

Written by: Assist. Prof. Sulochana Pradhan

Chapter 1: Ionic Equilibria and electrochemistry

The objective of an Ionic Equilibria and electrochemistry is:

- to describe how the amounts of reactants and products change in a chemical system at equilibrium.
- to understand standard electrode potential value and how to use this value to calculate E^0 cell for a galvanic cell.
- To predict the E^0 cell for the feasibility of chemical reaction.
- To apply the Nernst equation to calculate the emf of given chemical reaction.

Lecture 1. Buffer solution and its types, Mechanism of acidic buffer solution and buffer solution with suitable examples.

Definition of Buffer solution: Buffer solution is that solution which can resist the change in PH on addition of small amount of acid or base .

Types of Buffer solution: The buffer solution are divided into two types depending upon the its PH value .If the PH of buffer solution is less than 7 , it is called acidic buffer and if it is more than 7, it is called basic buffer.Actually two common types of buffer solutions are :

- 1) A mixture of weak acid and its salt with a strong base. These are called **acidic buffer** e.g. , $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$
- 2) A mixture of weak base and its salt with a strong acid. These are called **basic buffer** e.g. , $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$

Mechanism of Acidic Buffer solution :

Let us consider the common buffer system consisting of acetic acid and sodium acetate solution.



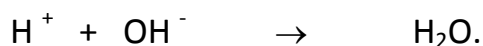
Since acetic acid is a weak acid , it slightly dissociates to give few H^+ ions and few CH_3COO^- ions in solution where as CH_3COONa being a strong electrolyte , it dissociates to form the excess of Na^+ and CH_3COO^- ions. When few drops of strong acid is added to the system, the H^+ ion in the acid will combine with the

CH_3COO^- to form the unionized CH_3COOH molecule. The reaction is



Since the addition of H^+ ions are neutralized by acetate ion, there would be no change in pH value.

When a strong base (NaOH) is added to the system, the OH^- ion combines with H^+ ion to form water. The reaction is



This reduces the H^+ ion in the buffer solution. This would result in greater ionization of acetic acid in order to restore the concentration of H^+ to its original value. The reaction is



So there is no change in pH at all.

Mechanism of basic buffer solution :



Since NH_4OH is a weak base, it slightly dissociates to form few NH_4^+ and OH^- ions whereas NH_4Cl being a strong electrolyte, it fully dissociates to give excess of NH_4^+ and Cl^- ions. When a few drops of strong acid are added to the system, H^+ ion in the acid will combine with OH^- ions to form water. The reaction is



This reduces the concentration of OH^- ion which would result in greater ionization of NH_4OH in order to restore to its original value. So the reaction is



So there is no change in pH at all.

Again when a few drops of NaOH are added to this basic buffer system, the concentration of OH^- ion will increase. So OH^- ion will react with NH_4^+ to form NH_4OH . The reaction is $\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_4\text{OH}$

Since addition of OH^- ions are neutralized by NH_4^+ , there would be no change in pH value.

Lecture 2. Calculation of pH of acidic buffer solution:

Let us consider a weak acid as HA and its salt as MA . Their dissociations are as follows. $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$ and $\text{MA} \rightarrow \text{M}^+ + \text{A}^-$. Then the dissociation constant of a weak acid can be written as

$$K_a = \frac{[H^+] \times [A^-]}{[HA]}$$

$$\text{Or } [H^+] = K_a \times \frac{[HA]}{[A^-]} \quad \text{-----(1)}$$

The weak acid slightly dissociates and its dissociation is further depressed by the addition of the salt which provides the A^- ion (common ion effect). As a result the equilibrium concentration of unionized acid is nearly equal to the initial concentration of the acid. The equilibrium concentration of A^- ion is nearly equal to the initial concentration of the salt added since it is completely dissociated into ions. So the equation (1) becomes

$$[H^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]} \quad \text{-----(2)}$$

Taking negative logarithm in both sides, we get

$$-\log_{10} [H^+] = -\log_{10} K_a - \log_{10} \frac{[\text{acid}]}{[\text{salt}]}$$

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{salt}]}{[\text{base}]}$$

This is called simply Henderson equation or Henderson - Hasselbalch equation.

Similarly the Henderson - Hasselbalch equation for basic buffer solution can be derived as $\text{pOH} = \text{p}K_b + \log_{10} \frac{[\text{salt}]}{[\text{base}]}$

Then pH can be determined applying this equation i.e. $\text{pH} + \text{pOH} = 14$.

Significance of Henderson - Hasselbalch equation :

1. pH can be calculated from initial concentration of acid and salt provided that K_a is given.

2. We have the equation

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{salt}]}{[\text{base}]}$$

When $[\text{salt}] = [\text{acid}]$, then the term $\log_{10} \frac{[\text{salt}]}{[\text{acid}]} = 0$. Therefore $\text{pH} = \text{p}K_a$ i.e., the dissociation constant of acid can be determined by measuring the pH of a buffer solution containing equimolar concentration of the acid (or base) and salt.

3. The buffer solution of desired pH can be prepared by adjusting the concentration of the salt and the acid added for the buffer solution.

Application of buffer solution :

Used to correct the pH of enzymes in many organisms to work.

Used in fermentation process.

Used in setting the appropriate condition for dyeing fabrics

Used in chemical analysis, syntheses, and calibration of pH meter.

Note : The pH of human blood is maintained at 7.4. If pH of human blood is less than 6.8 and greater than 7.8, the human death will occur. The pH is

maintained by carbonic acid and bicarbonate ion system in human blood .

Lecture 3 : Electrochemistry :

Introduction of electrochemistry : It is a branch of science which deal with relationship between electrical energy and chemical energy and inter conversion of electrical energy into chemical energy and vice versa.

Basic concept of electrochemistry :

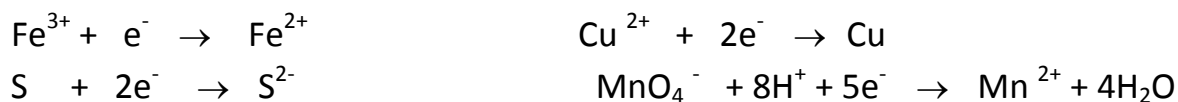
Electrolytes : electrovalent substances forming ions in solution can conduct electricity e.g. NaCl, CuSO₄, KNO₃ solution etc.

Nonelectrolytes : Covalent compounds forming neutral solution which don 't conduct electricity eg. Sugar,alcohol,glycerol.

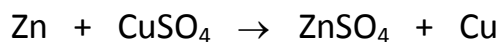
Oxidation reaction : Loss of electron is oxidation. In another word, Oxidation is a chemical reaction in which the any chemical species (atom , molecule or ion) will lose electrons in order to be oxidized e.g.:



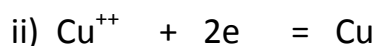
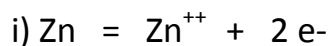
Reduction reaction :Gain of electron is reduction. In another word,oxidation is a chemical reaction in which the any chemical species (atom ,molecule or ion) will gain electrons in order to be reduced e.g.:



Redox reaction: It is a chemical reaction in which oxidation and reduction reactions occur simultaneously .In this reaction one of the substance loses e-s while other gains the same no .of electrons e.g., reaction between Zn and CuZO₄



The half reactions can be written as



The over- all balanced redox reaction is $\text{Zn} + \text{Cu}^{++} \rightarrow \text{Zn}^{++} + \text{Cu}$.

The Cell terminology :

1. Current : It is the flow of electrons through a wire or any conductor .
2. Electrode: It is the metallic rod which conducts electrons into or out of solution.
3. Anode : It is an electrode at which oxidation reaction occurs .It sends electrons into the outer circuits.

4.Cathode :It is an electrode at which reduction reaction occurs. During reduction, it receives electrons from the outer circuits.

5.Electrolyte : It is salt solution in a cell.

6.Anode compartment: It is the compartment of the cell in which the oxidation half reaction occurs. It contains anode

7.Cathode compartment : It is the compartment of the cell in which the reduction half reaction occurs. It contains cathode .

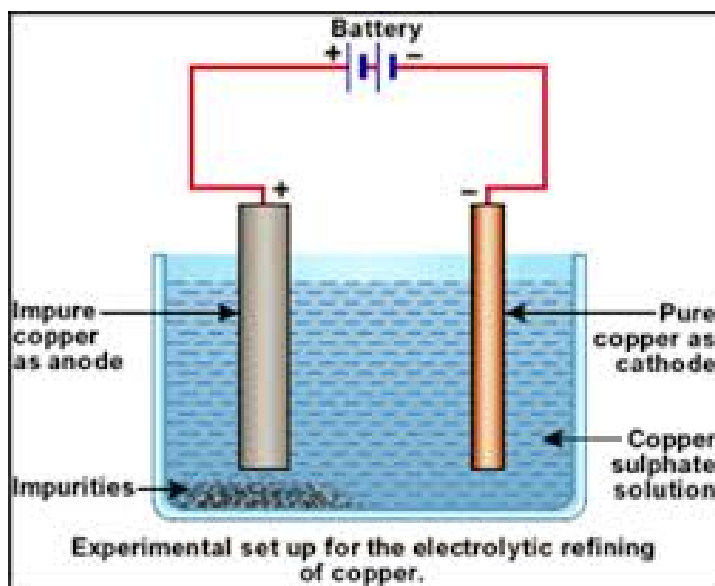
8.Half –cell: Each half of an electrochemical cell is known as half cell where either oxidation or reduction reaction occurs.

Electrochemical Cell :

It is a device for the conversion of electrical energy into chemical energy or chemical into electrical energy. It can be divided into two types a) galvanic cell and b) electrolytic cell

Galvanic cell : A device which converts chemical energy into electrical energy eg. Dry cell, lead acid battery, voltaic cell, fuel cell

Electrolytic cell : A device in which external supply of electrical energy is required in order to bring a chemical reaction e.g. Electrolysis of CuSO_4 solution between Cu electrodes and electrolytic refining of copper



The electrolysis of copper sulphate is carried in a vessel/beaker known as electrolytic cell in which two rods made up of copper are dipped into its electrolytic solution that is copper sulphate solution. Each end of the electrodes are connected to the battery. The electrode which is connected to the positive terminal of the battery is known as anode and another electrode which is connected to the negative terminal of the battery is known as cathode. Anode and cathode are made up of impure copper and pure copper respectively . When all the circuits are completed as shown in the figure,first of all the electrolyte copper sulphate dissociates into copper ion and sulphate ion.Then sulphate ion will be attracted towards anode and copper (II) ion will be attracted towards cathode. During this time, amount of energy evolved is not sufficient to oxidize the sulphate ion which is attracted to the anode.So the anode dissolves to give Cu^{2+} ion liberating the electrons .As soon as these electrons comes in contact with cathode ,these electrons are utilized to reduce copper(II) ion into metallic copper which are deposited on the cathode.So the reactions are as follows.

At anode : $\text{Cu} = \text{Cu}^{++} + 2\text{e}^{-}$

At cathode: $\text{Cu}^{++} + 2\text{e}^{-} = \text{Cu}$

In summary when copper sulphate solution is electrolyzed between copper electrodes, copper gradually dissolves and equivalent quantity of pure copper is deposited at cathode .This process is utilized in the purification of impure copper in commercial scale.

Lecture 4 Galvanic cell: A device which generates the electrical current by a spontaneous redox reaction. For this cell, let us consider the spontaneous redox reaction of zinc metal with an aqueous solution of CuSO_4 i. e. $\text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$

Explanation of galvanic cell with well-labeled diagram: This cell can be set up easily by taking two beakers, one of which contains a zinc rod dipped in 1M zinc sulphate solution and other contains a copper rod dipped in 1M copper sulphate solution. The temperature of both the beakers are maintained at 25°C . The zinc and copper are called electrodes which are connected to galvanometer by means of copper wire. The solutions in two beakers are connected to an inverted U-shaped glass tube known as salt bridge which is filled with electrolytic solution such as KCl

or KNO_3 or K_2SO_4 or NH_4NO_3 with agar agar. These chemicals do not undergo a chemical change during process. The salt bridge allows the movement of ions from one solution to other solution without intermixing two solutions. The two beaker containing metal rods, dipped in their respective salt solution are called half- cells. The reaction taking place in one half-cell is called oxidation reaction and the another half -cell is called reduction reaction. A neat and welled labeled diagram of this cell is shown in this figure. When the circuit is completed, the electrons flow from Zn to Cu electrode. As a result, Zn dissolves in anode solution to form Zn^{2+} ion i.e. $\text{Zn} \rightarrow \text{Zn}^{++} + 2\text{e}^-$ (oxidation). The Cu^{2+} ions in another half cell accepts electrons and are reduced or converted

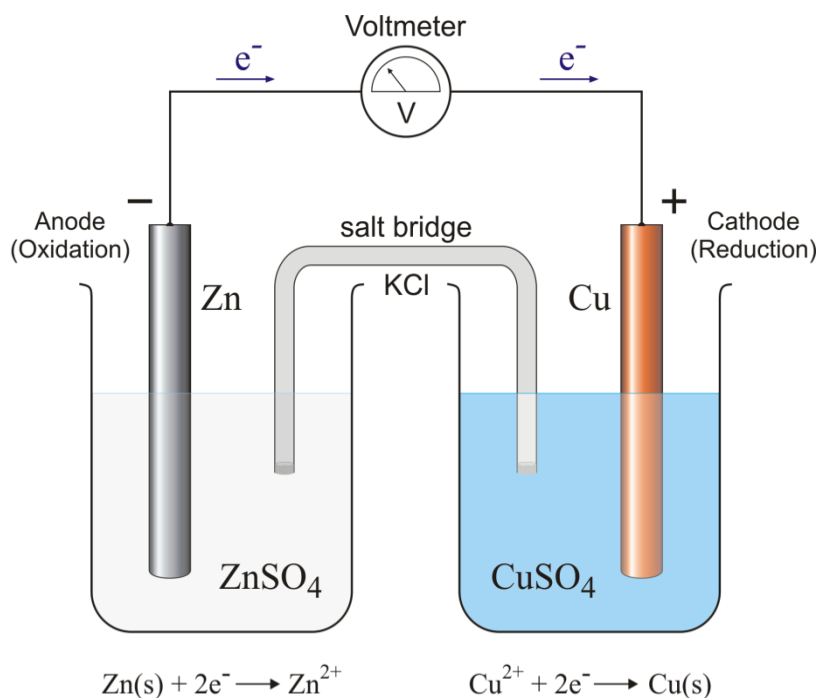


Figure : Zn /Cu galvanic cell with 1M ZnSO_4 solution and 1M CuSO_4 solution at 25°C

to Cu atoms which are deposited on Cu electrode i.e. $\text{Cu}^{++} + 2\text{e}^- \rightarrow \text{Cu}$

The over balanced redox reaction is $\text{Zn} + \text{Cu}^{++} \rightarrow \text{Zn}^{++} + \text{Cu}$

At the same time, the concentration of Zn^{2+} increases in L.H.S. and the concentration of SO_4^{2-} increases in R.H.S.beaker. So the SO_4^{2-} ions will migrate

from R.H.S. to L.H.S. beaker through a salt bridge. Likewise Zn^{2+} ions will migrate from L.H.S. to R.H.S. beaker through a salt bridge. This flow of ions from one half cell to other half cell completes the electrical circuit which ensures the continuous supply of current. The cell will operate till either the Zn metal or copper ion completely used up.

Use of salt bridge:

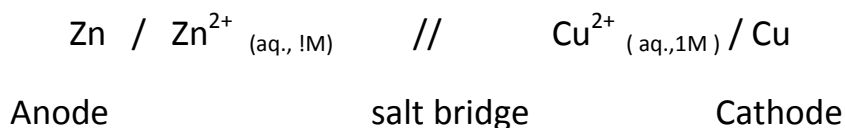
It restores the electrical neutrality of two electrolytic solutions in each half –cell. It prevents the intermixing of two solutions as well as the ions in the two halfcells. It also completes the electrical circuit.

Lecture 5

Differentiate between galvanic cell and electrolytic cell : Galvanic cell – Defⁿ, two compartments, presence of salt bridge in order to remove the accumulation of charges in each half cell, anode being –vely charged electrode & cathode being +vely charged electrode, use of two separate electrolyte.

Electrolytic cell – Defⁿ, Only one compartment, no salt bridge, anode being +vely charged electrode & cathode being -vely charged electrode, use of one type of electrolyte.

IUPAC system of representation of galvanic cell and its significance:

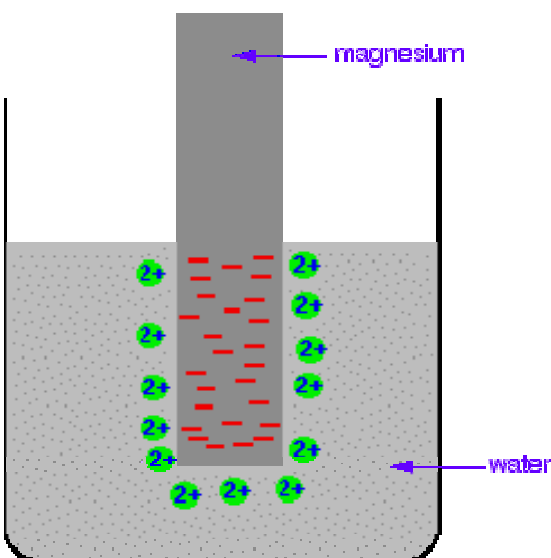


1. Anode- It is written in the extreme left hand side. When the anode is written , first of all the metal is written and then the electrolytic solution . In between metal and the electrolytic soluion, there is a one single line which is known phase boundary. T he phase boundary gives us an information that the metal is in contact with its electrolytic solution. For example : $\text{Zn} / \text{Zn}^{2+} \text{(aq., 1M)}$
2. Cathode – It is written in the extreme right hand side. When the cathode is written , first of all the electrolytic solution is written and then the metal. In between metal and the electrolytic soluion, there is a one single line which is known phase boundary. The phase boundary gives us an information that the metal is in contact with its electrolytic solution. For example : $\text{Cu}^{2+} \text{(aq., 1M)} / \text{Cu}$
3. Salt bridge - It is written in between anode and cathode. It is represented by two vertical lines. It actually separates two half cells.

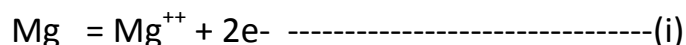
4. The half cell acting as anode in one galvanic cell may act as cathode in another galvanic cell depending upon their combination.
5. For representing a galvanic cell, anode and cathode formation are combined.

Lecture 6

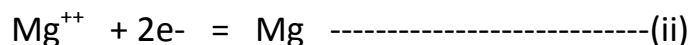
Electrode potential and EMF of a galvanic cell : experimental explanation, its def, types - oxidation and reduction potential



When the magnesium metal is taken and dipped in the 1M magnesium sulphate solution at 25°C, it undergoes oxidation reaction giving magnesium(II) leaving to the solution. So the reaction will be as



The electrons lost by the electrode would be accumulated on the metal electrode and cause the metal to develop negative charge. The negative charge developed on the electrode does not only allow metal to lose further electrons but it will reattract the metal ions from the solution to neutralize its charge immediately. So this reaction will occur as



Finally reaction (i) and (ii) will come to an equilibrium at which there will be formation of electrical double layer (or net charge separation). Due to the formation of electrical double layer, the potential difference set up between

metal and its electrolytic solution is known as electrode potential. The electrode potential depends upon the concentration of ions in solution, tendency / nature of metal to reduce or oxidize and the temperature of electrolytic solution.

Types of electrode potential: There are two types of electrode potential.

i) Oxidation Potential : It can be defined as tendency of metal to lose electrons in order to be oxidized eg: $\text{Zn} = \text{Zn}^{++} + 2\text{e}^-$: $E_{\text{oxidation}} = + 0.76 \text{ V}$

ii) Reduction Potential : It can be defined as tendency of metal to gain electrons in order to be reduced eg: $\text{Cu}^{++} + 2\text{e}^- = \text{Cu}$: $E_{\text{reduction}} = + 0.34 \text{ V}$

It may be noted that the oxidation potential is the reverse of reduction potential. For example, If the reduction potential of Zn is -0.76 volts, then its oxidation potential is +0.76 volts.

If the cell reaction is carried out under standard conditions (i.e. 25°C , 1M concentration of ions) with reference to standard hydrogen electrode(H_2 gas at 1atm. pressure, 1M H^+ ions and 25°C), the electrode potential measured is called **standard electrode potential** denoted by E° . The reduction potential under the above mentioned condition is called standard reduction potential. The standard reduction potential of standard hydrogen electrode is taken as zero. The electrode potential depends upon Nature of metal to be oxidised or reduced and its ion ,concentration of the electrolytic solution and temperature.

EMF and its expression

A galvanic cell is made up of two half cell i.e. two electrodes. One of these electrodes must have higher electrode potential than another electrode. So the electrons flow from one electrode at higher potential to another electrode at lower potential. This difference between electrode potential of two half cells constituting an electrochemical cell is known as electromotive force (EMF) or cell potential. So the EMF can be defined as driving force which causes to flow electrons from one half cell to another half cell. Mathematically it can be represented as

$\text{EMF} = \text{Reduction potential of cathode} - \text{Reduction potential of anode}$

Or $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

Since cathode is always written on the right- hand side and anode on the left- hand side,

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$

Where E_{R} stands for reduction potential of that electrode which is kept at right hand side and E_{L} stands for potential of that electrode which is kept at left hand side.

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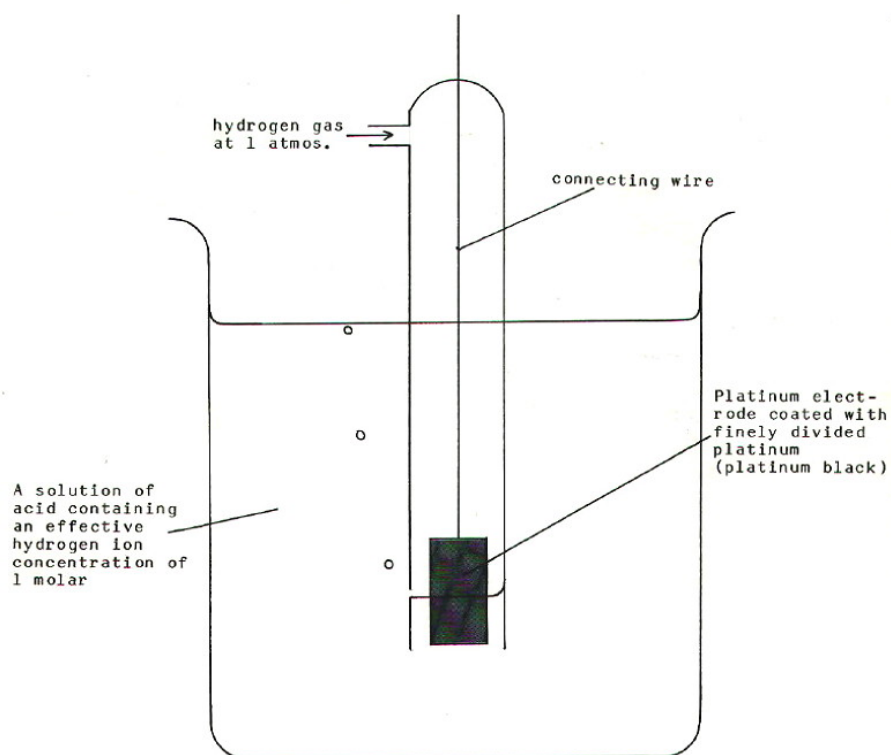
Measurement of electrode Potential :

It is impossible to determine the electrode potential of a single electrode. When two electrodes are coupled, the reaction takes place. Therefore the electrode potential of an electrode can be determined with reference to a reference electrode. The common reference electrodes are standard hydrogen electrode. The other reference electrodes are calomel electrode and silver – silver chloride electrode.

Standard hydrogen electrode :

It is a redox electrode which is widely used as primary reference electrode to determine the standard electrode potential of unknown electrode. So it is combined with unknown electrode to make a galvanic cell. It can be used either as an anode or a cathode depending upon the other electrode in a half cell.

FIG. 11.12. A diagram of a standard hydrogen electrode



It consists of platinum wire sealed in a glass tube and has a platinum foil attached to it. It is immersed in 1M HCl solution at 25⁰ C .This platinum electrode is covered by glass hood which consists of an inlet for hydrogen gas at top and a number of holes at the base for the escape of excess hydrogen gas. Pure hydrogen gas is circulated at one atmospheric pressure and is bubbled into the solution. A part of the gas is adsorbed on the surface of Pt electrode and the rest escapes through holes .This gives an equilibrium between the adsorbed hydrogen gas and hydrogen ions in the solution It acts as anode as well as cathode when it is coupled with the experimental electrode. So it depends upon the nature of new or experimental electrode. So if it acts as anode ,the half cell reaction will be : $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$.Similarly if it acts as cathode , this half cell reaction will be : $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

The cell notation of anode will be $\text{Pt}, \text{H}_2(\text{g}, 1 \text{ atm}) / 2\text{H}^+(\text{aq}, 1\text{M})$

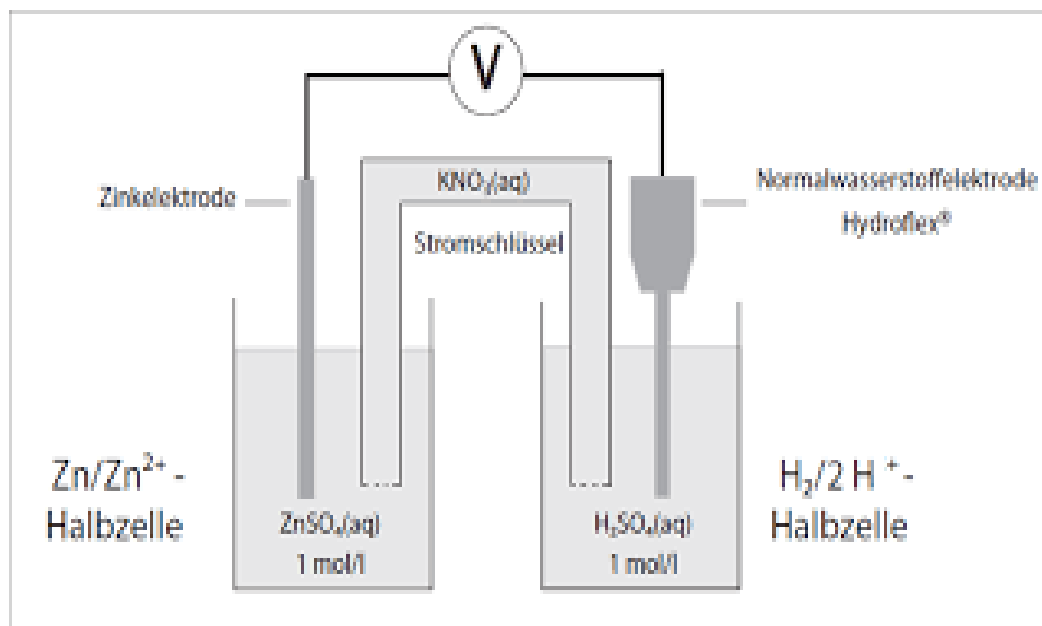
The cell notation of cathode will be $2\text{H}^+(\text{aq}, 1\text{M}) / \text{H}_2(\text{g}, 1 \text{ atm}), \text{Pt}$

The electrode potential of new electrode can be determined by coupling the new half cell with a standard hydrogen electrode.

Lecture -7 Determination of Standard Electrode potential of Zn electrode :

The standard electrode potential of Zn (which is taken as a new electrode) can be determined by constructing a galvanic cell in such a way that one half cell consists of Zn electrode and another half cell consists of standard hydrogen electrode. The zinc metal is dipped in the beaker containing 1M zinc sulphate solution and temperature is maintained at 25 °C. This constitutes the zinc half cell. The other half cell constitutes the normal or standard hydrogen electrode. Since hydrogen has greater tendency to reduce rather than zinc, the reduction reaction occurs at standard hydrogen electrode and oxidation reaction occurs at zinc half cell. As soon as all the circuit is completed, the electrons will flow from left hand side to right hand side and the following reaction will occur i.e. $\text{Zn} \rightarrow \text{Zn}^{++} + 2\text{e}^-$ and $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$

Therefore the overall redox reaction is $\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{++} + \text{H}_2$



Since E_{mf} observed in above galvanic cell is + 0.76V, the SEP of Zn can be calculated as follows. $E_{\text{mf}} = E_{\text{R}} - E_{\text{L}}$

$$0.76 = 0 - E_{\text{L}}$$

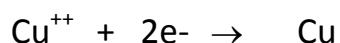
Therefore, $E_L = -0.76\text{V}$ i.e., Standard electrode potential of Zn electrode is -0.76V . That means it has less tendency toward the reduction. So the standard electrode potential of zinc electrode can be determined by coupling its half cell with standard hydrogen electrode (or commonly known as normal Hydrogen electrode) and it is found to be -0.76V . The cell notation of this galvanic cell is $\text{Zn} / \text{Zn}^{++} (\text{aq}, 1\text{M}) // 2\text{H}^+ (\text{aq}, 1\text{M}) / \text{H}_2(\text{g}, 1\text{atm}), \text{Pt}$

Determination Standard Electrode Potential of Cu electrode :

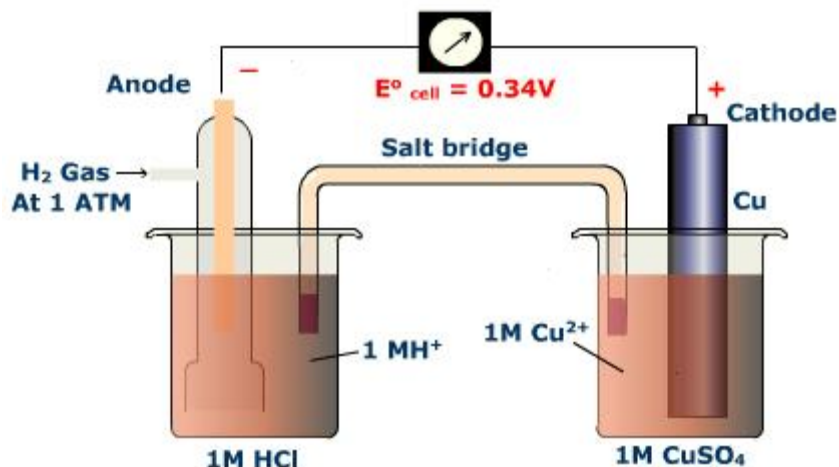
The standard electrode potential of zinc (which is taken as a new electrode) can be determined by constructing a galvanic cell in such a way that one half cell consists of copper electrode and another half cell consists of standard hydrogen electrode. The copper metal is dipped in the beaker containing 1M copper sulphate solution and temperature is maintained at 25°C . This constitutes the copper half cell. The another half cell constitutes the normal hydrogen electrode

Since copper has greater reduction potential than standard hydrogen electrode, the reduction reaction occurs at copper half cell and oxidation reaction occurs at standard hydrogen electrode half cell.

As soon as all the circuit is completed, the electrons will flow from left hand side to right hand side and the following reaction will occur



Therefore the over redox reaction is $\text{H}_2 + \text{Cu}^{++} \rightarrow 2\text{H}^+ + \text{Cu}$

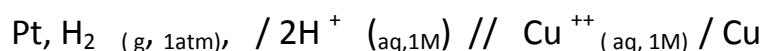


Since Emf observed in above galvanic cell is + 0.34 V, the SEP of Zn can be calculated as follows.

$$\text{Emf} = E_R - E_L$$

$$0.34 = E_R - 0$$

There fore , $E_R = +0.34\text{V}$ i.e., Standard electrode potential of Cu electrode is + 0.34 V. That means it has greater tendency toward the reduction. So the standard electrode potential of copper electrode can be determined by coupling its half cell with standard hydrogen electrode (or commonly known as normal Hydrogen electrode) and it is found to be + 0.34V. The cell notation of this galvanic cell is



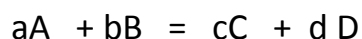
Lecture – 8

Nerst Equation : Derivation of this equation and its application.

The emf of the electrode or cell depends upon the activities of constituents (i.e. concentration of reactants and products) and the temperature of the solution.

When the activities of constituents are unity and temperature is 25^0C , the emf of electrode or cell is called standard emf or cell potential.

Let us consider the general reversible reaction.



$K_c = \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$ where a represents the activities of reactants and products. According to Vant Hoff reaction isotherm,

$$-\Delta G = RT \ln K - RT \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b} \text{-----(1)}$$

Where ΔG = Gibb's free energy

K = equilibrium constant, a = activity of components

R = gas constant

T = temperature

At standard state, the activities of all the reactants and products are unity and then free energy will be

$$\begin{aligned} -\Delta G^0 &= RT \ln K - RT \ln 1 \\ -\Delta G^0 &= RT \ln K \text{-----(2)} \end{aligned}$$

By substituting the value of $RT \ln K$ in equation (1), we get

$$-\Delta G = -\Delta G^0 - RT \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b} \text{-----(3)}$$

There is relation between Gibb's free energy and emf of the cell. So we have

$-\Delta G = nFE$ (i.e. by the system decrease in Gibb's free energy is equal to the electrical work by the system)

$$-\Delta G^0 = nFE^0$$

Where E and E^0 are the emf of the cell at certain concentration and at the standard state respectively. Again substituting the value of $-\Delta G$ and $-\Delta G^0$ in equation 3, we get

$$nFE = nFE^0 - RT \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$$

Dividing both sides by nF , we will get

$$E = E^0 - \frac{RT}{nF} \times \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$$

$$E = E^0 - \frac{2.303 \times R T}{n \times F} \times \log_{10} \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$$

$$E = E^0 - \frac{0.059}{n} \times \log_{10} \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b} \text{----- (4) nerst equation.}$$

For dilute solution, it can be written as

$$E = E^0 - \frac{0.059}{n} \times \log_{10} \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

Where $R = 8.3145 \text{ J/mol. K}$

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

$$T = 25^{\circ}\text{C} = (25 + 273) \text{ K}$$

n = number of electrons involved in redox reaction

Application of Nerst equation

It can be applied to a single electrode reaction.

It can be applied to cell reaction as a whole.

Lecture - 9

Electrochemical series: The sequential arrangement of electrodes with increasing order of standard electrode potential (i. e. reduction potential value) is known as electrochemical series. e.g.

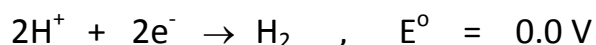


Figure: table of electrochemical series

Application of electrochemical series :

1.To predict anode and cathode e.g. $E^{\circ}_{\text{Zn}^{++}/\text{Zn}} = -0.76 \text{ V}$ and $E^{\circ}_{\text{Cu}/\text{Cu}^{++}} = +0.34 \text{ V}$
In Zn/Cu galvanic cell, Zn acts as anode and Cu acts as cathode. So it can be generalized that metals having smaller reduction potential acts as anode and metals having larger reduction potential acts as cathode in the electrochemical series.

2. Displacement of one species by other e.g. $\text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$

When zinc reacts with copper sulphate solution, it displaces copper to form zinc sulphate solution. So it can be generalized that metals having lower reduction potential can displace the metal having higher reduction potential.

The SEP of zinc has negative value which shows that it has greater tendency to get oxidized whereas the SEP of copper has positive value which shows that it has greater tendency to get reduced.

3. Calculation of standard emf of the cell :

The electrochemical cell is based on a redox chemical reaction which can be split into two half reactions. One half cell is for oxidation reaction and another half cell is for reduction reaction. For example, E°_{cell} of Zn/Cu galvanic cell can be calculated by this formula.

$$\begin{aligned}
 E^{\circ}_{\text{cell}} &= E_R - E_L \\
 &= 0.34 - (-0.76) \\
 &= 1.1\text{V}
 \end{aligned}$$

4.Spontaneity of redox reaction:

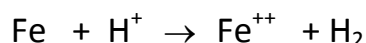
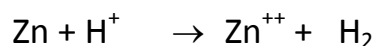
We have , $\Delta G = -nFE$

i) If $\Delta G = -ve$, i.e. $E = +ve$, then the reaction is spontaneous .Hence the cell reaction will be feasible)

li) If $\Delta G = +ve$, ie. $E = -ve$,then the reaction is non spontaneous .Hence the cell reaction will not be feasible)

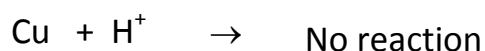
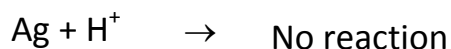
5.Prediction of reaction of metal with acids to liberate H_2 gas or not.

The metals like zinc and iron will react with dilute mineral acids to liberate hydrogen gas. For example:



So it can be generalized that metals having lower reduction potential react with dil. acid to liberate hydrogen gas. These metals are above the hydrogen in electrochemical series and they are strong reducing agent.

The metals like silver and copper will not react with dilute mineral acids to liberate hydrogen gas .For example.



So it can be generalized that metals having higher reduction potential do not react with dil. acid to liberate hydrogen gas. These metals are below the hydrogen in electrochemical series and they will act as weaker reducing agent.

6 . Determination of strength of Oxidising agent and Reducing agent

The metals/elements at the top of the table have lower reduction potential and have less tendency to get reduced. So lower the reduction potential, greater is the reducing strength of the metals /elements. $Li + K^+ = K + Li^+$

Here, Li is strong reducing agent.

The metals/elements at the bottom of the table have higher reduction potential and have greater tendency to get reduced. So higher the reduction potential,

greater is the oxidising strength of the metals /elements.

$F_2 + 2 Cl^- = Cl_2 + 2F^-$ Here, F_2 is strong oxidising agent.

7. To construct a galvanic cell: A galvanic cell is constructed by the combination of any two redox couples or half cells given in electrochemical series. If the standard electrode potential of these two half cells chosen are greatly separated, then there will be greater cell emf so that reaction will be easier.

e.g. Zn/Cu , Zn / Ag , Mg/Cu

Lecture 10

Corrosion - The gradual disintegration of metal by chemicals or electrochemical reactions with environment is known as corrosion e.g. rusting of iron i.e.

$Fe_2O_3 \cdot xH_2O$ (red brown precipitate or hydrated ferric oxide) .

Causes of corrosion: Most of the metals are found in combined state(ie. oxide , sulphide, carbonate, chloride or silicate) as their minerals. These minerals are more stable than metals. The pure metals are obtained from the extraction process in which lot of energy is used. As the energy is consumed in this process, it shows that the metals are in higher energy state than minerals. So if the metal is not alloyed immediately, it has natural tendency to revert back to its stable and natural combined form.

Minerals	=====	pure metal
(natural & stable state)		(Unstable state)
Lower energy state		(higher energy state)
(O^{2-} , S^{2-} , CO_3^{2-} , Cl^- , SiO_3^{2-})		

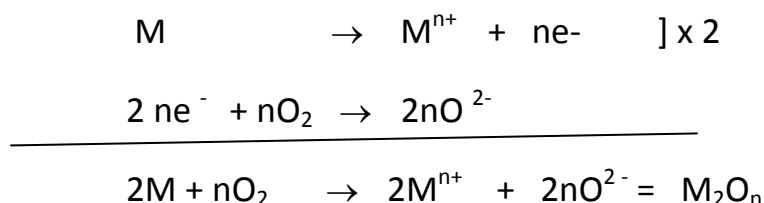
Consequences of Corrosion :

- plant shut down due to any failure in the system
- replacement of corroded equipment
- preventive maintainace (eg painting)
- loss of efficiency
- contamination or loss of products
- safety rules
- Health hazard.

Theories of corrosion

1.Direct chemical attack : It is a dry corrosion in which metal is attacked by dry

gases at high temperature to form oxide layer except Ag, Au, & Pt. Metal can form porous or non porous oxide layers. The reactions are as follows.



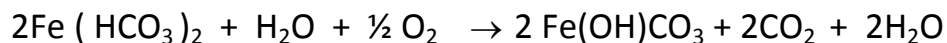
Mechanism of direct chemical attack:

First of all, oxygen molecule is adsorbed on the surface of metal by physical adsorption. In nature when the temperature of environment rises, the physical adsorption turns into chemical adsorption. During chemical adsorption, metal atom gets oxidized to metal ion and the electrons are taken by oxygen molecule and reduced to form oxide ion. Finally the metal ion and oxide ion combine to form metal oxide.

2. Acid theory: According to this theory, the rusting of iron occurs in presence of moist air as well as carbon dioxide converting metal into a soluble ferrous bicarbonate which is further oxidized by moist air to basic ferric carbonate and finally to hydrated ferric oxide. The reactions are as follows.



Ferrous bicarbonate



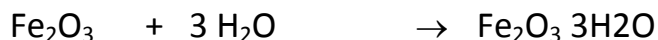
Basic ferric carbonate



Ferric hydroxide.

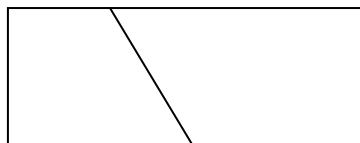


Ferric oxide



Hydrated ferric oxide

3. Electrochemical theory: This theory is most advanced and convincing theory. According to this theory, corrosion is electrochemical process in which rusting of iron occurs in presence of moist air. The reactions are as follows.



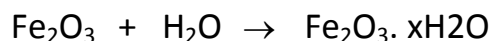
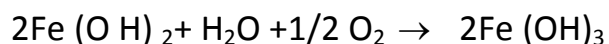
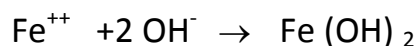
At anodic area,
 $\text{Fe} \rightarrow \text{Fe}^{++} + 2\text{e}^-$

(anodic product)

At cathodic area,
 $\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$

(cathodic product)

Once the anodic and cathodic product are formed, they migrated together to form the ferrous hydroxide which is further oxidized by moist air to form ferric hydroxide. The ferric hydroxide decomposes to give oxide which absorbs moisture from atmosphere to form brown rust. Thus rusting of iron can be well explained with help of this theory. The reactions are as follows.



Classification of corrosion : 3 types

(a) On the basis of nature of corrodent :

i) dry corrosion eg; direct chemical attack and ii) wet corrosion eg; electrochemical theory, acid theory

(b) On the basis of mechanism of corrosion

direct chemical attack and ii) indirect chemical attack

i)

(c) on the basis of appearance of corroded metal

i) Galvanic corrosion – It is wet corrosion where electrochemical reaction occurs.

It occurs when two metals in contact are exposed to a conducting solution. Larger

the reduction potential difference between metals, greater will be the galvanic corrosion. Anodic area will be less than cathodic area.

ii) Erosion corrosion – It is corrosion in which the movement of corrodent occurs. The main cause of corrosion is the removal of protective surface layer.

iii) Crevice corrosion – It is corrosion produced in between metal and metal or metal and non metal due to deposition of dirt, debris, corrosion products, cracking in coated area.

iv) Pitting corrosion - It is a localized corrosion in which there is formation of holes due to the cracking of protective layer on the surface of metal.

v) Stress corrosion – It is due to the combined effect of mechanical stresses and corrosive environment during manufacture of alloy (eg. Rolling and drawing etc.)

vi) Microbiological corrosion- It is the deterioration of materials caused by microbes like bacteria, algae, fungi, moulds etc. They may come singly or in combination. If microbes grow in presence of oxygen, this condition is called aerobic condition. Another if they grow in absence of oxygen, this condition is known as anaerobic condition. In aerobic condition, the aerobic bacteria (i.e. oxygen consuming bacteria) will consume the oxygen when it is in contact with metals. They will produce their metabolites as mineral acids or organic acids along with ferric oxide and ferric hydroxide during corrosion. Anaerobic bacteria will not grow even in traces of oxygen. They will produce their metabolites as black corrosive products with strong smell of hydrogen sulphide gas, ferrous sulphide and ferrous hydroxide.

vii) Intergranular corrosion- It occurs in alloy due to the heat treatment (i.e. welding)

Preventive measures of corrosion.

Galvanization – It is process of coating the sheet of iron by thin layer of Zn or Mg which are highly electropositive metals. It takes a long time to corrode the iron sheet rather than zinc or magnesium.

Tin plating - It is process of coating the sheet of iron by thin layer of tin which is less electropositive. It takes long time to corrode the tin rather than iron sheet.

Application of edible oil, grease, enamel and paints - These things can be applied on the surface of different objects depending upon their specific use.

Use of sacrificial anode - The sacrificial anodes are Zn and Mg. Since they are

being highly electropositive metal, they are connected to the large ships, underground tanks, underground pipe lines etc. as a sacrificial anode. During this time, instead of oxidising these large materials, the sacrificial anode will undergo oxidation and it can be easily replaced to preserve these large things. So it is very cost effective.

Natural formation of protective oxide layer $\text{--Al}_2\text{O}_3$ is very hard, inert toward O_2 , H_2O and other corrosive reagent. So once this oxide layer is formed on the surface of metal, it acts as a protective oxide layer.

Chapter 6: ANALYTICAL CHEMISTRY

The objective of an analytical chemistry is

- to identify the chemical components of various substances.
- to identify and isolate the chemical elements and compounds for research or informational purposes.
- to perform qualitative analysis.

Introduction and application of following analytical techniques : Fractional distillation , Chromatography (paper, thin layer), Nuclear magnetic resonance,

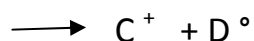
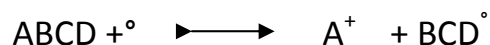
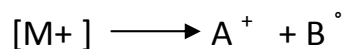
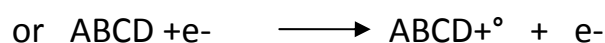
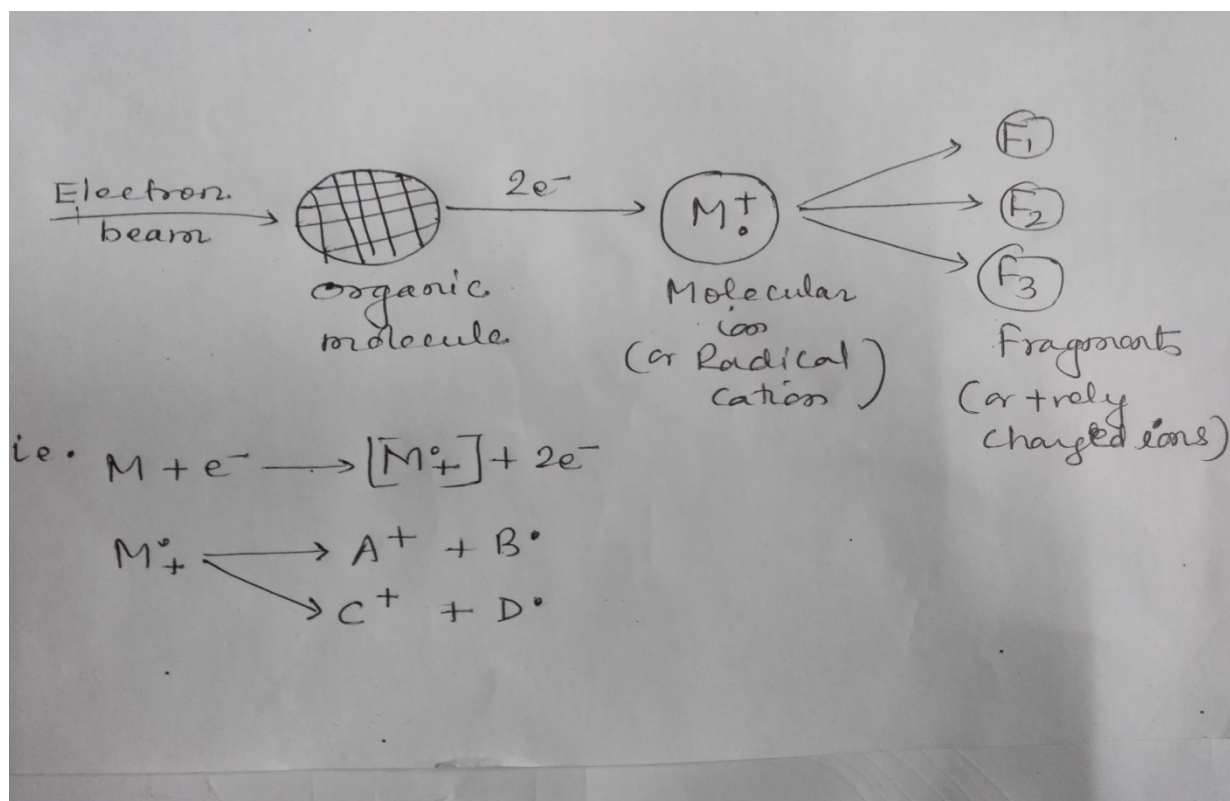
Mass Spectroscopy

Introduction :- It is versatile technique to determine the composition of chemical species(i.e. organic and inorganic compounds) either at atomic or molecular level

-High cost instrument

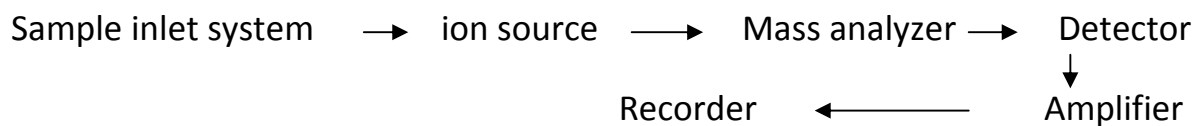
-More precise than chemical method

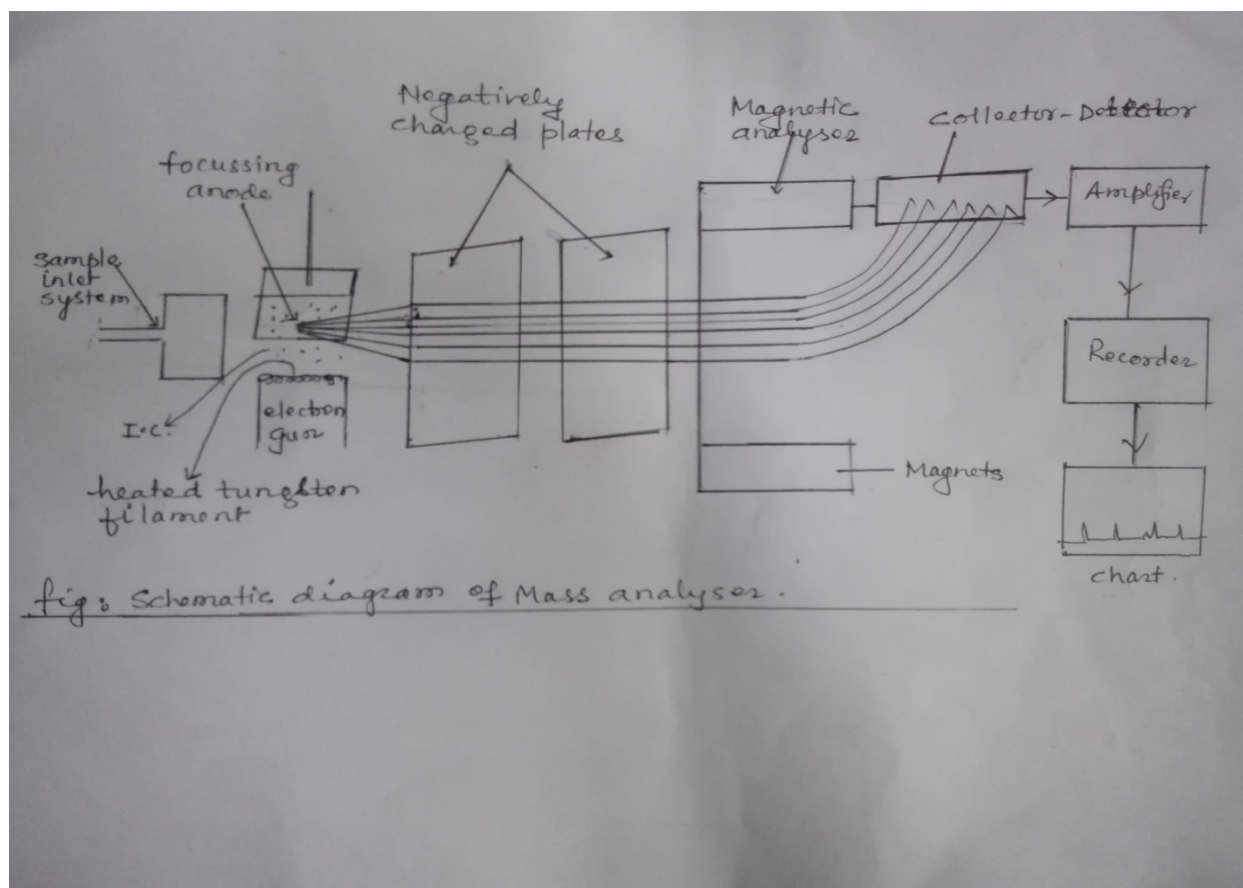
Basic principle :- In mass spectroscopy, the sample is vaporized as well as bombarded with a beam of electrons (having high energy) which collide with sample molecules to produce positively charged radicals cation (or molecular cation or radical cation having unpaired electron and positive charge) . Since this radical cation being highly energetic, it may further undergo fragmentation producing small fragments.



When these positive ions (i.e. fragment ions) are accelerated in electrical field, they are separated in magnetic field on the basis of m/z ratio where m = mass of ion and z = charge of ion. The ions with particular m/z ratio are detected by a detector. Then the detector output (i.e. electrical signal) is amplified and recorded as a band in the spectrum.

Basic Instrumentation and procedure of mass spectroscopy:





Procedure:

1. **Inlet system:** First of all, the sample enters into ionization chamber so that sample is converted into gaseous state.
2. **Ion source:** It is a source of ionization which refers to an electron gun. It produces the beam of electrons. The ionization of sample is mostly carried by using **electron impact** (i.e. electron ionization is harder than chemical ionization).
3. **Mass analyzer:** It consists of three components. These are ionization chamber, negatively charged accelerating plates and magnetic analyzer.
 - (i) **Ionization chamber** consists of tungsten filament which emits electrons. These electrons are accelerated across a small chamber between filaments and focusing anode. During electron ionization, the bombardment of vapour sample produces molecular cation which will further produces fragment ions.
 - (ii) The ions generated in ionization chamber are accelerated in the electrical field in presence of negatively charged plates by accelerating the ions of different masses (i.e. m_1 and m_2 etc.) to their final velocities (or high velocities) and to gain final kinetic energy.

Finally the fragment ions can be easily separated from negative as well as neutral particles. (iii) From negatively charged accelerating plates, the fragment ions are passed through the magnetic analyzer in which a magnet is used which reflects them in a curved path. By varying the magnetic field, ions of different masses (i.e. fragment ions) can be recorded.

4. Collector – Detector: The fragment ion with particular m/z value will be converted into an electrical signal.

5. Amplifier and recorder: Then the electrical signal is amplified by amplifier and then graphically recorded in a recorder. Finally the graph between m/z value and relative abundance is plotted to analyze the sample.

Application of mass spectroscopy:

- i. To find out the exact mass of molecular masses of organic compound.
- ii. To find out the structure determination of organic compound.
- iii. To elucidate the structure of organic and biological molecules.
- iv. To identify the components in TLC and paper chromatography.
- v. To analyze the petroleum products.

Note: Most elements are found naturally as several isotopes. Generally the lightest one predominates over the heavier ones eg.

Isotopes	% of natural abundance
^{12}C	98.93
^{13}C	1.07
^{35}Cl	75.77
^{37}Cl	24.23

Nuclear Magnetic Resonance (NMR) spectroscopy:

Introduction of electromagnetic radiation: All types of electromagnetic radiations travel with the same speed as the velocity of light but they have different wavelength. Since we have this relation, i.e. $\nu = c/\lambda$, frequency

of electromagnetic radiation decreases with increasing wavelength. So the radiowaves are least energetic and cosmic rays are highly energetic.

Definition of NMR : NMR stands for nuclear magnetic resonance where nuclear transition occurs by the absorption of electromagnetic radiation in radio frequency region.

Basic principles of NMR:
1. Spinning proton acts as a tiny bar magnet:

Hydrogen having one proton in its nucleus spins along its own axis. The spinning of proton produces a circulating electric current which in turn produces magnetic field. So the spinning proton acts as a tiny bar magnet.

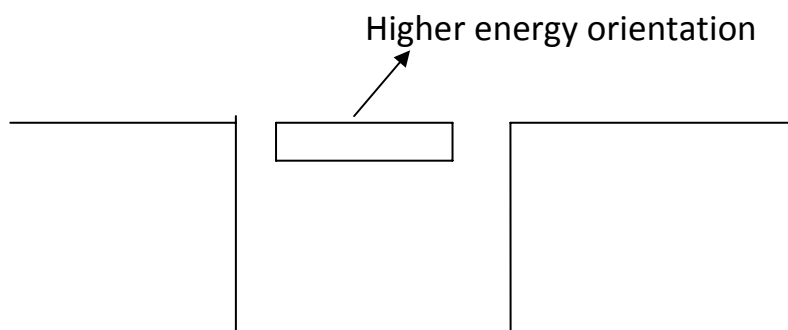
2. Nuclear spin: The principle of NMR is based on the fact that if the nucleus contains odd no of protons or odd no of neutrons, it has the property of nuclear spin. So the nucleus of such atom has nuclear spin. According to quantum mechanics, all sub atomic particles like proton, neutron and electrons have their spins. For example; ^1H , ^{13}C and ^{19}F nuclei have spin. But ^{12}C and ^{16}O nuclei do not have spin.

3. Types of spin due to neutron and proton:

- i) If any nucleus has even number of protons and even number of neutrons, it has no spin.
- ii) If the sum of protons and neutrons of nucleus is odd, it has a non integer spin (i.e. $1/2$, $3/2$, $5/2$ etc).
- iii) If the number of protons and neutrons are both odd, the nucleus has an integer spin (i.e. 1, 2, 3.....etc).

4. Energy orientation of proton:

When a proton/nucleus is placed in a magnetic field, it produces induced magnetic field which can align along the applied magnetic field or oppose the applied magnetic field. That means the proton may have either lower energy orientation or higher energy orientation.



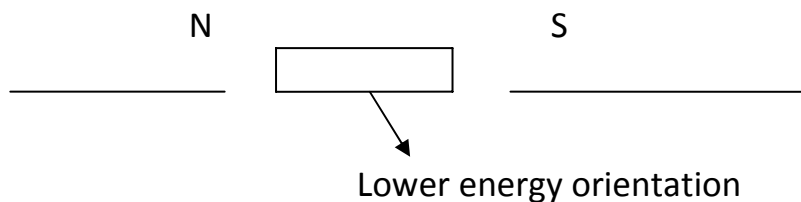


Figure : Energy orientation of nucleus

When the magnetic field of nucleus and the applied magnetic field are in the same direction, it is said to be lower energy orientation of nucleus. In other words, lower energy orientation of nucleus is the state of nucleus in which the magnetic field of nucleus is in the same directions as the direction of applied magnetic field. When both magnetic field opposes each other, it is said to be in higher energy orientation of nucleus.

5. Transition:

When the proton moves from lower state to higher state, a transition will occur. And there will be certain energy difference between these states. When the energy corresponding exactly to the energy gap between these states is absorbed by the nuclei, the nuclei are said to be in resonance with applied radio frequency. Hence this spectroscopy is known as NMR.

6. Energy:

The energy is based upon the magnitude of applied magnetic field. So the external magnetic field can be chosen to give absorption of electromagnetic radiation in a suitable part of spectrum.

7. Working principle of NMR:

When radiofrequency of 60 MHz (ie. 60 million cycles /second) is kept constant and the magnetic field is varied, nuclei or protons will absorb energy. The energy absorbed in this process produces a signal at the detector which after amplification is recorded as a band in the spectrum.

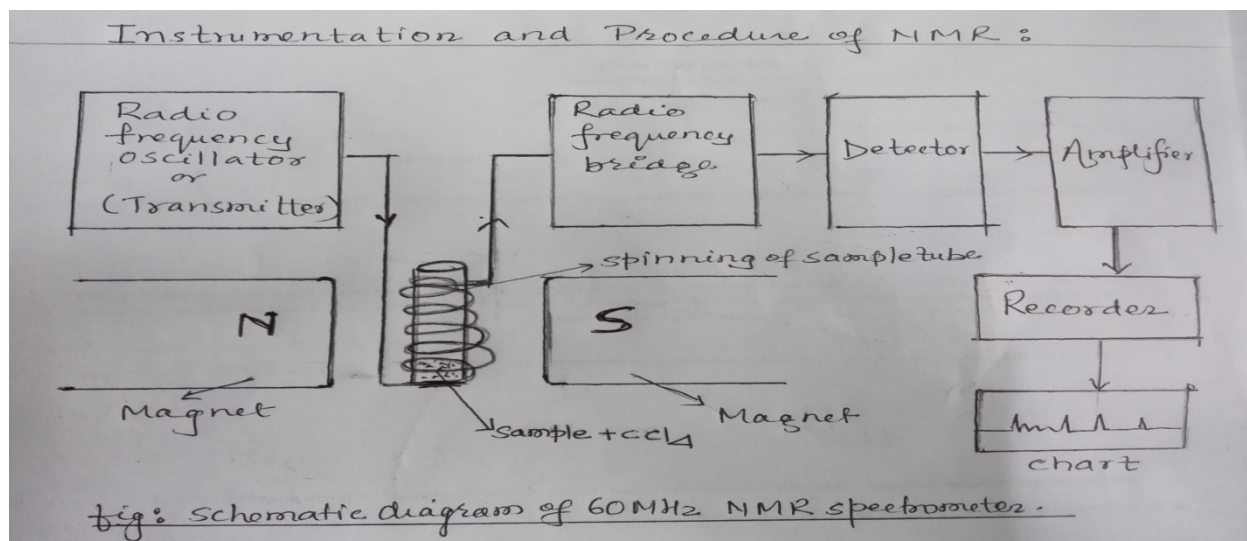
Instrumentation and procedure :

- i) The NMR spectrometer consists of magnets, radiofrequency source, detection system and recording device.
- ii) First of all, the sample is dissolved in suitable solvent and sample tube is placed in between the strong poles of magnet.

iii) The sample tube is held in such a way that all the nuclei of a sample can experience or feel a uniform magnetic field.

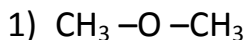
iv) Most commonly when the radio frequency of 60 MHz is kept constant and the magnetic field is varied, nuclei or proton will absorb energy. The energy absorbed in this process produces a signal at detector.

v) Finally that resulting electrical signal is amplified by amplifier and recorded on recorder.



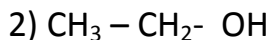
Understanding of the application of NMR:

NMR is determined by the nuclear properties and chemical environment of protons. That means the NMR depends on the total number of equivalent and non equivalent protons in the particular compounds. The equivalent protons are in structurally and chemically equivalent position in the molecule. For example:



1 signal

(Dimethyl ether)

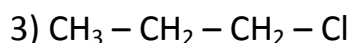
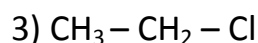


3 signals

(Ethyl chloride)

Because of one equivalent proton

because of three nonequivalent protons



2 signals

(ethyl chloride)

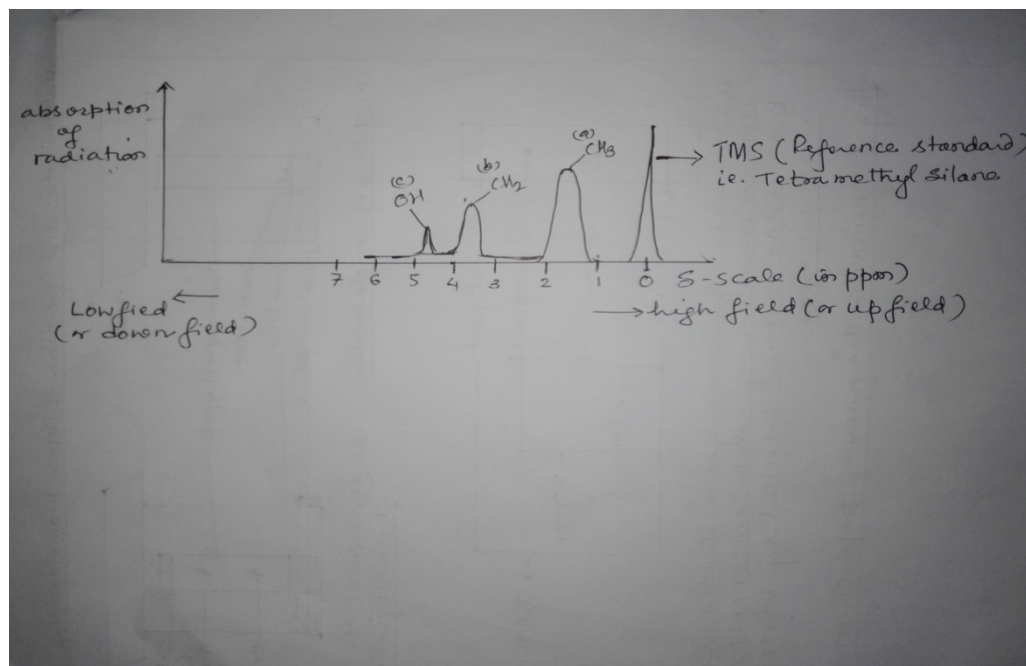
Because of two non equivalent protons

3 signals

(propyl chloride)

because of 3 non equivalent protons

Illustration of NMR spectrum of ethyl alcohol in low resolution:



Information Regarding NMR signal:

1. No. of peak or No. of signal refers to no. of different types of protons.
2. Position of each signal refers to the chemical environment of each kind of protons. For example: Ethanol contains three kinds of protons in - CH₃, -CH₂, -OH groups.
3. The relative area of peak refers to the intensities of the signals which depend upon the no. of protons in each kind.
4. Splitting patterns refers to the splitting of a signal into several peaks which depends upon the environment of a proton with respect to other nearby protons.

Chemical Shift :

Definition of chemical shift : It is defined as shift in position of signal or peak from TMS (due to a small change in chemical environment).

When a molecule is placed in a magnetic field, its circulating electric current produces the induced magnetic field. Then induced magnetic field may either oppose the applied magnetic field or align the applied magnetic field.

1. Oppose the applied magnetic field:

When the induced magnetic field oppose the applied magnetic field, the protons is said to be **shielded** (because the effective field experienced by proton is decreased). So the shielded protons give the absorption peak in up field. This effect is called **diamagnetic effect**. It means **more amount of energy** is required to bring this nucleus in the resonance.eg; acetylene protons.

2. Aligned the applied magnetic field :

When the induced magnetic field aligns the applied magnetic field, the proton is said to be deshielded (because the effective field experienced by proton is increased). So the deshielded protons give the absorption peak in down field. This effect is known as paramagnetic effect. It means less amount of energy is required to bring the nucleus in the resonance.

Expression of chemical shift :

The chemical shift is measured with rest to standard i.e. TMS and expressed in delta units.

Mathematically it is represented as

$$\delta = \frac{\nu_s - \nu_0}{\nu}$$

ν_s = frequency of the sample
 ν_0 = frequency of TMS
 ν = operating frequency

Use and application of NMR:

- In structure determination of organic compounds
- In chemical composition determination
- In compound identification and confirmation
- In sample purity determination

Fractional distillation :

It is a technique for separating a mixture of two miscible liquids with almost same boiling point eg. Mixture of water and alcohol, mixture of hydrocarbons in crude oil. It is most important process of crude oil refining in which boiling point difference between two liquids is less than 10°C .

Principle of fractional distillation :

When the mixture of two liquids are heated to a high temperature, the mixture boils forming vapour. The vapour enters fractionating column. As the vapour rises through the fractionating column, it cools and the vapour of the boiling mixture gradually becomes richer in the lower boiling point components. Then it will condense to form a liquid. And the collected liquid is passed into condenser which cools it further and finally collected in a receiver.

So it is based upon the principle of rectification in which the evaporation is followed by condensation. The fractionating column provides a large surface area for multiple condensation and evaporation to occur as the liquid ascends the column .

Instrumentation and Procedure for fractional distillation

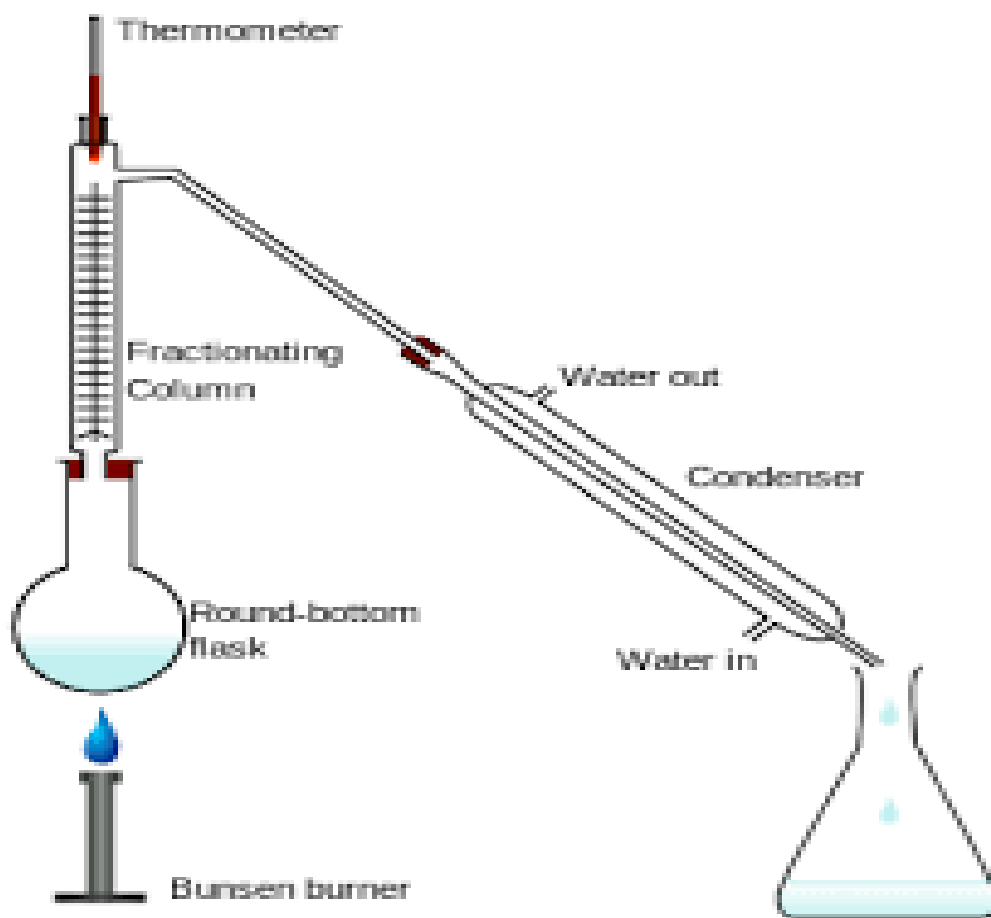


Figure : schematic diagram for fractional distillation.

The round bottom flask is fitted with two third volume of given mixture to be separated. About few pieces of porcelain chips should be added to prevent explosion reaction or bumping. Then round bottom flask containing mixture is connected to a fractionating column in which thermometer is kept to maintain the temperature constant. The fractionating column is further connected to the simple condenser which has an inlet and outlet. The inlet is joined to tap through rubber pipe. An outlet is connected to rubber pipe and left free to flow hot water after circulation through the condenser. So there must be continuous and steady flow of water to condense the fractions. When all the apparatus are ready and fitted as shown in the figure, distillation should be started. The heating is continued until there is small amount of mixture liquid left in round bottom flask. Lastly different fractions can be obtained condensing the vapour drawn from different levels of column.

Uses of fractional distillation

It is used

to prepare ethanol (95 % ethanol and 5% water) ,

to separate components in crude oil refining ,

to separate cyclohexane (b.pt.= 80°C) and toluene (b.pt.= 110°C) from a given mixture ,

to separate the ethanol(b.pt.= 78.5°C) and water (b.pt.= 100°C) etc

Chromatography

Introduction: Most organic compounds are not pure where they are obtained from natural sources or synthesized .So these compounds are purified by various methods. The method of purification are based on the nature of compounds and the impurities present in it.

Definition of chromatography: Chromatography is one of the most important separation technique used to separate mixture into their components and used to purify the compounds.

In greek, chroma means colour and graphein means to write. So chromatography means colour writing which is first employed by Russian scientist ,Mikhail Tswette in 1906. **In chromatography technique**, the phase in which the mixture of substance is applied is called stationary phase. The stationary phase may be solid or liquid. A moving phase that can be a pure solvent or gas, is allowed to move over the stationary phase. This moving phase is called mobile phase. When the mobile phase is moved over the mixture on the stationary phase, the components of the mixture gradually separates from one another.

Classification of chromatography:

Depending on the basic principle involved in chromatography , it is mainly classified into two types. (a) adsorption chromatography and (b) partition chromatography.

(1)Adsorption chromatography: It is based on the differential adsorption of compounds on the adsorbent (i.e. stationary phase).This means the different

compounds are adsorbed on the adsorbent at different degrees. So depending upon the differential adsorption, it is again divided into two types. These are column chromatography (CC) and thin layer chromatography (TLC)

(2) Partition chromatography: It is based on the distribution of sample mixture between two immiscible liquid phase i.e. stationary and mobile phase. For example: paper chromatography.

Thin Layer Chromatography (TLC):

Definition of TLC: Thin layer chromatography is another type of chromatography which involves the separation of a mixture over a thin layer of an adsorbent coated in a glass plate.

The principle of TLC

In this technique, there are two phases (a) stationary phase: the stationary phase is a glass plate coated with thin layer of silica gel or alumina. This plate is called chromatoplate. (b) mobile phase: The mobile phase is pure solvent or mixture of solvents.

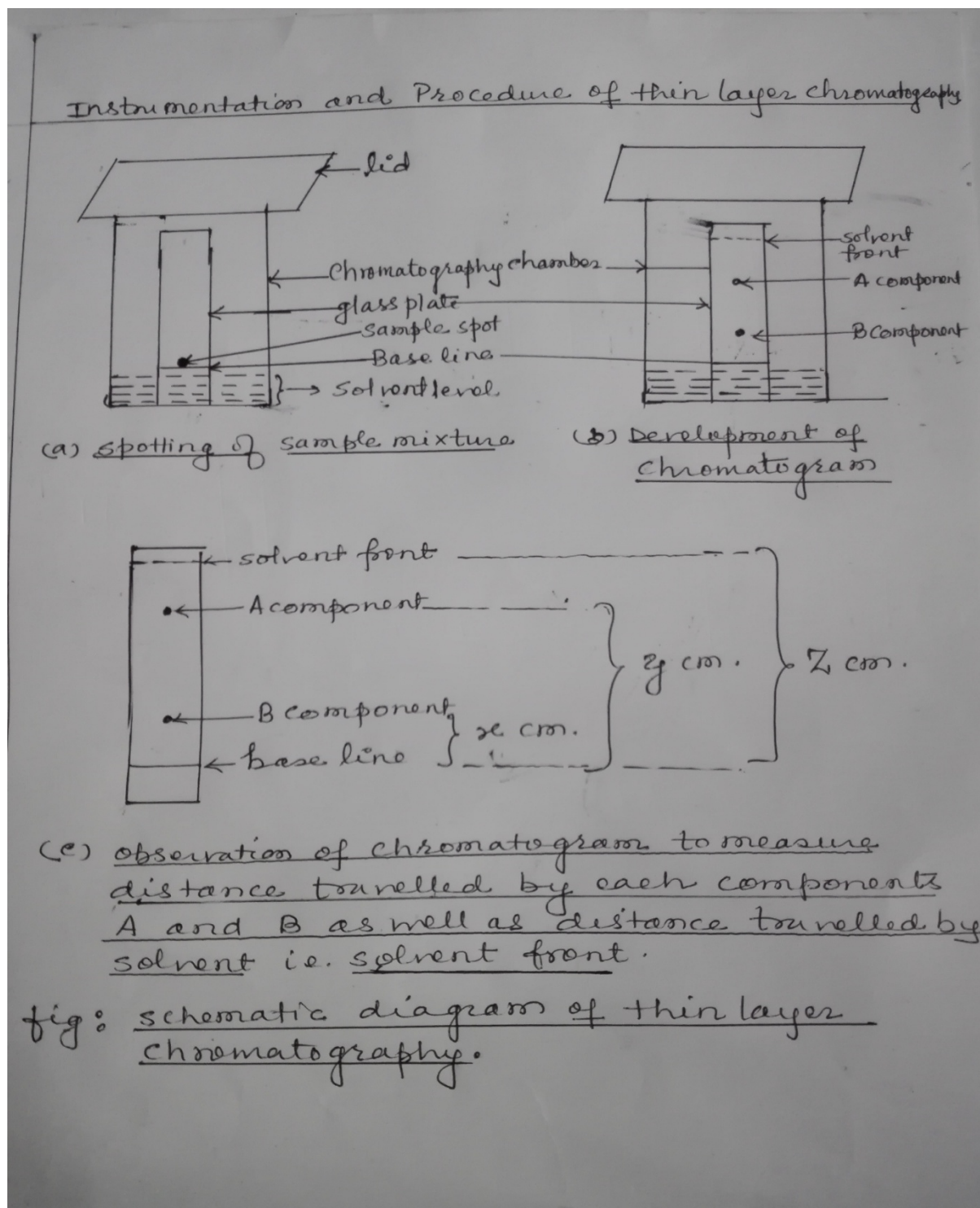
The sample to be separated is applied a spot above 2cm above from the bottom of TLC plate called base line. The glass is then placed in a closed jar (chromatography chamber) containing mobile phase. As the mobile phase rises up the plate by capillary action, the components of the sample mixture move up along with the solvent to different degrees which depends on the adsorption and solubility of the components. The spots of separated coloured components may be observed in chromatogram due to their original colour. If the compounds are colourless, they can be visualized under UV or Iodine vapour or by using any appropriate spraying reagent. The relative adsorption of each component of the sample mixture is expressed in terms of its retention factor (R_f). The R_f is defined as ratio of distance travelled by the component from the base line to the distance travelled by the solvent from the base line. So mathematically, it is expressed as follows.

$$R_f = \frac{\text{Distance travelled by the component from base line}}{\text{Distance travelled by the solvent from base line}}$$

Distance travelled by the solvent from base line

This technique is simple, rapid and cheap.

Instrumentation and procedure of thin layer chromatography:



Procedure: First of all, a slurry of silica gel is made in a beaker and it is spread over a thin plate of glass. Thus coated glass plate is now allowed to dry in oven and is ready for use. A horizontal line known as a **base line** is drawn about 2cm above from the bottom of TLC plate with the help of a pencil. The sample is applied as a small drop at the centre of the base line and this glass plate is kept in a chamber (i.e. beaker containing suitable solvent) in such a way that the sample spot is just above the surface level of solvent in the chamber. The chamber is sealed with a lid to prevent the evaporation of solvent. As the solvent travels up the coated glass plate, it moves the components of the mixture at different degrees. Then there is result of separation of the components of sample mixture known as **chromatogram** by the ascending technique as it is immersed in the solvent. The development of chromatogram is allowed to proceed until the solvent front has travelled the required distance. Then this plate is removed from the chamber and solvent front reached is marked with the pencil. At the same, distances travelled by different components are also marked with the pencil and these distances travelled by solvent and components are measured in centimeter. Then this plate is allowed to dry simply in lab temperature. Then finally the R_f value of each component are calculated using the given formula.

Uses and application of TLC

It is used

- to determine the purity of sample
- to identify and isolate the natural products like volatile oil/ essential oil, alkaloids, steroids etc.
- to examine the reaction mixture that whether the rxn is complete or not.

Advantage of TLC:

- less equipment is required
- very little time for separation is required .
- very small amount of sample is sufficient
- More sensitive

Paper chromatography

Definition : It can be defined as analysis of unknown substance by the flow of solvent on a chromatographic paper .It is based partly on adsorption and partly on distribution.

The principle of TLC

In this technique , there are two phases (a) stationary phase : the stationary phase is a special quality paper i.e. chromatographic paper. (b) mobile phase : The mobile phase is pure solvent or mixture of solvents.

The sample mixture is spotted on a line 2cm above from the bottom of paper called **base line**. This paper is suspended in a chromatographic chamber containing suitable solvent. The solvent rises up the paper by capillary action and flows over the spot. As solvent travel / rises up the paper , it carries the components of mixture at different degrees and causes them to separate. The paper strip so developed is called chromatogram in which spots of separated coloured compounds are visible at different distances from base line. The spots of separated coloured components may be observed in chromatogram due to their original colour. If the compounds are colourless , they can be visualized under UV or Iodine vapour or by using any appropriate spraying reagent. The relative adsorption of each component of the sample mixture is expressed in terms of its retention factor (R_f) . The R_f is defined as ratio of distance travelled by the component from the base line to the distance travelled by the solvent from the base line .So mathematically, it is expressed as follows.

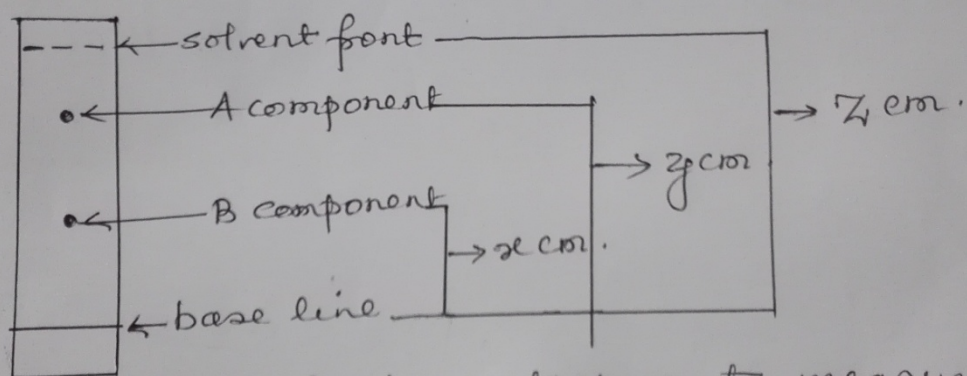
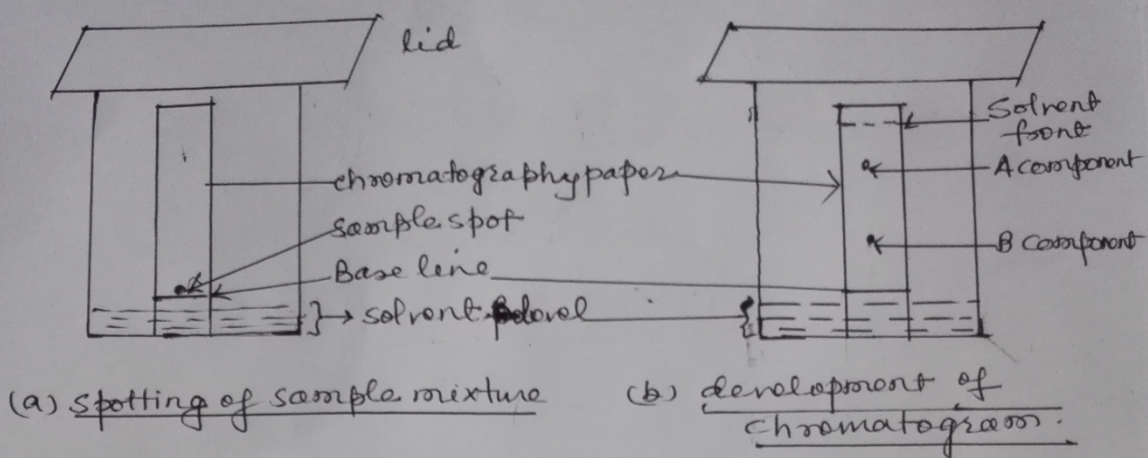
$$R_f = \frac{\text{Distance travelled by the component from base line}}{\text{Distance travelled by the solvent from base line}}$$

Distance travelled by the solvent from base line

The type of paper chromatography in which the solvent rises up is called ascending paper chromatography. Alternately the solvent may be taken on the top in a container and be allowed to come down in which it is termed as descending paper chromatography.

Instrumentation and procedure of paper chromatography:

Instrumentation and Procedure of Paper chromatography



(c) observation of chromatogram to measure distance travelled by each components A and B as well as distance travelled by solvent i.e. solvent front.

Fig: schematic diagram of paper chromatography

A horizontal line known as a **base line** is drawn about 2cm above from the bottom of TLC plate with the help of a pencil. The sample is applied as a small drop at the centre of the base line and this paper is hung vertically in chromatographic chamber (i.e. beaker/tank containing suitable solvent) in such a way that the sample spot is just above the surface level of solvent used. The chamber is sealed with a lid to prevent the evaporation of solvent. As the solvent travels up the paper, it moves the components of the mixture at the different distances. Then there is result of separation of the components of sample mixture known as **chromatogram** by the ascending technique as it is immersed in the solvent. The development of chromatogram is allowed to proceed until the solvent front has travelled the required distance. Then after 10-15 mins., this paper is removed from the chamber and solvent front reached is marked with the pencil. At the same, distances travelled by different components are also marked with the pencil and these distances travelled by solvent and components are measured in centimeter. Then this plate is allowed to dry simply in lab temperature. Then finally the R_f value of each component are calculated using the given formula.

Use and application of Paper chromatography

- to separate the amino acid in urine.
- to separate the pigments from natural colours.
- to separate colours in dyes.
- to monitor active ingredient in drugs.
- to identify the unknown organic and inorganic compounds in a mixture.

