The polymerized gases are passed through a cooler to get heavy oil
- It is then subjected to fractional distillation to get the gasoline fraction at the top portion
- At the bottom heavy oil fraction left out can be made use for making the coal paste again
- The yield of gasoline obtained by this process is 60%



Cracking of Petrol:

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

Cracking is defined as the "decomposition of bigger hydrocarbon molecules into simpler, low boiling hydrocarbons of low molecular weight".

Ex.

$$\underset{\text{Decane}}{C_{10}H_{12}} \xrightarrow{\text{Cracking}} \underset{\text{Pentane}}{C_5H_{12}} + \underset{\text{Pentene}}{C_5H_{10}}$$

Advantages

- The yield of petrol is higher.
- The quality of petrol produced is better.
- No external fuel is necessary for cracking.
- Cracking can be easily controlled, so we can get desired products.
- Evolution of by-product gases can be minimized.
- Product contains very less quantity of undesirable sulphur content. So it is very useful.

Objectives:

A product from crude oil, gasoline has greater demand as motor fuel. But yield is only upto 20%, more over fractional distillation have high content of sulphur. To overcome these problems middle and heavy oil fractions are cracked to get petrol. The main objective of cracking is to get desired products. Petrol made by cracking as good characteristics than straight run petrol

Cracking is mainly two types:

1. **Thermal cracking:** In this process, heavier hydrocarbon molecules are converted into lighter hydrocarbon molecules at high temperatures and pressures. Thermal cracking is carried out in two ways. The cracked products are then separated by fractional distillation. Generally, the yield is from 7 to 30%.

   1) Liquid phase thermal cracking 2) Vapour phase thermal cracking

Liquid phase thermal cracking: In this method, cracking takes place at 475^0C to 530^0C and at a high pressure of 100kg/cm^2. The cracked components have octane number up to 70.

Vapour phase thermal cracking: It is conducted for oils having low boiling temperatures. The cracking occurs at 600 to 650^0C and comparatively at low pressure of 10 to 20 kg/cm^2. It requires less time and the petrol obtained has better antiknock properties and poor stability than the petrol obtained from liquid phase thermal cracking.

1. Catalytic Cracking:

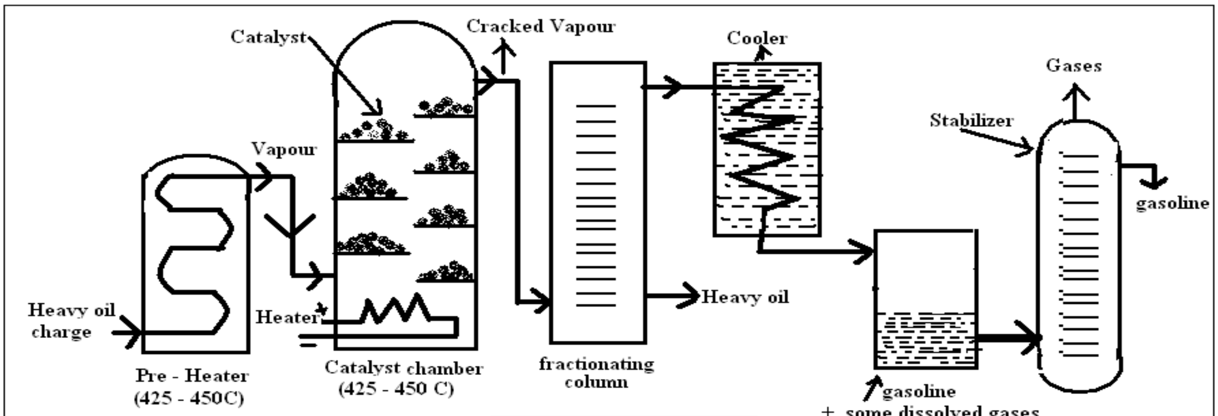
In this type of cracking catalysts are used. The suitable catalysts used are Al_2O_3 and $Al_2(SiO_3)$. This process completes at lower temperatures and low pressures compared to thermal cracking (300-450^{o}C; 1-5kg/cm^2 pressure). The petrol sample produced contains higher content of aromatics, hence quality of petrol with better antiknock properties. The petrol sample contains less percentage of sulphur, hence less corrosive.

Catalytic cracking may be:

1) Fixed bed catalytic cracking
2) Moving bed catalytic cracking

Fixed bed catalytic cracking:

- The oil vapours are heated in a pre-heater to cracking temperatures (420 – 450^0C) then forced through a catalytic chamber maintained at 425 – 450^0C and 1.5 kg/cm^2 pressure.
- During their passage through the tower, about 40% of the charge is converted into gasoline and about 2 – 4% carbon is formed. The latter adsorbed on the catalyst bed.
- The vapour produced is then passed through a fractionating column, where heavy oil fractions condense.
- The vapours are then led through a cooler, where some of the gases are condensed along with gasoline and uncondensed gases move on.
- The gasoline containing some dissolved gases is then sent to a 'stabilizer', where the dissolved gases are removed and pure gasoline is obtained.
- The catalyst, after 8 to 10 hours, stops functioning, due to the deposition of black layer of carbon, formed during cracking. This is re-activated by burning off the deposited carbon.



Fixed-bed catalytic cracking

Knocking-Petrol Knock :

1. In internal combustion engine, diesel or gasoline mixed with air is used as fuel
2. The power output and efficiency of internal combustion engine depends on a factor called compression ratio
3. CR is the ratio of volume of gases at the end of suction stroke to the volume of gases at the end of compression stroke: C.R = Vs.s/Vc.s
4. The efficiency of engine increases with increase in CR ratio which depends on the constituents present in petrol
5. Due to higher compression ratio fuel air mixture is heated to higher temperatures; the fuel ignites even before the regular spark occurs. This pre-ignition is called knocking
6. Some constituents of petrol, the rate of CR raises fast so that the last drops of the fuel air mixture gets instantaneously ignited producing a loud noise.
7. This rattling noise produced in the internal combustion engine is known as knocking.

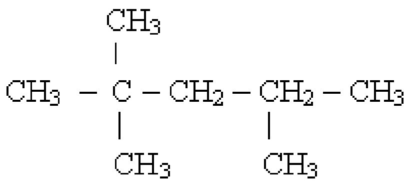
Octane number:

1. The performance of gasoline in internal combustion has been rated on the basis of octane number
2. The higher the octane number, lower is knocking and better is its performance
3. The knocking is maximum for n-heptane and has lowest antiknock value and its octane number is assigned as zero
4. Knocking is minimum for iso-octane (2,2,4-trimethyl pentane), has highest anti-knocking value and its octane number is given as 100.
5. Octane number of gasoline is the percentage of iso-octane in the mixture of isooctane and n-heptane which has same knocking as the gasoline itself
6. The higher the octane number, lower is knocking
7. The octane number of poor fuels can be raised by the addition of extremely poisonous materials such as tetraethyl lead $(C_2H_5)_4Pb$ and diethyl-telluride $(C_2H_4)_2Te$
8. The tendency of knocking is based on the chemical structure of hydrocarbons

n-paraffins > isoparaffins > Olefins > cycloparaffins > naphthalenes > aromatics

$$\xrightarrow{\hspace{12em}}$$

Decreasing order of knocking



$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\underset{\displaystyle CH_3}{|}}{C}}}-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

$CH_3-(CH_2)_5-CH_3$

2,2,4- trimethyl pentane **n-heptane**

(isooctane) octane number 100 (good fuel) octane number zero (bad fuel)

Diesel Knock:

Cetane Number:

1. The quality or rating of diesel is expressed by cetane number. Cetane is n- Hexadecane ($C_{16}H_{34}$)
2. Diesel knock is due to post-ignition (delayed ignition) of fuel air mixture with the application of heat and pressure but not by spark as in petrol I.C engine
3. n-Hexadecane has a short ignition lag as compared to any commercial diesel fuel. Its cetane number is 100
4. α -methyl naphthalene has very long ignition lag as compared to any commercial diesel oil. Its cetane number is taken as zero
5. ***Cetane Number is the percentage of n-hexadecane in a mixture of n- hexadecane and α-methyl naphthalene which has the same ignition characteristics as that of the sample under test.***
6. The order of cetane number for the following is given as:
7. n-alkanes > naphthalenes > alkenes > branched alkanes > aromatics
8. n-alkanes have good anti-knock value and aromatics have least anti-knock value

2-methyl naphthalene **n-hexadecane**

Cetane number = 0 (bad fuel) *Cetane number = 100 (good fuel)*

Petrol knocking is defined as the rattling sound produced in petrol engine due to pre-ignition of fuel air mixture

Diesel knocking is defined as the rattling sound produced in diesel engine due to ignition lag of fuel air mixture

- Knocking is due to improper ignition of fuel –air mixture.
- Knocking decreases the efficiency of engine.
- Petrol Knock is maximum in open chain straight paraffins and least in aromatics
- For internal combustion engine a fuel is said to be a good fuel if it has least knocking

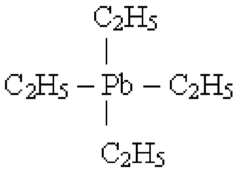
S. No	Petrol Knocking	Diesel Knocking
1	Petrol knocking is due to pre-ignition of the fuel	Diesel knocking is due to post-ignition (ignition–lag) of the fuel
2.	Octane number is the rating of petrol knock	Cetane number is the rating of diesel knock
3	Straight chain hydrocarbons causes maximum petrol knock where as aromatics causes least knock	Aromatic hydrocarbons causes maximum diesel knock where as straight chain hydrocarbons causes least knock
4	To improve anti-kock value TEL, and diethyl telluride are added	To improve antiknock value pre-ignition dopes like ethyl nitrite, isoamyl nitrite and acetane peroxide are added

Prevention of Knocking: To improve the antiknock value of the petrol sample, Tetraethyl lead (TEL) and diethyl telluride [$(C_2H_5)_2Te$] are added

Knocking can be prevented by using:

i) Good quality fuel with higher octane number
ii) By adding anti-knocking agents like tetraethyl lead, diethyl telluride etc.
iii) By retarding spark plug ignition

Leaded petrol: The variety of petrol in which tetra ethyl lead is added is called leaded petrol.



$$\begin{array}{c} C_2H_5 \\ | \\ C_2H_5 - Pb - C_2H_5 \\ | \\ C_2H_5 \end{array}$$

Tetra ethyl lead (TEL)

Advantages: Usually petrol with low octane number is not good quality petrol. It often knocks (i.e., produces huge noise due to improper combustion). As a result of knocking, petrol is wasted; the energy produced cannot be used in a proper way.

When tetraethyl lead is added, it prevents knocking, there by saves money and energy. Usually 1 to 1.5 ml of TEL is added per 1lit of petrol.

The mechanism of action is as follows:

First TEL will be transformed into finely divided particles of PbO which looks like a cloud. This takes place in the cylinder. Then the PbO particles react with hydrocarbon peroxide molecules formed, thus slowing down the oxidation process and prevent early detonation. Thus either knocking may be stopped or greatly reduced.

Disadvantages: Deposits of PbO are harmful to engine. So PbO must be eliminated from the engine. For this purpose, little amount of ethylene dibromide is added to petrol. It converts the harmful PbO to volatile $PbBr_2$ and eliminated through exhaust. Presence of any sulphur compounds reduces the efficiency of TEL. However lead bromide is harmful to environment

Gaseous fuels

Eg: Natural Gas

1. Natural gas is primary gaseous fuel. It is a fossil fuel
2. It is obtained from oil wells dug in the earth crust during mining of petroleum
3. It is mainly composed of methane and small quantities of ethane along with other hydrocarbons
4. It is also known as *methane gas or marsh gas* as it majorly contains methane
5. Composition of Natural gas:

CH_4 - 88.5% C_2H_6 - 5.5% Propane - 3.7%

Butane - 1.8% H_2, CO, CO_2 - 0.5%

6. Calorific value varies from 12000-14000 Kg/m^3

7. It is used as a very good domestic fuel
8. It is used in the preparation of ammonia
9. It is used to prepare carbon black for rubber industry
10. It is used to prepare some synthetic proteins which are used as animal feed

Secondary Gaseous Fuels:

LPG (Liquified Petroleum Gas):

Characteristics

1. LPG is obtained as byproduct during refining of crude oil or from natural gas
2. It mainly contains n-butane , isobutane, butylene and propane
3. It has high calorific value: 27800 kcal/m^3
4. It gives less CO and least un-burnt hydrocarbons. So it causes least pollution
5. It gives moderate heat which is very useful for cooking
6. It has a tendency to mix with air easily
7. Even though it is toxic, on combustion it gives no toxic gases
8. It neither gives ash or smoke content
9. It is cheaper than gasoline. Hence used as motor fuel
10. It is dangerous when leakage is there. It is highly knock resistant
11. LPG is used as domestic fuel and as a fuel in internal combustion engines
12. It is used as fuel in some industries

- LPG can be compressed under pressure in containers and sold under the trade name like Indane gas, Bharath gas etc.
- Traces of smelling organic sulphides (mercaptons) are added to LPG for safety measures (to give warning of gas leakage)

CNG (Compressed Natural Gas):

1. Natural gas mainly contains CH_4. CNG is made by compressing natural gas to less than 1% of the volume it occupies at STP
2. It is stored in a cylinder made of steel at a pressure of 200-248Kg/cm^3
3. It is odourless, non toxic gaseous mixture
4. Composition of CNG is CH_4 (90%), other constituents are ethane, propane and gases like N_2, CO etc.
5. Calorific value of CNG is 900KJ/mole

Advantages:

1. Due to higher temperature of ignition, CNG is better fuel than petrol and diesel
2. Operating cost is less
3. It releases least pollutants like CO and unburnt hydrocarbons
4. It mixes with air easily and undergoes regular combustion
5. No anti-knocking agent is required as it has high octane number
6. It is used as fuel in automobiles like cars, trucks, buses etc.
7. It is also used as fuel for locomotive diesel generators to generate electricity that drive the motors of train

Flue Gas Analysis:

Gases after combustion contain CO, CO_2, N_2 etc. In order to know the exact details about any fuel it is essential to analyze the flue gases. The mixture of gases mostly CO_2 issuing out of the combustion chamber is called flue gas. The efficiency of combustion can be well understood by the analysis of flue gas. For instance, if the presence of CO is indicated then carbon is suffering incomplete combustion due to insufficient supply of oxygen. But if the analysis shows the excess of CO_2, more of O_2, it implies that oxidation is complete and the supply of oxygen may be excessive. The analysis of flue gases is carried out with the help of Orsat's apparatus.

1. Flue gas is a mixture of gases produced from the products of combustion of a fuel
2. Its major constituents are CO, CO_2,O_2, and N_2
3. The efficiency of combustion can be understood by the qualitative analysis of flue gases
4. Orsat's apparatus is used for flue gas analysis

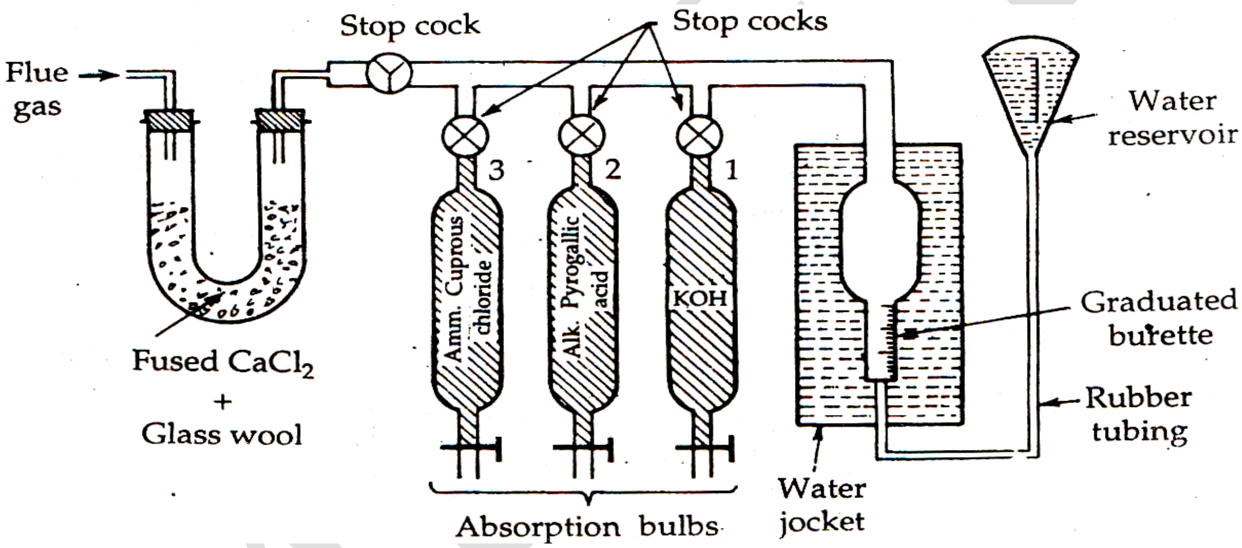


Fig: Orsat's Apparatus

Flue gas ⟹ **KOH sol** ⟹ **Alk. Pyrogallic sol** ⟹ **ammm.Cu_2Cl_2 sol**

-CO_2 **–O_2** **-CO**

Orsat's Apparatus: It consists of water – jacketed measuring burette, connected in series to a set of three absorption bulbs, through stop cocks. The other end is provided with a three way stop cock, the free end of which is further connected to a U – tube packed with glass wool (for avoiding the incoming of any smoke particles, etc.) The graduated burette is surrounded by a water jacket to keep the temperature constant of gas during the experiment. The lower end of the burette in connected to a water reservoir by means of a long rubber tubing. The absorption bulbs are usually filled with glass tubes, so that the surface area of contact between the gas and the solution is increased.

The absorption bulbs have solutions for the absorption of CO_2, O_2 and CO respectively. First bulb has potassium hydroxide solution (250g KOH in 500ml of boiled distilled water), and it absorbs only CO_2. The second bulb has solution of alkaline pyrogallic acid (25g pyrogallic acid + 200g KOH in 500 ml of distilled water) and it can absorb CO_2 and O_2. The third bulb contains ammonium cuprous chloride (100g cuprous chloride + 125ml liquor ammonia + 375 ml of water) and it can absorb CO_2, O_2 and CO.

Hence, it is necessary that the flue gas is passed first through potassium hydroxide bulb, where CO_2 is absorbed, then through alkaline pyrogallic acid bulb, where only O_2 will be absorbed (because CO_2 has already been removed) and finally through ammonical cuprous chloride bulb, where only CO will be absorbed.

Working:

Step 1:

- To start with, the whole apparatus is thoroughly cleaned, stoppers are greased and then tested for air tightness. The absorption bulbs are filled with their respective solutions to level just below their rubber connections. Their stop cocks are then closed.
- The jacket and leveling reservoir are filled with water. The three way stop cock is opened to the atmosphere and reservoir is raised, till the burette is completely filled with water and air is excluded from the burette.
- The three way stop cock is now connected to the flue gas supply and the reservoir is lowered to draw in the gas, to be analyzed, in the burette.
- However, the sample gas mixed with some air present in the apparatus. So the three way stop cock is opened to the atmosphere, and the gas expelled out by raising the reservoir. This process of sucking and exhausting of gas is repeated 3-4 times, so as to expel the air from the capillary connecting tubes etc.
- Finally, gas is sucked in the burette and the volume of the flue gas is adjusted to 100ml at atmospheric pressure.
- For adjusting final volume, the three way stop cock is opened to atmosphere and the reservoir is carefully raised, till the level of water in it is the same as in the burette, which stands at 100ml mark. The three ways stop cock is then closed.

Step 2:

The stopper of the absorption bulb, containing caustic potash solution, is opened and all the gas is forced into the bulb by raising the water reservoir. The gas is again sent to the burette. This process is repeated several times to ensure complete absorption of CO_2 [KOH solution]. The unabsorbed gas is finally taken back to the burette, till the level of solution in the CO_2 absorption bulb stands at the fixed mark and then its stop cock is closed. The levels of water in the burette and reservoir are equalized and the volume of residual gas is noted. The decrease in volume gives the volume of CO_2 in 100ml of the gas sample.

Step 3:

The volumes of O_2 and CO are similarly determined by passing the remaining gas through alkaline pyrogallic acid bulb and ammonical cuprous chloride bulb respectively. The gas remaining in burette after absorption of CO_2, O_2 and CO is taken as nitrogen.

Knowing the volume of the gases absorbed and volume of original gases, their percentages can be calculated

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

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

m = mass of gas in bulb (**m** = m_1, m_2, m_3 – mass of gas in bulbs 1, 2, 3, respectively)

Calorific value: The prime property of a fuel is its capacity to supply heat. Fuels essentially consists of carbon, hydrogen, oxygen and some hydrocarbons and the heat that a particular fuel can give is due to the oxidation of carbon and hydrogen. Normally when a combustible substance burns the total heat depends upon the quantity of fuel burnt, its nature, air supplied for combustion and certain other conditions governing the combustion. Further the heat produced is different for different fuels and is termed as its calorific value.

Calorific value of a fuel may be defined as “the total quantity of heat liberated, when a unit mass (or volume) of a fuel is burnt completely”. Or

“Calorific value is the amount of heat liberated by the complete combustion of a unit weight of the fuel and is usually expressed as cal gm^{-1} or kcal gm^{-1} or B.Th.U. Or

The calorific value of a fuel can be defined as “the total quantity of heat liberated when a unit mass of the fuel is completely burnt in air or oxygen”.

There are different units for measuring the quantity of heat. They are:

1. Calorie
2. Kilocalorie
3. British thermal unit (B.Th.U)
4. Centigrade heat unit (C.H.U)

1. **Calorie:** It is the amount of heat required to increase the temperature of 1 gram of water through one degree centigrade.

2. Kilocalorie: This is the unit of heat in metric system, and is defined as the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade.

1 k.cal = 1000 cal
1 k.cal = 3.968 B.Th.U

3. British thermal unit (B.Th.U): This is the unit of heat in English system, it is defined as “the quantity of heat required to increase the temperature of one pound of water through one degree Fahrenheit.

1 B.Th.U = 252 cal = 0.252 k.cal

4. Centigrade heat unit (C.H.U): It is the quantity of heat required to raise the temperature of one pound of water through one degree centigrade.

1 k.cal = 3.968 B.Th.U = 2.2 C.H.U

Inter conversion of various units of heat:

1 k.cal = 1000 cals = 3.968 B.Th.U = 2.2 C.H.U 1 B.Th.U = 252 cals

Units of calorific value:

For solid or liquid fuels: cal/g or k.cal/kg, B.Th.U/lb

For gaseous fuels: k.cal/cubic meter or k.cal/m^3

B.Th.U/ft^3 or B.Th.U/cubic feet

There are two types of calorific values of a fuel

1) Higher Calorific value (HCV) or Gross calorific value (GCV)
2) Lower Calorific value (LCV) or Net calorific value (NCV)

Higher or Gross calorific value (HCV):

It is defined as the total amount of heat produced when unit mass or unit volume of fuel is completely burnt and the products of combustion are allowed to cool to room temperature. When a fuel containing hydrogen is burnt, the hydrogen present is converted to steam. As the products of combustion are cooled to room temperature, the steam gets condensed into water and the latent heat is evolved. Thus the latent heat of condensation of steam, so liberated, is included in the gross calorific value.

Net calorific value or lower calorific value (LCV):

Whenever a fuel is subjected to combustion, the water vapour and moisture etc., escape along with the hot combustion gases and hence there is no chance for them to condense. So the net or lower calorific value is defined as “the net heat produced, when unit mass or unit volume of the fuel is burnt completely and the combustion products are allowed to escape.

Relationship between HVC and LCV

LCV or NCV = HCV – Latent heat of water vapour formed

$$H_2 + 1/2O_2 \longrightarrow H_2O$$

2 gm	18 gm
1 gm	9 gm

Since 1 part by mass of hydrogen produces 9 parts by mass of water
Hence LCV = HCV – mass of hydrogen x 9 x latent heat of steam

Latent heat of steam is 587kcal/g.

Net calorific value = Gross calorific value – 9 x H/100 x 587

$$\boxed{\textbf{NCV = GCV – 0.09 x H x 587}}$$

Where H = % of hydrogen in the fuel

Determination of Calorific Value:

The calorific value of a fuel is determined by an apparatus called calorimeter
Different types of calorimeter

a) Bomb calorimeter: for solids and liquid fuels
b) Boy's calorimeter: liquid fuels which get easily vapourised
c) Junker's calorimeter: for gaseous fuel

Junker's Gas Calorimeter:

The gas calorimeter functions based on the principle of burning a known volume gas and supplying heat with maximum efficiency to steadily flowing water and finding out the rise in temperature of a measured volume of water

Junker's principle:

Calorific of gaseous fuel x Volume of gas = Vol of water x Rise in temperature of water

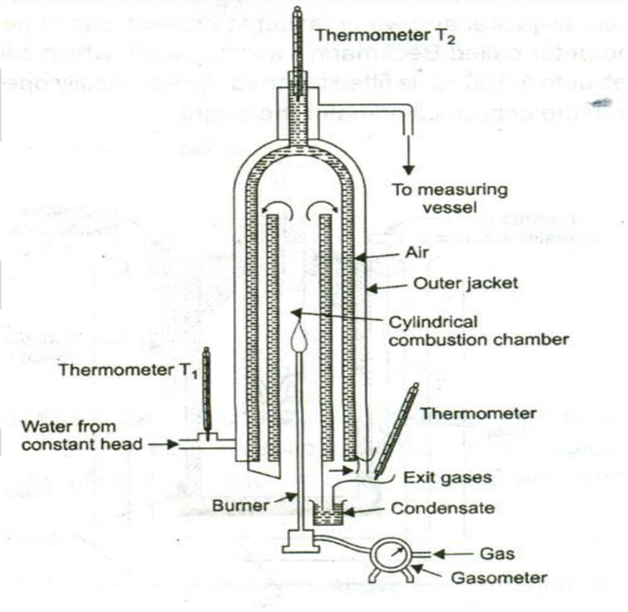


Fig. 6.14 : Junker's gas calorimeter

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

- Vertical metallic cylindrical combustion chamber where combustion of gaseous fuel occurs
- Bunsen burner clamped at the bottom to regulate the combustion which can be pulled out or pushed into the combustion chamber

- Supply of gas is regulated with the help of manometer which controls the supply of gas at a given pressure and gasometer is used to measure the volume of gas flowing in a particular time
- Combustion chamber is surrounded by annular space for water circulation
- Heat loss is prevented with the help of an outer jacket made of chromium plate
- Two thermometers are placed to measure the temperature of outlet and inlet water.

Procedure:

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

Experimental calculations

V = Volume of gas burnt in certain time ‘t’
W = Weight of water collected in time ‘t’
t_1 = Temp of incoming water
t_2 = Temp of outgoing water
Rise in temp = $t_2 - t_1$

If L kcal/m^3 is the calorific value of gaseous fuel,
Heat produced by fuel = V x L

Heat absorbed by water = W x ($t_2 - t_1$)

By principle, Heat given = Heat absorbed

$$V \times L = W \times (t_2 - t_1)$$

$$\text{C.V of gas (L) HCV} = \frac{W \times (t_2 - t_1)}{V} \ \text{kcal/m}^3$$

Mass of steam condensed in certain time ‘t’ = m/v
If Latent heat of steam = 587kcal/kg,
= m/v x 587

LCV = HCV – m/v x 587 kcal/m^3

****