

Ionic Equilibrium and Electrochemistry

Ionic Equilibrium

Buffer Solution

The solution which can resist the change in pH value even after addition of few drops of acids like HCl or few drops of bases like NaOH is known as buffer solution.

The ability to maintain pH value constant by a solution after adding small amount of HCl or NaOH is known as buffers action.

Types of Buffer Solution: On the basis of composition of buffer solution, it is classified into two types.

A. Acidic Buffer Solution

The buffer solution which consists of mixture of weak acid and its salt with strong base is known as acidic buffer solution. pH value of acidic buffer solution is always less than 7.

For e.g.: Mixture of acetic acid (CH_3COOH) and sodium acetate (CH_3COONa)

Mixture of formic acid (HCOOH) and potassium formate (HCOOK)

Mixture of propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$) and Sodium propanoate ($\text{CH}_3\text{CH}_2\text{COONa}$)

B. Basic Buffer Solution:

The buffer solution which consists of mixture of weak base and its salt with strong acid is known as basic buffer solution. pH value of basic buffer solution is always less than 7.

For e.g. Mixture of ammonium hydroxide (NH_4OH) and ammonium chloride (NH_4Cl)

Mixture of ammonium hydroxide (NH_4OH) and ammonium sulphate (NH_4SO_4)

Mechanism of Buffer Solution

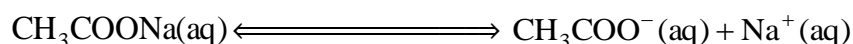
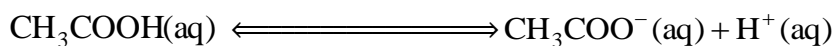
Acidic buffer solution maintains concentration H^+ protons and basic buffer solution maintains concentration of OH^- ions in the solution after adding either HCl or NaOH.

A. Mechanism of Acidic Buffer Solution

Acidic buffer solution consists of feebly ionizable weak acids and strongly ionizable it's salt with strong base.

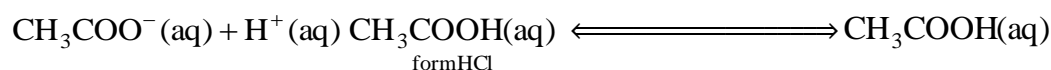
Let us consider an acidic buffer solution contains mixture of weak acids CH_3COOH and its salt with strong base CH_3COONa . Weak acid CH_3COOH gets feebly ionized in the solution in order to form small amount of CH_3COO^- ions and H^+ ions where salt

CH_3COONa gets strongly ionized in order to furnish large amount of CH_3COO^- ions and Na^+ ions as given below.



On addition of few drops of HCl

HCl gives H^+ ions and Cl^- ions in the solution by complete ionization and H^+ ions formed from HCl combines with acetate ions (CH_3COO^-) so as to give back weakly ionizable acetic acid (CH_3COOH) due to which concentration of H^+ ions remains constant in the solution and therefore pH value remains same as before adding of HCl in the solution.

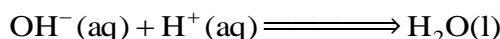
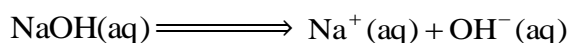


$$\text{pH} = -\log[\text{H}^+]$$

Since, $[\text{H}^+]$ is constant. pH value is also constant.

On addition of few drops of NaOH

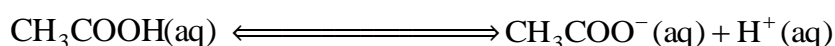
NaOH gives Na^+ ions and OH^- ions when it is added to the buffer solution and OH^- ions combines with H^+ ions of the buffer solution so as to form water.



Formation of water increases the dilution of buffer solution and according to Ostwald's dilution law, more amount of acetic acid further undergoes dissociation to regenerate H^+ ions in same concentration as it was before.

On the other hand, according to Le-chaterlier's principle when concentration of product H^+ ions decreases, more amount of reactant (CH_3COOH) get dissociated to maintain concentration of H^+ ions in the solution.

Therefore pH value of acidic buffer solution remains constant even after addition of few drops of NaOH in the solution.



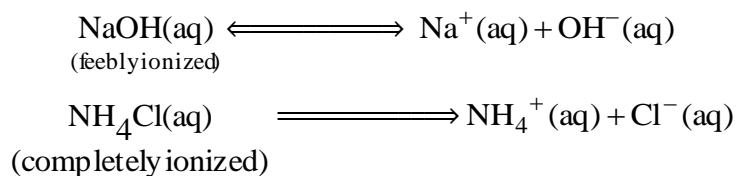
$$\text{pH} = -\log[\text{H}^+]$$

Since, the concentration of $[\text{H}^+]$ ions remains unchanged in the solution, therefore pH value of the solution remains unaffected.

B. Mechanism of Basic Buffer Solution

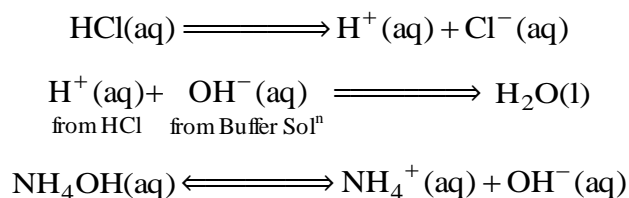
Basic buffer solution consists of feebly ionizable weak base and strongly ionizable its salt with strong base.

Let us consider a basic buffer solution contains weakly ionizable weak base NH_4OH and strongly ionizable its salt with strong acid NH_4Cl . Weak base NH_4OH partially gets ionized in order to form small amount of NH_4^+ ions and OH^- ions while NH_4Cl is completely ionized to form large amount of NH_4^+ ions and Cl^- ions in the solution as given below.



On addition of few drops of HCl

HCl is ionized completely to H^+ ions and Cl^- ions when it added to buffer solution. H^+ ions thus formed combines with ions of buffer solution so as to give water molecules due to which concentration of solution is decreased and according to Ostwald's dilution law, weak electrolyte NH_4OH gets further ionized to regenerate OH^- ions at the same concentration as it was before. Therefore the concentration of OH^- ions remains constant forever even after addition of few drops of HCl.

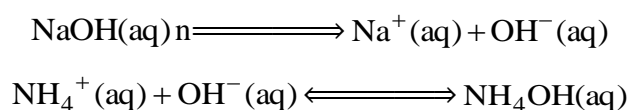


therefore $\text{pOH} = -\log[\text{OH}^-]$
 $\text{pH} = 14 - \text{pOH}$

Since concentration of OH^- ions remains same after addition of few drops of HCl. pH value of buffer solution also remain constant.

On addition of NaOH

NaOH is ionized to give Na^+ ions and OH^- ions in the solution and OH^- ions combines with NH_4^+ ions of buffer solution in order to give back feebly ionizable NH_4OH .



therefore $\text{pOH} = -\log[\text{OH}^-]$
 $\text{pH} = 14 - \text{pOH}$

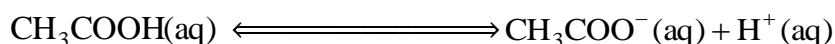
Since, concentration of OH^- ions remains constant in the solution, therefore pH value of buffer solution doesn't change after addition of NaOH.

Henderson-Hazel-Balch Equation

This equation is used to determine pH of Buffer solution and is derived from concept of common ion effect on the dissociation of weak electrolyte present in buffer solution.

Let us consider an acidic buffer solution of weak acid CH_3COOH and CH_3COONa .

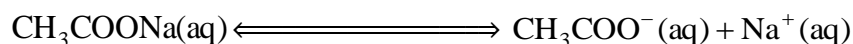
The CH_3COOH feebly dissociates



Hence,

$$\text{Dissociation constant for acid } K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} \dots\dots\dots \text{eq.1}$$

Salt CH_3COONa is completely dissociated in the solution to give common ion (CH_3COO^-)



Common ions CH_3COO^- suppress the dissociation of weak acid CH_3COOH and hence concentration of CH_3COOH at equilibrium becomes equal to that of initial CH_3COOH .

$$\underset{\text{at equilibrium}}{[\text{CH}_3\text{COOH}]} = \underset{\text{at initial}}{[\text{CH}_3\text{COOH}]}$$

Since, CH_3COONa gets complete dissociated in the solution, therefore concentration of CH_3COO^- is just equal to the concentration of CH_3COONa .

$$\text{CH}_3\text{COONa} = \text{CH}_3\text{COO}^-$$

Therefore, eq.1 will be

$$K_a = \frac{[\text{CH}_3\text{COONa}][\text{H}^+]}{\text{CH}_3\text{COOH}}$$

$$\text{H}^+ = \frac{K_a [\text{CH}_3\text{COOH}]}{\text{CH}_3\text{COONa}}$$

taking logarithm in both sides

$$\log[\text{H}^+] = \log K_a + \log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COONa}]}$$

taking negative sign in both sides

$$-\log[\text{H}^+] = -\log K_a - \log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COONa}]}$$

Since, $\text{pH} = -\log[\text{H}^+]$ and $\text{p}K_a = -\log K_a$

therefore,

$$\text{pH} = \text{pK}_a - \log \left[\frac{\text{CH}_3\text{COOH}}{\text{CH}_3\text{COONa}} \right]$$

$$\text{pH} = \text{pK}_a + \log \left[\frac{\text{CH}_3\text{COONa}}{\text{CH}_3\text{COOH}} \right]$$

As $[\text{CH}_3\text{COONa}] = [\text{Salt}]$ (concentration of Salt)

and $\text{CH}_3\text{COOH} = [\text{Acid}]$ (concentration of Acid)

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{pH} = \text{pK}_a + \log \left[\frac{\text{concentration of Salt}}{\text{concentration of Acid}} \right]$$

This is Henderson equation for acid buffer solution.

Similarly, for basic buffer solution

$$\text{pOH} = \text{pK}_a + \log \left[\frac{\text{concentration of Salt}}{\text{concentration of Base}} \right]$$

then $\text{pH} = 14 - \text{pOH}$

Significance of Henderson Equation

1. It helps to calculate pH value of acidic and basic buffer solution.
2. It helps to calculate dissociation constant for weak acid and weak base.
3. It helps to calculate the amount of salt, acid or base to prepare buffer solution of certain pH value.

Possible Questions

- Qn.1 What is buffer Solution?
- Qn.2 Write reaction mechanism of Acidic buffer solution with one suitable example.
- Qn.3 What is buffer action? How does a basic buffer solution can resist the change in pH even after addition of few drops of HCl or NaOH.

Solved Numerical on Ionic Equilibrium

1. Calculate pH of the buffer solution containing 0.01M acetic acid and 0.02 M sodium acetate. (K_a for acetic acid $= 1.8 \times 10^{-5}$)

Solution:

Given, concentration of Acetic acid = 0.02 M

concentration of Sodium acetate = 0.2 M

dissociation constant $K_a = 1.8 \times 10^{-5}$

$$\text{pK}_a = -\log(1.8 \times 10^{-5})$$

$$pK_a = 4.74$$

form Henderson equation.

$$\begin{aligned}\text{Here, } pH &= pK_a + \log \frac{[CH_3COONa]}{[CH_3COOH]} \\ &= 4.74 + \log \frac{0.2}{0.02} \\ &= 4.74 + \log 10 \\ &= 4.74 + 1 \\ &= 5.74\end{aligned}$$

- 2. Calculate the pH of the buffer solution containing 0.01M ammonium hydroxide and 0.1M ammonium chloride. ($pK_b=4.74$)**

Solution:

Given, concentration of NH_4OH = 0.01M

concentration of NH_4Cl = 0.1M

$$pK_b = 4.74$$

$$pOH = pK_b + \log \frac{0.1}{0.01}$$

$$pOH = 4.74 + 1$$

$$pOH = 5.74$$

$$pH = 14 - 5.74$$

$$pH = 8.26$$

- 3. Find out the value of buffer solution which is formed by mixing 200ml of 0.01M acetic acid and 300 ml of 0.02M sodium acetate.**

Solution:

Given, concentration of CH_3COOH = 0.01M

Volume of acetic acid $V_1 = 200\text{ml}$

Final volume of buffer solution $V_2 = 200 + 300$

$$= 500\text{ml}$$

Final concentration of $CH_3COOH(S_2) = ?$

From the Normal Equation

$$S_1 V_1 = S_2 V_2$$

$$S_2 = \frac{S_1 V_1}{V_2} = \frac{0.01 \times 200}{500} = 0.004\text{M}$$

Initial concentration of $CH_3COONa = 0.02\text{M}$

Initial volume of $CH_3COONa = V_1 = 300\text{ml}$

Final volume = 500ml

Final concentration of $\text{CH}_3\text{COONa}(\text{S}_2) = ?$

$$\text{S}_2 = \frac{\text{S}_1 \text{V}_1}{\text{V}_2} = \frac{0.02 \times 300}{500} = 0.012$$

Here, $[\text{CH}_3\text{COOH}] = 0.004\text{M}$

$[\text{CH}_3\text{COONa}] = 0.012\text{M}$

$\text{pK}_a = 4.47$

From Henderson Equation

$$\begin{aligned}\text{pH} &= \text{pK}_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} \\ &= 4.74 + \log 3 \\ &= 5.217\end{aligned}$$

- 4. Calculate pH value of basic buffer solution containing 100ml of 0.1M of hydroxide and 200ml of 0.2M of NH_4Cl . [dissociation constant $= 1.8 \times 10^{-5}$]**

Solution:

Given, For ammonium hydroxide (NH_4OH)

initial concentration of $\text{NH}_4\text{OH}(\text{N}_1) = 0.1\text{M}$

initial volume of $\text{NH}_4\text{OH}(\text{V}_1) = 100\text{ml}$

final concentration of buffer solution (N_2) = ?

final volume of buffer solution (V_2) = $100 + 200 = 300$

Now from Normal Equation,

$$\begin{aligned}\text{N}_1 \text{V}_1 &= \text{N}_2 \text{V}_2 \\ \text{N}_2 &= \frac{\text{N}_1 \text{V}_1}{\text{V}_2} = \frac{0.1 \times 100}{300} = 0.033\text{M}\end{aligned}$$

For ammonium chloride (NH_4Cl)

initial concentration of $\text{NH}_4\text{Cl}(\text{N}_1) = 0.2\text{M}$

initial volume of $\text{NH}_4\text{Cl}(\text{V}_1) = 200\text{ml}$

final volume of buffer solution (V_2) = $100 + 200 = 300$

final concentration of buffer solution (N_2) = ?

Now from Normal Equation

$$\text{N}_1 \text{V}_1 = \text{N}_2 \text{V}_2$$

$$N_2 = \frac{N_1 V_1}{V_2} = \frac{0.2 \times 200}{300} = 0.133M$$

Here, $[NH_4OH] = 0.033M$

$[NH_4Cl] = 0.133M$

$$pK_a = -\log(K_a) = 4.74$$

Now, from Henderson equation

$$\begin{aligned} pOH &= pK_a + \log \frac{[Salt]}{[Base]} \\ &= 4.74 + \log \frac{[0.133]}{[0.033]} \\ &= 4.74 + 0.605 = 5.34 \end{aligned}$$

Now, $pH = 14 - pOH$

$$= 14 - 5.34 = 8.65$$

Alternatively

$$\begin{aligned} pH &= pK_a + \log \left[\frac{\frac{300 \times 0.02}{500}}{\frac{300 \times 0.01}{500}} \right] \\ &= 4.74 + \log 3 = 5.217 \end{aligned}$$

- 5. Find out the pH of buffer solution containing 200ml of 0.02M of Sodium acetate and 100ml of 0.01M acetic acid. What will be the change in pH after addition of 0.01M of few drops of HCl.**

Solution:

Given, For CH_3COOH

Initial volume CH_3COOH $V_1 = 100ml$

Initial concentration of CH_3COOH $S_1 = 0.01M$

Final volume of buffer solution $V_2 = 100 + 200 = 300ml$

Final concentration of CH_3COOH $S_2 = ?$

$$\begin{aligned} S_2 &= \frac{S_1 V_1}{V_2} \\ &= \frac{0.01 \times 100}{300} \\ &= 0.033 \end{aligned}$$

For CH_3COONa

Initial volume of CH_3COONa $V_1 = 100\text{ml}$

Initial concentration of CH_3COONa $S_1 = 0.02\text{M}$

Final volume buffer solution $V_2 = 300\text{ml}$

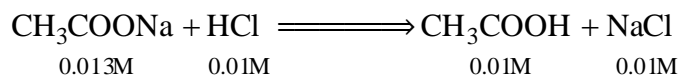
Final concentration CH_3COONa $S_2 = ?$

$$\begin{aligned} S_2 &= \frac{S_1 V_1}{V_2} \\ &= \frac{0.02 \times 200}{300} \\ &= 0.013 \end{aligned}$$

Now, Initial pH of the buffer solution

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ &= 4.74 + \log \left[\frac{0.013}{0.033} \right] \\ &= 4.74 + 0.59 \\ &= 5.33 \end{aligned}$$

Now, after the addition of HCl



$$\begin{aligned} \text{Concentration of } \text{CH}_3\text{COONa} &= 0.013 - 0.01 \\ &= 0.003\text{M} \end{aligned}$$

$$\begin{aligned} \text{Concentration of } \text{CH}_3\text{COOH} &= 0.022 + 0.01 \\ &= 0.043\text{M} \end{aligned}$$

Now, pH after the addition of HCl

$$\begin{aligned} \text{pH} &= 4.74 + \left[\frac{0.0033}{0.043} \right] \\ &= 4.74 - (-1.15) \\ &= 3.59 \end{aligned}$$

$$\begin{aligned} \text{Thus the change in pH} &= 5.33 - 3.59 \\ &= 1.74 \end{aligned}$$

- 6. Calculate the buffer solution containing 0.2M NH_4Cl and 0.1M NH_4OH solution. Find out change in pH after addition of 0.01M NaOH solution.**

Solution:

Given, concentration of $\text{NH}_4\text{Cl} = 0.02\text{M}$

concentration of $\text{NH}_4\text{OH} = 0.01\text{M}$

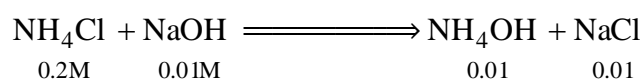
$$\text{pK}_a = 4.74$$

Now,

$$\begin{aligned}\text{pOH} &= \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Base}]} \\ &= 4.74 + \log \frac{[0.2]}{[0.1]} \\ &= 5.04\end{aligned}$$

$$\text{therefore, pH} = 14 - 5.04 = 8.96$$

After the addition of NaOH



$$\text{concentration of } \text{NH}_4\text{Cl} = 0.2 - 0.01 = 0.19$$

$$\text{concentration of } \text{NH}_4\text{OH} = 0.01 + 0.1 = 0.11$$

Now

$$\begin{aligned}\text{pOH} &= \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Base}]} \\ &= 4.74 + \log \frac{[0.19]}{[0.11]} \\ &= 4.977\end{aligned}$$

$$\text{pH} = 14 - 4.977 = 9.02$$

$$\text{therefore, change in pH} = 9.02 - 8.96 = 0.06$$

- 7. Calculate pH of buffer solution containing 500ml of 0.4M acetic acid and 500ml of 0.6M sodium acetate. Find out change in pH after addition of 1M of 20ml HCl**

Solution:

Given, **For acetic acid,**

$$\text{initial concentration of } \text{CH}_3\text{COOH}(N_1) = 0.4\text{M}$$

$$\text{initial volume of } \text{CH}_3\text{COOH}(V_1) = 500\text{ml}$$

$$\text{final volume of buffer solution } V_2 = 500 + 500 = 1000\text{ml}$$

$$\text{final concentration of buffer solution } (N_2) = ?$$

We Know,

$$N_2 = \frac{V_1 N_1}{V_2} = \frac{0.4 \times 500}{1000} = 0.2M$$

For sodium acetate,

initial concentration of $\text{CH}_3\text{COONa}(N_1) = 0.6M$

initial volume of $\text{CH}_3\text{COONa}(V_1) = 500\text{ml}$

final volume of buffer solution (V_2) = 1000ml

final concentration of buffer solution (N_2) = ?

We Know,

$$\begin{aligned} N_2 &= \frac{V_1 N_1}{V_2} \\ &= \frac{0.6 \times 500}{1000} = 0.3M \end{aligned}$$

Now, $[\text{CH}_3\text{COOH}] = 0.2M$

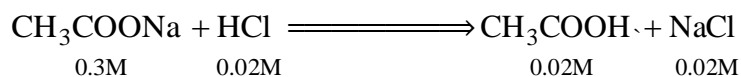
$[\text{CH}_3\text{COONa}] = 0.3M$

$$\begin{aligned} \text{Now, } \text{pH} &= \text{pK}_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]} \\ &= 4.74 + \log \frac{[0.3]}{[0.2]} \\ &= 4.74 + 0.176 = 4.916 \end{aligned}$$

After the addition of 20ml of 1M HCl

1M HCl means 1000ml of solution contains 1M

20ml of solution contains $\frac{1 \times 20}{1000} = 0.02M$



concentration of $\text{CH}_3\text{COOH} = 0.02 + 0.2 = 0.22$

concentration of $\text{CH}_3\text{COONa} = 0.3 - 0.02 = 0.28$

$$\begin{aligned} \text{Now, } \text{pH} &= \text{pK}_a + \log \left[\frac{0.28}{0.22} \right] \\ &= 4.74 + 0.104 = 4.845 \end{aligned}$$

Now, change in pH value = $4.916 - 4.845 = 0.071$

Alternatively

$$\text{pH} = \text{pK}_a + \log \left[\frac{500 \times 0.6}{500 \times 0.4} \right] \text{ and see above solution}$$

Electrochemistry

Electrochemical Cell

The cell consisting of two metallic electrodes dipping into the same or different electrolytes whereby either energy is produced or consumed in order to bring about chemical change is known as electrochemical cell.

Types of Electrochemical Cell

1. Electrolytic Cell
2. Galvanic Cell

Electrolytic Cell

The electrochemical cell which requires external supply of electricity in order to bring about chemical change is known as electrolytic cell. Such type of cell performs its work as long as the supply of electrical energy is continued.

- For e.g. i) Electroplating of Copper
ii) Electrolysis of Solution

Galvanic Cell

The cell which produces electrical energy by the spontaneous Redox chemical reaction in the cell is known as Galvanic cell or Voltaic cell.

for e.g. Dry Cell, Daniel Cell

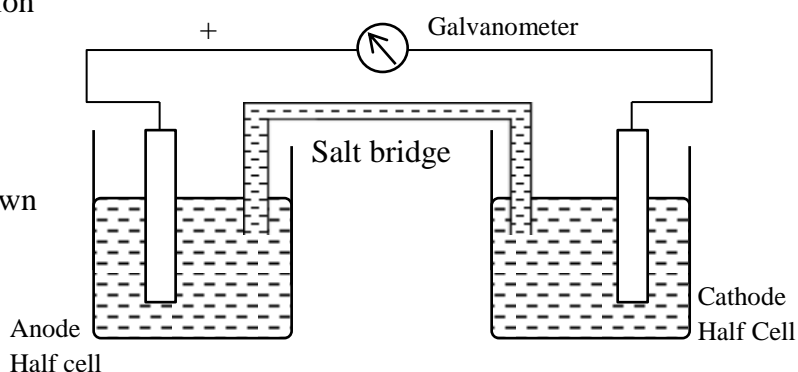


Fig. Galvanic or Voltaic Cell

Galvanic Cell	Electrolytic Cell
It converts chemical energy into electrical energy.	It converts electric energy into chemical energy.
Electrical energy is produced as a result of Redox reaction.	Electrical energy is supplied to bring about chemical change.
Reaction occurs simultaneously	Reaction occurs non-simultaneously
Cell contains same or different electrolytes	Cell contains same electrolytes
Anode and Cathode are present in different half cells	Anode and Cathode are present in same electrolytes in a cell.
Anode and cathode are of different materials	Anode and cathode are of same or of different materials
Electrode with oxidation is called anode and that with reduction is called Cathode	Electrode connected with negative terminal of electrical source is called cathode and that connected with positive is called anode.
Salt bridge is used	No salt bridge is used.

Cell notation of Galvanic Cell

There is a certain way of representation of electrochemical cell. According to the universal accepted convention, cell notation is done as following points.

- Anode half cell is written in left hand side.
- Cathode half cell is written in right hand side.
- Both half cells are separated by double vertical lines which represents the salt bridge.
- Each electrode is represented by single vertical line from its electrolyte.
- Electrolytes are expressed in ionic or molecular form with their concentration in aqueous medium.

General Representation

The examples of Cell Notation are given below.



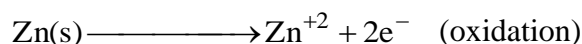
Cell Reaction

The chemical change obtained from the sum of chemical reactions occurred in anode half cell and cathode half cell is termed as cell reaction of single electrochemical reaction. The flow of electron from one electrode to another in the electrochemical cell is caused by the half cell reaction in the anode and cathode compartment.

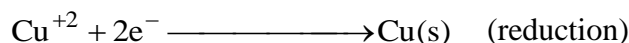
Let us consider a galvanic cell constructed by following pair of half cell.



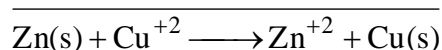
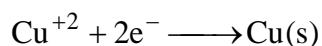
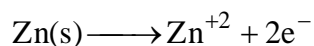
At anode



At cathode



Net Cell Reaction



Single Electrode Potential

The potential difference between any electrode and its ions due to formation of double electrical layers around the electrode as a result of oxidation or reduction is called single electrode potential simply electrode potential.

When metal is dipped into its salt solution metal gets oxidized into metal cation (i.e. positive) and electrons lost from it are deposited over metal due to positively charged metal ions surround the metal surface so as to form double electrical layers. The separation of double electrical layers results the development of potential difference which is known as single electrode potential.

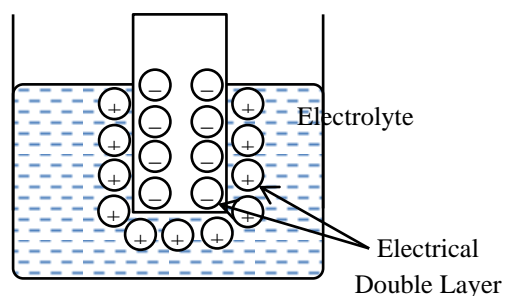


Fig. Formation of electrical double layer causing Electrode Potential

Single electrode potential is categorized into two types.

Oxidation Potential

The potential difference developed between the electrodes and its ions as a result of oxidation is called is known as oxidation potential. It is represented by E_{red} . Higher the value of oxidation potential higher will be the tendency of species (metal) to get oxidized.

For zinc electrode it is represented by $E_{\text{Zn}|\text{Zn}^{+2}}$ and standard oxidation potential is expressed by $E^{\circ}_{\text{Zn}|\text{Zn}^{+2}}$.

Similarly, oxidation potential of copper electrode is expressed by $E_{\text{Cu}|\text{Cu}^{+2}}$ and standard oxidation potential is expressed by $E^{\circ}_{\text{Cu}|\text{Cu}^{+2}}$

Reduction Potential

The potential difference between the electrode and its ions are result of reduction reaction is called reduction potential. It is denoted by E_{red} and standard reduction potential is expressed by E°_{red} .

For example, Reduction potential of Zinc $E_{\text{Zn}^{+2}|\text{Zn}}$.

Standard Reduction potential of Zinc $E^{\circ}_{\text{Zn}^{+2}|\text{Zn}}$.

Standard Electrode Potential

The potential difference of an electrode which it is dipped into 1M solution of its ions at 25°C (98K) under 1 atmospheric pressure is known as standard electrode potential.

Standard oxidation potential is denoted by E°_{ox} and standard reduction potential is represented by E°_{red} .

Cell Potential or emf

The driving force of cell which can push electrons through the circuit is termed as cell potential or emf. It is also defined as the sum of oxidation potential of anode half cell and reduction half cell. It is denoted by E_{cell} and standard cell potential by E°_{cell} .

$$E_{cell} = \text{Oxidation Potential} + \text{Reduction Potential}$$

$$E_{cell} = (E_{ox})_{anode} + (E_{red})_{cathode}$$

Now,

$$E_{cell} = (-E_{red})_{anode} + (E_{red})_{cathode}$$

$$E_{cell} = (E_{red})_{cathode} - (E_{red})_{anode}$$

$$E_{cell} = E_R - E_L$$

Or,

$$E_{cell} = (E_{ox})_{anode} + (-E_{ox})_{cathode}$$

$$E_{cell} = (E_{ox})_{anode} - (E_{ox})_{cathode}$$

$$E_{cell} = E_L - E_R$$

Solved Numerical on Emf of cell

1. Find out the emf of cell from the given pair of electrode. $E^{\circ}_{Zn|Zn^{+2}} = 0.76 \text{ volt}$
 $E^{\circ}_{Cu^{+2}|Cu} = -0.34 \text{ volt}$

Solution: Here, Oxidation potential of Zinc $E^{\circ}_{Zn|Zn^{+2}} = 0.76 \text{ volt}$

and Reduction potential of Copper $E^{\circ}_{Cu^{+2}|Cu} = -0.34 \text{ volt}$

$$\begin{aligned} E_{cell} &= E_R - E_L = (-E_{red})_{anode} + (E_{red})_{cathode} \\ &= E^{\circ}_{Cu^{+2}|Cu} - E^{\circ}_{Zn|Zn^{+2}} \\ &= -0.34 + 0.74 \\ &= 0.34 \text{ volt} \end{aligned}$$

2. Find out the emf of cell from the given pair of electron. $E^{\circ}_{Zn|Zn^{+2}} = 0.76 \text{ volt}$
 $E^{\circ}_{Pb^{+2}|Pb} = -0.13 \text{ volt}$

Solution: Here, Oxidation potential of Zn $E^{\circ}_{Zn|Zn^{+2}} = 0.76 \text{ volt}$

and Reduction potential of Pb $E^{\circ}_{Pb^{+2}|Pb} = -0.31 \text{ volt}$

$$\begin{aligned} E_{cell} &= E_R - E_L = (-E_{red})_{anode} + (E_{red})_{cathode} \\ &= E^{\circ}_{Pb^{+2}|Pb} - E^{\circ}_{Zn|Zn^{+2}} \\ &= -0.13 + 0.74 \\ &= 0.63 \text{ volt} \end{aligned}$$

3. Find out the emf of cell from the given pair of electron. $E^\circ_{\text{Cu}^{+2}|\text{Cu}} = -0.34 \text{ volt}$

$$E^\circ_{\text{Ag}|\text{Ag}^+} = 0.84 \text{ volt}$$

Solution: Here, Oxidation potential of Silver $E^\circ_{\text{Ag}|\text{Ag}^+} = 0.84 \text{ volt}$

and Reduction potential of Copper $E^\circ_{\text{Cu}^{+2}|\text{Cu}} = -0.34 \text{ volt}$

$$\begin{aligned} E_{\text{cell}} &= E_R - E_L = (-E_{\text{red}})_{\text{anode}} + (E_{\text{red}})_{\text{cathode}} \\ &= E^\circ_{\text{Cu}^{+2}|\text{Cu}} - E^\circ_{\text{Ag}|\text{Ag}^+} \\ &= -0.34 + 0.84 = 0.5 \text{ volt} \end{aligned}$$

Standard Hydrogen Electrode (SHE)

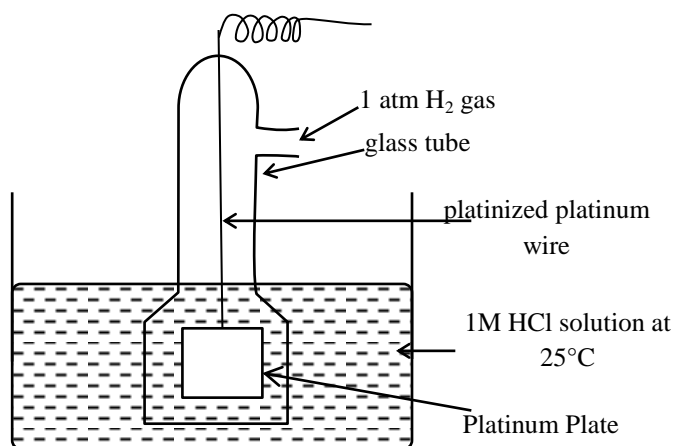


Fig. Standard Hydrogen Electrode

The standard hydrogen electrode which consists of platinized platinum dipped in 1M HCl solution to which pure hydrogen gas under 1 atmospheric pressure is bubbled over it at 25°C is known as standard hydrogen electrode. The emf of SHE is assigned as 0 volt at 25°C.

Uses of SHE

It is used to calculate single electrode potential of anode.

It is used to calculate single electrode potential of cathode

It is used to calculate pH of the solution.

Limitations of SHE

It is difficult to maintain 1 atmospheric pressure by passing hydrogen gas for a long time.

It is difficult to maintain 1 M concentration of HCl for a long time.

Hydrogen electrode gets poisoned if trace amount of impurities present in HCl

It is difficult to maintain standard temperature 25°C for every condition.

Measurement of Standard Electrode Potential of Anode (Zinc)

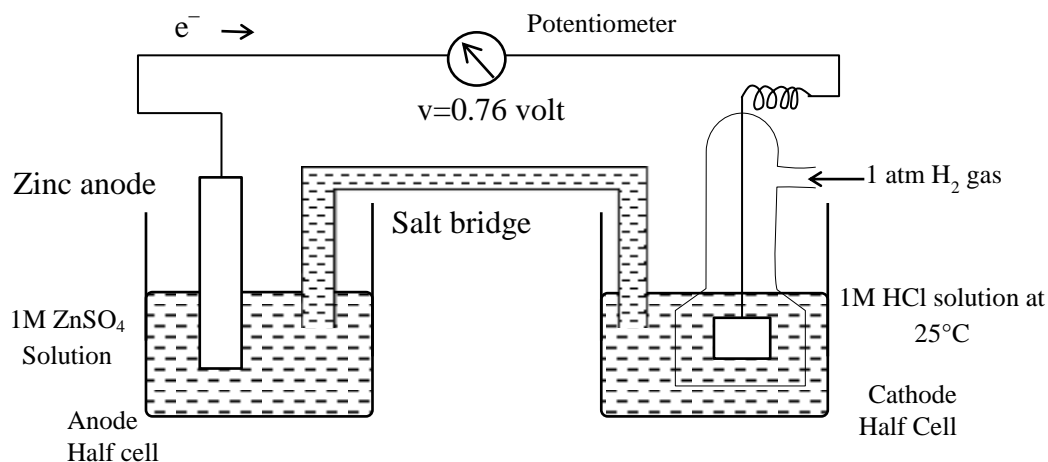


Fig. Measurement of Standard Electrode Potential of Anode

In order to measure single electrode potential of anode, the half cell containing zinc rod dipped into 1M zinc sulphate solution is connected with standard hydrogen electrode by external circuit through a voltmeter/potentiometer and solution of both half cell are connected by salt bridge. After completion of circuit the deflection of needle of voltmeter indicates the conventional flow of current from SHE towards Zinc electrode. This means the actual flow of electron occurs from zinc electrode to SHE. Therefore oxidation occurs in Zinc electrode and it act as anode while reduction occurs in SHE which act as cathode. It has been experimentally found that the emf of cell from voltmeter at standard condition is equal to 0.76 volt.

Therefore emf of cell $E^\circ_{\text{cell}} = 0.76 \text{ v}$

Standard Electrode Potential of anode $E^\circ_{\text{Zn}^{+2}|\text{Zn}}$

Standard Electrode Potential of SHE $E^\circ_{\text{H}^+|\text{H}_2} = 0 \text{ v}$

We Know that

$$E^\circ_{\text{cell}} = -E^\circ_{\text{Zn}^{+2}|\text{Zn}} + E^\circ_{\text{H}^+|\text{H}_2}$$

$$0.76 = -E^\circ_{\text{Zn}^{+2}|\text{Zn}} + 0$$

$$E^\circ_{\text{Zn}^{+2}|\text{Zn}} = -0.76 \text{ v}$$

$$\text{or, } E^\circ_{\text{Zn}|\text{Zn}^{+2}} = 0.76 \text{ v}$$

In this way, standard reduction potential of Zn electrode is determined by using SHE which is equal to -0.76 volt .

Measurement of Standard Electrode Potential of Cathode (Copper)

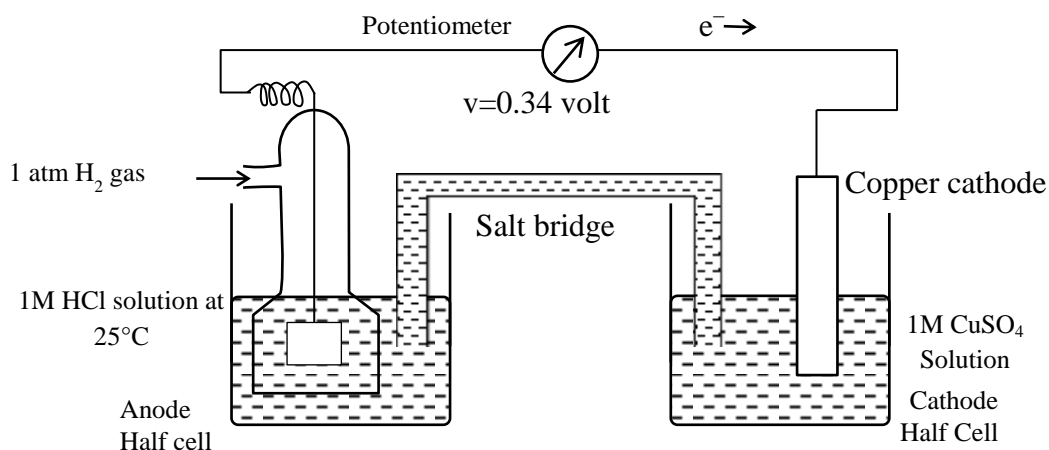


Fig. Measurement of Standard Electrode Potential of Anode

In order to determine standard electrode potential of cathode, a half cell containing copper electrode dipped in 1M CuSO_4 solution is connected with SHE by an external circuit through potentiometer/voltammeter and electrolyte of both half cells are connected through salt bridge. After completion of circuit, deflection of needle of voltammeter shows the conventional current flow from copper electrode towards SHE but actually electron flows from SHE to the copper electrode therefore oxidation occurs in SHE and it act as anode while reduction occurs in copper electrode which serve as cathode. Experimentally it has been found that emf of cell at standard condition is equal to 0.34 volt from voltammeter.

Therefore emf of cell $E^\circ_{\text{cell}} = 0.34 \text{ v}$

Standard Electrode Potential of SHE $E^\circ_{\text{H}^+|\text{H}_2} = 0 \text{ v}$

Standard Electrode Potential of anode $E^\circ_{\text{Cu}^{+2}|\text{Cu}}$

We have

$$E^\circ_{\text{cell}} = E^\circ_{\text{Cu}^{+2}|\text{Cu}} - E^\circ_{\text{H}^+|\text{H}_2}$$

$$0.34 = E^\circ_{\text{Cu}^{+2}|\text{Cu}} - 0$$

$$E^\circ_{\text{Cu}^{+2}|\text{Cu}} = 0.34 \text{ v}$$

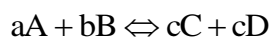
$$\text{therefore } E^\circ_{\text{Cu}^{+2}|\text{Cu}} = 0.34 \text{ v}$$

In this way standard electrode potential of Copper is determined by using SHE as reference which is equal to 0.34 volt.

Nernst's Equation

Emf of cell depends upon concentration of electrolytes and temperature. Nernst's equation provides relationship between concentration of electrolytes and emf of cell.

Let us consider a reversible reaction.



Applying law of mass action

$$\text{Equilibrium constant, } K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where,

[A] = concentration of A [B] = concentration of B

[C] = concentration of C [D] = concentration of D

From Van't Hoff reaction isotherm, Gibb's free energy change is related with equilibrium constant as,

$$\Delta G = \Delta G^\circ + RT \ln K \dots\dots\dots(i)$$

where, ΔG = Gibb's free energy change

ΔG° = Standard Gibb's free energy change

Substituting value of K

$$\Delta G = \Delta G^\circ + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Again, Gibb's free energy is related with emf of cell.

$$\Delta G = nFE$$

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

therefore,

$$-nFE = -nFE^\circ + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Taking negative sign in both sides

$$nFE = nFE^\circ - RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Dividing both sides by nF

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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

This is Nernst's Equation.

At 25°C (298K)

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Solved Numerical on Nernst's Equation

1. Calculate the emf of cell containing zinc electrode and lead electrode at 30°C.

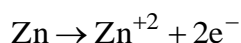
$$E^{\circ}_{\text{Zn}^{+2}|\text{Zn}} = -0.76 \text{ volt} \quad [\text{Zn}^{+2}_{(\text{aq})}] = 0.01\text{M}$$

$$E^{\circ}_{\text{Pb}^{+2}|\text{Pb}} = -0.13 \text{ volt} \quad [\text{Pb}^{+2}_{(\text{aq})}] = 0.1\text{M}$$

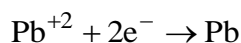
Solution: The reduction potential of zinc is less than Zinc ($E^{\circ}_{\text{Zn}^{+2}|\text{Zn}}$) is less than that of lead electrode ($E^{\circ}_{\text{Pb}^{+2}|\text{Pb}}$). Therefore zinc electrode act as anode and lead act as cathode

$$\begin{aligned}\text{Standard emf of cell } E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{Pb}^{+2}|\text{Pb}} - E^{\circ}_{\text{Zn}^{+2}|\text{Zn}} \\ &= -0.13 - (-0.76) \\ &= 0.63\text{volt}\end{aligned}$$

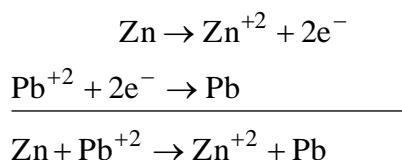
Oxidation Reaction at Anode



Reduction Reaction at Cathode



Net Cell Reaction



Cell Notation



No of electrons involved in reaction (n) = 2

$$F = 96500\text{C}$$

$$R = 8.313$$

$$T = 30 + 273 = 303\text{K}$$

From Nernst Equation,

$$\begin{aligned}E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[\text{Zn}^{+2}][\text{Pb}]}{[\text{Zn}][\text{Pb}^{+2}]} \\ &= 0.63 - \frac{2.303 \times 8.313 \times 303}{2 \times 96500} \log \frac{[0.01] \times 1}{1 \times [0.1]} \\ &= 0.63 - 0.03 \times \log(0.1) \\ &= 0.63 + 0.003 \\ &= 0.633\end{aligned}$$

2. Calculate the emf of the cell constructed by the following pair of electron at 25°C.

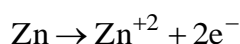
$$E^{\circ}_{\text{Zn}^{+2}|\text{Zn}} = -0.76 \text{ volt} \quad [\text{Zn}^{+2}_{(\text{aq})}] = 0.1 \text{ M}$$

$$E^{\circ}_{\text{Ag}|\text{Ag}^{+}} = -0.84 \text{ volt} \quad [\text{Ag}^{+}_{(\text{aq})}] = 0.1 \text{ M}$$

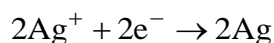
Solution: Since reduction potential of Zinc electrode ($E^{\circ}_{\text{Zn}^{+2}|\text{Zn}}$) is less than that of Silver electrode $E^{\circ}_{\text{Ag}|\text{Ag}^{+}}$. Therefore zinc electrode act as anode and silver electrode as cathode.

$$\begin{aligned} \text{Standard emf of cell } E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{Ag}^{+}|\text{Ag}} - E^{\circ}_{\text{Zn}^{+2}|\text{Zn}} \\ &= -0.84 - (-0.76) \\ &= 1.6 \text{ volt} \end{aligned}$$

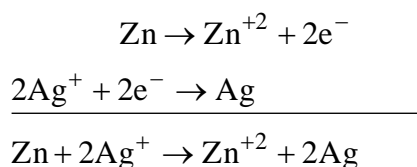
Oxidation Reaction at Anode



Reduction Reaction at Cathode



Net Cell Reaction



Cell Notation



No of electrons involved in reaction (n) = 2

$$F = 96500 \text{ C}$$

$$R = 8.313$$

$$T = 25 + 273 = 298 \text{ K}$$

From Nernst Equation,

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[\text{Zn}^{+2}][\text{Ag}]}{[\text{Zn}][\text{Ag}^{+}]^2} \\ &= 1.6 - \frac{2.303 \times 8.313 \times 298}{2 \times 96500} \log \frac{[0.1] \times 1}{1 \times [0.1]^2} \\ &= 1.6 - 0.0295 \times \log 10 \\ &= 1.57 \text{ volt} \end{aligned}$$

3. Calculate the emf of cell 20°C constructed by following pairs of electrode.

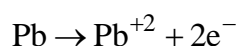
$$E^\circ_{\text{Pb}^{+2}|\text{Pb}} = -0.13 \text{ volt} \quad [\text{Pb}^{+2}_{(\text{aq})}] = 0.01\text{M}$$

$$E^\circ_{\text{H}^{+2}|\text{H}_2} = -0.0 \text{ volt} \quad [\text{H}^{+}_{(\text{aq})}] = 0.1\text{M}$$

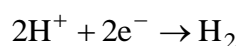
Solution: Since reduction potential of Lead electrode ($E^\circ_{\text{Pb}^{+2}|\text{Pb}}$) is less than that of Hydrogen electrode $E^\circ_{\text{H}^{+}|\text{H}_2}$. Therefore Lead electrode act as anode and Hydrogen electrode as cathode.

$$\begin{aligned} \text{Standard emf of cell } E^\circ_{\text{cell}} &= E^\circ_{\text{H}^{+}|\text{H}} - E^\circ_{\text{Pb}^{+2}|\text{Pb}} \\ &= 0 - (-0.13) \\ &= 0.13 \text{ volt} \end{aligned}$$

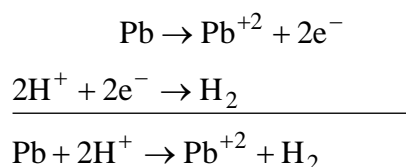
Oxidation Reaction at Anode



Reduction Reaction at Cathode



Net Cell Reaction



Cell Notation



No of electrons involved in reaction (n) = 2

$$F = 96500 \text{ C}$$

$$R = 8.313$$

$$T = 20 + 273 = 293\text{K}$$

From Nernst Equation,

$$\begin{aligned} E_{\text{cell}} &= E^\circ_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{[\text{Pb}^{+2}][\text{H}_2]}{[\text{Pb}][\text{H}^{+}]^2} \\ &= 0.13 - \frac{2.303 \times 8.313 \times 293}{2 \times 96500} \log \frac{[0.01] \times 1}{1 \times [0.1]^2} \\ &= 0.13 \text{ volt} \end{aligned}$$

Electrochemical series or Emf of series

The arrangement of elements in order of increasing reduction potential as compared to that of standard hydrogen electrode is known as electrochemical series or emf of series. It is also called activity series.

Elements	Electrodes	E_{red} at 25°C
Lithium	$\text{Li}^+ \text{Li}$	- 3.05
Potassium	$\text{K}^+ \text{K}$	- 2.93
Magnesium	$\text{Mg}^{+2} \text{Mg}$	- 2.37
Zinc	$\text{Zn}^{+2} \text{Zn}$	- 0.76
Cadmium	$\text{Cd}^{+2} \text{Cd}$	- 0.40
Lead	$\text{Pb}^{+2} \text{Pb}$	- 0.13
SHE	$\text{H}^+ \text{H}_2$	0
Copper	$\text{Cu}^{+2} \text{Cu}$	0.34
Silver	$\text{Ag}^+ \text{Ag}$	0.84

Application of Emf of series

Electrochemical series are applicable for following purposes.

1. To compare the relative reduction potential of oxidation or reduction

Lighter the reduction potential of element, higher is the oxidation strength of it and vice versa. **E.g.:** Reduction potential of copper is higher (0.34v) than that of lead (- 0.13v) therefore copper has higher oxidation strength than lead.

2. To choose the proper metal for electrode

Proper metal should be chosen for cathode and anode to construct galvanic cell. Metal with low reduction potential or higher oxidation potential is used as anode and metal having higher reduction potential (lower oxidation potential) is used as cathode. **E.g.:** zinc has reduction potential (-0.76 v) and copper has (0.34 v). Therefore Zinc act as anode and Copper act as cathode in the cell.

3. To determine the emf of cell:

From the proper value of reduction potential of metal, emf of cell can be calculated by formula. $E^\circ_{\text{cell}} = (E^\circ_{\text{red}})_{\text{cathode}} - (E^\circ_{\text{red}})_{\text{anode}}$

E.g.: $E^\circ_{\text{Zn}^{+2}|\text{Zn}} = -0.76 \text{ v (anode)}$

$E^\circ_{\text{Cu}^{+2}|\text{Cu}} = 0.34 \text{ v (cathode)}$

$$\begin{aligned}\text{therefore } E^\circ_{\text{cell}} &= E^\circ_{\text{Cu}^{+2}|\text{Cu}} - E^\circ_{\text{Zn}^{+2}|\text{Zn}} \\ &= 0.34 - (-0.76) \\ &= 1.1 \text{ volt}\end{aligned}$$

4. To predict whether the cell does work or not

The cell work only when emf of cell is positive. It depends upon the correct choose of electrode.



$$E^{\circ}_{\text{Pb}^{+2}|\text{Pb}} = -0.13 \text{ (anode)} \quad \{\text{according to cell}\}$$

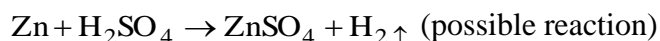
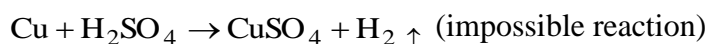
$$E^{\circ}_{\text{Mg}^{+2}|\text{Mg}} = -2.34 \text{ v (cathode)}$$

$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{Mg}^{+2}|\text{Mg}} - E^{\circ}_{\text{Pb}^{+2}|\text{Pb}} \\ &= -2.34 + 0.13 \\ &= -2.21 \text{ volt} \end{aligned}$$

Since, emf of cell is negative, therefore above cell doesn't work.

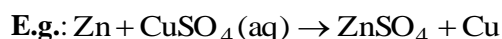
5. To predict whether the metal can liberate hydrogen gas from dilute acid

Lower the reduction potential or higher the oxidation potential of metal then that of hydrogen can displace hydrogen from mineral acid. **E.g.** Oxidation potential of copper is lower (0.34 v) than that of hydrogen (0 v). Therefore Copper can't displace hydrogen from acid.



6. To predict whether a metal can displace another metal from its aqueous solution:

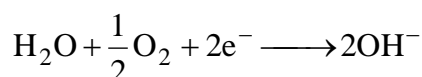
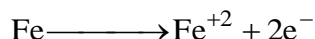
Metal with high oxidation potential can displace having low oxidation potential.



Corrosion

Corrosion is the process of redox reaction due to which metals or alloy of metals gets oxidized by season in the presence of moisture. It is reverse process of extraction of metal since metal turns into while pure metal is obtained from compound in extraction process.

Therefore, Corrosion is slow electrochemical reaction of metal or alloy of metal in which electrons are released by metal and gained by non-metallic components



Types of Corrosion

Corrosion is of mainly two types.

Dry corrosion

The corrosion which occurred by direct reaction of metal surface with agent like oxygen of air, anhydrous acid and gaseous like H_2S , SO_2 , HBr etc. is known as dry corrosion.

For e.g. rusting of iron, when it is exposed to atmosphere for long time.

Wet Corrosion

The corrosion which occurs in the aqueous environment is known as wet corrosion or electrochemical corrosion.

For e.g. Corrosion of water pipes

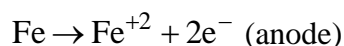
Rusting of iron when it is dipped into water for long time

Mechanism of Corrosion (Rusting)

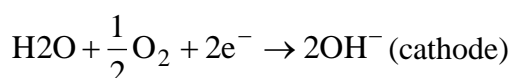
Various theories are put forward to explain the mechanism of corrosion of iron, Among them the electrochemical theory is most convincing one.

Corrosion is the electrochemical process in which chemical reaction is accompanied by the flow of current from metal to non-metal compound.

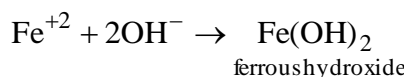
Metal iron act as anode which gets oxidize and dissolved in the solution.



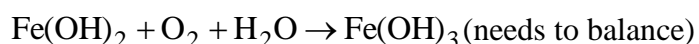
Thus produced electrons migrate to the solution or moisture and reduce oxygen as well as other cations which act as cathode.



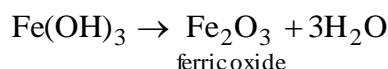
The Fe^{+2} ion formed at anode and OH^- ions formed at cathode migrate together and combine to form ferrous hydroxide.



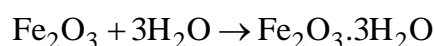
Thus formed ferrous hydroxide gets oxidized to ferric hydroxide in the presence of oxygen and water or moisture.



Thus, formed above ferric hydroxide loss water molecule to give ferric oxide.



Ferric oxide slowly absorbs moisture to form brown scale of hydrated ferric oxide which is called rust.



Prevention of Corrosion

Protective Coating

Metal can be protected from rusting by coating the surface of metal with oil, grease, paint, varnishes, metallic thin film etc. which act as barrier between metal surface and atmosphere.

Application of Inhibitor

In this process metal is treated with certain solution like potassium chromate phosphate etc. which inhibit the corrosion.

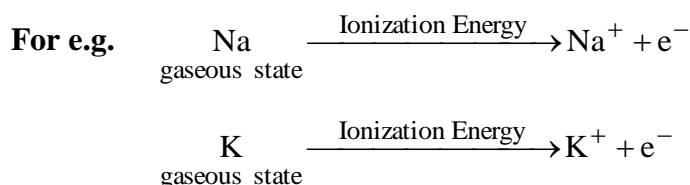
Galvanization

The coating of iron surface with thin film of zinc is known as galvanization. The galvanization process prevents metal from rusting by separating metal surface and atmosphere. This is the most convincing method of prevention of corrosion. In this method, Iron is kept in the contact with more electropositive other metal. The electropositive metal gets oxidized prior than iron and hence it is rusted before iron. This method is also known as sacrificial method. It is used for huge equipment like ship, iron bridge etc.

General Inorganic Chemistry

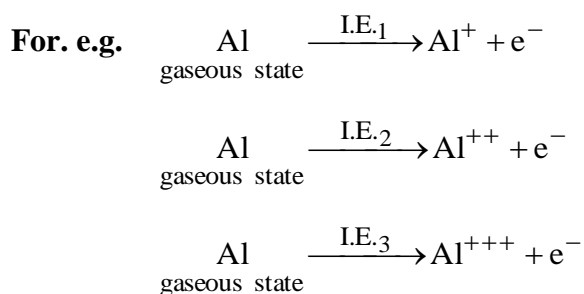
Ionization Energy

The minimum amount of energy to remove the loosely bounded valance electron from isolated gaseous atom in order to convert it into cation is known as ionization energy or ionization potential. It is denoted by I, E or I.P. Its unit is e.v., KJmol^{-1} , KJ^{-1}



Successive ionization energy

The amount of energy required to remove more than one loosely bounded valance electron successively from isolated gaseous atom is known as successive ionization energy. Successive ionization energy is called 1st, 2nd, 3rd and so on ionization energy which refers to removal of first, second, third and so on electron.



Qn. Order of ionization energy is $\text{I.E.}_1 > \text{I.E.}_2 > \text{I.E.}_3$. **If asked why?**

Reason: After the removal of first electron, atom has one lower number of electron but nucleus contain same positive charge which attract more tightly due to which higher amount of energy is required to remove second electron than the first electron. Similarly there becomes less number of electron in an atom after removal of second electron as a result remaining electron more tightly held by same magnitude of nucleus and therefore higher energy required for removal of third electron than second electron. Therefore successive ionization energy follows the order of $\text{I.E.}_1 > \text{I.E.}_2 > \text{I.E.}_3$.

Factors affecting Ionization Energy

Ionization energy depends upon the following factors.

Atomic Size: The size of atom greater will be distance between nucleus and valance electron due to which valance electron are loosely held by nucleus and less amount of energy is required to remove them. Therefore ionization energy decreases as atomic size increases and vice versa.

$$\text{Ionization Energy} \propto \frac{1}{\text{Atomic Size}}$$

Nuclear Charge: Ionization energy is directly affected by magnitude of nucleus charge. Larger the magnitude of nuclear charge of an atom is directly proportional to ionization energy.

Shielding or Screening Effect: The electron present in the inner shell cause repulsive intervening electron which cause repulsion among them and shield the attraction force of nucleus due to which attraction between nucleus and valance shell electrons decreases. As a result it becomes easy to remove them by the supply of less amount of energy. Therefore higher the shielding effect. Lower will be ionization energy and vice versa.

$$\text{Ionization Energy} \propto \frac{1}{\text{Shielding Effect}}$$

Note: The phenomenon by which electrons of outermost shell are shielded from nucleus due to repulsive interaction of intervening electrons is called shielding effect or screening effect.

Penetration of Electrons: The probability of electron being nearer to the nucleus of an atom is known as penetration of electrons. since the order of orbitals nearer to nucleus shows $s > p > d > f$. Therefore penetrating power of electrons towards nucleus occurs in same manner and hence ionization energy for removal of electron from ns is greater than np and ionization energy of electron of np is greater than that of nd and so on where n is valance shell.

Electronic Configuration: According to Hund's rule half-filled ns^1 , np^3 , nd^5 and nf^7 and completely filled ns^2 , np^6 , nd^{10} and nf^{14} orbitals are comparatively more stable and hence more energy is required to remove electron from such orbitals. Therefore energy of an atom having half-filled or completely filled orbital is relatively higher than that atom having normal electronic configuration.

Periodic Trend of Ionization Energy

Variation along Period: On proceeding from left to right in a particular period, nuclear charge increases by one unit and electron progressively at to the same valance shell which cause the decrease of atomic size and electrons are more lightly bounded by nucleus. Therefore ionization energy goes on increasing from left to right in period. On the other word ionization energy is inversely proportional to atomic size and atomic size decreases gradually from left to right in a period. Therefore ionization energy increases in the same manner.

However in some cases, the general trend is avoided by some elements due to stability of half-filled and completely filled orbitals. **For example**, ionization energy of nitrogen is greater than that of oxygen because of half-filled p orbital of nitrogen atom.

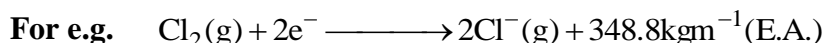
Qn. Ionization energy of nitrogen is greater than that of oxygen. justify it.

Ans: According to Hund's rule half-filled and full filled orbitals are comparatively more stable than that of normal condition. Since nitrogen has half-filled p orbital ($2p^3$) which is more stable normal condition of p -orbital of oxygen ($2p^4$). Therefore more energy is required to remove electron from half-filled orbital of nitrogen than that of oxygen and hence ionization energy of nitrogen is greater than oxygen.

Variation along Group: Along a group from top to bottom, atomic size as well as shielding effect increases due to addition of extra cell in each step. Hence attraction between nucleus and valance electrons decreases from top to bottom and lower energy is required to remove valance electron. On the other way both atomic size and shielding effect are inversely proportional of ionization energy and both of them gradually increases from top to bottom. Therefore ionization energy decreases in a particular group from top to bottom.

Electron Affinity (E.A.)

The amount of energy released while an electron is added to the valance shell of an isolated gaseous atom so as to change into anion is called electron affinity. It is denoted by E.A. and its unit is e.v. KJmol^{-1} etc



Factors Affecting Electron Affinity

Important factors which affects magnitude of electron affinity values of atom are as follows.

Atomic Size: Smaller the size of atom, greater is the attraction of the nucleus of nucleus for incoming electron from outside. Thus electron affinity decreases with increase in size of an atom and vice versa. Therefore electron affinity inversely proportional to atomic size.

Nuclear Charge: Atom of higher magnitude of nuclear charge can attract more strongly to the incoming electron from the outside than with smaller nuclear charge. Thus electron affinity increases as the magnitude of nuclear charge increases and vice versa. Electron affinity is directly proportional to nuclear charge.

Shielding Effect or Screening Effect: As the number of inner shell increases, shielding effect due to intervening electron also increases which cause less attraction of nucleus to incoming electrons from outside. Therefore electron affinity is inversely proportional to shielding effect.

$$\text{E.A.} = \frac{1}{\text{Shielding Effect}}$$

Electronic Configuration: Electron configuration has effective role on the variation of electron affinity. Completely filled orbitals are more stable than the normal condition of electronic configuration. Thus the atom with completely filled orbitals as lowest affinity to add electrons from outside due to higher stability of orbitals. **For example,** of noble gases have zero or very very less value since they have complete electronic configuration.

Periodic trend of Electron Affinity

Variation along Period: On moving from left to right in particular period, size of atom decreases and nucleus charge increases progressively. Both these factors cause the increase in force of attraction between nucleus and the electron being added to valance shell and hence the atom has greater tendency to accept incoming electron. Therefore electron affinity increases from left to right but zero group element have zero or very very low value of electron affinity due to their stable electronic configuration. In the other way, electron affinity is inversely proportional to the atomic size and atomic size decreases from left to right in the particular period. Therefore electron affinity increases from left to right in the periodic table.

Variation along Group: On moving down a group, size of an atom increases due to addition of new valance shell and increase of shielding effect by intervening electron. This results the decrease in attraction between nucleus and electron to be added in the valance shell. Therefore electron affinity decreases from top to bottom in a particular group. On the other hand, electron affinity is inversely proportional to both atomic size and shielding effect. Both the shielding effect and atomic size goes in particular group. Therefore electron affinity decreases from top to bottom in the periodic table.

Qn. Electronic Affinity of chlorine is higher than fluorine? Why?

Ans: Atomic size of fluorine is extremely small ($r = 0.72\text{\AA}$) and therefore electron density per unit volume is high due to which it has more electronic repulsion and incoming electron from outside feels large repulsion by the electrons. But chlorine has larger atomic size in comparison to fluorine and there is no or less electronic repulsion due to which it can easily add incoming electrons in the valance shell. Therefore electron affinity of chlorine is higher than fluorine.

Electronegativity

The tendency of an atom to attract bounded pair (shared pair) of electron towards it's center in a molecule is known as electronegativity. The term electronegativity has been defined in different ways by different chemist such as, Mullikan, Pauling, Allred and Reshow.

Pauling Approach: According to Pauling electronegativity of an atom in a molecule is relative tendency to attract bonded pair of electrons towards itself.

Mullikan's Approach: According to Mullikan's electronegativity is the average of 1st ionization energy and electron affinity of an atom. It can be calculated by given relation.

$$\text{Electronegativity} = .0344 \left(\frac{\text{I.E.}_1 + \text{E.A.}}{1} \right) + 0.17$$

Factors Affecting Electronegativity

Atomic Size: Smaller the size of atom, lower the distance between nucleus and bond pair of electron than in larger atom. Therefore nucleus of smaller can attract more strongly to bonded pair of electrons than larger atom. Thus electronegativity of an atom increases when size of atom decreases. Therefore

$$\text{Electronegativity} \propto \frac{1}{\text{Atomic size}}$$

Nuclear Charge: Larger the magnitude of nuclear charge of an atom, higher will be the attraction between nucleus and bonded pair of electrons which pull strongly towards its center. Therefore electronegativity increases as the nuclear charge increases.

$$\text{i.e. Electronegativity} \propto \text{Nuclear Charge}$$

Ionization Energy and Electron Affinity: Higher the ionization energy and electron affinity represents smaller size of atom on the other hand smaller atom has higher electronegativity and therefore atom with higher ionization energy and electronegativity has also higher electronegativity and vice versa.

Hybridization: The hybrid orbitals which has higher percentage of *s*-character is shorter and hence bond pair of electron formed by such hybrid orbitals is nearer to nucleus and are more strongly attracted by nucleus. Therefore atom with *sp* hybridization has higher electronegativity than the *sp*² hybridization and similarly atom with *sp*² hybridization has higher electronegativity than the atom with *sp*³ hybridization as percentage of *s*-character is 50%, 33% and 25% in *sp*, *sp*², and *sp*³ hybrid orbitals respectively.

Periodic Trend of Electronegativity

Variation along period: Size of atom decreases and nuclear charge increases from left to right in a particular period. Electronegativity is inversely proportional to atomic size but directly proportional with nuclear charge and therefore, electronegativity increases from left to right in particular period of periodic table.

Variation along Group: Atomic size increases from top to bottom in a group due to addition of new valance shell in each step and electronegativity is inversely proportional to atomic size. Therefore electronegativity goes on decreasing from top to bottom in a particular group. The decrease in electronegativity in the group is mainly due to

- a. atomic size increases from top to bottom in a group and

$$\text{electronegativity} \propto \frac{1}{\text{AtomicSize}}$$

- b. attraction between nucleus and bonded pair of electron decreases from top to bottom in a group.

Exception; Electronegativity of Gallium is higher than Aluminum: Though Aluminum and Gallium lie in the same group, Gallium also includes *d* orbital in its electronic configuration but aluminum does not include *d* orbitals, due to inability of expansion of *d* orbitals in the Gallium, it has higher tendency to pull bonded pair of electron towards it's center than the Aluminum. Therefore electronegativity of Gallium is higher than Aluminum.

General Characteristics of s-block elements

Atomic Radii (Atomic Size): Atomic radii increases on moving down from lithium (Li) to cesium (Cs) in IA group and from beryllium (Be) to Radium (Ra) in IIA group due to addition of extra shell and increase of shielding effect. As the atomic size decreases from left to right in a periodic table and s-block elements lie in extreme left side, therefore atomic size of s-block elements have largest in a particular period.

Melting and Boiling Point: Melting and boiling point depend upon the interatomic force of attraction in a crystal lattice but atoms of s-block elements are loosely packed in their lattice due to their larger size and hence low temperature is required to melt and boil these elements. Therefore they have lower melting and boiling point.

Metallic Character: Generally elements of IA and IIA group are metals. They show luster property due to presence of one or two loosely bonded valance electron in the elements of IA and IIA group respectively which absorbs light and give reflection back. Due to large size of atom of IA and IIA group. They have low ionization energy and high electronegativity and therefore they show metallic character.

Electropositivity: Since IA and IIA group elements have larger size and lower attraction between nucleus and valance electrons, therefore they attract bonded pair of electron less tightly and hence they are electropositive in nature.

Ionization Potential: Since size of atom of group I and II elements is larger in comparison to other elements in a particular period. Valance electron are less tightly hold by nucleus. And low energy required to remove valance electron. Therefore they have low ionization potential.

Reducing Property: Since size of atom of s-block elements is larger and valance electron are loosely bounded by nucleus. Therefore they have higher tendency to loss valance electron in order to reduce other atom in chemical combination. Hence s-block elements are reducing agent and reducing power increases from top to bottom in a group of s-block elements.

Oxidation State: All elements of IA group possess +1 oxidation state and all elements of IIA possess +2 oxidation state which is equal to no of valance electron in their outermost shell.

Formation of Cation: Since alkali metals have low ionization energy, they have strong tendency to change into positive cation with unit positive charge. Similarly elements of group IA have lower ionization energy due to their large size. So they have tendency to loss electron form valance shell from valance shell and change into M^{+2} ion. e.g. $Mg \rightarrow Mg^{+2} + 2e^{-}$

General Characteristics of p-block elements

p-block consists of groups IIIA, IVA, VA, VIA, VIIA and zero group. It lies right side of the periodic table.

Atomic Size: As atomic size decreases from left to right and p-block elements are situated at right belt of periodic table. Therefore atomic size of p-block elements is smaller in a particular period.

Melting and Boiling Point : Melting point and Boiling point of *p*-block elements do not show regular trend. The MP and BP of IIIA and IVA group elements generally decreases from top to bottom due to lower interatomic attraction and loosely packing in the lattice. On the other side MP and BP of VA, VIA and VIIA and zero group elements increases from top to bottom due to increase in atomic size. As a result of which Vander's wall's force of attraction increases. It has been found that MP and BP of zero group elements has very low due to weak Vander's wall's force of attraction between their atoms.

Electronegativity: As the size of atom decreases from left to right in a period, attraction between nucleus and bonded pair of electron increases in the same manner. Therefore elements of *p*-block elements higher electronegativity than the *s* and *d* block elements. Elements of VIIA (Halogen) are most electronegative elements, among the period, however zero group elements have very low electronegativity to their stable electronic configuration.

Nonmetallic character: Metallic or nonmetallic character of an element is measured by Electropositivity of that element which depends upon ionization potential. Higher the value of ionization potential, less is the electropositivity. i.e. more is the electronegativity and less will be the metallic character *p*-block elements have smaller size and higher I.P. in a particular period. Therefore they have nonmetallic character. Hence almost all *p*-block elements (except N, Be, Si, etc.) are nonmetallic in nature.

Magnetic Property: Mostly *p*-block elements are diamagnetic in nature. Diamagnetism arises due to presence of paired electron in an orbitals. Spin moment of one electron is canceled by spin moment of other electron present in same orbital and net momentum becomes zero. Most of the *p*-block elements have pair electrons in the orbitals and hence they show magnetic property.

General Characteristics of *d*-block elements

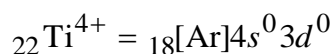
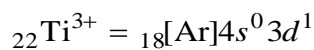
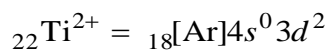
Variable Oxidation state or Valency : Variable oxidation state of transition elements is one of the most important distinguished property which keeps them different from *s*-block and *p*-block elements. Almost all the transition elements exhibit variable oxidation state or valencies. The reason for the variable oxidation state of transition elements is that they can give off different number of electrons from valance shell (*ns*-orbital) with addition of different no of electrons from *d*-orbitals of penultimate shell $\{(n-1)d\}$. **For example,** Scandium possess Sc^{+2} oxidation state when it loss 2 electrons from 4*s* orbital and exhibit Sc^{+3} oxidation when it loss two electron from 4*s* and one electron from 3*d*-orbital.

Here : ${}_{21}\text{Sc} = {}_{18}[\text{Ar}]4s^2 3d^1$

$${}_{21}\text{S}^{2+} = {}_{18}[\text{Ar}]4s^0 3d^1$$

$${}_{21}\text{S}^{3+} = {}_{18}[\text{Ar}]4s^0 3d^0$$

Similarly, Titanium (Ti) has Ti^{+2} , Ti^{+3} and Ti^{+4} oxidation state as it loses two electrons from 4s with one electron from 3d orbital respectively as shown below.



Following two points should be considered for variable oxidation state.

- Lowest oxidation state is equal to total number of electrons of ns orbital.
- Highest oxidation state is equal to the sum of number of electrons of ns and (n-1)d orbitals.

For example, Ti has +2 lowest oxidation state and highest +4 oxidation state.

Color Properties: Most of the transition elements form coloured compounds. Color of compounds appear due to promotion of electrons of partially filled d-orbital from lower d-level (t_{2g} level) to higher d-level (e_g). i.e. d-d transition of the electrons. When light falls on the compound it absorbs light of particular colour of wavelength 4000Å-7000Å of visible region and reflects the remaining light of complementary colour of absorbed light. The colour of reflected light of the compound is the actual colour of the substance.

According to Crystal Field Theory (CFT) when light falls on the compound unpaired electron of d-orbital gets excited and jumps from lower t_{2g} level to upper e_g level within the same d-orbital i.e. d-d transition colour is transmitted which appears as colour of that compound.

For example, Ti^{3+} in a compound.

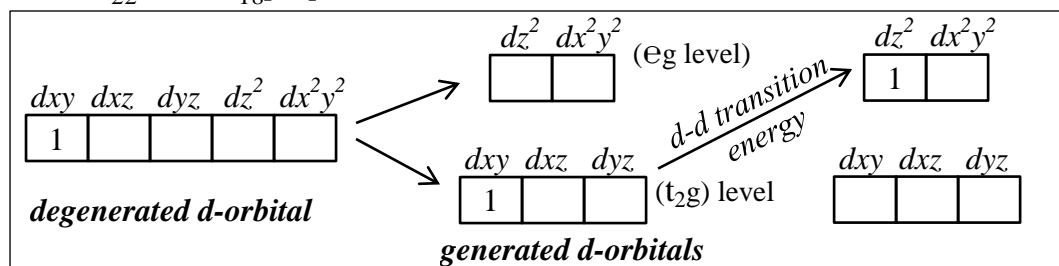
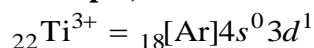


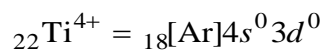
Fig: Stability of d-orbital in compound of Ti^{3+}

Compounds of ions which have completely filled d-orbital or empty are colourless because there is no vacant d-orbital in completely filled and there is no electron for d-d transition in empty d-orbital. Hence compound of $\text{Cu}^{+1}(3d^{10})$ and $\text{Zn}^{+2}(3d^{10})$ ions are colourless.

In contrast to d-block elements, compounds of s and p block elements are colourless since these elements have no partially filled d-orbital and electron cannot undergoes d-d transition. However electrons can undergo transition only from one major energy level (shell) to another energy level which requires very high amount of energy reflects light in ultraviolet region. Therefore compounds of s and p block elements are colourless.

Qn.Compound of Ti^{3+} are coloured (purple) but compounds of Ti^{4+} are colourless. Why?

Ans: Ti^{3+} has one pair of electron in d -orbital which gets excited from lower (t_{2g}) level to upper level within the d -orbital (i.e. $d-d$ transition). When compounds absorbs radiation of visible region of wavelength (5000\AA to 5600\AA) and transmitted light at this visible region is complementary colour are coloured but Ti^{4+} has empty d -orbital and there is no $d-d$ transition. Hence compound of Ti^{4+} are colourless.



Magnetic Property: Almost all d -blocks elements are paramagnetic. Paramagnetism arises due to spinning of unpaired electron in its orbital around the nucleus and in its own axis. The spinning of electron in its own axis creates magnetic moment called spin moment and spinning of it in orbital produce another magnetic moment called orbital moment. The observed magnetic moment in the substance is the sum of these two moments created by unpaired electron. Most of the d -block element are partially filled d -orbital and have maximum probability of unpaired electrons. Therefore they are paramagnetic in nature and allow the magnetic lines of force of applied magnetic field to pass through them rather through vacuum.

And paramagnetic substance are attracted by magnet. Magnetic moment of unpaired electron is determined by spin only formulae as

$$\mu = \sqrt{n(n+2)}BM \text{ (Bohr's Magnetum)}$$

where n = no of unpaired electrons

BM = Bohr's magnetum

for e.g. $n=1$

$$\begin{aligned} \text{(magnetic moment)} \quad \eta &= \sqrt{3}BM \\ &= 1.731BM \end{aligned}$$

On the basis other hand mostly s and p -block elements are diamagnetic since they have paired electrons in the orbitals and therefore spin momentum produced by one electron is cancelled by spin momentum of another electron. Net magnetic moment possessed by substance is zero and such substance allow the magnetic lines of force of applied magnetic field to pass through vacuum rather through themselves and these substance show no attraction towards magnetic field.

Complex Formation: The cation of transition elements have greater tendency to form complex with several ligands (negative ions, neutral species having electron density). The tendency of d -block elements for formation of complex is mainly due to the following two reasons.

- i) Cations are relatively very small in size and hence they have very high positive charge density which makes easy to accept pair of electrons from ligands.
- ii) The cations have almost vacant $(n-1)d$ orbital which are of approximate energy to accept lone pair of electrons from the ligands.

For example: Hexamine Cobalt(III) chloride $[Co(NH_3)_6]Cl_3$

Diamino Silver(I) chloride $[Ag(NH_3)_2]Cl$

In contrast to *d*-block elements *s* and *p* block elements cannot form complex since they have no vacant *d*-orbital as well as their cations have less or no tendency to accept lone pair of electron from ligands due to their large size.

Some Possible Questions

1. What is ionization energy? How do various factor effect the ionization energy?
2. What is electronegativity and electron affinity? Write their periodic trend in a periodic table.
3. Give reasons.
 - a. *d*-block elements have variable oxidation state.
 - b. *d*-block elements have tendency to form complex.
 - c. *d*-block elements mostly form colour compounds.
 - d. *d*-block elements are paramagnetic but *p*-block elements are diamagnetic.
 - e. Ti^{+3} forms coloured compounds but Ti^{+4} forms colourless compounds.
 - f. *p*-block elements are mostly non-metal but *s*-block elements are mostly metal.
 - g. Ionization energy of nitrogen is higher than that of oxygen.
 - h. Electron affinity of Gallium (Ga) is higher than aluminum.
 - i. Electron affinity of fluorine is less than chlorine.

General Organic Chemistry

Intermediate

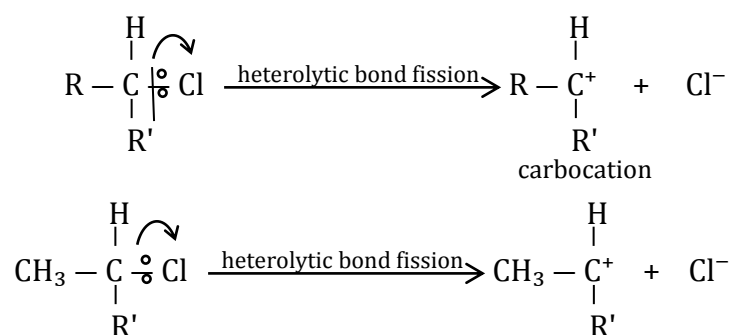
The species which are formed as an intermediate agent during the course of reaction are known as Intermediate or Reaction Intermediate. They are very reactive and have tendency to become stable. Reaction intermediate are of following types.

- Carbocation
- Carboanion
- Carbon free-radical

Carbocation

The intermediate species which contain positively charged carbon atom formed after heterolytic bond fission of organic compound is known as carbocation.

For example



Carbocation are very reactive intermediate due to the fact that positively charged carbon contains only six electron in its outermost shell and it has higher tendency to attain octet state. Therefore carbocation rapidly combines with electron rich species.

Types of Carbocation

Carbocation are of following types:

Methyl Carbocation: The carbocation which contains positive carbon in methyl group is known as methyl carbocation. **E.g.** CH_3^+

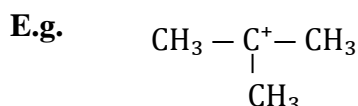
Primary carbocation: The carbocation in which positively charged carbon is directly bonded with single carbon atom.

E.g. $\text{CH}_3 - \text{CH}_2^+$ (ethyl-carbocation), $\text{CH}_3 - \text{CH}_2 - \text{CH}_2^+$ (propyl-carbocation)

Secondary Carbocation: The carbocation in which positively charged carbon is directly bonded to carbon atom is known as secondary carbocation.

E.g. $\text{CH}_3 - \text{CH}^+ - \text{CH}_3$ (iso propyl carbocation, 2°)

Tertiary Carbocation: The carbocation in which positively charged carbon is directly bonded with three carbon atom is known as tertiary carbocation.



Stability of carbocation

Carbocation is stabilized mainly by two phenomenon

- 1. Inductive Effect:** Stability of carbocation depends upon the types of substitute present in carbocation. There are mainly two types of substituent which has marked effect on the stability of carbocation.

a. Effect due to electron releasing groups

Electron releasing group like alkyl group ($-\text{R}$), ($-\text{OH}$), ($-\text{OR}$), ($-\text{NH}_2$) etc. increases the stability of carbocation by dispersing positive charge of carbocation throughout the molecule. Therefore stability of carbocation follows the order of $3^\circ\text{carbocation} > 2^\circ\text{carbocation} > 1^\circ\text{carbocation} > \text{methyl carbocation}$.

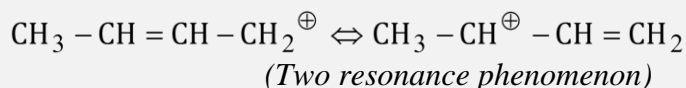
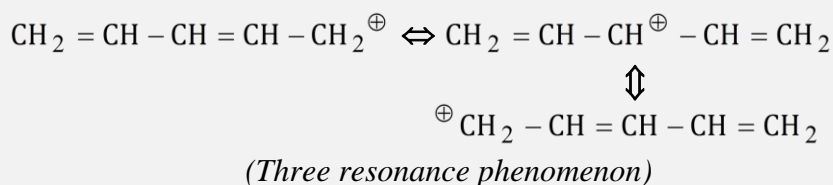
As 3° carbocation has three releasing alkyl group and can distribute positive charge throughout the molecule in larger extent than 2° carbocation as it contains only two electron releasing alkyl groups and similarly 2° carbocation has more possibility of dispersion of positive charge than primary carbocation.

b. Effect due to electron withdrawing group

Electron withdrawing groups like ($-\text{NO}_2$), ($-\text{CN}$), ($-\text{X}$), etc. decrease the stability of carbocation by intensifying positive charge of carbocation. Stability of carbocation increases as the distance of withdrawing group increases from positively charged carbon.

- 2. Resonance effect (only in case of multiple bond):** The phenomenon of delocalization of π -bond or lone pair of electron in the molecule is known as resonance effect. Higher the number of resonance structure of carbon more is the stability of it.

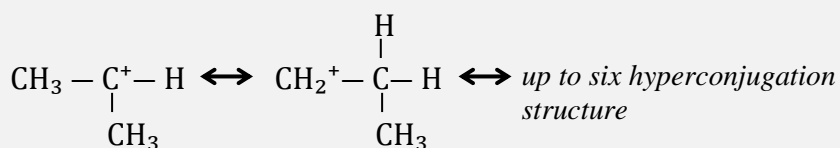
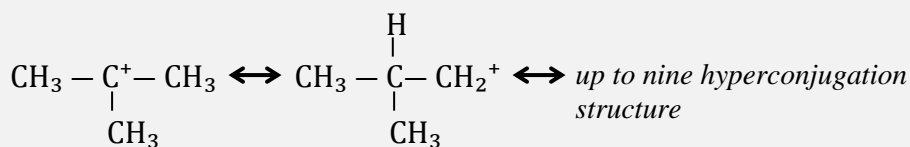
For example



Hence, $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH} - \text{CH}_2^+ > \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2^+$ in case of stability

- 3. Hyperconjugation:** The phenomenon of interaction of vacant p -orbital with σ -bond of adjacent carbon of carbocation is known as hyperconjugation. Higher the number of alkyl group directly bonded with carbocation greater will be the possibility of of hyperconjugation and consequently more will be stability. Therefore $3^\circ\text{carbocation}$ is more stable than $2^\circ\text{carbocation}$ and $2^\circ\text{carbocation}$ is more stable than $1^\circ\text{carbocation}$ since $3^\circ\text{carbocation}$ has nine possibility of hyperconjugation and $2^\circ\text{carbocation}$ has

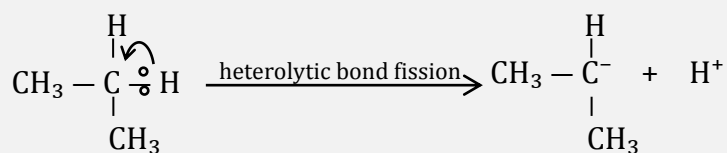
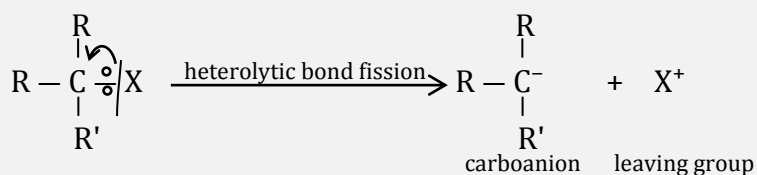
six possibility of hyperconjugation and 1° carbocation has three possibility of hyperconjugation.



Carboanion

The intermediate species that contain negatively charged carbon atom produced after heterolytic bond fission in the hydrocarbon is known as carboanion. During bond fission pair of electron goes to carbon atom and hence it gets negative charge and leaving group gains positive charge.

For example



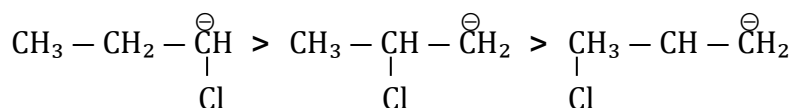
Carboanion are reactive species due to presence of negative charge at carbon atom and are readily attracted by electrophile.

Stability of Carboanion

Stability order of carboanion is methyl carboanion > 1° carboanion > 2° carboanion > 3° carboanion. Stability of carboanion is markedly affected by inductive effect.

+I Effect: Electron groups like alkyl group shows +I effect which increase negative charge of carboanion-carbon by releasing electron and decreases stability of carboanion.

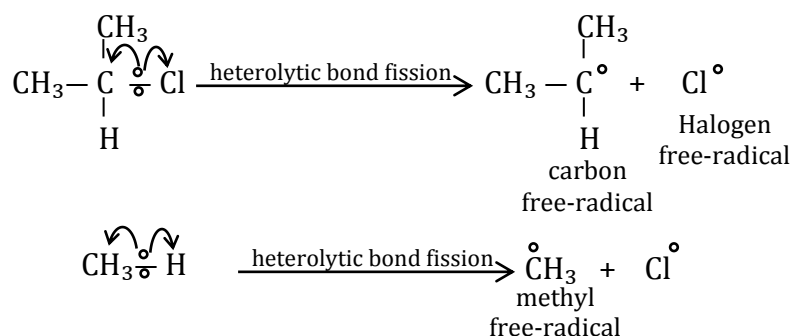
-I Effect: Electron withdrawing groups shows -I effect which increases stability of carboanion by dispersing negative charge throughout the molecules. **For example,** (-X), (-NO₂), etc. group increases stability of carboanion. But stability decreases as their distance from carboanion-carbon



Carbon free-radical

The reaction intermediate which contains odd electron on carbon atom formed by heterolytic bond fission is known as carbon free-radical.

For example



Types of Carbon free-radical

Carbon free-radical are of following types on the basis of carbon atom directly bonded with carbon free-radical.

- i) Methyl free-radical **E.g.** $\overset{\cdot\cdot}{\text{CH}_3}$ methyl free-radical
- ii) Primary free-radical **E.g.** $\text{CH}_3 - \text{CH}_2^\cdot$ ethyl free-radical
- iii) Secondary free-radical **E.g.** $\text{CH}_3 - \overset{\cdot\cdot}{\text{CH}} - \text{CH}_3$ iso-propyl free-radical
 $\text{CH}_3 - \overset{\cdot\cdot}{\text{CH}} - \text{CH}_3$ sec-butyl free-radical
- iv) Tertiary free-radical **E.g.** $\text{CH}_3 - \overset{\cdot\cdot}{\underset{\text{CH}_3}{\text{C}}} - \text{CH}_3$ tert-butyl free-radical
 $\text{CH}_3 - \overset{\cdot\cdot}{\underset{\text{CH}_3}{\text{C}}} - \text{C}_2\text{H}_5$ tert-pentyl free-radical

Stability of carbon free-radical

Stability of carbon free-radical follows the order of $3^\circ\text{free-radical} > 2^\circ\text{free-radical} > 1^\circ\text{free-radical} > \text{methyl free-radical}$. Free-radical is stabilized by hyperconjugation. Higher the hyperconjugation in the molecule, more will be the stability of free-radical. Since, possibility in $3^\circ\text{free-radical}$ is nine which is greater than possibilities of hyperconjugation of $2^\circ\text{free-radical}$ i.e. six possibilities. Therefore $3^\circ\text{free-radical}$ is more stable than $2^\circ\text{free-radicals}$. Similarly $2^\circ\text{free-radical}$ is more stable than $1^\circ\text{free-radical}$ as $2^\circ\text{free-radical}$ has six possibilities of hyperconjugation and $1^\circ\text{free-radical}$ has a possibilities of hyperconjugation.

On the other hand stability of free-radical is measured from bond-dissociation energy of alkyl free-radical. $3^\circ\text{alkyl free-radical}$ are more stable than 2° and 1° because bond-dissociation energy is 92kcal, 95kcal, and 98kcal.

Stereoisomerism

The spatial arrangement of atoms or groups of atoms of a molecule in the space is known as stereoisomerism. And the molecules having same molecular formulae but different relative arrangement of atoms in the space are called stereoisomerism.

(In Greek; Stereo=space, meros=parts)

In fact stereoisomerism is exhibited by the compounds which have the same molecular formulae but differ in configuration (3-dimensional arrangement of atoms).

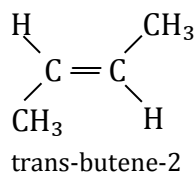
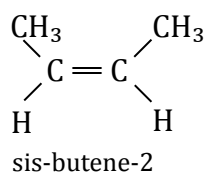
Stereoisomerism is of following types.

- i) Geometrical Isomerism
- ii) Optical Isomerism

Geometrical Isomerism

The stereoisomerism which occurs due to the restriction of rotation of carbon-carbon multiple bonds or due to restriction of rotation of cyclic compounds is known as geometrical isomerism.

Geometrical isomerism in alkene: In alkene carbon-carbon double bond consists of a σ -bond and a π -bond which locks the molecule in fixed position and restricts the rotation of carbon-carbon double bond. Rotation of carbon-carbon double bond is not possible it ruptures the π -bond. Alkene has two geometrical isomers i.e. *cis* isomers and *trans* isomers. **For example**

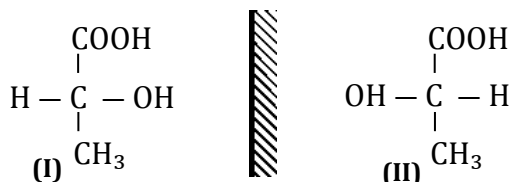


Optical isomerism

The stereoisomerism in which molecules have same molecular formulae, molecular mass, and most of physical and chemical properties are same but are differ in direction of rotation of polarized light is known as optical isomerism. Optical isomers are of two types.

Enantiomers

The isomers having same molecular formulae, molecular mass and identical most of physical and chemical properties but are mirror image and non-superimposable to each other are known as Enantiomers. **For example**



Structure I and II are mirror image of each other but non-superimposable. Therefore structure I and II are enantiomers.

Properties of Enantiomers

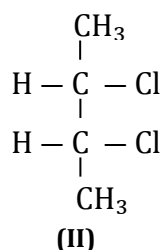
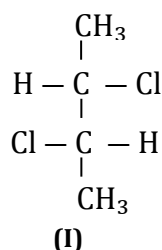
- i. They have similar physical properties.
- ii. They rotate polarized light into opposite direction.
- iii. They poses different chemical properties towards optically active reagents.

Distereoisomers

The molecule having similar molecular formulae, similar mass and different physical properties as well as chemical properties but are not mirror image and non-superimposable to each other are called distereoisomers.

On the other way distereomers are pair of isomers which have opposite configuration at one or more chiral centers but are not mirror image to each other's.

For example



Above structure I and II are not mirror image of each other. Therefore structure I and II are distereomers.

Properties of Distereomers

- They have different physical properties like M.P., B.P., density, etc.
- They have different chemical reactivity towards most of reagents.
- They have opposite configuration at one or more chiral centers.

Differentiate Between Enantiomers and Distereomers.

Enantiomers

- They are mirror image of each other.
- They are superimposable to each other.
- They have same physical properties except direction of rotation of polarized light.
- They have opposite configuration at all asymmetric(*chiral*) centers.
- They have same reactivity rates.
- They have same activation energy.
- It contains at least one chiral centers.

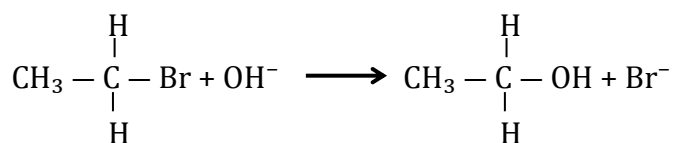
Distereomers

- They are not mirror image of each other.
- They may or may not be superimposable.
- They have different physical properties like M.P., B.P., density, etc.
- They have opposite configuration at one or more asymmetric center but not at all centers.
- They have different reactivity.
- They have different activation energy
- It contains at least two chiral centers.

Nucleophilic Substitution Reaction

The reaction in which the leaving group is replaced from substrate molecule by a nucleophile (negative or electron rich species).

For example



Essential of Nucleophile Substitution reaction

- Nucleophile
- Solvent
- Substrate Molecule

Types of Nucleophilic Substitution reaction.

On the basis of molecules involved in the determining step, nucleophilic substitution reaction are of two types.

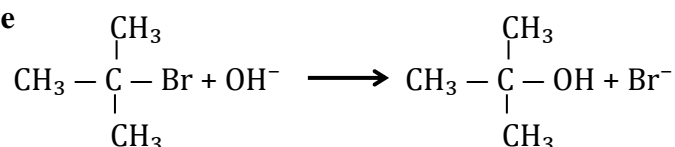
SN^1 or also written SN_1 reaction

SN^2 or also written SN_2 reaction

SN^1 reaction (Unimolecular Nucleophilic Substitution Reaction)

The nucleophilic substitution reaction whose rate depends upon the concentration of substrate only is known as SN^1 reaction or unimolecular nucleophilic substitution reaction. It shows first order kinetics.

For example



$$\text{Rate} \propto [\text{Substrate}]$$

$$\text{Rate} \propto \left[\text{CH}_3 - \underset{\text{H}}{\overset{\text{CH}_3}{\text{C}}} - \text{Br} \right]$$

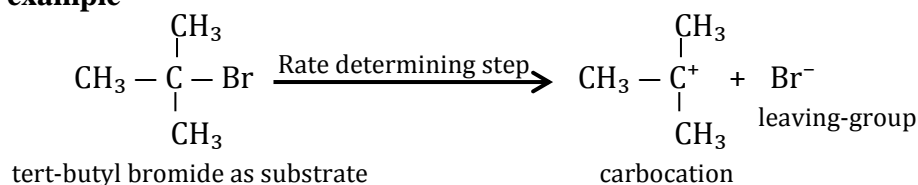
$$\text{Rate} = k \left[\text{CH}_3 - \underset{\text{H}}{\overset{\text{CH}_3}{\text{C}}} - \text{Br} \right]$$

Reaction Mechanism of SN^1 Reaction

SN^1 reaction proceed through 3 steps reaction mechanism

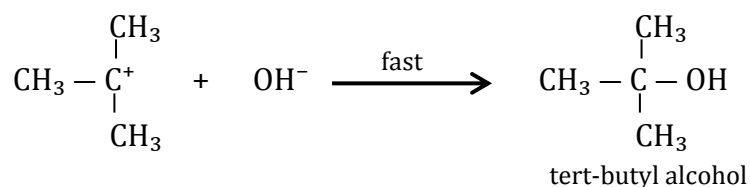
Departure of leaving group: Leaving group detaches from substrate molecule so as to form carbocation. This process is very slow and therefore it is known as rate-determining step (rds).

For example



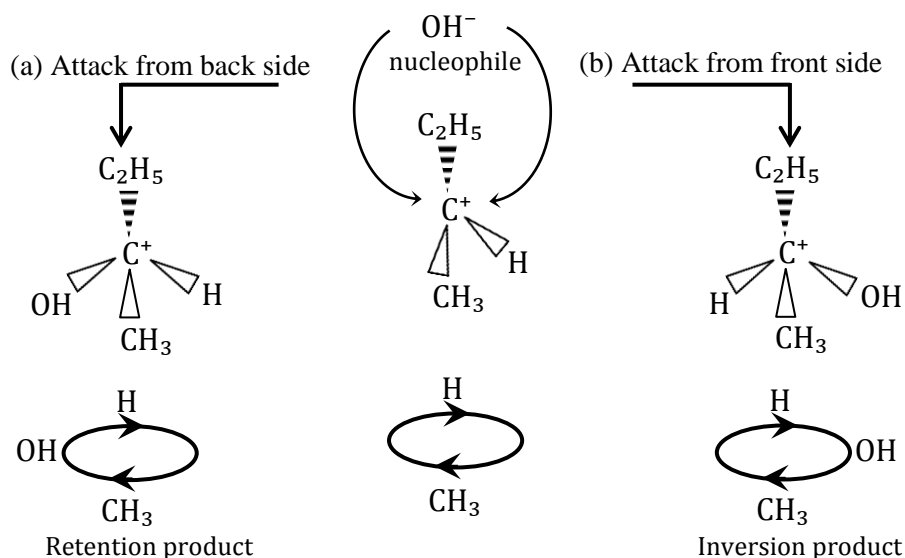
Attack by Nucleophile: Nucleophile attack on the planar carbocation formed in Rate determining step from backside or front side so as to form final product. This step is very fast.

For example



Stereochemistry of SN^1

There is possibility to attack on the planar carbocation by nucleophile from backside and from front side in order to give a racemic mixture of products with retention of configuration. Since the products are formed with some retention of configuration and some inversion of configuration. The net optical activity of product is zero or very low.



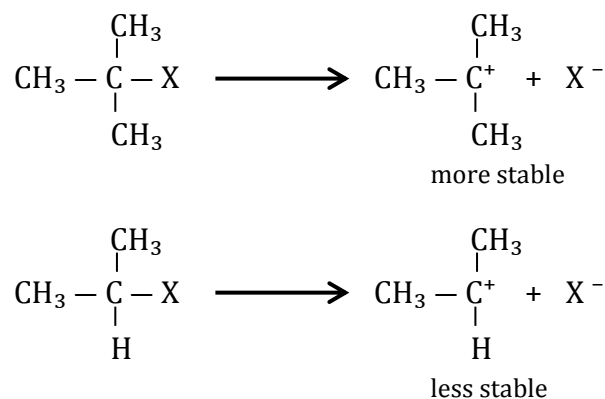
Since some products are obtained with retention configuration and some products are with inversion configuration. Therefore mixture of product is not optically 100% pure.

Reactivity Order of SN^1 Reaction

Order of SN^1 reaction flows as 3° alkyl halide $>$ 2° alkyl halide $>$ 1° alkyl halide $>$ methyl halide because leaving group (halide) leaves substrate molecule faster in 3° alkyl halide than 2° alkyl halide and so on as.

3° carbocation formed by 3° alkyl halide is more stable than that of 2° carbocation formed from 2° alkyl halide and so on.

For example



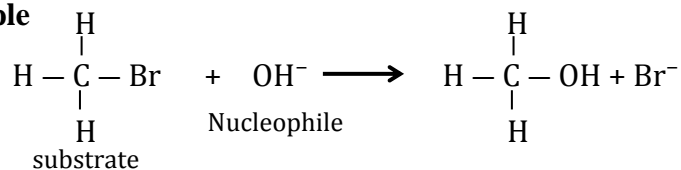
SN² Reaction (Bi-molecular Nucleophilic Substitution Reaction)

In nucleophilic substitution reaction whose rate depends upon the both concentration of substrate as well as nucleophile is known as SN² reaction. It follows:

$$\text{Rate} \propto [\text{Substrate}][\text{Nucleophile}]$$

$$\text{Rate} = k[\text{Substrate}][\text{Nucleophile}]$$

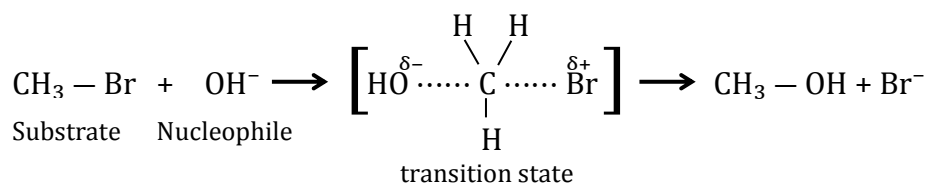
For example



$$\text{Rate} = k[\text{CH}_3\text{Br}][\text{OH}]$$

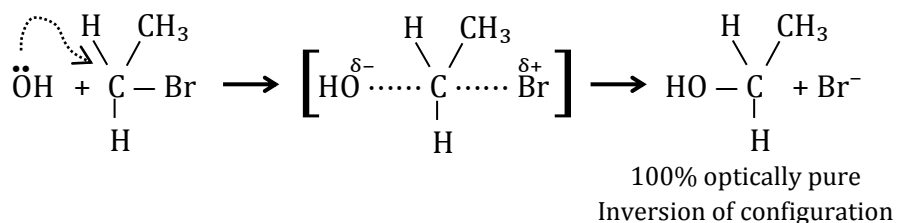
Reaction Mechanism of SN² Reaction

SN² reaction is a single step reaction mechanism in which nucleophile attacks on substrate molecule and leaving group leaves from substrate molecule simultaneously. Reaction proceed through transition state (T.S.) in which nucleophile-substrate bond is partially formed and substrate-leaving group is partially broken. Finally a product of inversion of configuration is formed.



Stereochemistry of SN² Reaction

SN² reaction proceeds through transition state (T.S.) in which nucleophile-substrate bond is partially formed and substrate-leaving group is partially broken and nucleophile attack from back side only. Therefore product is obtained of inversion of configuration only which is 100% optical pure.



Reactivity Order of SN² Reaction

The reactivity order of SN² is methyl alkyl halide > 1° alkyl halide > 2° alkyl halide > 3° alkyl halide because there are more (three) bulky groups in 3° alkyl halide than (two) in 2° alkyl halide which causes steric hindrance and makes difficult for nucleophile to attack and reaction becomes slower in 2° alkyl halide. Similarly SN² reaction is faster in 1° alkyl halide than in 2° alkyl halide because 2° alkyl halide has more bulky group than primary alkyl halide and cause more steric hindrance which makes difficult for nucleophile to attack on 2° alkyl halide than 1° alkyl halide.

Differentiate Between SN¹ and SN²

SN¹ Reaction

- a. It follows the first order kinetics
- b. It gives racemic mixture of products
- c. Its rate depends upon concentration of substrate only.

$$\text{Rate} \propto [\text{Substrate}]$$

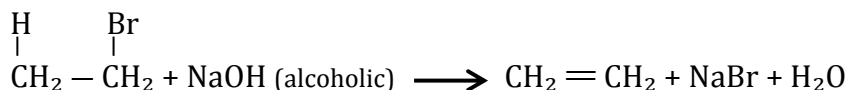
- d. Reactivity order is 3° alkyl halide > 2° alkyl halide > 1° alkyl halide > methyl alkyl halide.
- e. It involves two step reaction mechanism.
- f. It does not include transition state (T.S.)
- g. It gives retention as well as inversion configuration of products.
- h. Nucleophile may attack either from front side or back side.

SN² Reaction

- a. It follows second order kinetics.
- b. It gives 100% optical pure products.
- c. Its rate depends upon concentration of both substrate and nucleophile.
- d. Reactivity order is methyl halide > 1° alkyl halide > 2° alkyl halide > 3° alkyl halide.
- e. It involves single step reaction mechanism.
- f. It includes transition state (T.S.)
- g. It gives 100% inversion configuration of products.
- h. Nucleophile attacks only from back side.

Elimination Reaction

The reaction which involves the removal of hydrogen along with leaving group so as to form multiple bonds is known as elimination reaction. A typical example is the dehydrohalogenation of alkyl halides with alcoholic NaOH or KOH.



Types of Elimination Reaction.

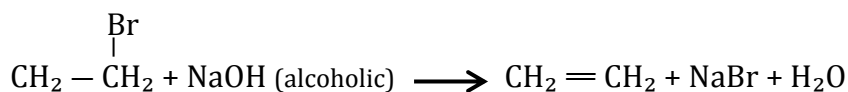
Elimination reaction are of following two types.

1. E₁ elimination reaction. (Unimolecular Elimination Reaction)
2. E₂ elimination reaction (Bimolecular Elimination Reaction)

E₁ elimination reaction. (Unimolecular Elimination Reaction)

The elimination reaction whose rate depends upon concentration of substrate molecule only and the reaction proceed through first order kinetics is known as E₁ elimination reaction.

$$\text{Rate} = k[\text{Substrate}]$$

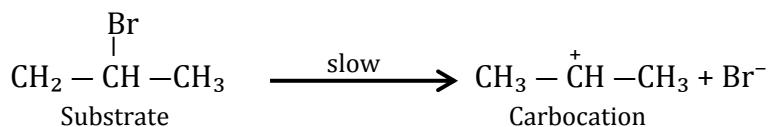


$$\begin{aligned} \text{Rate} &= k[\text{Substrate}] \\ &= k[\text{CH}_2 - \text{CH}_2\text{Br}] \end{aligned}$$

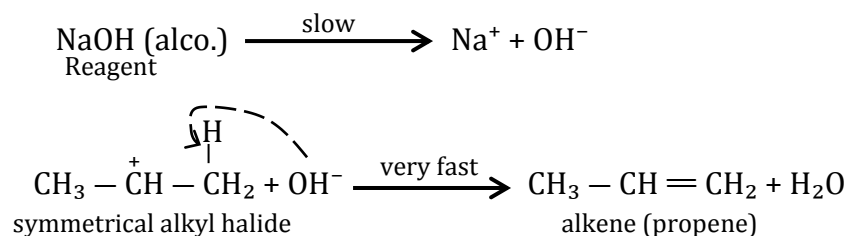
Reaction Mechanism of E₁ Elimination reaction

E₁ Elimination reaction proceed through 2 step reaction mechanism viz.

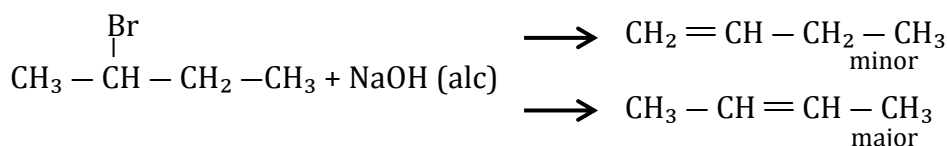
- i) **Ionization of substrate molecule :** Leaving group first leaves first leaves substrate molecule in solution. It is slow and hence rate determining step (rds).



- ii) **Abstraction of β-hydrogen :** Negative part of reagent abstracts hydrogen atom from β-carbon atom of carbocation so as to form multiple bonds. This is fast step reaction.



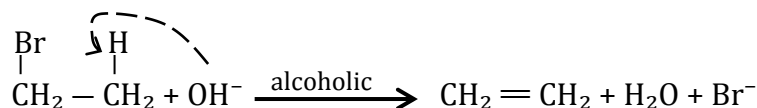
Sayzeff's Rule : If there is possibility of formation of more than one kinds of alkene then highly substituted alkene is the major product.



E₂ Elimination Reaction. (Unimolecular Elimination Reaction)

The elimination reaction whose rate depends upon concentration of both substrate molecule and reagent molecule in which abstraction of β-hydrogen and removal of leaving group takes place simultaneously is known as E₂ Elimination reaction.

E₂ elimination reaction proceed through second order kinetics. **For example**



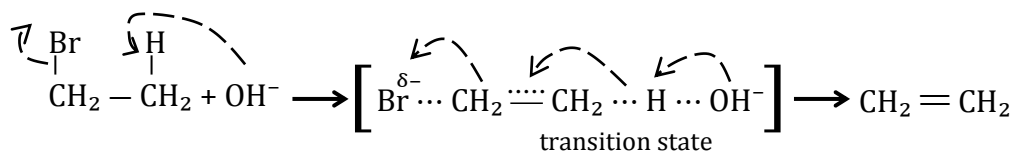
$$\text{Rate} \propto [\text{Substrate}][\text{Reagent}]$$

$$\text{Rate} = k [\text{Substrate}][\text{Reagent}]$$

$$\text{Rate} = k[\text{CH}_2\text{BrCH}_3][\text{OH}^-]$$

Reaction Mechanism of E₂ Elimination Reaction

E₂ Elimination reaction proceeds through single step reaction in which β-hydrogen is abstracted by reagent and leaving group from α-carbon is removed simultaneously so as to form multiple bond in the product. This elimination reaction passes through transition state (T.S.) as shown in figure below.



Difference between E₁ and E₂ Elimination Reaction.

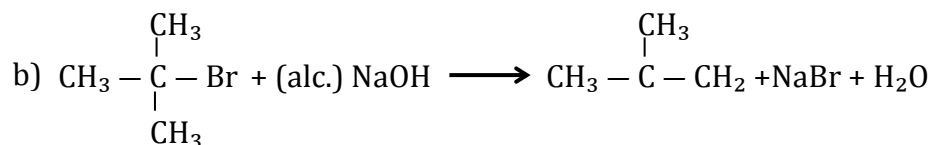
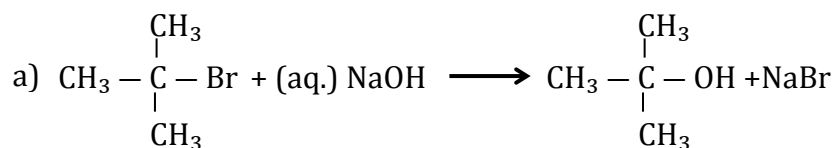
E₁ Elimination Reaction

- a. Its rate depends upon concentration of substrate only.
- b. It proceeds through first order kinetics.
- c. It involves two step reaction mechanism.
- d. It proceeds through formation of carbocation.
- e. It shows rearrangement of carbocation.
- f. Reagent does not take part in rate determining step (rds).

E₂ Elimination Reaction

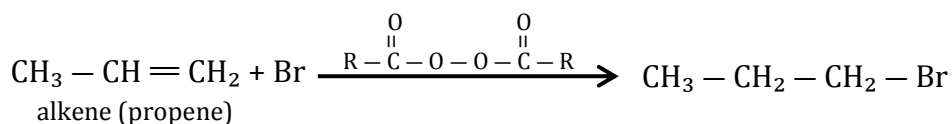
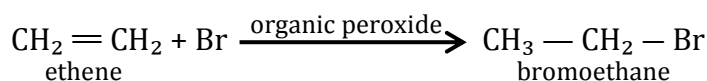
- a. Its rate depends upon concentration of both substrate and reagent.
- b. Its process through second order kinetics.
- c. It involves single step reaction mechanism.
- d. It proceeds through (T.S) transition state.
- e. No carbocation is formed.
- f. Reagent takes part in rate determining step.

Complete the following reaction and write their reaction mechanism.



Free-radical addition reaction

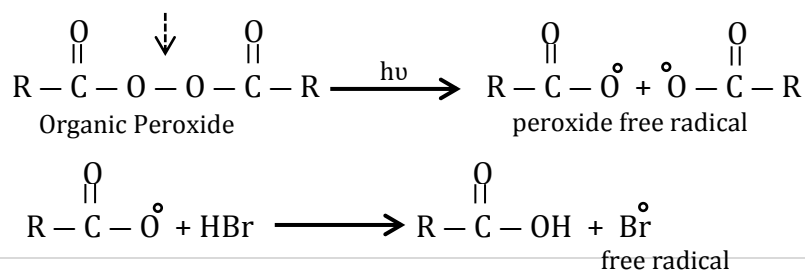
The reaction which proceeds by the addition of free-radicals to the carbon-carbon multiple bonds is known as free-radical addition reaction. It occurs in the presence of organic peroxide.



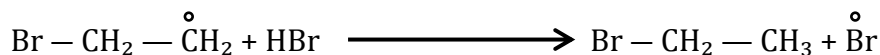
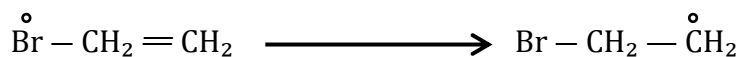
Mechanism of free radical addition reaction

Free radical addition reaction proceeds in the direction of Anti-markonikovs rule in the presence of organic peroxide reaction mechanism in three step.

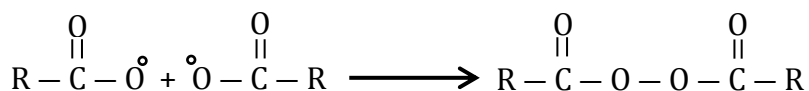
Chain Initiation State : Organic peroxide gets dissociated homologically in presence of sunlight to generate free-radical which attacks to the reagent HBr as



Chain propagation step : Thus produced free-radical Br in the chain initiation step attack on unsaturated hydrogen to propagate chain of reaction.

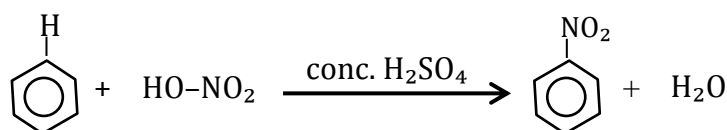


Chain Termination : In this step peroxide is regenerated and reaction become complete.



Electrophilic Aromatic Substitution Reaction

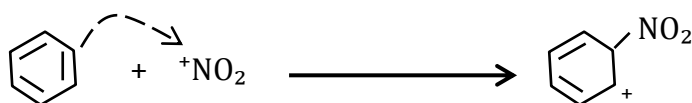
The substitution reaction in which positive species like H^+ is substituted by electrophilic (electron efficient or positively charged species) formed from benzene ring is known as electrophilic aromatic substitution reaction. **For example**



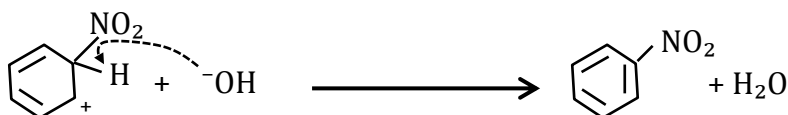
Mechanism of Electrophilic Substitution Reaction

Electrophilic Aromatic substitution reaction proceeds through two step reaction mechanism.

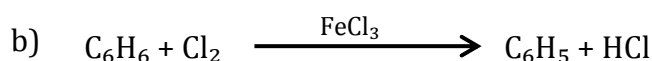
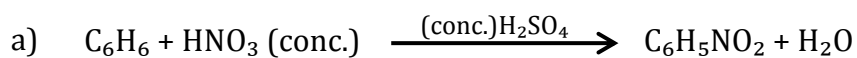
Attack by electrophilic : Electrophile first attack the benzene ring through π -bond



Abstraction of Proton H from α -carbon : Negative part of reagent abstracts H^+ proton from α -carbon



Write the reaction Mechanism of following reaction.



Polymer chemistry

Polymer

The macromolecule formed by the combination of large numbers of similar or different monomer units is known as polymers. For example cellulose, starch, protein, silk, rubber, nylon, Bakelite, polythene P.V.C etc.

On the basis of source of polymers, they are classified into following two types.

Natural polymers: The polymers which are naturally synthesized in the animals or plants by spontaneous phenomenon are known as natural polymers. **For example** starch, protein, cellulose, Natural rubber, etc.

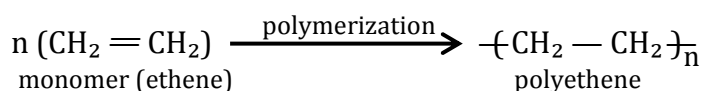
Synthetic Polymer: The polymers which are synthesized in the industries by human beings as required are known as synthetic or artificial polymers.

For example Polythene, P.V.C. Nylon.6.6, Polystyrene, Bakelite, etc.

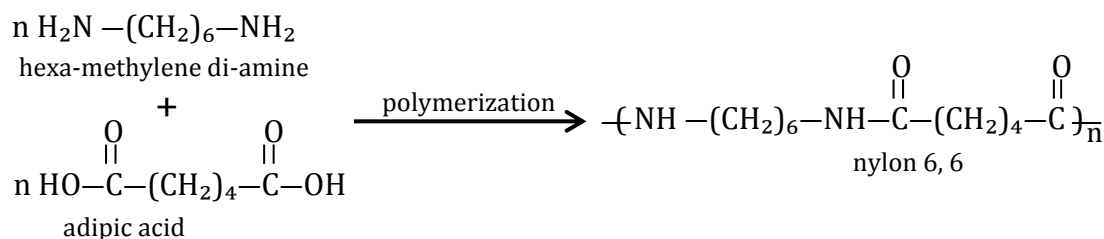
Further polymers are classified into following two groups on the basis of monomer units.

Homo-polymers : The polymers which contain large numbers of similar monomer units are known as homo-polymers.

For example polythene, P.V.C., Polystyrene, natural rubber, etc.



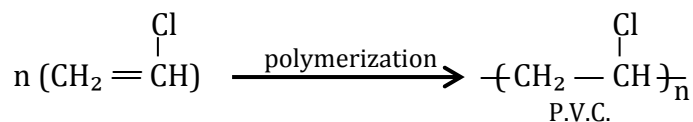
Co-polymer : The polymers which are synthesized by the combination of two or more different monomers units are known as co-polymers. **For example** Nylon 6,6. Bakelite, etc.



Polymerization

The phenomenon of synthesis of macromolecules by the combination of large numbers of similar or dissimilar monomer units is known as polymerization.

For example Formation of P.V.C



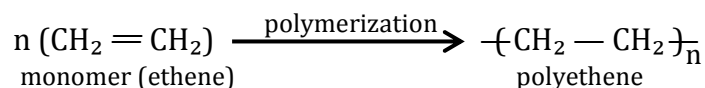
There are two types of polymerization.

Addition Polymerization and Condensation Polymerization

Addition Polymerization

The phenomenon of formation of polymers by addition of large numbers of similar or dissimilar monomer units having at least one multiple bond without elimination of small molecules like H_2O , HCl , NH_3 etc. as byproduct is known as addition polymerization.

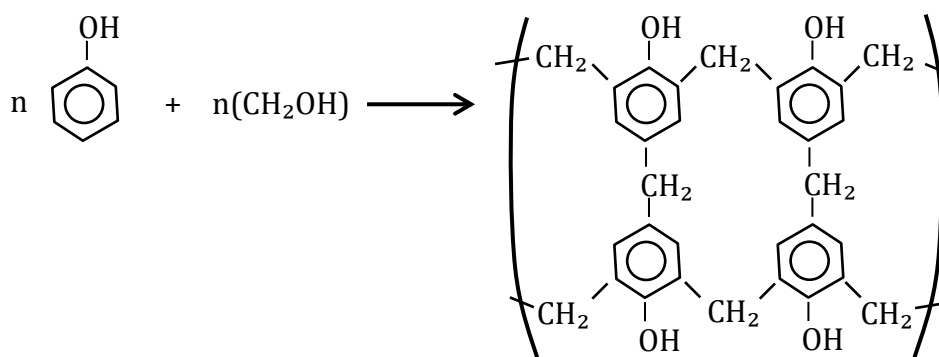
For example : Formation of polythene



Condensation Polymerization

The polymerization of large number of monomer units having at least two functional group with elimination of simple molecule like HCl , H_2O , NH_3 etc. as byproduct is known as condensation polymerization.

For example Formation of Bakelite.



Difference Between Addition and Condensation Polymerization

Addition Polymerization

- Monomer units contain at least one multiple bond.
- Small molecules like H_2O , HCl , NH_3 are not produced as byproducts.
- It gives usually thermo-plastic polymer.
- Multiple participate in combination.
- It forms linear chain structure of polymer.
- It proceeds either by free-radical addition or by cationic or by anionic reaction mechanism.
- It gives generally soft polymer.

Condensation Polymerization

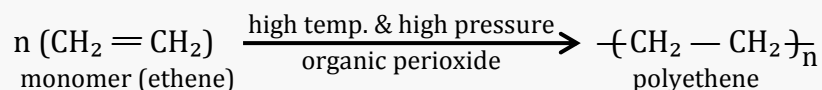
- Monomer units contain at least two functional group.
- Small molecules like HCl , NH_3 , H_2O are produced as byproducts.
- It gives usually thermosetting polymers.
- Functional group participate as reactive sites for condensation.
- It forms three-dimensional cross-linked polymer.
- It gives polymer through condensation mechanism.
- It gives generally hard polymers.

Preparation of synthetic polymers and their uses

Polythene

Preparation

It can be prepared by heating large numbers of ethane monomers at high temperature under high pressure in presence of organic peroxide.



Properties

- It is soft having plastic in nature.
- It is insoluble in water but soluble in certain chemicals.
- It is addition type of polymer.
- It is homo-polymer and thermoplastic.
- It is bad conductor.

Uses

It is used as bag and used in packaging.

It is used for insulation of cable and formation of flexible bottles.

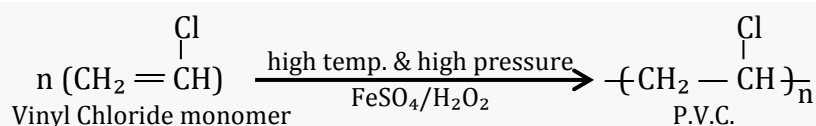
It is used in the manufacture of flexible bottles.

It is used in the manufacture of household products like dustbin, soft bucket and as wrapping material.

P.V.C.

Preparation

It is prepared by adding vinyl chloride monomer under high temperature and pressure.



Properties

- It is homopolymer and thermosetting plastic.
- It is bad conductor of heat and electricity.
- It is insoluble in water but soluble in chemicals.
- It has self-extinguishing properties.

Uses

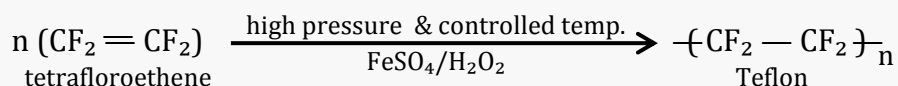
- It is used in making pipes, bottles, films sheets.
- It is used for making floor tiles, and floor covering.
- It is used in electrical and thermal insulators.

Teflon

(Polymer of Tetra-floro-ethene :PTFE)

Preparation

It is prepared by adding number of tetra-floro-ethene monomers in aqueous suspension using ferrous sulphate (FeSO_4) and (H_2O_2) as catalyst at high pressure and controlled temperature.



Properties

It is homopolymer and addition polymer. It is insulator, It is insoluble in water but soluble in most of organic compounds. It becomes hard on heating and cannot be remolded.

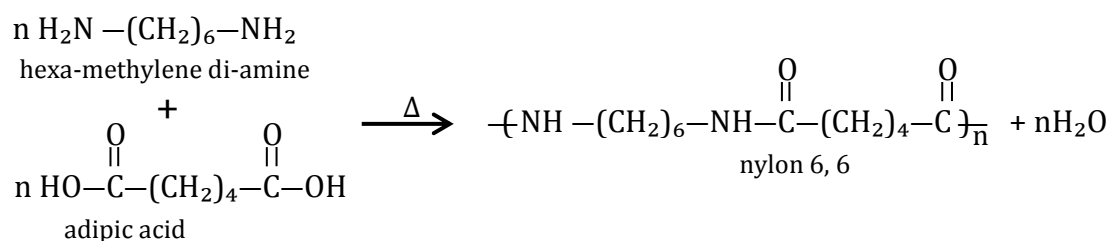
Uses

It is used in nonstick coating pans, handles of cooker, It is used as insulator, It is used in the manufacture of gaskets and valves. It is used in manufacture of artificial limbs.

Nylon 6, 6

Preparation

It is prepared by heating hexamethylene diamine monomers and adipic acid.



Properties

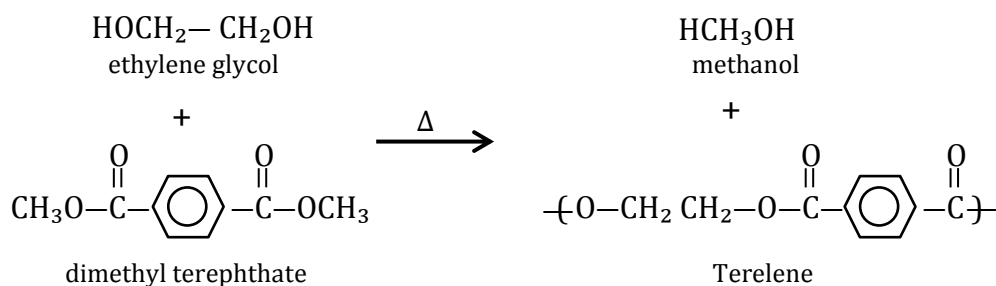
It is soft translucent with high melting point.
It possess high avrasion resistance and are thermally stable.
It is insoluble in organics solvent except phenol and formic acid.
it is thermoplastic resins.

Uses

It is used to make fabrics, carpets, ropes, thread.
It is used to make bristle of toothbrush.
It is used to make bag.
It is used in molding purpose of gears and bearings.

Terelene (Polystyrene)

It is obtained by heating ethylene glycol with dimethyl terephthalate.



Properties

It is soft and translucent. It is high tensile in nature.

It is bad conductor of electricity and is condensation polymer.

Uses

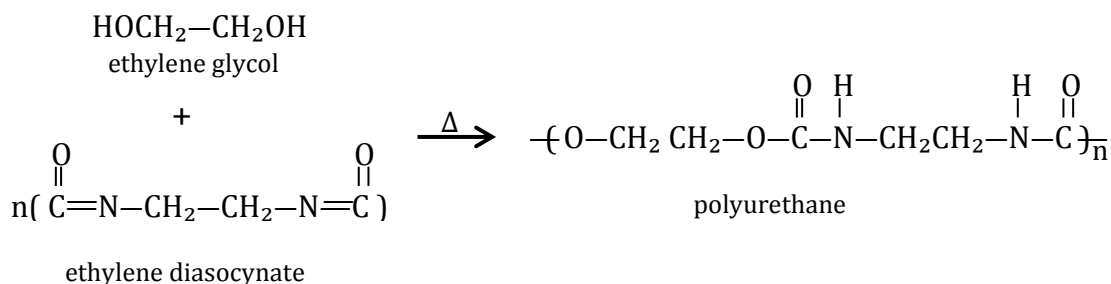
It is used for making fabrics of high crease resistance.

It is used for making ropes and nets of high tensile strength.

Polyurethane (isocyanate rubber)

Preparation

It is prepared by condensation of ethylene glycol and ethylene diisocyanate.



Properties

It is highly resistance to oxidation. It is resistant to organic solvent.

Uses:

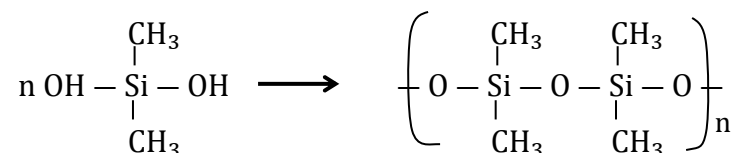
It is used for making pillows mattresses. It is used to prepare thermal insulating materials and surface covering.

Silicone (Polymer)

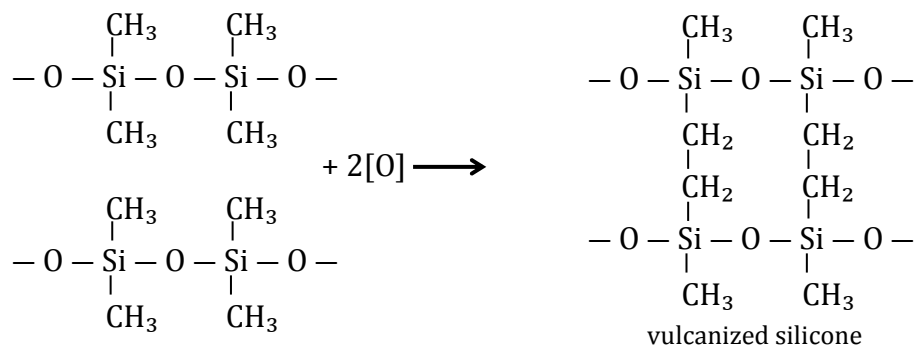
It was first produced by F.S Kipping during study about organosilicone compounds.

Preparation

It is manufactured by intermolecular condensation of d-methyl silicon hydroxide. The chain of polymer can be further vulcanized to form cross-links between two neighboring chains.



Vulcanization of silicone



Properties

Silicone rubbers are exceptional resistance to weather, boiling water, and prolonged exposure to sunlight.

It is also resistance to chemicals like dilute acids and alkalis.

It is a bad conductor. It remains flexible in the temperature of 90°C to 250°C.

Uses:

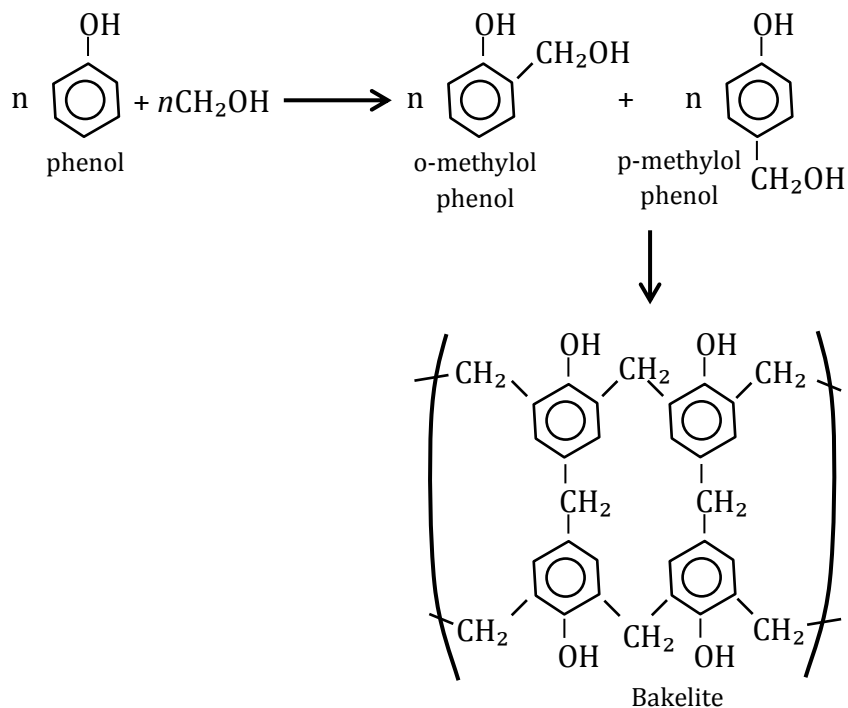
It is used in making tyres of fighter air crafts.

It is used as sealing material as search light.

It is used for insulating the electric wiring in ship and washing machine. It is used for making artificial heart valve, transformation tube and in important surgery.

Bakelite

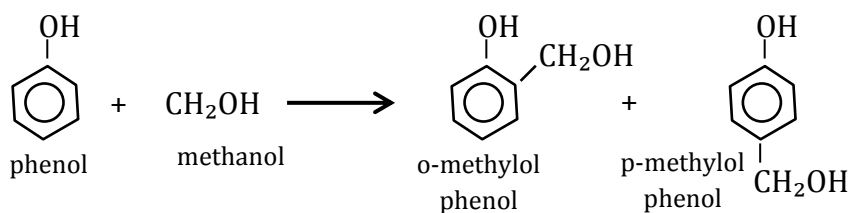
It is prepared by heating phenol monomers and methanol (formaldehyde monomer) in either acidic or alkaline medium.



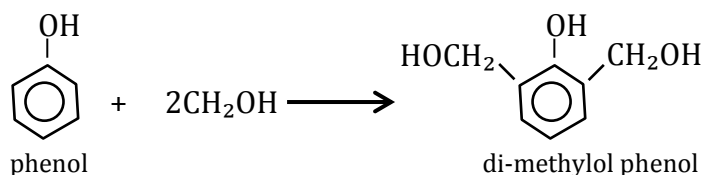
Stepwise formation of Bakelite

Bakelite formation involves following steps

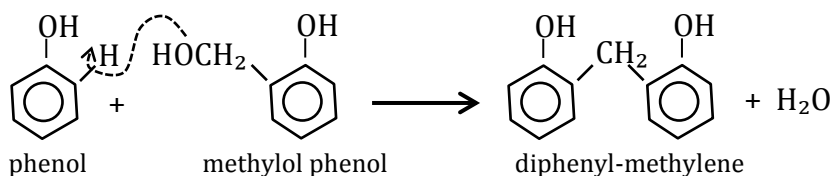
- a. **Methylation** : Phenol and methanol react to give o-methylol phenol and p-methylol phenol.



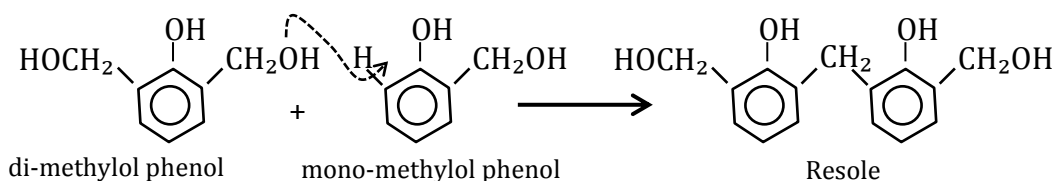
It also gives dimethylol phenol in some extent.



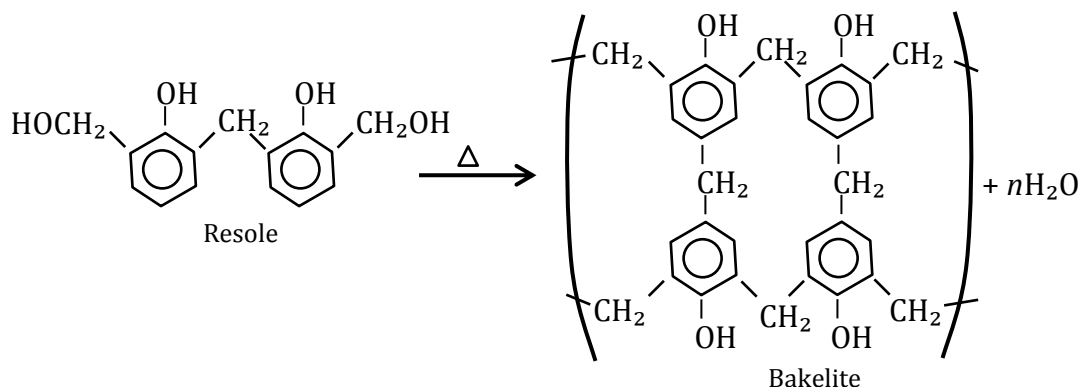
- b. **Formation of Novaloc** : If ratio of phenol and methanol is greater than unity, then methylol phenol reacts with phenol to give dihydroxy, di-phenyl, methylene which further undergoes to form Novaloc.



- c. **Formation of Resole** : If ratio of phenol and methanol is less than unity then mono-methylol phenol combines with dimethylol phenol to give resole in alkaline medium.



- d. **Resite formation** : When resole is heated, formation of 3-dimensional cross link called resite occurs. The resite is known as Bakelite.



Properties

- It is thermosetting plastic & very hard.
- It is a bad conductor.
- It is insoluble in most of organic compound and water.
- It is 3-dimensional solid.

Uses

- It is used for making handles for cooking utensils.
- It is used as electric equipment like switch, electric plate, adaptor, plug, etc.
- It is used for making comb, fountain pen, bucket. etc.

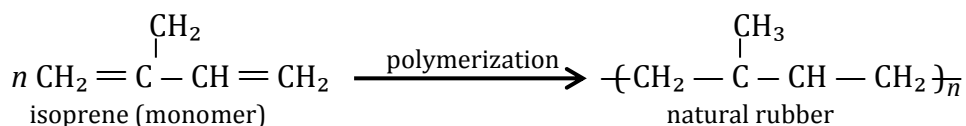
Rubber

Rubber is the polymer having high elasticity and stretching properties. They can be stretched up to 4-10 times of its original length but it reverse back to its initial state as soon as the stretching force is released. the name of "rubber" was given by Joseph Priestley who first time use it to rub pencil mark.

Types of Rubber : According to the source of monomer rubbers are classified into following two types: Natural Rubber & Synthetic Rubber

Natural Rubber

The rubber which are synthesized by latex(milky sap) of rubber tree. Latex contains organic compound isoprene as a constituent unit. Therefore natural rubber is a polymer by the combination of isoprene monomer.

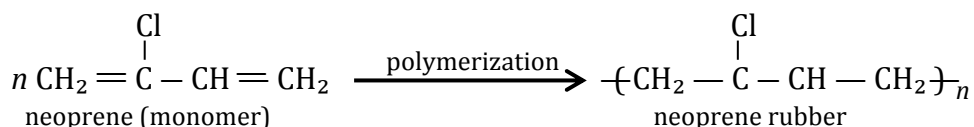


Synthetic Rubber

The rubber which are synthesized in the industry by the combination of different types of monomer units.

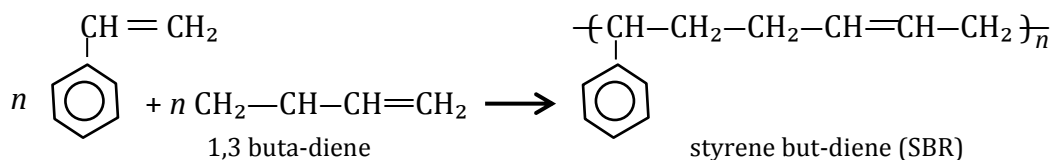
Neoprene rubber

It is synthesized by addition polymerization of neoprene monomer unit.



Styrene buta-diene

It is synthesized by adding styrene monomers with 1,3-buta-diene monomer.



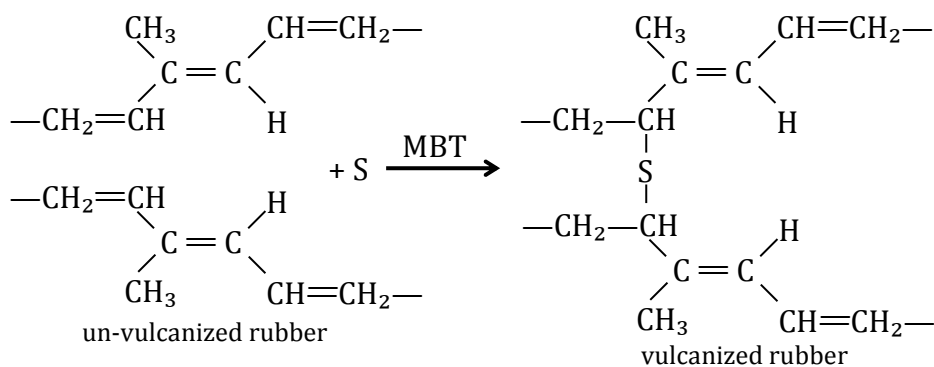
Vulcanization of Rubber

The process in which rubber transformed from its plastic condition into highly stretchable elastic form by improving degree of cross links between chain of polymers of rubber is known as vulcanization. Sulphur, H₂S and benzoyl chloride etc. are used as compounding agent among which mostly used vulcanizing agent is sulphur.

Process of vulcanization

In this process a mixture of rubber polymers and sulphur (1-13%) by weight of rubber is heated about 200°C. The rate of vulcanization can be enhanced by adding sulphur or nitrogen containing compounds, like **2-mercaptobenzothiozole (MBT)**, **zinc-diethyl dithio-carbamate**, **diphenyl guanidine** etc.

Vulcanization increases the strength, elasticity, and stretching properties of Rubber.



Structure of Vulcanized and Un-vulcanized Rubber



Processing of Natural Rubber

In order to collect rubber latex, small incisions (cuts) are made on the barks of rubber trees and the sap is allowed to flow in small vessels. The tapping is usually done once in six month. The latex is diluted to contain 15% to 20% of rubber and filtered to remove any dirt if present. It is then coagulated in a tank fitted with irregular partition by adding acetic acid or formic acid (1kg/200kg). The coagulated mass obtained in the form of sheet is pressed well to free excess acid and then it is treated with smoking at a temperature of 40°C - 50°C which gives a ribbed pattern to the sheet. The rubber sheet is translucent and amber in colour. The rubber thus obtained is not elastic which is carried out for vulcanization in order to get more elastic rubber.

Mechanism of Addition Polymerization.

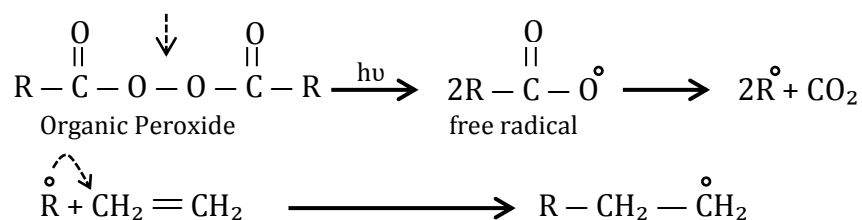
Mechanism of Addition polymerization are of following types.

- Addition mechanism of free radical
- Ionic addition mechanism
 - Cationic addition mechanism
 - Anionic addition mechanism

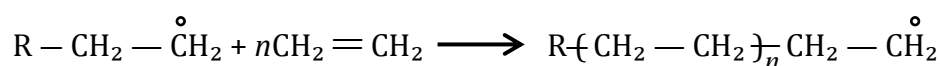
Free Radical Addition Polymerization

Free radical addition polymerization proceeds through following three steps

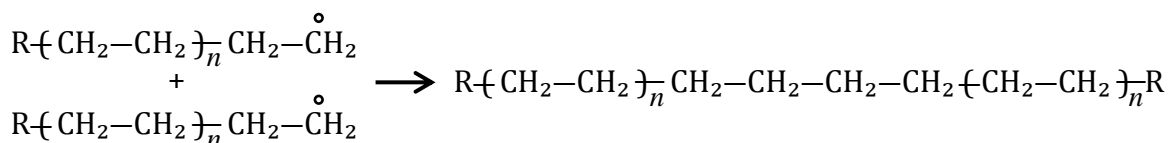
Chain Initiation: In this step, free radical is generated by the influence of sunlight upon the organic peroxide.



Chain Propagation: Free radical thus generated in chain initiation step undergoes goes addition to the large number of monomer



Chain Termination: In this step alkyl free radical generated in chain propagation step



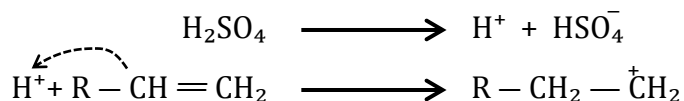
combine together to form long chain of polymer.

Ionic Addition Mechanism

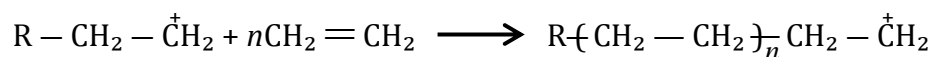
Cationic Addition Mechanism

It involves following three steps.

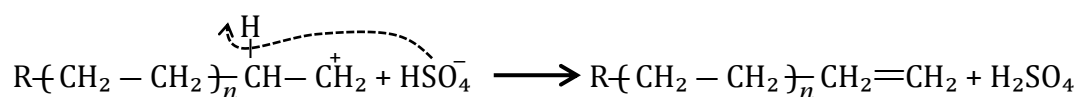
Chain Initiation: In this step cation is formed by heterolytic bond fission of reagent.



Chain propagation: Thus formed carbocation radical attack on number of monomer unit to give chain reaction.



Chain termination: The negative part of reagent (HSO_4^-) abstracts H^+ proton from β -carbon of carbocation.



Analytical Chemistry

The branch of science which deals with the identification, elucidation of structure of compound and separation of mixture in the pure form, etc. is known as analytical chemistry.

For example

- i) Fractional distillation technique
- ii) Chromatography
- iii) Nuclear magnetic Resonance (NMR)
- iv) Mass Spectroscopy

Chromatography

The analytical technique to distinguish the components of mixture by distributing them between stationary phase and flowing mobile phase accordingly to their rates of transportation on the stationary phase is known as chromatography. It is one of the major analytical tools for chemist. There are many types of chromatography used in analysis. Out of them important methods are.

- i) Paper Chromatography
- ii) Thin layer Chromatography
- iii) Gas Chromatography
- iv) High Pressure Liquid Chromatography

Principal of Chromatography

Chromatography technique based on different absorption ability of various components of mixture on absorbents such as Alumina, Cellulose, Silica gel, kieselguhr, magnesium oxide, paper etc.

The absorbents are termed as stationary phase and the liquid which carries components is termed as mobile phase. The components of mixture are separated in the stationary phase according to retention factor value.

$$R_f = \frac{\text{distance travelled by compound}}{\text{distance travelled by solvent}}$$

Components having high R_f value have lower absorption ability and can cover higher distance while compounds having lower R_f value have more absorption ability and can cover lower distance. In this way, different compounds are separated in stationary phase.

Paper Chromatography

An analytical chemistry technique which is applied for distinguishing of components in the mixture and for determination of purity of components by allowing them to flow up the stationary phase paper along with solvent is known as paper chromatography.

Principle

Paper chromatography is based on different absorption ability of various components of mixture on the stationary phase paper. During flow of solvent and components are separated according to their different retention factor value.

$$R_f = \frac{\text{distance travelled by compound}}{\text{distance travelled by solvent}}$$

Higher the value of R_f more is the distance covered by the components and vice versa.

R_f value depends upon:

- Nature of Solvent
- Nature of Substance
- Temperature
- Porosity grade of filter paper employed

Procedure

Paper chromatography involves following steps.

- i) **Preparation of strip of paper :** A thin strip about 1.5 cm to 2cm wide and nearly 5cm long of filter paper is prepared by cutting properly and line is drawn at above 1cm from the lower edge by pencil.
- ii) **Deployment of Chromatogram:** The solution of mixture under interest is applied on the paper strip as spot at the bottom on the line 1cm above. The spotted paper strip is placed in the suitable solvent like ethanol, ether, etc. so that spot remains above solvent. The solvent moves up the paper strip by the capillary action and carries the components of mixture present in the spot. Different components of mixture travel at different rates, due to their different absorption ability to the fiber of paper. When the solvent covers $3/4^{\text{th}}$ distance of the paper height then paper is removed out the developing tank.

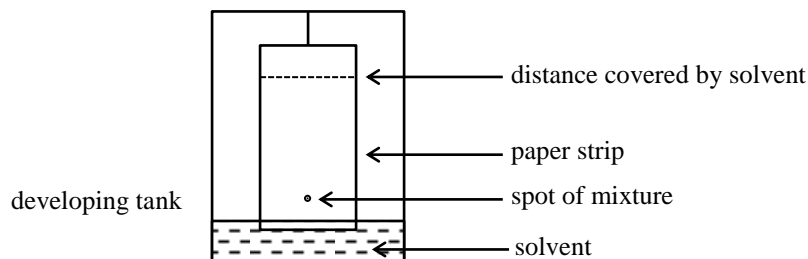


Fig: Paper Chromatography

- iii) **Detection/ Observation:** The paper strip is observed so as to identify the spots of the several components. If the components of the mixture are coloured then different spots are observed in the paper but for the colourless component locating agent like iodine, ninyhydrine can be used for better observation.

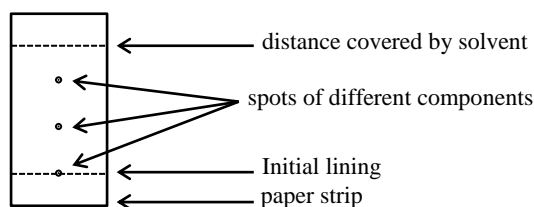


Fig: Development of Paper Chromatography

Application of Paper Chromatography

- i) It is used to determine purity of compound.
- ii) It is used to determine numbers of components present in mixture.
- iii) It is used to identify the compounds by comparing with the standard chromatography.

Thin Layer Chromatography

The analytical technique by which the components of mixture are separated on the stationary phase by migration along with solvent is known as thin-layer chromatography. In this technique, thin layer absorbents are applied on the glass plates for the preparation of stationary phase. This technique is primarily used in bio-chemical pharmaceutical, chemical and forensic areas for qualitative analysis by the comparison of R_f values of solutes with those of standard run on the sample plate.

Principle

Components of mixture are separated in TLC plate due to their different absorption ability on the stationary phase during flow up with proper solvent. The components can cover distance from initial lining on the basis of their retention factor value.

$$R_f = \frac{\text{distance travelled by compound}}{\text{distance travelled by solvent}}$$

Procedure

Thin Layer Chromatography involves following steps.

- i) **Preparation of TLC Plate:** Two glass slides are held back to back and dipped in slurry of absorbent like silica gel, alumina, cellulose, etc. prepared in solvent like chloroform or methanol. The plates are then separated and are dried in air oven.
- ii) **Application of Sample:** The sample is dissolved in suitable solvent and applied in the plate by the help of capillary tube on a line drawn by a pencil at least 1.5cm above from the lower edge.
- iii) **Development of Chromatogram:** The lower edge of the plate is dipped in the solvent in inclined position in such a way that spot of sample should not be merged into solvent gradually rises up in the plate. When the solvent reaches to $3/4^{\text{th}}$ of the plate, then it is taken out from the developing chamber and is dried.

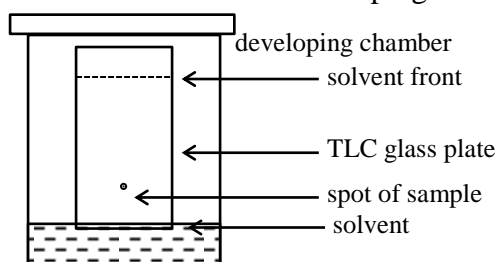


Fig: Thin Layer Chromatography

- iv) **Detection/Observation:** The dried TLC plate is observed so as to identify the different separated spots of components present in mixture. If the plate components are coloured, spots are visible on the plate. But if components are not visible then some locating agent like iodine vapour, ninyhydrine, rhodamine-b, 2-4 DNP are used.

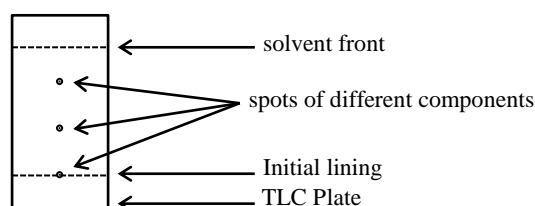


Fig: Development of TLC

Application of TLC

- i) To separate mixture in pure form.
- ii) To examine the purity of compound.
- iii) To identify the compound by co-relating with reference.

Fractional Distillation

The process of separation of volatile components having different boiling points of mixture of liquids in the pure form by distillation and condensation in separate fractionating columns is known as fractional distillation.

Principle

Volatile mixtures of liquid mixture get converted into vapour at different temperature. According to their boiling point and are condensed separately in the different column.

Mixture of Components [A,B,C,D] \rightarrow [A,B,C,D] In different columns.

Procedure

The liquid mixture to be distilled is taken in a distillation flask so that flask should not be more than $2/3^{\text{rd}}$ full otherwise content may boil over the fractionating column is fitted vertically of the top of distillation flask and condenser in joined to the outlet of fractionating column.

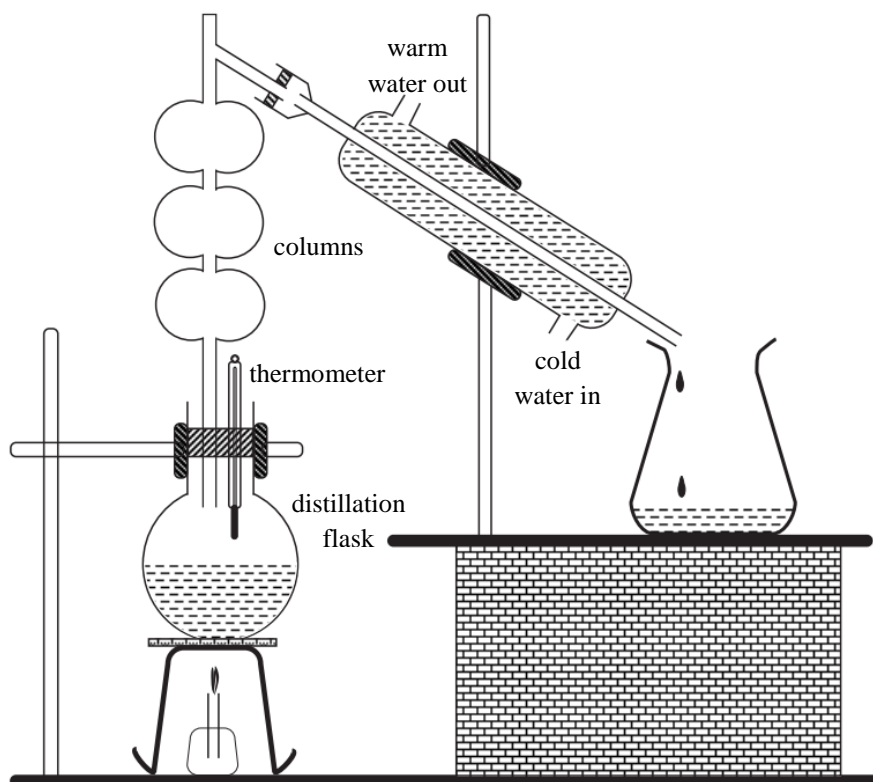


Fig : Fractional Distillation

After making air tight distillation flask is gently heated up to different temperature indicated by thermometer. Different component liquids distill off at their boiling points and get condensed at the different parts of fractionating column. Less volatile liquids are collected in lower parts and high volatile liquids are collected at upper part of fractionating column while extremely volatile liquids vapour passes through water condenser and are collected into the receiver as pure form.

Application of fractional distillation

- i) It is applied for the purification of crude petroleum.
- ii) It is applied to separate volatile components of liquid mixture.
- iii) It is used to purify organic volatile solvent like ether alcohol, chloroform, etc.
- iv) It is used to separate acetone from ethanol.
- v) It is applied to test the purity of alcohol in distillery, Beverage Company.

Spectroscopy

The analytical technique which is applied for more evidential analysis for identification and elucidation of compound by displaying spectra of corresponding compound in the various wavelength regions is known as spectroscopy. It has three major advantages over most of other chemical methods.

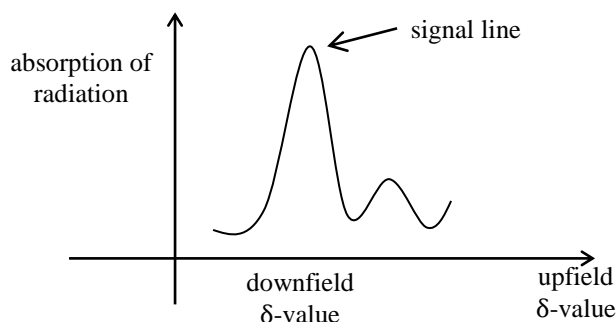
- It is easier and faster than most of chemical methods.
- It provides far more information about molecular structure.
- It is not destructive and if necessary the entire sample can be recovered.

Nuclear Magnetic Resonance Spectroscopy (NMR)

It is the analytical technique which provides information about the arrangement, chemical environment, types and number of hydrogen atom present in a molecule through spectral lines displayed by the spinning of nuclei against applied magnetic field. Nucleus of hydrogen atom is considered in NMR spectroscopy.

Principle

Nuclei of hydrogen atom is considered as spinning like an electron which generates the magnetic moment along the axis that magnetic moment either align with or against the external magnetic field. It is the magnetic moment produced by nuclei of hydrogen atom is against is against applied magnetic field, then it opposes the applied magnetic field and spectral lines are produced at up-field (high-field) while absorption of spectral lines are appeared at down-field when induced magnetic field of nuclei of hydrogen atom is aligned with applied magnetic field.



The proton whose induced magnetic-field oppose the applied magnetic field are called shielded proton. An requires higher applied field strength to give absorption at up-field while the proton whose induced magnetic field reinforce the applied field are called de-shielded proton and require lower applied field strength so as to give absorption at down-field.

Signals of NMR gives following information

- Number of signal tells about kinds of proton in the molecule.
- Position of signals tells about electronic environment of each of proton.
- The intensities of signals tell the number of protons of each kind.
- The splitting of signal tells about environment of proton with respect to others.

Application of NMR

- It is used to determine structure, arrangement of protons in a molecule.
- It is used to identify the compound.
- It is used to know the reaction path.
- It is used in stereoisomerism.
- It is used to know the number and types of protons.
- It is used to drug screening and designing.
- It is used to determine the structure of biological macromolecules, DNA, RNA, protein, etc.
- It is used to compare geometry of isomers.
- It is used to distinguish enantiomers and di-stereoisomers.
- The area of peak gives the idea of number protons.

E.g. Find out the number of NMR spectra in the given molecule.

- i) $\text{CH}_3\text{—CH}_2\text{—OH}$ ii) $\text{CH}_3\text{—O—CH}_3$ iii) $\text{CH}_3\text{—CH=OH}$

Solution: i) $\text{CH}_3\text{—CH}_2\text{—OH}$
(a) (b) (c)

therefore, number of spectra are three signal

ii) $\text{CH}_3\text{—O—CH}_3$
(a) (a)

therefore, number of NMR spectra is one

iii) $\text{CH}_3\text{—CH=OH}$
(a) (b) (c)

there are three NMR signals

Chemical shift

The shifting of the position of NMR absorption spectra due to shielding and de-shielding phenomenon of proton is called chemical shift.

Spin-spin Coupling

The splitting of signals of one type of proton by the influence of number of neighboring hydrogen atom is known as spin-spin coupling.

E.g. i) $\text{CH}_3\text{—CH}_2\text{—CH}_3$
 (a) (b) (a)

Splitting of (a) protons $2+1=3$

Splitting of (b) protons $6+1=7$

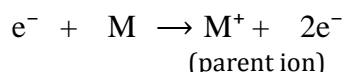
Mass Spectroscopy

It is the analytical technique used to identify geometry of molecule and to establish the arrangement of molecules in a new compound by absorbing spectral lines displayed by several factor of ions having certain value of ratio of mass and charge.

$$\text{i.e. } \frac{m}{e} \text{ value}$$

Principle

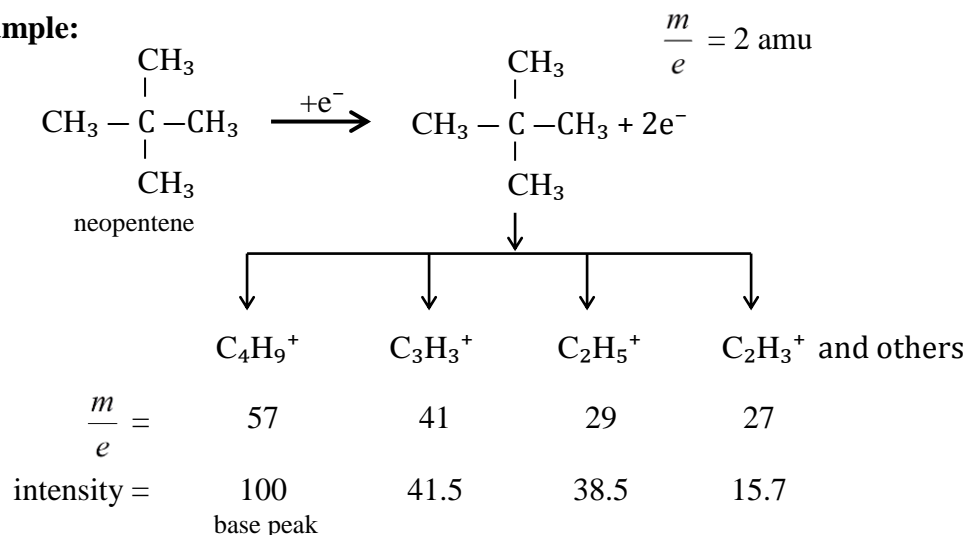
In the mass spectrometer, a molecule is bombarded with a beam of energetic electrons due to which molecule gas ionize and broken into many fragment ions having particular value m/e . Mass of ions have unit charge. Therefore value differs to mass of ions. The fragmentation occurs as.



$$\frac{m}{e} = \text{molecular mass of } M$$

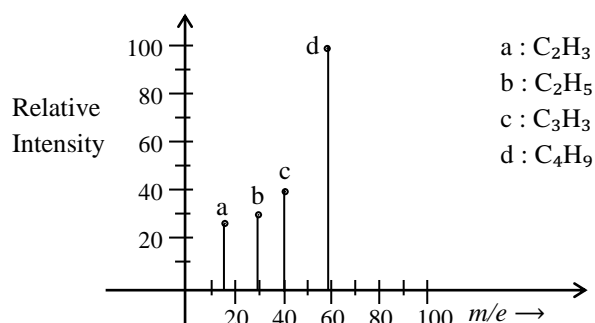
In many cases peak given by M^+ is the base peak but sometimes M^+ even splits to give smaller value of base peak

For example:



Large peak is called base peak and its intensity is taken as 100. The intensities of the other peaks are expressed relative to it. The intensity of each signal expresses the relative abundance of ions producing that signal.

Spectra of each ion can be represented in the plot as:



Application of Mass Spectroscopy

- i) It is used to determine the structure of unknown compound.
- ii) It is used to compare structure of two compounds.
- iii) It is used to determine the molecular mass of unknown compound.
- iv) It is used to determine the isotopes of compounds.
- v) It is used to determine molecular mass.
- vi) It is used in pharmaceutical.

Industrial Chemistry

Paint

Paint is defined as the decorated and protective liquid or semi liquid product which holds solid colouring materials in suspension.

Parts Of Paint

There are five essential parts of paint such as

Pigments: The colour of the paint depends upon the colour of the pigment in it. These may be either natural pigment or manufactured pigment.

Drying Oils: Dry Oils make dispersion of paint for fast drying of paint. Generally Turpentine oil and Tung oil (chine wood oil) are used for drying of paint.

Driers: In order to dry paint readily and properly, some addition substance known as driers or siccative are added. They act as oxygen carrier to the oils and are added in the quantities from 0.5% — 2% of the oil in the paint. These are usually metallic derivatives, particularly of cobalt, iron and manganese.

Thinner: Thinning of the prepared paints is usually done by mixing solvents as petrol, benzene, naphtha liquid.

Fillers: These are inert solid substance like china clay, talc, asbestos, etc. which are added to the paint to increase their durability.

Requisites for a good paints

A good paint must have following properties.

- i. It should be resistance to heated light.
- ii. It should be resistant to the corrosive action of acid and alkalis.
- iii. It should be resistance to atmospheric changes such as: rain, winter, summer

Uses of Paints

- i. It is used for decoration.
- ii. It is used for protection of metal from rusting.
- iii. It is used for protection of surface of materials from climate change.
- iv. It is used for durability of substance.

Lubricants

The substance or chemicals which are applied to reduce frictional resistance on the surface are known as lubricants. A lubricant performs the following functions.

- i) It reduces the loss of energy due to friction.
- ii) It doesn't allow the direct contact between two rubbing surface.
- iii) It acts as coolant or heat transformer.
- iv) It acts as sealing material in internal combustion engine.

Types of Lubricants

Oil lubricants are following types.

- i) Oil Lubricants
- ii) Grease
- iii) Solid Lubricants

Oil Lubricants

Oil lubricants are of following types

Mineral Lubricants

Mineral lubricants oils are residual mass left behind during distillation of crude petroleum. It consists of many impurities like dissolved wax, asphaltic substances and resinous materials which are removed either by solvent refining or by dewaxing.

Fatty oils

Fatty oils obtained from animals and vegetables are sometimes used along but are mixed with mineral oils, non-drying oils such as olive oil, lard and fish oil are mainly used for lubricating purpose.

Synthetic Lubricating Oils

Synthetic lubricants are derived due to need by both industry and military. They have better viscosity, higher degree of resistance to oxidation, temperature and thermal decomposition. Some examples are :

dibasic ester : Used in jet engine, hydraulic fluid

Silicate ester : Condensation pump, for highly loaded bearing

Grease

Grease is a semisolid dispersion of a thickening agent in liquid lubricant. These are normally used under conditions of lubrication for which oil is not suitable.

Grease perform better than oil under several conditions. Such as:

- i) For high bearing loads and shock loads.
- ii) For slow general speed.
- iii) For extreme temperature.
- iv) A seal against external contamination

Types of Grease

Calcium Soap Grease: Calcium soap grease is widely used as cup and pressure-gun grease for lubrication plain bearing which operate as normal temperature. Its water proof nature is primary advantages.

Sodium Soap Grease: They are useful for higher temperature and are fibrous.

Aluminum Soap Grease: They are extremely soft fibrous and smooth.

Barium Soap Grease: They are resistant to water but melt at fairly high temperature. They are characterized by multipurpose grease.

Lithium Soap Grease: They are considered to be superior to other grease as multipurpose lubricant.

Solid Lubricants

Solid Lubricants are solid materials having strong adherence to metals, very low shear strength and good elastic properties.

Some solid lubricants are useful in the high temperature at which oil or grease may not be used.

The disadvantage of solid lubricant is did not flow lecture in the lubricant film. Solid lubricant are

Laminar Solid

- Graphite Solid:** It is most commonly used lubricant and can be used in nearly up to 370°C.
- Molybdenum di-sulphide :** It is thermally stable and retains lubricity up to 400°C in air. It is used as an extreme pressure agent in grease or liquid lubricant.

Organic Compounds

These consist of dry soaps, waxes, fats or fatty acids. High melting point wax are not extremely probably because a poor adherence of metals. Soaps are in general used as lubricants in wire drawing.

Explosives

The substance which release enormous amount of energy violently in very brief period when it is subjected to sudden electrical shock is known as explosive.

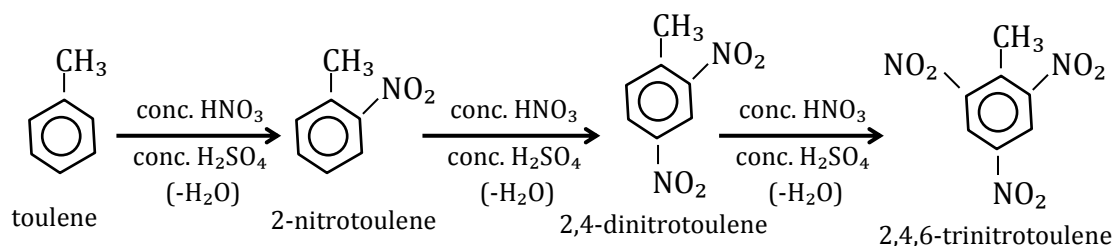
Varieties of inorganic & organic compound can serve as explosive. They are generally in the form of nitrate chlorates, peroxides, perchlorates, etc. Some of them are TNG and TNT.

TNT (trinitrotoluene)

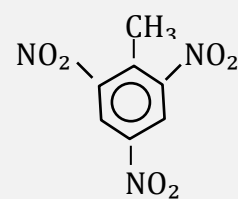
It is principal military explosive since 1920. It's economic and safe to prepare, low sensitivity to impact, high stability and low melting point make it a preferred explosive.

Preparation

It can be prepared by nitration of toluene in 3 stages.

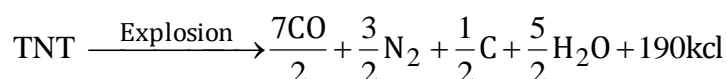


Structural Formulae



2,4,6-trinitrotoluene

Many commercial explosives contain TNT as one of their component. It decompose to give carbon monoxide, nitrogen, water(H_2O), & carbon with evolution of 190Kcal.



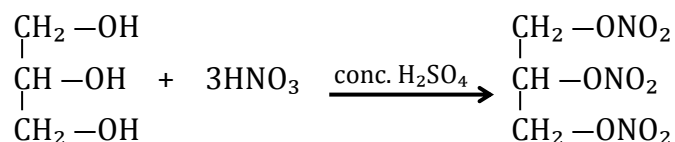
Uses of TNT

- i. It is used for shell of rocket launcher.
- ii. It is used in air bond demolition.
- iii. It is used as gun powder & as dynamite.
- iv. It is used in rock blasting, subsoil blasting.

(TNG) trinitroglycerol

Preparation

Trinitroglycerol can be prepared by nitration of glycerol with conc. HNO_3 in presence of H_2SO_4 .



In the industry glycerol is added by well stirring cooling of mixture of conc. HNO_3 and conc. H_2SO_4 ensuring that temperature of reaction mixture does not rise up to 15°C otherwise it may result serious explosion. The reaction mixture is then quenched in a large volume of water and the product is washed & and purified. It is very sensitive to electric shock and can decompose readily.

It can be absorbed on a porous material like kieselguv and safely handled. TNG has a very high freezing point 13°C and frozen TNG is less sensitive. Therefore ethylene glycol di-nitrate is used as antifreeze for use in low freezing dynamite.

Uses

- i. It is used as direct explosive
- ii. It is used as dynamite.

Application of Explosive

- i. They are used in subsoil blasting, rock blasting.
- ii. Some explosive are used to shape the material as desire shape, that are not achievable by other methods.
- iii. They are used for dislodging the coal mines.
- iv. Some explosives are used as dynamite in shell, gunpowder, etc.
- v. They are used for construction of road in hilly areas.

Cements

Introduction

The important constructive material which is employed for the construction of building, bridge, roads, tunnels, cannels, etc. is known as Cement.

It was first time introduced in England in 1924 by Joseph Aspdin. It is also called Portland cement. Since it resembles with the famous stone found near Portland in England.

Composition of Portland Cement

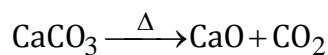
Different Types of Cement have different compositions of metal oxide. The average composition of different oxide found in Portland Cement are:

Line (CaO)	50 – 60 %
Silica (SiO ₂)	20 – 25%
Alumina (Al ₂ O ₃)	5 – 10%
Magnesia (MgO)	2 – 3%
Ferric Oxide (Fe ₂ O ₃)	1 – 2%
Sulphur trioxide (SO ₃)	1 – 2%
Sodium Oxide (Na ₂ O)	1%
Potassium Oxide (K ₂ O)	1%

Manufacture of Cement

For the manufacture of cement following materials are used.

Limestone: It provides CaO



Clay: Clay is a salt of Al₂O₃.SiO₃.FeO₃.H₂O. It supplies Silica (SiO₂), Alumina(Al₂O₃), and ferric oxide (Fe₂O₃).

Gypsum Salt: It gives the strength to the setting of the cement.

Various steps involved in manufacture of cement

Preparation of Slurry of raw meal : In the first step, lime stone is broken into small pieces and then it is mixed with paste of clay in the proper proportion (limestone 75% & clay 25%). Finally it is pulverized to fineness and made homogeneous so as to produce slurry or raw meal by adding about 40% water.

Calcination of Slurry (Formation of Clinker) : Raw meal or slurry prepared as above is allowed to introduce into the rotatory kiln with the help of screw conveyer. The rotatory kiln consists of long cylindrical 6–8 feet in diameter and 100–250 in length

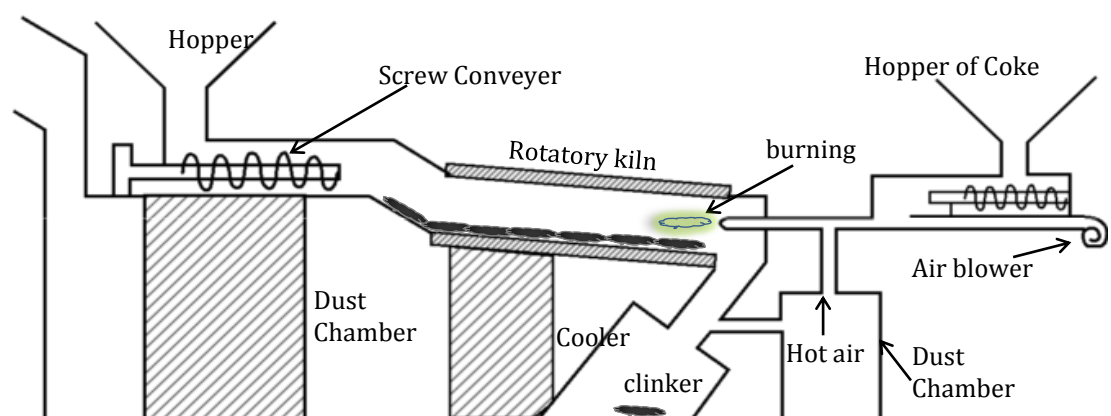
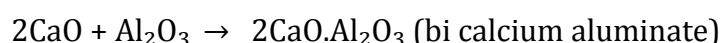
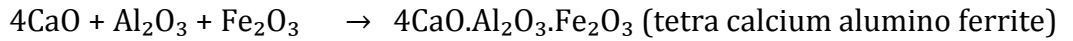
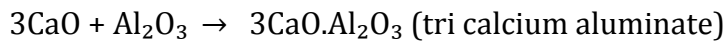


Fig : Formation of Clinker

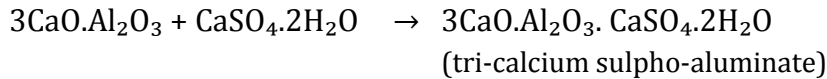
made of steel and lined inside with fire bricks. As the kiln rotates the slurry moves downward and is heated up to 1500°C by burning coal dust at the lower part of the kiln where reaction occurs to form clinker as:





The resulting mixture is then cooled in the cooler so as to get clinker.

Addition of Gypsum Salt $\text{CaSO}_4.2\text{H}_2\text{O}$: The clinker is cooled and then mixed with 2-3% of its weight of gypsum salt. It reacts with tri-calcium aluminate to give crystal of tri-calcium sulpho-aluminate



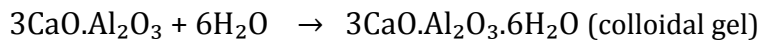
Packing of Cement : Finally thus manufactured cement is weighed and packed into packs and it is ready for selling.

Setting of Cement

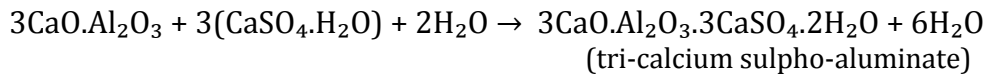
The phenomenon of changing paste of cement into hard mass and resistant pressure by allowing it to stand with water for certain period is known as setting of cement.

Setting of cement involves following reaction in different period.

Reactions in first 24 hours : When water is added to the cement tri-calcium aluminate absorbs water so as to give hydrated colloidal gel.

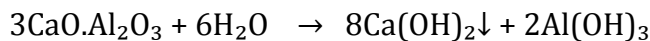
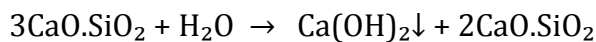


Tri-calcium aluminate which is fast setting material reacts with gypsum salt to form crystal of tri-calcium sulpho aluminate.



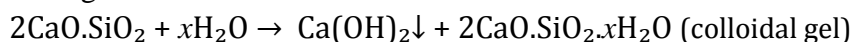
The formation of calcium sulpho-aluminate retards setting of cement and better strength in setting.

Reaction within one week : Within the seven days period tri-calcium silicate & tri-calcium aluminate gets hydrolyzed with water to give calcium hydroxide.



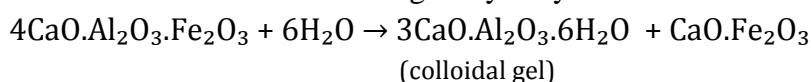
Calcium hydroxide starts to change into needle shaped crystal and aluminum hydroxide fills interstices resulting hardening of the mass.

Reaction between 7-28 days : In this period, bi-calcium silicate gets hydrolyzed to give colloidal gel.



Needle of calcium hydroxide formed above get studded in the colloidal gel to impart strength.

Tetra-calcium alumino-ferrite also gets hydrolyzed to form colloidal gel



The gel formed above start to lose water partially by evaporation and partially by forming hydrates. In this way cement set into hard mass in the construction work.