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B.Sc. CHEMISTRY

THIRD YEAR

PAPER - VI : PHYSICAL CHEMISTRY

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PAPER-VI : PHYSICAL CHEMISTRY

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UNIT – I

1.1 Solutions:

A solution is a homogenous mixture of 2 or more non reacting components relative amounts can be varied up to certain limits.

(Ex) salt – water

Alcohol – water

Solution of gases in liquids:

Solubility of gas in a liquid depends on pressure, temperature, nature of gas, nature of liquid and other soluble component present in the solution.

Henry's law

The mass of a gas dissolved in a given volume of the liquid at constant temperature are directly proportional to the pressure of the gas present in equilibrium with the liquid.

If w is the mass of the gas then

$W \propto P$

$\therefore$ W = KP. Where K is a constant.

Dependence of the solubility of gas at a given temperature

We know that

W = KP

$$K = \frac{W}{P} \qquad ------1$$

$$W = \frac{MPV}{RT} \qquad ------2$$

Where W = Mass of the gas

M = Molecular weight

Substituting 2 in 1 we have

$$K = \frac{MPV}{RT\,P} = \frac{MV}{RT}$$

At constant temperature

$$V = \frac{KRT}{M} = k^1.$$

Thus the volume of a gas absorbed by a define volume of the liquid, does not depend on the pressure of the gas.

Application:

It is applicable to ideal gases & not for real gases. Since real gases behave like ideal gases at low pressure, Henry's law should be applied at low pressures only.

Limitations:

Henry's law is applicable to gases which don't under go any chemical change with the solvent. For example this law is not applicable in the case of dissolution of ammonia in water because it under goes compound formation

$$NH_{3\,(g)} + H_2O \rightarrow NH_4\,OH.$$

Similarly, the law is not applicable to dissolution of the Hcl gas in water because it undergoes dissociation.

$$Hcl_{(g)} + H_2O \rightarrow H^+ + Cl^-$$

Solution of liquids in liquids:

RAOULT'S LAW:

The partial vapour pressure of any volatile constituent of solution at a given temperature is equal to the product of the vapour pressure of the pure constituent and its mole fraction in solution.

Let us consider a solution of liquid 1 in liquid 2 then at a given temperature

$$P_1 = X_1 P_1^0$$

$$P_2 = X_2 P_2^0$$

Where

P_1, P_2 = Partial pressure of pure liquids 1& 2

P^0_1, P^0_2 = Vapour pressure pure liquids 1 and 2

X_1, X_2 = Mole fraction of liquids 1 & 2 in solution

Binary liquid mixtures:

IDEAL SOLUTION:

A solution is said to be an ideal solution if the molecules in it attract one another with equal force, irrespective of their nature. For an ideal solution of B in A, the forces between A - A, B - B and A - B should be the same.

Further the solution formed on mixing the two liquids is ideal if

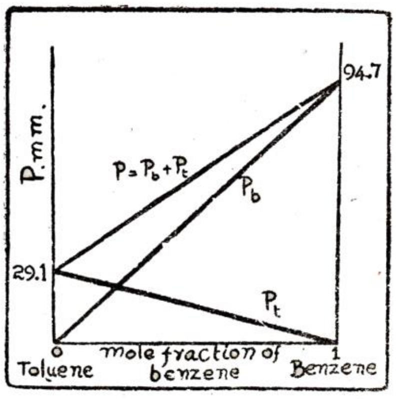
i. There is no volume change i,e., ΔV mix = 0

ii. There is no enthalpy change i,e., ΔH mix = 0

For example, if 50 ml of n-hexane is mixed with 50 ml of n- heptane, the total volume of the solution is found to be 100 ml and no heat is evolved or absorbed on mixing. Such a solution is called an ideal solution.

e.g 1. Benzene – toluene

Let us consider Benzene – Toluene system. This system behaves ideally to a good degree of accuracy. In this system the total vapour pressure is always equal to the sum of the vapour pressures of pure components. So this is called the ideal system.



Deviation from ideal Behavior:

Most of the solutions, however, show appreciable deviation from ideal behavior. These are called real or non- ideal solutions.

A solution formed by mixing two liquids is said to be non- ideal if it does not obey Raoult's law or the interactions of A and B molecules in the solutions are not similar to those of pure A and B or $\Delta V_{mix} \neq 0$ and $\Delta H_{mix} \neq 0$.

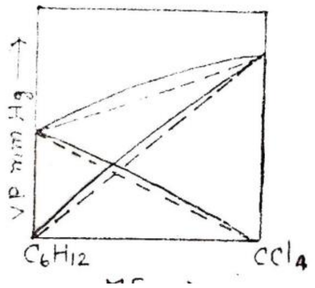
In the case of non- ideal solution, the plots of vapour pressure Vs composition (mole fraction) are curved lines instead of straight lines. Non-ideal solutions are divided into the following three types.

Type: I

Those, which show small positive deviation from Raoult's law. The vapour pressure –

Composition graphs of these solution curve are slightly upwards as shown in the figure. The dotted line plots are for ideal solution, calculated by using Raoult's law.

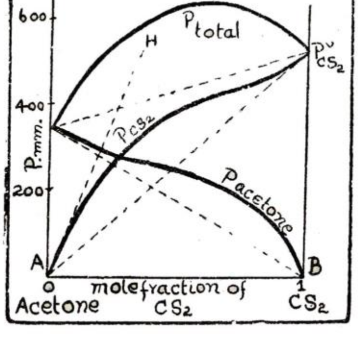
e.g. cyxlo hexane – ccl_4 system.



Type:II

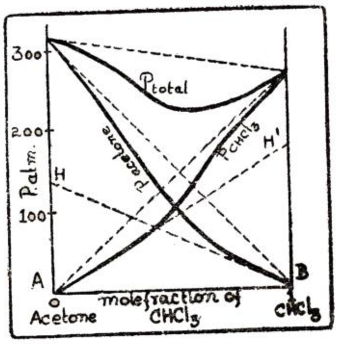
They show large positive deviations. In these system the individual partial pressure curves fall well above the ideal line. i,e.,the partial pressures are more than those calculated from Raoult's law. The Raoult's law predictions are shown by the dashed lines. The total vapour pressure shows a a maximum

e.g Acetone-CS_2



Type: III

They show negative deviations. In these system The vapour pressure carves fall below the Raoult's law. Predication. The system exhibits negative deviation from Raoult's law. The total vapour pressure has a minimum value.



e.g. 1) Acetone - $CHcl_3$.

2) Hydrochloric acid- Water.

Thermodynamics of ideal solution:

Gibbs free energy charge of mixing (ΔG_{mix}) for an ideal solution:

Let us consider n_A moles of liquid A and n_B mole of a liquid B mixed to form a solution.

The free energy (G) of the solution at given temperature and pressure is

$$G = n_A\ \bar{G}_A + n_B\ \bar{G}_B \quad \text{-------1}$$

$\bar{G}_A$, $\bar{G}_B$ is partial moral free energies of A & B respectively. The free energy change of mixing ΔG_{mix} is given by

ΔG_{mix} = Free energy of solution – sum of free energies of pure A and pure B.

$$= G- (n_A G^\circ_A + n_B G^\circ_B) \quad \text{-------2}$$

G°_A, G°_B are free energy /Mole of pure A and B respectively.

Substituting 1 in 2

$$\Delta G_{mix} = (n_A\ \bar{G}_A + n_B\ \bar{G}_B) – (n_A G^\circ_A + n_B G^\circ_B)$$

$$= n_A (\bar{G}_A - G^\circ_A) + n_B (\bar{G}_B - G^\circ_B) \quad \text{-------3}$$

We know that chemical potential (μ)

$$\mu = \mu^\circ + RT\ l\ n\ a.$$

since μ identical with partial molal free energy $\bar{G}$

$\bar{G}_A = G^\circ_A + RT\ l_n\ a_A$ for A

$\bar{G}_B = G^\circ B + RT\ l_n\ a_B$ for B

$\bar{G}_A = G^\circ_A + RT\ l_n\ a_B$ ---------- 4

$\bar{G}_B = G^\circ_B + RT\ l_n\ a_B$ ---------- 5

Substituting 4 & 5 in 3

$\Delta G_{mix} = n_A RT\, l_n\, a_A + n_B RT\, l_n\, a_{B.}$ -------- 6

For ideal solution

$a_A = x_A$ and $a_B = x_B$

x_A, x_B mole fraction of A and B respectively,

$\therefore\ \Delta G_{mix} = n_A RT\, l_n\, x_A + n_B RT\, l_n\, x_{B.}$ --------- 7

For more than 2 component

$\Delta G_{mix} = n_A RT\, l_n\, x_A + n_B RT\, l_n\, x_B + n_C RT\, l_n\, x_C + \ldots\ldots\ldots\ldots$

$$\boxed{\Delta G_{mix} = RT \sum \mu\, l_n\, x_i}$$

Volume change of mixing (ΔV_{mix}) for an ideal solution:

We know that

$$(\partial (\Delta G) / \partial P)_T = \Delta V \text{ ----------- } 8$$

For free energy of mixing we may write the above equation as

$$(\partial (\Delta G_{mix}) / \partial P)_T = \Delta V_{mix}$$

The equation 7 does not has any pressure term. So ΔG_{mix} is independent of P. So differentiating equation 7 wrt pressure at constant T gives.

$$(\partial (\Delta G_{mix}) / \partial P)_T = 0 \text{ --------- } 9$$

On comparing 8 & 9

$$\Delta V_{mix} = 0.$$

Thus, if two pure liquids are mixed to gether to give an ideal solution, there is no change in volume.

Enthalpy change of mixing (ΔH_{mix}) for an ideal solution

We know $\Delta H_{mix} = n_A RT\, l_n\, x_A + n_B RT\, l_n\, x_B$

$= RT\, (n_A RT\, l_n\, x_A + n_B RT\, l_n\, x_B)$

$\therefore (\Delta G_{mix} / T)_P = R\, (n_A\, l_n\, x_A + n_B\, l_n\, x_B)$ ------ 10

On differentiating 10 wrt Temperature at constant P gives

$$[\partial (\Delta G_{mix} | T) / \partial T]_P = 0 \text{ -------------------------- } 11$$

An alternate expression by differentiating $\Delta G_{mix} / T$ with respect to T at constant P gives.

$$[\partial (\Delta G_{mix} | T) / \partial T]_P = T\, [\partial (\Delta G_{mix} | T) / \partial T]_P - \Delta G_{mix} / T^2 \text{ ----- } 12$$

We know that Gibbs Helm holtiz equation

$$\Delta G - \Delta H = T\, (\partial (\Delta G) / \partial T)_P \text{ -- } 13$$

Substituting 13 in 12

$$(\partial (\Delta G_{mix} / T) / \partial T)_P = \Delta G_{mix} - \Delta H_{mix} - \Delta G_{mix} / T^2$$

$$= -\Delta H_{mix} / T^2 \text{ --- } 14$$

Comparing 11 & 14

$$-\Delta H_{mix} / T^2 = 0 \qquad \text{Or} \qquad \Delta H_{mix} = 0.$$

Thus if two pure liquids are mixed together, to give an ideal solution, there is no change in enthalpy.

Vapour pressure- composition curves, V.P- temperature curves.

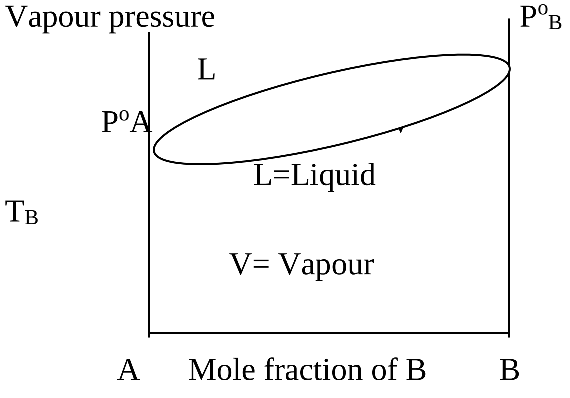
Boiling point is the temperature at which the total vapour pressure equal to the atmospheric pressure. Thus a liquid having low vapour pressure will have a higher boiling point because it will have to be heated more to make the vapour pressure equal to the atmospheric pressure. Thus pure liquid A which has less vapour pressure will have a higher boiling point and the pure liquid B which has higher vapour pressure will have lower boiling point. In between these two extremes, a solution of any composition having lower V.P will have higher boiling point. These facts help us to construct the boiling point – composition diagrams from the V.P – composition diagram as below.

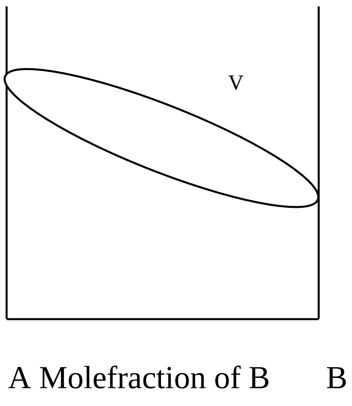
The point C in type II that corresponds to maximum vapour pressure represents the lowest boiling point. Similarly the point D in type III which represents the lowest vapour pressure corresponds to the highest boiling point. The liquid mixtures having compositions corresponding to points C & D have constant boiling points and are called a zoetrope's.

Vapour pressure – composition Diagrams

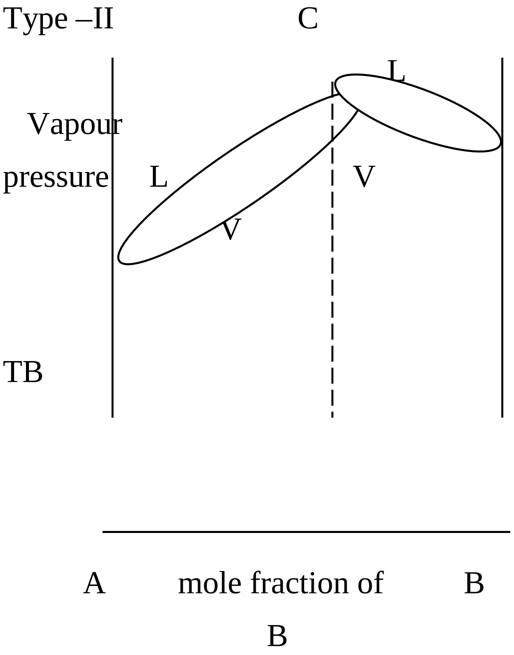
Boiling point – composition Diagrams

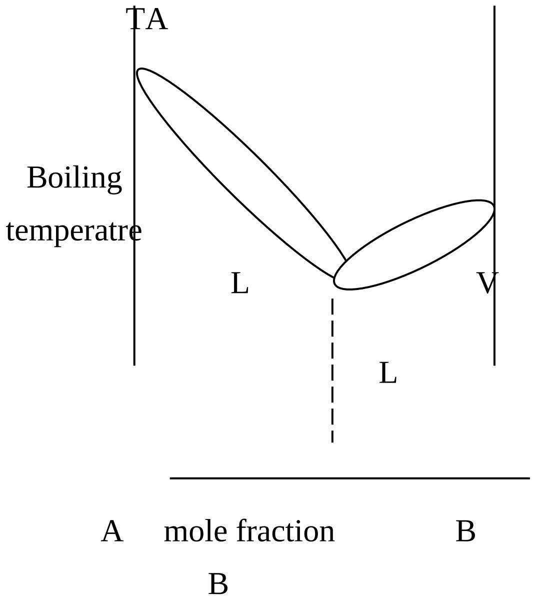
Type - I



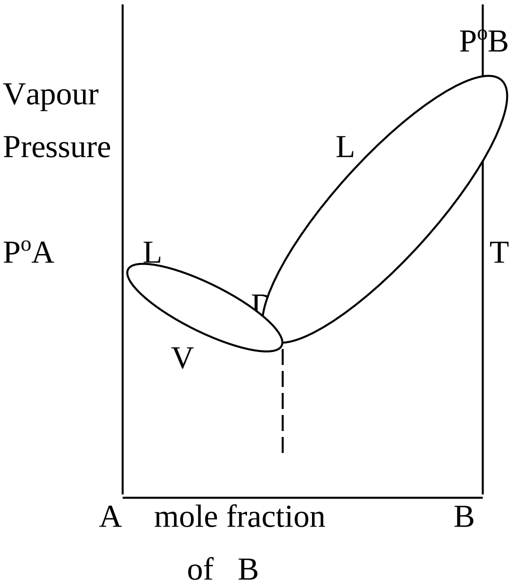


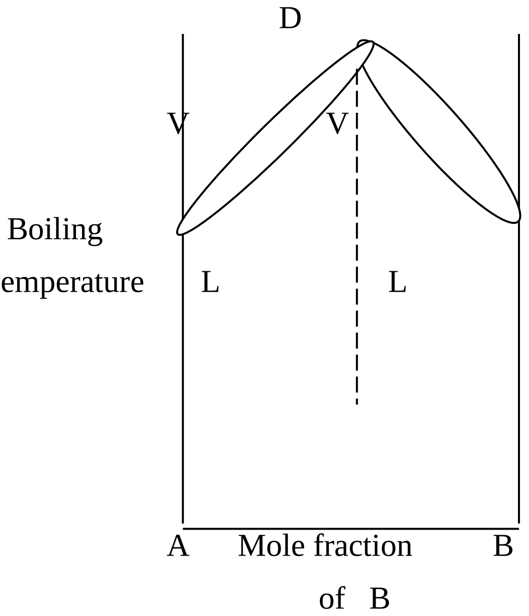
Type –II





Type - III





Azeotropic Distillation: (production of 100% alcohol)

Azeotropic mixtures of suitable components are mixed and distilled.. 100 % pure components have been obtained by such distillation. Such distillation are called azeotropic distillation.

Preparation of absolute alcohol:

Ethyl alcohol and water form an azeotropic mixture containing 95.6 % alcohol which boils at 351.2K. This is called rectified spirit. This is mixed with benzene and distilled. At 337.6K a ternary azeotropic mixture containing benzene, water and alcohol distils. At 340.8K a binary azeotropic mixture of alcohol & benzene distills. The residue in the flask is 100 % ethanol which distills at 351.2K. Thus we get pure alcohol.

1.2 Nernst's distribution law:

"A solid or liquid distributes it self between two immiscible solvents in such a way that the ratio of its concentration in the two solvents is constant. The ratio of the concentration in the two solvents is called partition Co-efficient (or) distribution Co-efficient."

Limitations:

This law holds good only when,

1. The temperature is constant.
2. The substance dissolves in both the solvents with out association or dissociation.
3. The concentration of the solute is low.
4. No chemical reaction takes place between the solute and either of the solvents.

Thermo dynamic derivation:

If a dilute solution of iodine in water is shaken with ccl_4, iodine distributed between the two solvents if μ_1d μ_2 are the chemical potentials of iodine in water and ccl_4 respectively, then at equilibrium.

$$\mu_1 = \mu_2$$

We know that,

$$\mu_1 = \mu^\circ_1 + RT\, ln\, x_1$$

$$\mu_2 = \mu^\circ_2 + RT ln\, x_2$$

$$\therefore \quad \mu^\circ_1 + RT\, ln\, x_1 = \mu^\circ_2 + RT ln\, x_2$$

$$\mu^\circ_1 - \mu^\circ_2 = RT ln\, x2 / x1.$$

$$-(\mu^\circ_2 - {}^\circ\mu_1) = RT ln\, x2 / x1.$$

Since μ°_2 &μ°_1 are independent of composition.

$$-(\mu^o{}_2 - \mu^o{}_1) = C \quad a\ constant$$

$$\therefore RT\ln\frac{x_2}{x_1} = C$$

$$\log\frac{x_2}{x_1} = \frac{C}{2.303RT}$$

$$\frac{x_2}{x_1} = anti\log\frac{C}{2.303RT} = K,\ a\,constant$$

$$\frac{x_2}{x_1} = K.$$

x_1 , x_2 are mole fraction of the solute in water and ccl_4. if the solution is dilute, then instead of mole fraction the molalities or molarities can be used.

ie. $\frac{M_2}{M_1} = K \qquad (or) \quad \frac{C_2}{C_1} = K$

K is called partition (or) distribution Co- efficient.

Applications:

1. Nernst distribution law helps us to determine the degree of hydrolysis and hydrolysis constant of salts of weak acids or weak bases.
2. It helps us to determine the molecular weight and molecular complexities of the compounds. It also helps to determine the degree of dissociation and the nature of complexity of substances.
3. The law helps us in the study of complexes. In distribution experiments we can find actual concentration of the various species at equilibrium. From these values equilibrium constant and the molecular formula of the complex can be found out.
4. The most important use of distribution law is the extraction of a substance from mixtures.

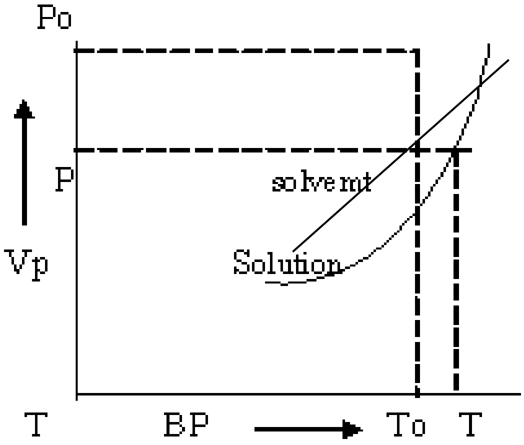
Solvent extraction:

This method is largely employed in extracting organic materials from plants and other natural resources.

In order to separate the constituents A and B from their solution in the solvent x, a suitable solvent, which is immiscible with x, and in which constituent A is relatively more soluble, is added to the solution. The mixture is then shaken vigorously and allowed to stand for some time. The two layers are then separated with the help of a separating funnel. One of these layers is the solvent X richer in the constituent B and the other is the solvent Y richer in the constituent A. the solvents are recovered by distillation and used again. By repeating the process A & B can be separated. Nowadays sox h let apparatus is often employed to make use of the solvent over and over again automatically.

1.3 Thermodynamic derivation of elevation of boiling point:

The boiling point of a liquid is the temperature at which its vapour pressure becomes equal to pressure over it which is normally one atmosphere.



The vapour pressure of a solvent is lowered when a non. Volatile solute is dissolved in it. Thus the vapour pressure

(VP) of the solvent (P_0) is higher than that of the solution. Hence the temperature needed to raise the vapour pressure of a solvent to one atmosphere is less than that needed to raise the vapour pressure of the solution to one atmosphere. In other words the boiling point (BP) of the solution (T) is higher than that of the solvent (T_o). We say that that non-volatile solute has elevated the B.P of the solvent. The difference between T and T_o ($T-T_o$) is called the elevation of boiling point. i,e, $T- T_o = \Delta T_b$

A relation between the elevations of boiling point of a solution ΔT_b and its molality can be derived by the application of clausius clapeyron equation. Which relates the variation of BP with the pressure.

$$\ln \frac{P_2}{P_1} = \frac{\Delta HV}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

If T_1 &T_2 are replaced by T_o and T the BPts of the solvent and solution respectively. P_2 and P_1 may be replaced by P_o and p, the VP of the solvent and the solution respectively.

$$ln \frac{P_0}{P} = \frac{\Delta HV}{R} \left[\frac{T - T_0}{TT_0}\right]$$

When the solution is dilute T will be nearly equal to T_o then $TT_o = T_o^2$

$$\therefore \; ln \frac{P_0}{P} = \frac{\Delta HV}{R}\left[\frac{\Delta Tb}{T_0^{\,2}}\right] \quad \text{----------------------------} \; 1$$

When ΔH_V = molar heat of vaporization

ΔT_b = elevation of boiling point.

We know that from Raoult's law

$$\frac{P}{P_0} = x_1 = 1 - x_2 \qquad \text{-------------------------------- } 2$$

Equation 1 can be written as

$$-ln \frac{P}{P_0} = \frac{\Delta HV}{R} \cdot \frac{\Delta Tb}{T_0{}^2} \qquad \text{------------------------------ } 3$$

Substitute 2 in 3

$$-ln\ (1 - x_2) = \frac{\Delta HV}{R} \cdot \frac{\Delta Tb}{T_0{}^2} \qquad \text{------------------------------ } 4$$

$$-ln\ (1 - x_2) = x_2 + \frac{x_2{}^2}{2} + \frac{x_2{}^3}{3} + \ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

neglecting the higher powers in series.

$$-ln(1 - x_2) = x_2$$

∴ the equation 4 becomes

$$x_2 = \frac{\Delta HV}{R} \cdot \frac{\Delta T b}{T_0{}^2}$$

$$\Delta Tb = \frac{x_2 . RT_0{}^2}{\Delta HV} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5$$

We know that

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n_1} = \frac{W_2 M_1}{M_2 W_1} \qquad \text{------------------ } 6$$

Substituting 6 in 5

$$\Delta Tb = \frac{W_2}{M_2} \cdot \frac{M_1}{W_1} \cdot \frac{RT_0{}^2}{\Delta HV} \qquad \text{---------------------- } 7$$

$\frac{\Delta HV}{M_1}$ = 1, the latent heat of vaporization of 1 gram of the solvent then equation 7 becomes

$$\Delta Tb = \frac{W_2}{M_2} \frac{RT_0^{\ 2}}{W_1.1}$$

Multiplying and dividing the above equation by 1000

$$\Delta Tb = \frac{W_2.1000 \times RT_0^{\ 2}}{M_2 W_1.1000} \text{ -------------- } 8$$

When $M = \dfrac{W_2.1000}{M_2 W_1}$

$$\Delta T_b = M.\ K_b \qquad \text{--------------------------- } 9$$

$$K_b = \frac{RT_0^{\ 2}}{1000}.$$

M is the molality of the solution. K_b is the modal elevation constant or ebullioscopy constant.

From the equation 8 the molecular weight of the dissolved solute can be determined from

$$M_2 = \frac{Kb\, W_2.1000}{\Delta Tb.W_1}$$

From the equation 9 the following Raoult's takes of elevation of B.Pt can be deduced.

1. The elevation in B.Pt (ΔT_b) of a solution of a non electrolyteis proportional to its molality (M).

   $$\Delta T_b \propto M$$

2. $\Delta Tb = \dfrac{1000}{W_1} . \dfrac{W_2}{M_2} .\ Kb.$

Unit of K_b = Kg $mol^{-1.}$

Thermodynamic derivation of depression in freezing point:

The freezing point of a solution is less than the freezing point of the pure solvent. This is a consequence of lowering of vapour pressure.

The relation between the depressions in freezing point of a solution ΔT_f and its molality can be derived by the application of clausius clapeyron equation.

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_f}{R} \left[\frac{T_2 - T_1}{T_1 . T_2} \right]$$

When this is applied to a solution.

$$\ln \frac{P_o}{P} = \frac{\Delta H_f}{R} \left[\frac{T - T_o}{T . T_0} \right] \qquad \text{------(1)}$$

Where ΔH_f is the molar heat of fusion. P_o and P are VP of the solvent & solution respectively. T_o and T are the freezing points of the solvent and solution. Since for a dilute solution $T_o = T \quad T_o T = T_o^2$

$$\ln \frac{P_o}{P} = \frac{\Delta H_f}{R} \left[\frac{T - T_o}{T_0^{\ 2}} \right] \qquad \text{------(2)}$$

∴

$$\ln \frac{P_o}{P} = \frac{\Delta H_f}{R} \ \frac{\Delta T_f}{T_0^{\ 2}}$$

∴

ΔT_f = depression in freezing point.

We know that from Raoult's law

$$\frac{P}{P_0} = x_1 = 1 - x_2 \qquad \text{------------------------------------- 3}$$

∴ Equation 2 becomes

$$- \ln \frac{P}{P_o} = \frac{\Delta H_f . \Delta T_f}{R \, T_0^{\ 2}} \qquad \text{--------(4)}$$

$$- ln\,(1 - x_2) = x_2 + \frac{x_2^{\ 2}}{2} + \frac{x_2^{\ 3}}{3} + \text{-----------------}$$

Neglecting higher powers

$$l_n\,(1 - x_2) = x_2$$

∴ Equation 4 becomes,

$$x_2 = \frac{\Delta H_f \,.\, \Delta T_f}{RT_0^{\,2}}$$

$$\therefore \qquad \Delta T_f = \frac{x_2 \;\; RT_0^{\,2}}{\Delta H_f} \text{ --------------------------------------- } 5$$

We know that

$$x_2 = \frac{W_2}{M_2} \,.\, \frac{M_1}{W_1}.$$

Substituting the value of x_2 in 5

$$\Delta T_f = \frac{W_2 \;.M_1 \, RT_0^{\,2}}{M_2 .W_1 \;\Delta H_f}$$

$$\frac{\Delta H_f}{M_1} = 1 \text{Latent heat of fusion per 1 gram of solvent}$$

$$\therefore \qquad \Delta T_f = \frac{W_2 \, RT_0^{\,2}}{M_2 \, W_1 .1}$$

Multiply and divide by 1000

$$\Delta T_f = \frac{W_2 \, RT_0^{\,2} .1000}{M_2 W_1 \times 1000} \qquad \text{------------------------ } 6$$

$$\Delta T_f = Kf .M \qquad \text{------------------------ } 7$$

When $K_f = \frac{RT_0^{\,2}}{1000}$: $\qquad M = \frac{W_2}{M_2} . \frac{1000}{W_1}.$

Where K_f is the molal depression constant or cryoscopic constant and M is molality of the solute.

From 6 we can get molecular weight of the solute.

$$M_2 = \frac{K_f .W_2 .1000}{\Delta T_f .W_1}$$

From 7 the following Raoult's laws of depression of freezing point can be deduced.

1) $\Delta T_f \propto M$

2) $\Delta T_f = \frac{1000}{W_1} \cdot \frac{W_2}{M_2} . K_f .$

Unit of K_f = kgm Mol^{-1}.

Van't Haff Factor

The ration between the experimental value of colligative property and the theoretical value is known as the van't Haff factor. i.

$$i = \frac{Experimental\ Colligative\ property}{Theoretical\ colligative\ property.}$$

(or)

$$i = \frac{Theoretical\ molecular\ weight}{Experimental\ moleculer\ weight.}$$

Calculation of i ;

Let 1 mole of an electrolyte be dissolved in a given quantity of water. Let $\propto$ be the degree of dissociation. When 1 mole dissociates n moles of ions are formed. Since $\propto$ is the degree of dissociation 'n$\propto$' moles of ions will be formed. There fore after ionization the total no. of ions will be

$$1-\propto + n\propto = 1+ \propto (n-1)$$

The ration of number of moles after dissociation to the number of moles expected.

$$i = \frac{1+(n-1)\propto}{1}$$

If i is known, $\propto$ can be calculated using the equation $\propto = \frac{i-1}{n-1}$

Abnormal molecular mass:

Molecular weights determined by measuring their properties gives (colligative) abnormal results in some cases. Such abnormal results are may be due to association or dissociation of solute in solution.

Degree of association:

Many organic solutes under go association, in non-aqueous solution. Due to association, two or more molecules of the solute form a bigger molecule. So the number of effective molecules or particles in the solution decreases. Thus the measured osmotic pressure, the elevation of boiling point or the depression in freezing point is less than the calculated values. The molecular weight of solutes in such cases will be higher than the true molecular weights as indicated by their formulas.

Solute	Solvent	Observed Mol.wt	Calculated Mol.wt
Acetic acid	Benzene	118	90
Benzoic acid	Benzene	242	122

Degree of dissociation:

Many inorganic acids, bases, salts undergo dissociation in aqueous solutions. Due to dissociation, the molecules break down into positively and negatively charged ions. So number of effective particles in the solution increases. Thus the measured colligative properties are more than the calculated values. The molecular weights of solutes in such cases will be less than the true molecular weights as indicated by their formula. E.g.

Solute	Solvent	Observed Mol.wt	Calculated Mol.wt
Kcl	Water	38.75	74.5
Na_2so_4	Water	49.84	142.0

CHEMICAL EQUILIBRIUM

1.4 Thermo dynamic derivation of equilibrium constants:

Let us consider a reversible reaction in which

$$aA + bB + \text{-------} \Leftrightarrow cC + dD + \text{--------}$$

At constant temperature and pressure the Gibb’s free energy of the system is equal to the sum of the chemical potential of the components present in the system.

$G_R = \quad a\,\mu_A + b\,\mu_B + \text{------------}$

$G_P = \quad c\,\mu_C + d\,\mu_D + \text{------------}$

∴ The change in Gibb’s free energy is

$\Delta G = G_P - G_R$

$= (c\,\mu_C + d\,\mu_D + \text{------}) — (a\,\mu_A + b\,\mu_B + \text{----------}) \text{-----------}1$

If P_A, P_B, P_C, P_D are the partial pressure of components A, B, C, D then

$\mu_A = \mu^o{}_{A+}RT\, l_n\, P_A \qquad \mu_C = \mu^o{}_C + RTl_n\, P_C$

$\mu_B = \mu^o{}_{B}+ RT \ln P_B$ $\qquad\qquad$ $\mu_D = \mu^o{}_{D}+ RT \ln P_D$

$\mu^o{}_A$, $\mu^o{}_B$, $\mu^o{}_C$, $\mu^o{}_D$ are standard chemical potentials of the components A, B, C& D

Substitute μ_A, μ_B, μ_C , μ_D in 1

$\Delta G = [c\,(\mu^o{}_C\ RT \ln P_C) + d\,(\mu^o{}_D\ RT \ln P_D)] – [a\,(\mu^o{}_A\ RT \ln P_A) + b\,(\mu^o{}_B\ RT \ln P_B)]$

$= (c\mu^o{}_C + D\,\mu^o{}_D + \text{-----}) – (a\,\mu^o{}_A + b\,\mu^o{}_B + \text{---}) + (c\,RT \ln P_C + d\,RT \ln P_D) – (a\,RT \ln P_A + b\,RT \ln P_B + \text{-------})$ ---------------------------2

Let $(c\mu^o{}_C + d\mu^o{}_D + \text{----}) – (a\,\mu^o{}_A + b\mu^o{}_B + \text{---}) = \Delta G^o$

$\therefore$ Equation 2 becomes

$\Delta G = \Delta G^o + (RT \ln P_C{}^c + RT \ln P_D{}^d) – (RT \ln P_A{}^a + RT \ln P_B{}^b)$

$= \Delta G^o + RT \ln P_C{}^c \text{ x } P_D{}^d$

For a Reversible reaction at equilibrium $\Delta G=0$

$$\therefore\ 0 = \Delta G^o + RT\,ln\frac{P_C{}^c . P_D{}^d}{P_A{}^a . P_B{}^b}$$

$$RT\,ln\frac{P_C{}^c . P_D{}^d}{P_A{}^a . P_B{}^b} = -\Delta G^o$$

$$ln\frac{P_C{}^c . P_D{}^d}{P_A{}^a . P_B{}^b} = -\frac{\Delta G^o}{RT}$$

$$ln\frac{P_C{}^c . P_D{}^d}{P_A{}^a . P_B{}^b} = e^{\frac{-\Delta G^o}{RT}}$$

At a particular temperature $e^{\frac{-\Delta G^o}{RT}}$ is a constant known as K_p the equilibrium constant then

$$K_p = \frac{P_C{}^c . P_D{}^d}{P_A{}^a . P_B{}^b}.$$

Equilibrium constant in term of concentration:

[Derivation is the same as above expect]

Substitute
$$\mu_A = \mu^o A + RT\ln C_A \qquad \mu_C = \mu^o C + RT\ln C_C$$
$$\mu_B = \mu^o B + RT\ln C_B \qquad \mu_D = \mu^o D + RT\ln C_D$$

Then $K_C = \dfrac{C_C{}^c . C_D{}^d}{C_A{}^a . C_B{}^b}$.

Equilibrium constant interm of mole fraction:

[Derivation is the same as above expect]

Substitute
$$\mu_A = \mu^o A + RT\ln X_A \qquad \mu_C = \mu^o C + RTl\,n X_C$$
$$\mu_B = \mu^o B + RT\ln X_B \qquad \mu_D = \mu^o D + RTl\,n X_D$$

Then $K_X = \dfrac{X_C{}^c . X_D{}^d}{X_A{}^a . X_B{}^b}$.

Relation ship between K_p and K_C

We know that

$$PV = nRT$$

$$\frac{n}{V} = C$$

$$P = \frac{n}{V} RT$$

$$\therefore \qquad K_P = \frac{(C_C RT)^c \times (C_D RT)^d}{(C_A RT)^a \times (C_B RT)^b}.$$

$$= \frac{C_C{}^c \times C_D{}^d}{C_A{}^a \times C_B{}^b} . \frac{RT^{c+d}}{RT^{a+b}}$$

$$= K_C . (RT)^{(c+d)-(a+b)}$$

$$\Delta n = (c+d)-(a+b)$$

$$K_P = K_C . RT^{\Delta n}.$$

Relationship between K_p and K_X

We know that $P_A = x_A . P$ from Raoult’s law lly $p_B = x_B.P, PC = xC.P,\ P_D = x_D.P$

$$\therefore \qquad K_P = \frac{(X_C P)^c \times (X_D P)^d}{(X_A P)^a \times (X_B P)^b}.$$

$$= \frac{X_C{}^c \times X_D{}^d}{X_A{}^a \times X_B{}^b}.\ P^{(c+d)-(a+b)}$$

$$K_P \ = K_C \cdot p^{\Delta n}.$$

Standard free energy:

It is defined as the free energy change that takes place when the reactants and products at 298k and 1 atm pressure. It is denoted by ΔG

$\Delta G^o = G^o(p) - G^o(R)$

If ΔG^O = -ve then the reaction is feasible

= +ve then the reaction is not feasible

= 0 then the reaction is at equilibrium

If we know standard entudalpy and stand entropy then we can calculate ΔG using

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

Derivation of van's Hoff Reaction Isotherm:

Let us consider a Reversible reaction in which

$$aA + bB \Leftrightarrow cC + dD$$

At constant temperature and pressure

$$G_R = a\mu_A + b\mu_B$$

$$G_P = c\mu_C + d\mu_D$$

$$\therefore \qquad \Delta G = G_P - G_R$$

$$= (c\mu_C + d\mu_D) - (a\mu_A + b\mu_B)$$

If a_A, a_B, a_C, a_D are the activities of the composes A, B, C & D then

$$\mu_A = \mu^o A + RT \ln a_A \qquad \mu_C = \mu^o C + RT \ln a_C$$

$$\mu_B = \mu^o B + RT \ln a_B \qquad \mu_D = \mu^o D + RT \ln a_D$$

Then

$$\Delta G = [c(\mu^o A + RT \ln a_C) + d(\mu^o D + RT \ln a_D)] - [a(\mu^o A + RT \ln a_A) + b(\mu^o B + RT \ln a_B)]$$

$$\Delta G = (c\mu^o C + d\,\mu^o D) - (a\mu^o A + b\,\mu^o B) + (c\,RT \ln a_C + d\,RT \ln a_D) - a\,RT \ln a_A + b\,RT \ln a_B$$

$$\Delta G = \Delta G^o + (RT \ln a_C{}^c + RT \ln a_D{}^d) - (RT \ln a_A{}^a + RT \ln a_B{}^b)$$

$$= \Delta G^o + RT \ln \frac{a_C{}^c \times a_D{}^d}{a_A{}^a \times a_B{}^b}$$

Let $\ln \dfrac{a_C{}^c \times a_D{}^d}{a_A{}^a \times a_B{}^b} = Ja$

Then,

$$\Delta G = \Delta G^o + RT \ln Ja$$

This reaction is commonly known as vant hoff reaction isotherm.

De-Donder’s concept of advancement of a reaction:

The progress of a chemical reaction can be understood by De-Donder’s concept as follows

Let us consider

$$aA + bB \Leftrightarrow cC + dD$$

The reaction proceeds in a closed vessel and the total mass of the system remain constant. Although the number of moles of reactants and products change. If the progress of the reaction is represented by ξ the small increase in the extent of reaction that takes place in any interval is dξ

Then

Decrease in amount of A = $- a\,d\,\xi$

Decrease in amount of B = $-b\,d\,\xi$

Decrease in amount of C = $c\,d\,\xi$

Decrease in amount of D = $d\,d\,\xi$

Mathematically

$dn_A = -ad\xi \qquad dn_C = cd\xi$

$dn_B = -bd\xi \qquad dn_D = dd\xi$

At constant temperature, pressure the change in Gibbs free energy for small progress that takes place in the system is given by

$(dG)\ T,P = (\mu_C dnC + \mu_D dnD) + (\mu_A dnA + \mu_B dnB)$

$= (c\mu_C d\xi + d\ \mu_D d\xi) + (-a\mu_A d\xi - b\mu_B d\xi)$

$= [(c\mu_C + d\ \mu_D) + (-a\mu_A - b\mu_B)]d\xi$

$= [(c\mu_C + d\ \mu_D - a\mu_A - b\mu_B)]d\xi$

$(dG/d\xi\ )_{T,P} = c\mu_C + d\ \mu_D - a\mu_A - b\mu_B$

$(dG/d\xi\ )_{T,P}$ was ntroduced by De-dander. Hence this equation is known as De=Donder's concept.

if $(dG/d\xi\ )_{T,P}$ = - ve reaction take place in the forward direction

= + ve reaction takes place in the backward direction

= 0 reactions is at equilibrium.

Chemical affinity:

Early chemist found that different substances exhibit either empathies (or) antipathies towards each other. Their reaction can be explained based on chemical affinity.

It is defined as the force that brings chemical reaction.

Greek scientist explained the chemical union by love and Decomposition by hate between the atoms. The scientist Geoffroy and Bergmann compiled a tables affinity "in which substances are arranged in order of their affinities but could not explain large no of reversible reactions. Later it was proved that not only affinity place important role but also depends on its concentration.

Temperature dependence of equilibrium constant- van't Hoff isochore

In a Reversible reaction if the reactants and products are in gaseous standard states then the standard free energy and equilibrium constant have the following relation.

$$\Delta G^{o} = -RT\,l\,n\,k_{P} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Differentiate work temperature at constant pressure

$$(\partial\frac{\Delta G^{o}}{dT})_{P} = -RT\,l\,n\,K_{P} - RT\frac{d|nK_{P}}{dT}$$

Multiply by T on both sides

$$T\,\partial\left(\frac{\Delta G^o}{dt}\right)_p = -RTl\,nK_P - RT^2\left(\frac{d\,l\,n\,k_p}{dT}\right)$$

$$= \Delta G^o - RT^2\left(\frac{d\,l\,n\,k_p}{dT}\right)\text{------------}2$$

We know that the Gibb's helm holtz equation in standard state as.

$$\Delta G^o = \Delta H^o + T\,\partial\left(\frac{\Delta G^o}{\partial T}\right)_P$$

$$T\left(\frac{\partial \Delta G^o}{\partial T}\right)_P = \Delta G^o - \Delta H^o \text{--------------------}3$$

Compare the equation (2) & (3)

$$\Delta G^o - \Delta H^o = \Delta G^o - RT^2\,\frac{d\,l\,n|n\,K_P}{dT}$$

$$\Delta H^o = RT^2\,\frac{d\,|n\,K_P}{dT}$$

$$\frac{d\,|n\,K_P}{dT} = \frac{\Delta H^o}{RT^2}$$

This equation is known as van't Hoff isochore (or) van't Hoff equation.

Keeping ΔH as constant and integrate the equation (4) between the intervals T_1, T_2 and Kp over P_1& p_2

$$\int_{P_1}^{P_2} d\,l\,nK_P = \frac{\Delta H^o}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

$$l\,nK_P)_{P_1}^{P_2} = \frac{\Delta H^o}{R}\left(\frac{-1}{T}\right)^{T_2}$$

$$l\,n\frac{KP_2}{KP_1} = \frac{\Delta H^o}{R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

kp1, kp2 are equilibrium constant when the temperature $T_1$and T_2. By knowing T_1, T_2 and Kp and Kp2 we can calculate Δ H

Van's Hoff equation in term of KC:

We know that

$$K_P = K_C . RT^{\Delta n}$$

Take in on both sides

$$l\,n K_P = l\,n K_C + \Delta n\, l\,n\, RT$$

Differentiate write temperature.

$$\frac{d\,l\,n K_P}{dT} = \frac{dl\,n K_C}{dT} + \frac{\Delta n}{T}$$

$$\frac{d\,l\,n K_C}{dT} = \frac{dl\,n K_P}{dT} - \frac{\Delta n}{T}$$

$$= \frac{\Delta H^o}{RT^2} - \frac{\Delta n}{T}$$

$$= \frac{\Delta H^o - \Delta n RT}{RT^2}$$

We know that

$$\Delta H^o = \Delta E^o + RT\,\Delta n$$

Then

$$\frac{d\,l\,n K_C}{dT} = \frac{\Delta E^o + \Delta n RT - \Delta n RT}{RT^2}$$

$$\frac{dl\,n K_C}{dT} = \frac{\Delta E^o}{RT^2}$$

Effect of pressure on equilibrium constant:

In a reversible reaction if the reactants and products are ideal gases then kp and kc do not depend on pressure. However the equilibrium constant kx does depend on pressure according to the equation.

$$K_P = K_X . P^{\Delta n}$$

Take ln on both sides

$$l\,n K_P = l\,n K_X + \Delta n l\,n P$$

$$l\,n K_X = l\,n K_P + \Delta n l\,n P$$

On differentiation

$$d\,l\,n K_X = dl\,n\ K_P - \Delta n\,dl\,n\ P$$

But $\quad d|nK_P = 0.$

$$\therefore \qquad d\,l\,n\ K_X = -\Delta n\,d\,l\,n P$$

$$d\,l\,n\ K_X = -\Delta n \frac{dP}{P} \qquad ------------1$$

Ideal gas equation

$$PV = nRT$$

$$P\Delta V = \Delta n RT$$

$$\frac{\Delta V}{RT} = \frac{\Delta n}{P} ------------------------2$$

Compare the Equation 1 & 2

$$\frac{d\,l\,n\ K_X}{dP} = \frac{-\Delta V}{RT}$$

When Δv = (volume at equilibrium – initial volume)

When Δ v is +ve(i.e.) there is increase in volume, kx will decrease with increase of pressure.

1) If Δ is –Ve (i.e.) there is decrease in volume, kx will increases with increase of pressure.

1.5 Adsorption:

Adsorption is a process in which one substance accumulates on the surface of another substance.

The substance on whose surface, adsorption takes place is called adsorbent.

The Substance which is adsorbed the surface of the adsorbent is called adsorbate.

Physical adsorption:

When a gas is adsorbed on the surface of a solid by van der waal's forces without resulting into the formation of any chemical bond between them is called physical adsorption.

This type of adsorption involves low heats of adsorption i.e., above 20-40 kJ/mole.

Physical adsorption of a gas by a solid is generally reversible

Increase of pressure causes more gas to be adsorbed and the release of pressure frees the adsorbed gas.

Decrease of temperature increases adsorption but the gas adsorbed at low temperature can be freed again by heating.

Chemical adsorption (or) Chemisorption:

When a gas is adsorbed onto the surface of a solid by forces similar to those of a chemical bond is called chemical adsorption. This type of adsorption results into the formation of surface compound.

This type of adsorption evolves high heat of adsorption i.e. about 40-400 KJ/mole.

Chemisorptions is usually irreversible.

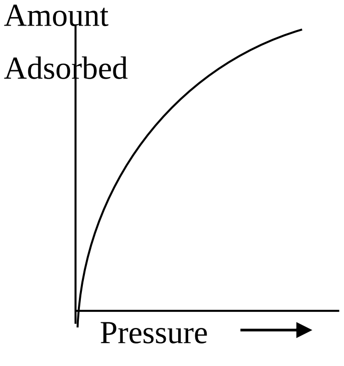
Increase of temperature increase the adsorption physical adsorption takes place between every gas and a solid i.e. not specific in nature, where as chemisorptions is specific in nature and occurs only where there is a tendency towards compound formation between the gas and the adsorbent.

Types of adsorption isotherms:

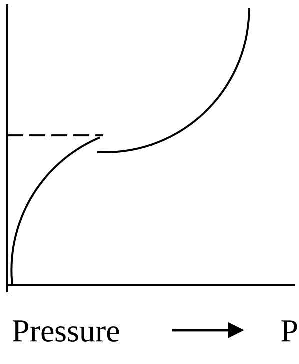
Amount of a gas adsorbed by a given amount of the adsorbent depends upon both temperature and pressure. At constant temperature there exist, some definite relationships between the amount of the gas adsorbed and the equilibrium pressure. Such relationships are known as adsorption isotherms.

Five different general types of adsorption isotherms have been observed for the adsorption of gases on solids. These are shown in the figure below.

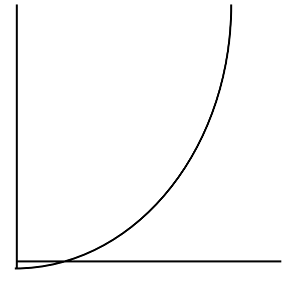
Type – I

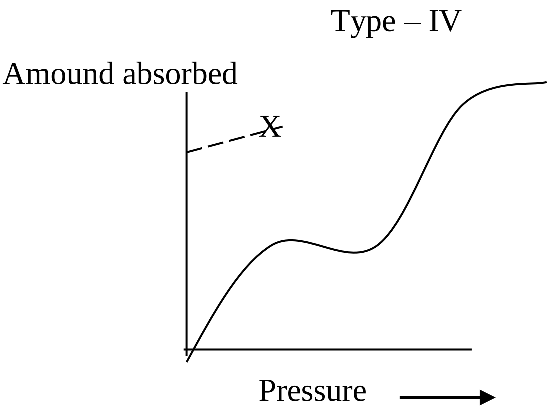


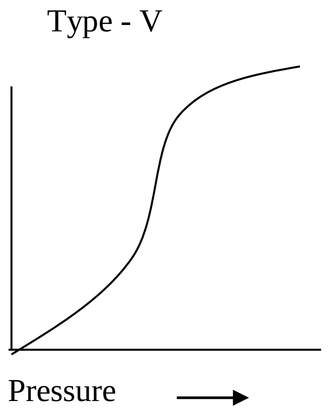
Type – II



Type – III







Freundlich Adsorption Isotherm:

Freundlich gave an empirical relationship between the amount of gas adsorbed on a solid adsorbent surface and pressure of the gas absorbed at a particular temperature.

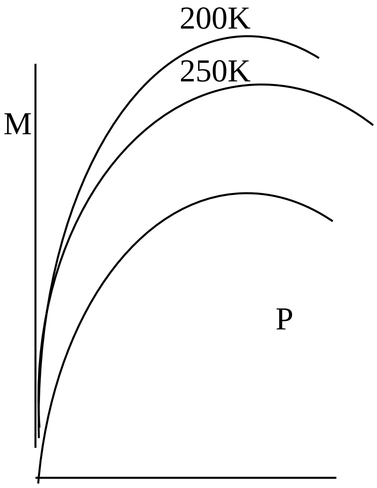
$X/m = KP^n$

Where x = weight of the gas adsorbed.

m = mass of the adsorbent at a pressure p

K ,n are constants for a particular adsorbent and gas

This relationship is called Freundrich adsorption Isotherm. From these curves we find that at a fixed Pressure, physical adsorption decreases with an increase in temperature. Taking logarithm for (1) we get.



$$\log {}^{x}\!/_{M} = \log K + n \log P \text{ --------- } 2$$

Thus, if we plot log (x/m) against log p we should get a straight line, the slope of which should be equal to n.

In practice the plot obtained at medium pressures is reasonably straight. The value of n is generally less then.

Deviation of langmuir adsorption isotherm:

Let as consider the fraction of the surface covered by the adsorbed molecules as θ and the fraction of the surface bare and available for adsorption =1-θ

Suppose the pressure of the gas at that instant = p

According to Langmuir’s theory of adsorption.

Rate of condensation $\propto (1-\theta)P$

$$= K_1 (1-\theta) P$$

Where k_1 is proportionality constant

Rate of evaporation $\propto \theta$.

$=K_2\theta$.

Where K_2 is another constant of proportionality.

When the adsorption is at equilibrium then

$$K_1 (1-\theta) P = K_2\,\theta.$$

$$\theta\,(K_2 + K_1 P) = K_1 P.$$

$$\theta = \frac{K_1 P}{K_2 + K_1 P}.$$

The above equation can be written as

$$\theta = \frac{{K_1}/{K_2}\;P}{1+\frac{K_1}{K_2}P} = \frac{bP}{1+bP}.$$

Where $\frac{K_1}{K_2} = b.$ is another constant.

As the gas molecules are assumed to form a layer, one molecule thick on the surface, the gas adsorbed per unit area or per gram of the adsorbent must obviously be proportional to the surface covered i.e.

$$\frac{x}{M} \propto \theta$$

$$x/M = K_3\,\theta.$$

Where x the mass of the gas absorbed on m gram of the adsorbent & k3 is proportionality constant.

$$\therefore \quad \frac{x}{M} = \frac{K_3 . bP}{bP}$$

$$\frac{x}{M} = \frac{aP}{1+bP}.$$

Where $k_3b = a$ is another constant. The above equation is known as Longmuir adsorption isotherm.

BET Isotherm (postulates)

Brunner, Emmett and Teller (B.E.T) extended the Langmuir approach and proposed a theory for multiplayer adsorption. This theory is based on the following postulate.

i) The Langmuir's approach assumed only monomolecular layer adsorption. BET isotherms is an extension to this approach.

ii) B.E.T is also based on kinetic model like langmuir's approach. In this model it is assumed that the condensation forces are the principal forces in adsorption

iii) Rate of evaporation from each succeeding layer is equal to the rate of condensation on the preceding layer.

iv) Rate of evaporation is equal to the rate of condensation.

v) The heat of adsorption is involved exponentially in each of the equilibrium rate expression.

vi) It is assumed that the heat of adsorption in each layer other than the first layer is equal to the heat of liquefaction of the bulk adsorb ate material.

BET equation:

$$\frac{P}{V(P^o - p)} = \frac{1}{V_m C} + \left[\frac{C-1}{V_m C}\right]\frac{P}{P^o}$$

It can also be written in the form

$$V = \frac{V_m C f}{1-f}\frac{1}{1+(C-1)f}$$

V = volume of the gas adsorbed at given pressure.

V_m = volume of the gas adsorbed when the surface is completely covered by a unimolcular layer.

f = $\frac{P}{P^o}$ where P^o is the vapour pressure at the experimental Temperature T.

C = Constant at the given temperature

E1 = Heat of adsorption of the gas in the first layer

EL = heat of liquefaction of the gas

If $E_1 > E_L$ so that c is considerably greater than 1, or (1) gives a curve of the type II. If $E_1 < E_L$, the curve of type III is obtained.

Determination of surface area:

The p lot of $f/V(1-f)\,Vs\, f\ (i,e.\ P/V(P^o - P)\ Vs\ P/P^O)$ is a straight line with slope = $(C-1)/V_mC$ and intercept on the y-axis = $1/V_mC$

From these quantities the value of Vm i.e., the volume of the gas required to completely cover the surface of the adsorbent with a unimolecular layer, can be calculated. As 22400 cc of the gas at STP contains Avogadro's number of molecules, therefore, the number of molecules in the volume Vm can be calculated. Further as the area of cross- section per single gas molecule used for adsorption is known, there fore the total area occupied by the gas molecules gives the area of the definite weight of the adsorbent taken.

Calculation:

Volume V_m as obtained from the graph is reduced to N.T.P conditions by using the general gas equation.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

The surface area of the adsorbent may be calculated directly from the value of V_m as follows.

22400 cc of the gas at STP contain = 6.022×10^{23} molecules.

V_m cc of the gas at STP will contain = $\dfrac{6.022 \times 10^{23} \times V_m}{22400}$ molecules.

If the area occupied by a single molecule is S, then the surface area of the adsorbent.

$$\frac{6.022 \times 10^{23}}{22400} \times V_m \times S$$

Suppose W gm of the adsorbent was used in the experiment then area per unit gram of the adsorbed is

$$\frac{6.022 \times 10^{23}}{W \times 22400} \times V_m \times S$$

Applications of adsorption:

1. In softening hard water: Hard water is passed thro' Zeolite. Ca $^{2+}$, Mg $^{2+}$are adsorbed by zeolite which releases Na^{+} to water. Thus water is softened
2. In decoloursing: Sugar, Vinegar etc., when manufactured is colored. Their colures are removed by adsorbents like charcoal.
3. Adsorption Indicators: Several dye like eosin, dichlorofluorescein etc, are used as adsorption indicators in titrations.
4. In chromatography: Entire chromatographic analysis is based on adsorption only.
5. In curing a disease: when drugs are administrated to cure diseases they get adsorbed on the germs and kill them.
6. Removal of unwanted gases or vapors: charcoal is used in gas masks to remove unwanted gases and vapours.

Questions:

1) Writes notes or Henry's law and its applications.
2) Write notes a Raoults law of binary mixtures and its deviations.
3) What are ideal and non ideal solutions?
4) Write notes on azetropic distillation.
5) Show how van's Hoff I is calculated for an electrolyte.
6) State and explain nernst distribution law and is limitations
7) Derive relationship between K_p& Kc
8) Derive equilibrium constant ka of a chemical reaction with the help of thermodynamies.
9) Derive van's Hoff isochroes equations.
10) Discuss Dedonders treatment of chemical equilibrium.
11) Explain the effect of temperature and pressure on equilibrium constant.
12) Distinguish between physisorption and chemisorptions.
13) Discuss Freundlich adsorption isotherm.
14) Explain Longmuir theory of adsorption,
15) What are the postulates of B.E.T Theory?

NOTES

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UNIT - II

CHEMICAL KINETICS

2.1 Derivation of rate constant of a second order reaction when the reactants are taken at different concentrations.

A reaction is said to be of the second order if the rate of reaction depends upon two concentration terms.

The general equation for such reaction is

$$A + B \rightarrow \text{Products}$$

Let the initial concentration of A is amoles and B is b moles after time interval t sees. X moles undergo reaction then the remaining concentration of A & B is (a-x) and (b-x) moles respectively.

$$\frac{dx}{dt} \propto [A][B]$$

Rate of reaction $\propto (a-x)(b-x)$

$$\frac{dx}{dt} = K(a-x)(b-x) --------1$$

Equation (1) may be re written as

$$\frac{dx}{(a-x)(b-x)} = K\,dt. ------------------2$$

Resolving the L.H.S into partialfractions eqn (2) may be rewritten as

$$\frac{1}{a-b}\left[\frac{1}{(b-x)(a-x)}\right]dx = K\,dt$$

Integrating this equation. We get

$$\frac{1}{a-b}\left(\int\frac{dx}{b-x}\int\frac{dx}{a-x}\right) = K\int dt$$

$$\frac{1}{a-b}\,[|n(b-x)-(-|n(a-x)] = Kt + C.$$

$$\frac{1}{a-b}\,[|n(a-x)-|n(b-x)] = Kt + C.$$

$$1\big/_{a-b}[|n\frac{a-x}{b-x}] = Kt + C. \qquad --------3$$

Where C is the integration constant.

But at t=0, x=0 substitute these values in 3 we get

$$\frac{1}{a-b}(l\,n\,a/b) = C.---------------4$$

Subsitute (4) in (3)

$$\frac{1}{a-b}\ln\frac{a-x}{b-x}=Kt+\frac{1}{a-b}\ln\frac{a}{b}$$

$$Kt=\frac{1}{a-b}\ln\frac{a-x}{b-x}-\frac{1}{a-b}\ln\frac{a}{b}$$

$$=\frac{1}{a-b}\left[\ln\frac{a-x}{b-x}-\frac{1}{a-b}\ln\frac{a}{b}\right]$$

$$=\frac{1}{a-b}\ln\left(\frac{a-x}{b-x}\times\frac{b}{a}\right)$$

$$K=\frac{2.303}{t(a-b)}\log\frac{b\,(a-x)}{a(b-x)}$$

Derviation of rate constant of a second order reaction – when the reactants are taken at the same initial concentration:

General equation for such reaction is

A + B → Products

Let the initial concentration of A and B is a moles after time t_1x moles undergo reaction then the remaining concentration of A, B will (a-x) moles

Applying the law of mass action

Rate of reaction $\frac{dx}{dt}\propto[A][B]$

$$\propto(a-x)(a-x)$$

$$\frac{dx}{dt}=K(a-x)^2 \qquad -------1$$

Equation (1) can be re written as

$$\frac{dx}{(a-x)^2}=K\,dt$$

On Integration $\int\frac{dx}{(a-x)^2}=K\int dt$

$$\frac{1}{a-x}=K\,t+C-------------2$$

When c is the Integration constant when t=0 x=0 subsitute these vales in (2)

then $C=\frac{1}{a}.$

Substitute C in (2) we get

$$\frac{1}{a-x} = Kt + \frac{1}{a}$$

$$Kt = \frac{1}{a-x} - 1/a.$$

$$= \frac{a-(a-x)}{a-(a-x)}$$

$$= \frac{x}{a(a-x)}$$

$$K = 1/t.\frac{x}{a(a-x)}$$

Unit: lit. mol^{-1} sec^{-1}

Determination of the rate constant of II order reaction:

E. g Saponification of esters.

The reaction of esters with Na0H is called saponification of esters. For Example, the reaction of ethyl acetate with sodium hydroxide solution takes place. As follows

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

The reaction involves Na0H as one of the reactants, the concentration of which decreases as the reaction progresses. Starting with known concentration of ethyl acetate and sodium hydroxide (preferably equal concentration), the concentration of Na0H at any instant of time can be found by with drawing a definite amount of the reaction mixture and titrating against a standard acid. The same volume if the reaction mixture with drawn at different intervals of time.

Calculation:

$$\left.\begin{array}{l}\text{Volume of the standard acid at}\\ \text{the Beginning of the experiment}\end{array}\right\} = Vo$$

∝ Initial concentration of Na0H

∝ a

a ∝ Vo ------- (1)

Volume of standard acid solution used

At any instant of time t_1, ∝ V_t

∝ Concentration of NaoH at that instant

∝ (a-x)

$$(a-x) \propto V_t \text{-------} (2)$$

From equation (1) (2) we get

$$x \propto \text{Vo-Vt} \text{-----------------------} (3)$$

Substituting the values of a, x and (a-x) from equation (1) , (2) & (3) in the second order equation.

K =1/t .a/a(a-x)

= 1/t. (Vo-Vt)/Vo.Vt

Derivation of rate constant of a Third order reaction;-

When the reactants are taken at the same initial concentration

A reaction is said to be of the third order if the rate of reaction depends upon three concentration terms.

The simplest case of this type can be represented as

$$3A \rightarrow \text{Products.}$$

Let a is the initial concentration of A and x is the concentration of A after time t. Then the remaining concentration of A is (a-x).

According to the law of mass action.

$$\frac{dx}{dt} \propto [A]^3$$

The rate of the reaction is $\frac{dx}{dt} \propto (a-x)^3$

$$\frac{dx}{dt} = K(a-x)^3 ----1$$

The equation (1) may be rewritten as

$$\frac{dx}{(a-x)^3} = Kdt$$

Integrating this equation, we get

$$\int \frac{dx}{(a-x)^3} = \int Kdt$$

$$\frac{1}{2(a-x)^2} = \int Kdt$$

Where c is the Integration constant.

When t=0, x=0 substitute these values in (2)

We get $C = \frac{1}{2a^2}$

Substituting this value in equation (2) we get

$$\frac{1}{2(a-x)^2} = Kt + 1/2a^2$$

$$Kt = \frac{1}{2(a-x)^2} - a^2$$

$$= 1/2\left[\frac{1}{(a-x)^2} - a^2\right]$$

$$K = 1/2t\left[\frac{1}{(a-x)^2} - a^2\right]$$

UnitL litre^2 mole^{-2} sec^{-1}

Examples;

1) $2NO + Cl_2 \rightarrow 2NOCl$
2) $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$

Determination of order of a Reaction:

1) **Trial and error method:**

The appropriate values of a, x and (a-x) are substituted into the integrated form of the rate equation for the first order, second order and third order one by one. The rate equation which gives the constant value of K gives the order of the reaction. This method involves trial of one equation after another till the correct one is found.

2) **Graphical method:**

In this method suitable function is plotted against time.

a) If the plot of log (a-x) against time is a straight line, the reaction is of the first order.

b) If the plot of $\frac{1}{(a-x)}$ against time is a straight line, the reaction is of the reaction is of the second order.

c) If the plot of $\frac{1}{(a-x)^2}$ against time is a straight line, the reaction is of the third order.

d) If the plot of x against time is a straight line, the reaction is of Zero order.

3) Half life Period method:

Half life period for nth order of a reaction is directly proportional to (n-1) of power to the initial concentration of the reactant

$$t\ 1/2 \propto \frac{1}{a^{n-1}}$$

For 2 different initial concentrations a_1, a_2 the half life period will be$(^t1/2)_1$ $(^t1/2)_2$ then.

$$(t_{1/2})_1 \propto \frac{1}{a_1^{\,n-1}} \qquad \text{---------------- } 1$$

$$(t_{1/2})_2 \propto \frac{1}{a_2^{\,n-1}} \qquad \text{----------------- } 2$$

2 / 1 we get

$$(^t\ ½)_1 / (^t\ ½)_2 = (a_1/a_2)^{n-1}$$

Take log on both sides

$$\log \frac{(^t1/2)_2}{(^t\ ½)_1} = (n-1) \log \frac{a_1}{a_2}$$

$$(n-1) = \frac{\log(t\ ½)_2 / (t\ ½)_1}{\log a_1 / a_2}$$

$$(n-1) = \frac{\log(t\ ½)_2 - \log(t\ ½)_1}{\log a_1 - \log a_2}$$

$$n = 1 + \frac{\log(t\ ½)_2 - \log(t\ ½)_1}{\log a_1 - \log a_2}$$

Thus starting with 2 different initial concentration and finding the half life period each case, the value of n can be calculated.

4) Use of Differential Rate equation (or) Van’t hoff method:

Rate for nth order is directly proportional to concentration of nth power of its concentration. i.e.,

$$\frac{-dc}{dt} \propto C^n$$
$$\frac{-dc}{dt} = KC^n$$

Let us consider the initial concentrations of reactants are C_1 and C_2 then the rates are $\frac{-dc_1}{dt}$, $\frac{-dc_2}{dt}$ then

$$\frac{-dc_1}{dt} = KC_1^{\,n} \text{ ----------------- } 1$$
$$\frac{-dc_2}{dt} = KC_2^{\,n} \text{ ----------------- } 2$$

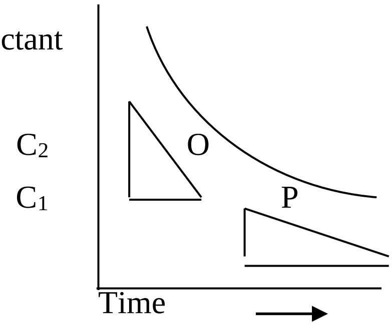
$$1 \div 2 \quad \frac{-dc_1/dt}{-dc_2/dt} = \left(\frac{C_1}{C_2}\right)^n$$

Take log on both the sides

$$\log \frac{-dc_1/dt}{-dc_2/dt} = n \log \frac{C_1}{C_2}$$
$$n = \frac{\log\,(-dc_1/dt) - \log\,(-dc_2/dt)}{\log C_1 - \log C_2}$$

Using this equation we can calculate the order of the reaction.

For different time intervals concentration of reactant are determined. Then a graph is drawn between concentration Vs time. For the concentrations C1 & C2 corresponding points 0 & p are marked on the curve. To this point a tangent is drawn. Slope of the tangent gives $-dc_1$ / dt & $-dc_2$/dt



Substitution of these values in equation (3) enables evaluation of n, the order of the reaction.

5) Ostwald's isolation method:

This method can be used for finding the order of those reaction which involves two or more reactants. The method is based upon the fact that the order of a reaction does not depend upon the concentration of those reactants which are taken in excess. Turn by turn, all reactants except one are taken in excess. The order thus observed is with respect to the reactant that has been isolated from the others. The total or the overall order of the reaction is the sum of the orders found with respect to the different reactants one by one by isolation.

For example, suppose a reaction involves three reactants A,B and C. In the first case B & C are taken in excess (so that A is isolated). The order thus observed is the order with respect to A. Similarly by taking A and C in excess, the order with respect to B can be found and by taking A and B in excess, the order with respect to C can be found. Suppose the orders with respect to A, B, C are found to be a, b, and c respectively. Then the overall order of the reaction is a+b+c.

Experimental methods in the study of kinetics:

1. Volumetry.

Principle: In this technique, the change in volume of the reactants or the products is determined at different intervals of time.

Example: The decomposition of hydrogen peroxide can be studied by this technique. In the presence of platinum black H_2O_2 decomposes as

The progress of the reaction can be followed in two ways

1. By cooling the oxygen gas evolved during the decomposition and measuring its volume at definite intervals.
2. Equal portions of H_2O_2 are titrated against standard $kMnO_4$ solution at regular intervals. The titre values give the amount of hydrogen peroxide which remains undecomposed. This method is more convenient. The experimental results show that the decomposition of H_20_2 follows first order kinetics.

Calculation;

$$\left.\begin{array}{r}\text{The volume of } KMnO_4 \text{ required by a particular}\\ \text{Volume of } H_2O_2 \text{ at the beginning.}\end{array}\right\} = V_1$$

$\propto$ the Initial concentration of H_2O_2

$= a.$

$$\left.\begin{array}{r}\text{The volume of } KmnO_4 \text{ required after}\\ \text{time interval t}\end{array}\right\} = V_2$$

$\propto$ the remaining concentration after time t secs.

$= (a-x)$

The values of a and (a-x) are substituted in the first order rate equation.

$$K = \frac{2.303}{t} \log \frac{a}{a-x}.$$
$$= \frac{2.303}{t} \log \frac{V_1}{V_2}$$

The value of k is found to be constant showing that the decomposition of H_20_2 follows first order kinetics.

Manometry:

Principle: In this technique, the change in pressure of the reactants or the products is determined at different intervals of time.

Example; $2\,N_2O_5 \leftrightarrow 4NO_2 + O_2$

Nitrogen pent oxide is taken in a round bottomed flask and it is kept in a thermostat. It is connected to a manometer. Initially the level of mercury is equal when the reaction takes place no. of. Molecules of products increases the pressure also increases. Hence mercury level will be pushed down in one limb and it is increased at the other. The distance between the two levels will give the pressure at different time interval. This method is applicable only if both the reactants and products are gases.

Calculation:

The pressure of the reaction at the beginning = P_O

$\propto$ the Initial concentration of N_2O_5

$a = P_\propto - P_O$

$\left.\begin{array}{l}\text{The pressure of the reaction after a time}\\ \text{Interval t secs}\end{array}\right\} = P_t$.

$\propto$ (a-x)

= The remaining concentration of N_2O_5 after time t secs

The pressure of the reaction at infinite level (a-x) = $P_\propto - P_t$

The value of a and (a-x) and substituted in the first order rate equation.

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$
$$= \frac{2.303}{t} \log \frac{P_\propto - P_O}{P_\propto - P_t}$$

The value of k is found to be constant showing that the decomposition of N_2O_5 follows first order kinetics.

Polarimetry:

In this technique, the change in optical rotation of the reactants or the products is determined at different intervals of time

Example: Inversion of cane sugar

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6 .$$

During the reaction dextro rotatory sucrose is converted to leavo rotatory products. Hence the name inversion of sucrose. This reaction is also example for pseudo unimolecular reaction.

20% cane sugar solution and 1 M Hcl are kept in a thermostat to attain equilibrium. Then equal volumes of both the solutions are mixed separately in a vessel, shaken well then transferred into a polarimeter tube with thermostatic arrangements. Then it is placed in the polarimeter and the angle of rotation is measured at the end of every 20 minutes for 3 hrs and the final reading is taken at the 24th hour.

Angle of rotation at the beginning = r_O

Angle of rotation after the time = r_t

Infinite angle of rotation = $r_\propto$

The initial concentration of sucrose = a

$\propto (r_O - r_\propto)$

The concentration of sucrose after the z Time interval t sees $\}$ = (a-x)

$= (r_t - r_\propto)$

The values of a and (a-x) are substituted in the first order rate equation

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$= \frac{2.303}{t} \log \frac{r_O - r_\propto}{r_t - r_\propto}$$

The value of k is found to be constant showing that the hydrolysis of cane sugar follows first order kinetics.

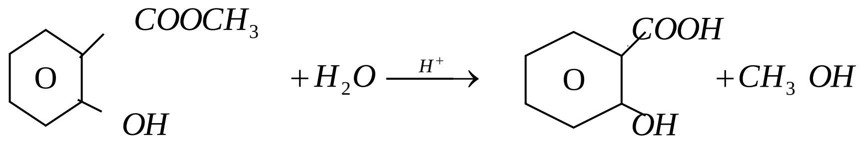
Colorimetry:

Principle: In this technique, the change in intensity of the colour of reactants (0r) products at different intervals of time. According to Beer Lambert's law.

$$I \; abs = I_O (1- e^{-Kcl})$$

Intensity of absorbed light is directly proportional to concentration.

Example: Hydrolysis of methyl salicylate



λ = 3320 A° λ = 3050 A°

Methyl salicylate and the catalyst are kept in equilibrium, then the equal volumes are taken in a colorimeter tube 3320 A° light radiation is passed. The intensity of light at different intervals is measured.

Intensity of light absorbed at the beginning = I_o
$\propto$ the Initial concentration
of the reactant.
= a.

Intensity of light absorbed after the time
Interval t sees } = I_t
= The remaining concentration of the reactant after time interval t secs.

The values of a and (a-x) are substituted in the first rate equation then

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$= \frac{2.303}{t} \log \frac{I_O}{I_t}$$

The value of k is found to constant showing that the hydrolysis of methyl salicylate follows I order kinetics.

Kinetics of fast reaction by temperature jump method:

Reaction that takes place in times shorter than the time required to mix the reactants can't be investigated by conventional methods. Such reactions are termed fast reactions.

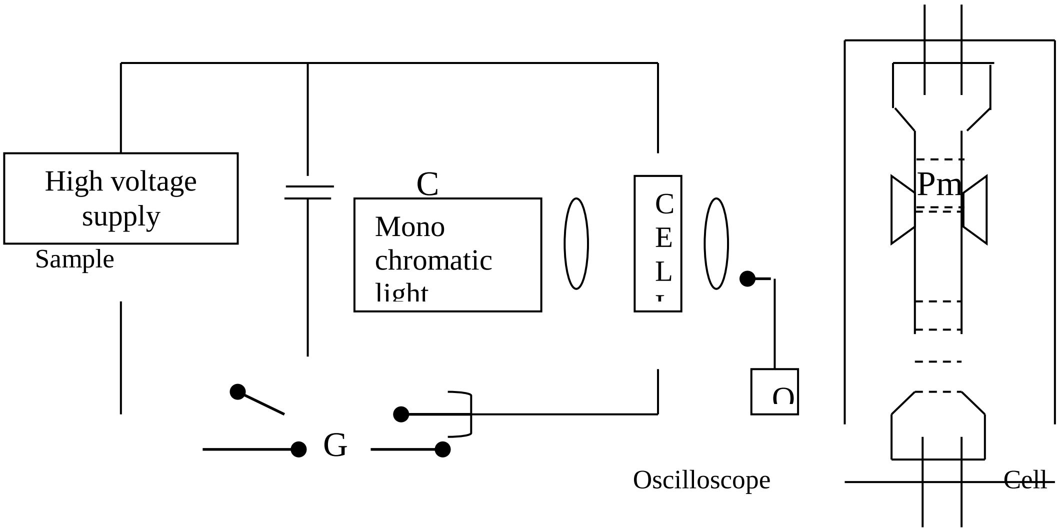
Relaxation technique to available to follow the kinetics of fast reactions.

In this technique the reacting system in equilibrium is subjected to a sudden variation in some physical parameter on which the equilibrium constant of the reaction depends. The system changes to a new state of chemical equilibrium. The rate of this change is called relaxation. Relaxation studies are carried out with such parameter as temperature, pressure and electric field.

Temperature jump method:

In this method, a temperature change of several degrees ($\approx 10^{o}C$) in 10^{-6} see is created by a discharge of a high voltage condenser (100kv) thro' a small quantity of the solution. Then the dependence of concentration is followed by the absorption spectroscopy (0r) by measuring electrical conductivity as a function of time. The following is the diagrammatic representation of temperature jump method.

A high voltage supply charges a capacitor c. When a certain voltage is reached, the spark gap G breaks down discharging the capacitor and sending the current through the cell containing the reactive system at equilibrium in a conducting aqueous solutions. As the current passes, the temperature of the system rises by about 10^0 c in a few microseconds.



In the ensuing time interval the concentration of the resulting species adjusts to the new equilibrium value appropriate to the temperature jump. Simultaneously a beam of monochromatic light is passed into the cell, then the intensity of the light beam leaving the cell and entering the detector (pm) photo multiplier tube) is charged. The output of the photomultiplier tube is displayed in the vertical axis of the oscilloscope.

In this way the curve showing the variation of the concentration vs time is plotted on the oscilloscope screen.

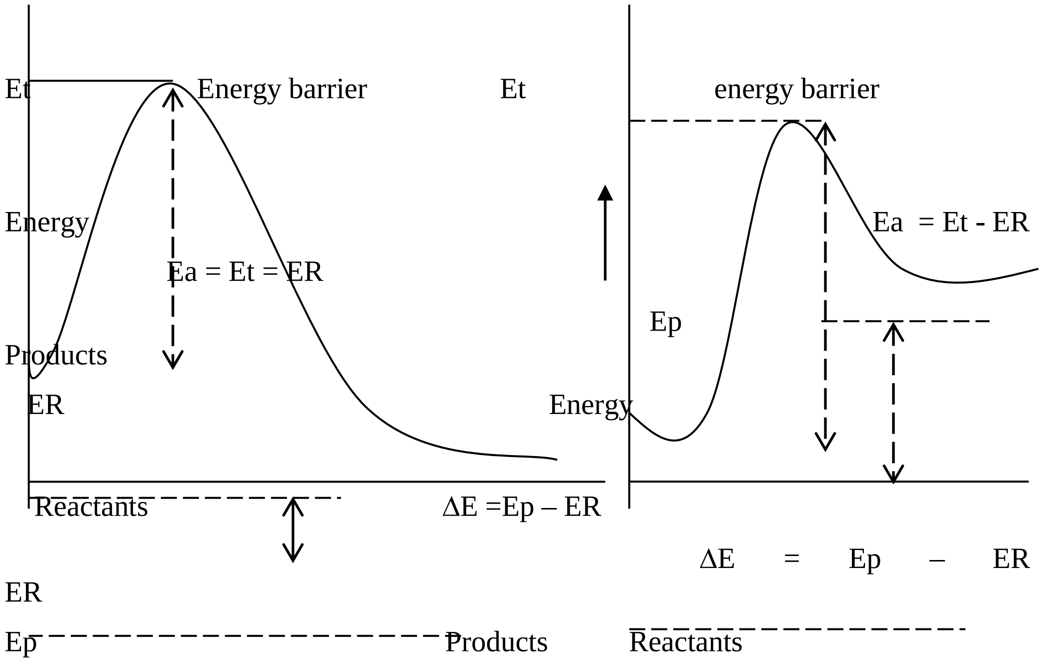
Concept of activation energy:

At room temperature, there is no molecule possessing energy greater than the threshold energy (the minimum amount of energy which the colliding molecules must possess in order that the collision between them is effective) and so there is no reaction. When temperature is increased the molecules of the reactants absorb heat energy and thus a number of molecules start attaining energy equal to (or) greater than the threshold energy and hence the reaction starts.

The extra amount of energy which the molecules of the reactants have to absorb so that their energy becomes equal to the threshold energy is called activation energy

Activation energy = Threshold energy -energy actually possessed by the reacting molecules.

Thus in order that the reactants may change over to products they have to absorb some energy and thus cross a barrier called activation energy barrier. The situation may be represented graphically for exothermic and endothermic reactions as follows.



Reaction Co- ordinate
For Exothermic Reaction
$\Delta E = -Ve$

Reaction Co- ordinate
For Endothermic Reaction
$\Delta E = +Ve$

Where E_t = Threshold energy

E_a = activation energy

E_R = Energy of Reactants

E_P = Energy of Products.

ΔE = Heat of Reaction

Effect of Temperature on the Rate:

The rate equation and the value of the rate constant for a reaction are deducted from measurements of the rate of reaction at a fixed temperature. Temperature has a considerable effect on the rate of chemical reaction. The rate of reaction generally increases with rise of temperature. In most cases a rise of

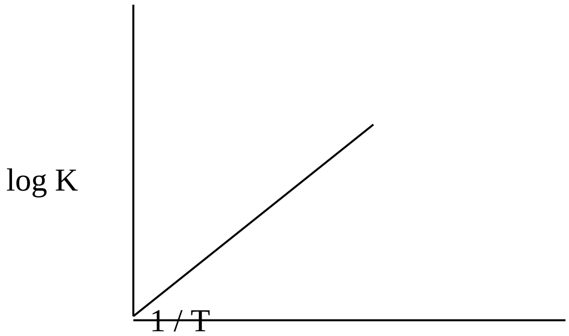
10^{o}C temperature doubles the rate of reaction. In some cases rate of the reaction increases three times.

Arrhenius found that the rate, or rate constant, increasingly exponentially with temperature. It is confirmed by potting log k vs 1/T. This gives a linear graph which shows that

$$\log K \propto 1/T$$

$$K \propto e^{Constant/T}$$

$$K = A.e^{-\Sigma a/RT}$$



Where A is a constant called the frequency factor. Ea is the activation energy.

Determination of energy of activation:

We know that

$$K = A.e^{-\Sigma a/RT}$$

Taking logarithm on both sides, we get

$$\ln K = \ln A - \frac{Ea}{RT}$$

If the values of the rate constant T_1 & T_2 are K_1 and K_2 respectively, then we have

$\ln K_1 = \ln A - Ea/RT_1$ ---------------------(1)

$\ln K_2 = \ln A - Ea/RT_2$ ------------------------(2)

Subtracting equation (1) from (2) we get

$$\ln K_2 = \ln K_1 - \frac{Ea}{RT_2} - \left(\frac{-\Sigma a}{RT_1}\right)$$

$$\ln K_2/K_1 = \frac{Ea}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$= \frac{Ea}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log K_2/K_1 = \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Thus knowing the values of the rate constants k_1 and k_2 at two different temperatures T_1, T_2 the value of E can be calculated

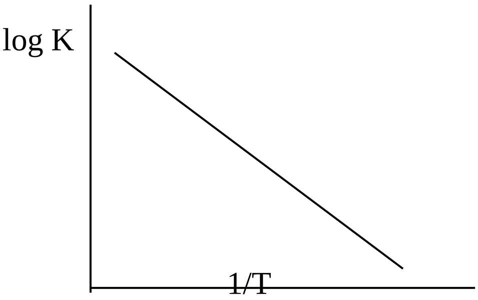
Equation (3) can be written as

$$\ln K = \frac{-Ea}{RT} + \ln A$$

$$\log K = \frac{-Ea}{2.303RT} + \log A$$

This equation is of the form y= mx + c the equation of a straight line. Thus a plot of log k Vs $1/T$ is a straight line.

Slope of the line = $\frac{-Ea}{2.303R}$



From this equation Ea can be calculated

DETERMINATION OF ARRHENIUS FREQUENCY FACTOR A

We know

That

$K = A. e^{-\Sigma a/RT}$

Taking log on both sides

$$\ln K = \ln A - \frac{Ea}{RT}$$

$$\ln A = \ln K + \frac{Ea}{RT}$$

$$\log A = \log K + \frac{Ea}{2.303RT}$$

Thus by knowing the values of Ea and the rate constant k at a particular temperature T we can able to calculate the Arrhenius frequency factor A.

Collision theory of reaction Rates:

Derivation of rate constant of a bimolecular reaction from collision theory:

According to Arrhenius

$$K = A.\, e^{-\Sigma a/RT}$$

The reactants after reaching the activated state it is getting converted to products. But he doesn't explain how they are activated. It can be explained on the basis of collision theory.

According to this theory activation is by collision between molecules. When two molecules involved in collision, their occurs exchange of energy between them. Therefore they acquired energy in excess possessed by it. If the acquired energy is greater then it will reach the activated state and give products.

The scientist W.C Mec. Lewis found that frequency factor A is identified with that of collision number Z. This is possible only the reacting spheres are hard. The rate of reaction depends on two factors.

$$V_{AA} = Z_{AA}\, e^{-\Sigma a/RT}$$

Z_{AA} – represent no. of collision between the two molecular of A Per cc / sec.

From the theory of gases

$$Z_{AA} = \tfrac{1}{2}\sqrt{2}\,\pi d^2 \bar{c} n^2$$

Since collisions involves 2 molecules, the no collision = 1.

$$\therefore \quad Z_{AA} = \tfrac{1}{\sqrt{2}}\,\pi d^2 \bar{c} n^2$$

Where $\bar{c}$ = average velocity of each molecule

n = no. of molecules/cc

d = effective collision diameter.

$C = \sqrt{\frac{8KT}{\pi M.}}$ $\quad M = Mass\, of\ Molecules$

$K = Boltz\, manncons\tan t$

$$\therefore \quad Z_{AA} = \frac{1}{\sqrt{2}} \pi d^2 n^2 \sqrt{\frac{8KT}{\pi M}}.$$

$$= 2n^2 d^2 \sqrt{\frac{\pi KT}{M}}.$$

Though every molecule is taking part in collision all of them are not activated. The fraction of the molecules which are activated i.e., which possess the required amount of activation energy for the reaction. According to Maxwell’s distribution of velocities.

If a gas contains n molecules per cc at a temperature T, the number of molecules (n) possessing the energy of activation Ea is

$$n' = n\, e^{-\Sigma a/RT}$$

$$q = \frac{n'}{n} = e^{-\Sigma a/RT}$$

$$\therefore\ \nu = Z_{AA} . e^{-\Sigma a/RT}$$

$$V = 2n^2\ d^2\ \sqrt{\frac{\pi KT}{M}} . e^{-\Sigma a/RT}$$

This is simple collision theory equation 2 idential molecules.

If A reacts with B (2 different atoms)

Then $Z_{AB} = n_A\, n_B\, d^2{}_{AB} \left[8\pi kt\ \frac{MA+MB}{MA.MB} \right]^2$

Where M_A, M_B = Masses of A & B.

n_A, n_B = no. of molecules/cc.

then rate

$$V = Z_{AB} .\ e^{-\Sigma a/RT}$$

$$V = n_A , n_B\, d^2 AB \left[8\pi kt\ \frac{MA+MB}{MA.MB} \right] 1/2\ .\ e^{-\Sigma a/RT}$$

$$\frac{V}{n_A , n_B} = K^1$$

$$K^1 = d^2 AB \left[8\pi kt\ \frac{MA+MB}{MA.MB} \right] 1/2\ .\ e^{-\Sigma a/RT}$$

Molecules / Cc /Sec

To covert number molecules /cc/ sec to moles /cc/ sec multiply by Avagadro number.

$$K = N\, d^2{}_{AB} \left[8\pi kt \, \frac{MA+MB}{MA.MB} \right]^{1/2} . \, e^{-\Sigma a/RT}$$

$K = e^{-\Sigma a/RT}$

Failures of collision theory:

In some reaction where the calculated and experimental values differ widely (Rate constant). For example

1. Reaction between ethanol vapor and acetic anhydride vapour, the calculated value of k is about 10^5 times greater than the experimental value.
2. In polymerization of ethylene, the calculated value of k is 2000 times greater than the experimental value.
3. In polymerization of 1,3 buta diene, the calculated value is s10,000 times greater than the experimental value

Thus we can say that this theory is applicable only to simple bimolecular reaction but not complex bimolecular reactions.

There fore for the above cases. The rate of the reaction to rewritten as

$$K = P.\, Ze^{-\Sigma a/RT}$$

Z = frequency factor

P = probability factor (or) steric factor

The value of p may vary from $1\text{-}10^{-9}$. It has been introduced to account for the discrepancy between the calculated and the observed value of

Here

$$PZ = N\, d^2{}_{AB} \left[8\pi KT . \frac{M_A + M_B}{M_A M_B} \right]^{1/2}$$

2.5 Lindemann theory of unimolecular reactions:

Collision theory of bimolecular reaction does not explain how the molecules are activated in unimolecular reactions. Therefore in 1922 lindemann proposed a hypothesis.

He accepted that like bimolecular reactions, in unimolecular reactions also molecules are activated by collisions but there is time lag between activation and their reaction (i.e) during this time the activated molecular either react or be deactivated to ordinary molecules this concept may be illustrated as follows:

$$\begin{tikzcd} A+A \arrow[r, shift left, "K_1"] & A^* + A \arrow[l, shift left, "K_2"] \arrow[d, "k_3"] \\ & \textit{prodects} \end{tikzcd}$$

Where K$_1$, K$_2$, K$_3$ are the rate constants of the different processed involved as shown above.

Rate of the reaction is

$$\frac{-d[A]}{dt} = \mathrm{K}_3[A^*]$$

Rate of formation of activated molecules = $K_1[A]^2$

Rate of disappearance of activated molecules =

$$K_2[A^*][A]+K_3[A^*]$$

According steady state principle

Rate formation of an intermediate = Rate of its destruction (or) disappearance

$$K_1[A]^2 = K_2[A^*][A]+K_3[A^*]$$

$$=[A^*][K_2[A]+K_3]$$

$$[A^*]=\frac{K_1[A]^2}{K_2[A]+K_3}$$

Substitute the value of [A*] in (1) then $\dfrac{-d[A]}{dt}=\dfrac{K_3.K_1[A]^2}{K_2[A]+K_3}$

If the pressure is high:

The rate of deactivation by collision is greater than Rate of formation of products then K2[A] >>>> K3 in the Denominator is neglected. Hence

$$\frac{-d[A]}{dt} = \frac{K_3.K_1}{K_2}[A].$$

At low pressure:

The rate of formation of products is higher than that of deactivation by collision then k3 >>> k2[A] Therefore k2[A] in the Denominator is neglected

$$\frac{-d[A]}{dt} = \frac{K \cdot K_3 [A]^2}{K_3}$$

$$= K.[A]^2$$

The reaction is then second order.

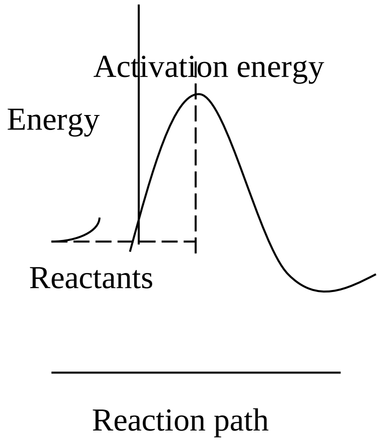
2.6 Theory of Absolute Reaction Rates:

Thermodynamic derivation of rate constant for a bimolecular reaction based on ARRT:

This theory is an alternative approach to reaction kinetics by Eyring and polanyi and their theory is known as absolute reaction rates (or) activated complex theory (or) Transition state theory.

According to this theory, it is believed that before the reacting molecules change into products they form an intermediate called activated complex. Which has higher energy than both Reactants and products. Activated complex

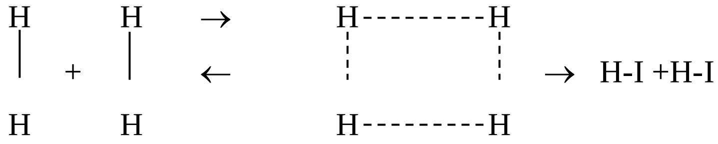
It is for this reason that this theory is called Transition state theory. The activated complex is in equilibrium with the reacting molecules and the rate of reaction is given by the rate of decomposition of the complex to form the products Thus we products represent the bimolecular reaction as follows



$$A + B \leftrightarrow [x^*] \xrightarrow{K} \text{Products.}$$

Reactants *Activated complex*

For example Dissociation of HI



If a reaction is unimoleculur i.e., it involves a single molecule, in that case some rearrangement of atoms and energy must occur yielding an activated complex before the reaction can proceed at all.

The rate of the reaction is so slow that it does not affect the equilibrium between the reacting molecules and the complex.

$$K_{eq} = \frac{[X^{*}]}{[A][B]}$$

K eq is the equilibrium constant for the formation of activated complex.

We know from the thermodynamic relationship that

$$\Delta G^{*} = -RT \ln Kequ.$$

$$\ln Kequ = -\Delta G^{*}/RT$$

$$Kequ = e^{-\Delta G^{*}/RT}$$

Substitute the value of $\Delta G^{*}\ as\, \Delta G^{*} = \Delta H^{*} - T\Delta S^{*}$

Then $$Kequ = e^{-(\Delta H^{*} - T\Delta S^{*})/RT}$$

$$= e^{\Delta S^{*}/R}\, .e^{\Delta H^{*}/RT}$$

The activated complex is a aggregate of atoms which is similar to an ordinary molecule, except that it has one special vibration with respect to which it is unstable. This vibration leads to dissociation of the complex into products. If the frequency of the vibration is then the rate at which the products are formed is given by.

$\text{Rate} = \gamma\, [x]^{*}$

$= \gamma [A]\, [B]\, Keq$ ---------------------------(1)

For an elementary reaction

$$A + B \rightarrow \text{Pr}oducts$$

$$rate \quad = \quad K[A]\,[B] \qquad -------------- 2$$

Compare (1) & (2) then

$K = \gamma\ Kequ.$ ------------------3

From statistical mechanics it was found

$\gamma = RT/Nh$

Where R is Bolzmann constant

H is planks constant

N is Avogadro’s number

Substituting the value of Kequ and in (3)

$$k = \frac{RT}{Nh}.e^{-\Delta H^*/RT}\ .e^{\Delta S^*/R}$$

The reactions which are taking place in solution, the enthalpy of activation and activation energy Ea is the same

$$\Delta H^* = \Sigma a$$

$$\therefore \qquad K = \frac{RT}{Nh}\, e^{\Delta S^*/R}\ .\ e^{-\Sigma a/RT}$$

Comparison between ARRT and CT

Sl.No	**Collision Theory**	**ARRT**
1.	This theory is due to w.c. Mec Lewis	It is an alternate approach to kinetics by Eyring and polanyi.
2.	This theory explain how reactants are getting converted into products (collision)	According to this theory before the reacting molecules change into products they form an intermediate Called activated complex.
3.	It is applicable only to simple molecules which behave as rigid spheres.	It is applicable to both simple and complex molecules
4.	It includes only translational energy while deriving the rate equation.	It includes all the internal degrees of freedom such as Translational, rotational and vibrational energies.
5.	$K = P.Z.e - \Sigma a/RT$ $A = PZ.$ i.e., rate or reaction depends on collision number, energy of activation and probability factor.	$K = \frac{RT}{Nh}\, e^{\Delta S^*/R}\ .\ e^{-\Sigma a/RT}$ $P = \frac{RT}{Zh}\, e^{\Delta S^*/R}.$ When compared with collision theory. Rate of reaction depends on entropy of activation and energy of activation.
6.	Compared to Arrhenius theory it is superior	Among all the theories it is superior.

Significance of free energy of activation (ΔG^{*})

The free energy that takes place when the reactant molecules are converted into activated complex is known as free energy of activation.

According to ARRT

$$K = \frac{RT}{Nh}\ K\,equ.$$

We know that

$$\Delta G^{*} = RT\,|n\ Kequ.$$

$$Kequ = e^{-\Delta G^{*}/RT}$$

$\therefore$ The rate of the reaction

$$K = \frac{RT}{Nh}\,.e^{-\Delta G^{*}/RT}$$

Rate of the reaction depends on free energy of activation. If ΔG^{*} is greater then the rate of reaction will be less and vie versa. Therefore in predicting the rate of reaction free energy of activation plays major role than the energy of activation.

Entropy of activation:

According to ARRT

$$K^{*} = e^{-\Delta H^{*}/RT}\ .\ e^{\Delta S^{*}/R}$$

We know that

$$K = \frac{RT}{Nh}\ K^{*}.$$

Substituting K^{*} in the above equation

$$K = \frac{RT}{Nh}\ e^{\Delta H^{*}/RT}\ .\ e^{\Delta S^{*}/R}$$

$$\Delta H^{*} = \Sigma a.\ energy\,of\ activation.$$

$$K = \frac{RT}{Nh}\ e^{-\Sigma a/RT}\ .\ e^{\Delta S^{*}/R}$$

When we compare this equation with.

$$\mathrm{K = PZ\ e^{-\Sigma a/RT}}$$

We can conclude that

$$PZ = \frac{RT}{Nh}\, e^{\Delta S^{*}/R}$$

Z_1 RT/Nh Are constants. Therefore the probability factor p is related to the entropy of activation ΔS^{*}. If that is positive p is large and if p is large k will also be large. If ΔS^{*} is positive reaction is fast. It ΔS^{*} is negative is small and so k is small. Thus the reaction is slow

2.7 Kinetics of complex reactions:

A reaction which may takes place in many steps or many reactions which take place simultaneously are known as complex reactions. Types of complex reactions are

1. Consecutive (or) Simultaneous reactions.
2. Parallel (or) Side reactions
3. Reversible (or) opposing Reactions.

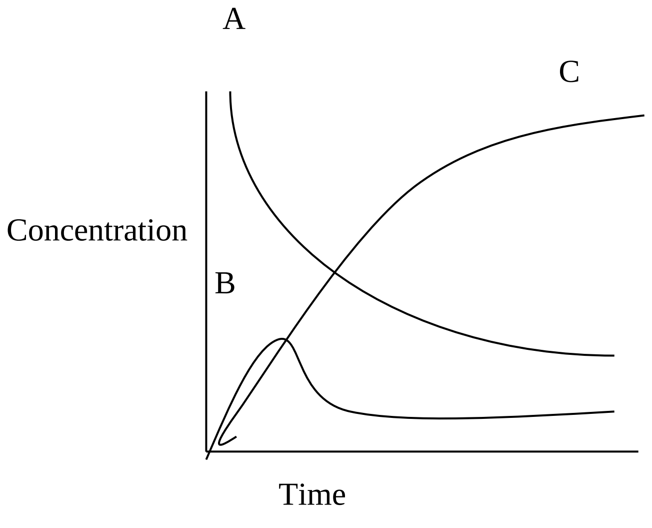
Consecutive Reactions:

The reaction which takes place in many steps is known as consecutive (or) simultaneous reactions.

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C.$$

The reactant A gives the product B which further react and give another product c. The product B is known as an intermediate.

The change in Concentration of A, B, and C with time is indicated in the graph. The slowest step is the rate determining step,



Examples:

1) Oxidation of HI by H_2O_2

$$H_2O_2 + 2HI \rightarrow 2H_2O + I_2$$

The reaction occurs in various stages.

$$H_2O_2 + I^- \rightarrow H_2O + IO^- \text{ (Slow)}$$

$$\left.\begin{array}{l} H + IO^- \rightarrow HIO \\ HIO + H^+ + I^- \rightarrow H_2O + I_2 \end{array}\right\} \text{(Fast)}$$

The rate equation is

$$\frac{dx}{dt} = K[H_2O_2][I^-]$$

The order is 2.

2) Reaction between Nitric oxide and Hydrogen

$$2\,NO + 2H_2 \rightarrow N_2 + 2H_2O$$

Mechanism

$$2NO + H_2 \rightarrow N_2 + H_2O_2 \text{ (Slow)}$$

$$H_2O_2 + H_2 \rightarrow 2H_2O \quad \text{(Fast)}$$

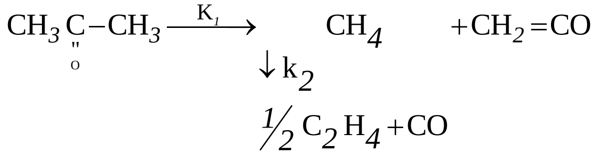
The rate of the reaction is

$$\frac{dx}{dt} = K[NO_2]^2[H_2]$$

The order of the reaction in 3.

3) Series of Radio active decay.

4) Thermal decomposition ion of acetone



$$\begin{array}{lll} CH_3\underset{\overset{\|}{O}}{C}-CH_3 \xrightarrow{K_1} & CH_4 & + CH_2=CO \\ & \downarrow k_2 & \\ & \tfrac{1}{2}C_2H_4 + CO & \end{array}$$

5) Decomposition of Di methyl ether

$$CH_3-O-CH_3 \xrightarrow{K_1} CH_4 + HCHO$$

$$HCHO \xrightarrow{K_2} H_2 + CO.$$

Parallel or side reactions:

If in a Reaction, the reactants react to form 2 different products by 2 different paths such that one product in large amount than the other, then the reaction giving the large amount is called main reaction while the other giving the small amount of product is called side reaction (or) parallel reaction.0

$$\begin{tikzcd}[row sep=small] & B \quad 90\% \quad \text{(Main Reaction)} \\ A \arrow[ur, "K_1"] \arrow[dr, "K_2"'] & \\ & C \quad 10\% \quad \text{(Side Reaction)} \end{tikzcd}$$

In these reactions, the most rapid rate determine predominate path of the over all reaction. If $K_1 >> K_2$ then $A \rightarrow B$.

Examples

1) Decomposition of ethanol vapour

$$\begin{tikzcd} C_2H_5OH \arrow[r, "K_1"] \arrow[dr, "K_2"'] & C_2H_4 + H_2O \text{ (Main)} \\ & CH_3CHO + H_2 \end{tikzcd}$$

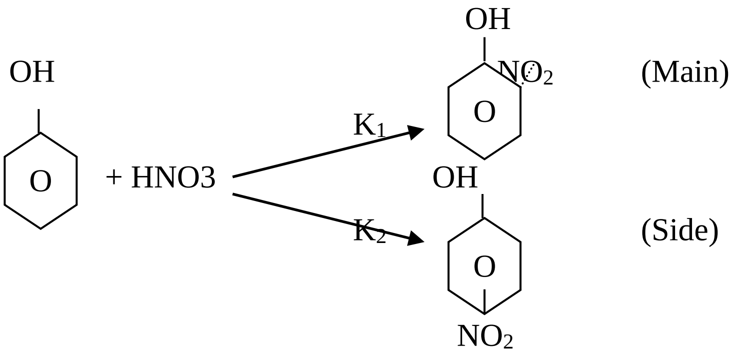
2) Chlorination of Benzene

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl \text{ (Main)}$$

$$C_6H_6 + 3\,Cl_2 \rightarrow C_6H_6Cl_6 \quad \text{(Side)}$$

BHC

3)



Opposing (OR) Reversible reactions:

If in a reaction, the reactants react to form the product and the products also recent to give back the original substances under the same conditions, it is called a reversible reaction.

In other words the reaction takes place not only in the forward direction but also in the backward direction.

$$A \underset{K_b}{\overset{K_f}{\rightleftharpoons}} B$$

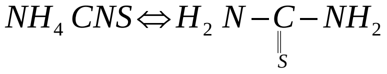
If the rate contents for the back ward reaction (K_f) is small as compared to that of the forward reaction (K_b) the former can be neglected in comparison with the latter. However the rate constants of both reactions are at comparable rates, the rate equation has to be changed.

Example:

1) $2HI \Leftrightarrow H_2 + I_2$

2) $2NO + O_2 \Leftrightarrow 2NO_2$

3) $CH_3COOH + C_2H_5OH \Leftrightarrow CH_3COOC_2H_5 + H_2O$

4) 
$NH_4CNS \Leftrightarrow H_2N - \underset{\underset{S}{\|}}{C} - NH_2$

5) $N_2 + 3H_2 \Leftrightarrow 2NH3.$

6) $CH_3COOC_2H_5 + NaOH \Leftrightarrow CH_3COONa + C_2H_5OH$

Questions:

1) Explain the effect of temperature on reaction rate

2) Define the expressions for rate constant and half life period for a second order reaction of the type 2A→P.

3) Explain the graphical method of determining order of a reaction.

4) Describe the temperature-jump method to follow the kinetics of fast reactions.

5) Discuss kinetics of a consecutive reactions.

6) Discuss the postulates of ARRT and derive the rate constant of a reaction using ARRT.

7) How the kinetics of a chemical reaction is studied by polarimetry method.

8) Write a note on lindemann hypothesis.

9) Explain and derive rate equation based on collision theory for a bimolecular reaction.

10) Compare ARRT and C/T.

NOTES

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UNIT –III

Grotthus –Draper law.

“Only those radiations which are absorbed by reacting systems are effective in producing the chemical change”.

When a light falls on a body, a part of it is reflected, a part of it is transmitted and the rest of it is absorbed. It is only the absorbed light which is effective in bringing about a chemical reaction.

But all the absorbed light not results into chemical reaction. The absorbed light may bring reemission in the form of fluorescence, phosphorescence etc., similarly the absorbed light is converted into thermal energy and in some cases the reacting substances does not absorbs energy but may be absorbed by some other substances present along with it. The energy thus absorbed by it is then passed onto the reacting substance which then starts reacting. (Photosensitization)

The stark Einstein law of photochemical equivalence

“Every atom or molecule that takes part in a photo chemical reaction absorbs one quantum of the radiation to which the substance is exposed.

If γ is the frequency of the absorbed radiation, then the energy absorbed by each reacting atom or molecule is one quantum i.e., $h\gamma$ where h is plank’s constant. The energy absorbed by one mole of the reacting molecules will then be given by.

$$E = Nh\gamma$$

Where N is Avogadro’s number

Putting

$$\gamma = C/\lambda$$

$$\therefore \quad E = \frac{NhC}{\lambda}$$

Where C is the velocity of light and λ is the wavelength of the absorbed radiation.

Substituting, $N = 6.022 \times 10^{23}, h = 6.626 \times 10^{-27}\, erg/see.\ C = 3 \times 10^{10}\, cm/see.$

$$E = \frac{6.022 \times 10^{23} \times 6.626 \times 10^{-27} \times 3.0 \times 10^{10}}{\lambda}$$

$$= \frac{119.7 \times 10^{6}}{\lambda} erg/mole.$$

$$(or) \quad = \frac{119.7 \times 10^{6}}{4.184 \times 10^{7}\, \lambda} cal/mole$$

$$= \frac{2.86}{\lambda}\ cal/mole.$$

Hence λ is expressed in cm. However λ is usually expressed in angstrom unib (A^o) 1 $A^o = 10^{-8}$ cm. therefore

$$E = \frac{2.86 \times 10^{8}}{\gamma} \text{cal/mole}$$

$$\lambda \text{ in Angstrom unit}$$

Further 10^3 cal $= 1$K.cal Hence

$$E = \frac{2.86 \times 10^{5}}{\lambda} \text{K cal/mole.}$$

Quantum efficiency (or) Quantum yield:

It is defined as the number of moles reacting per Einstein of the light absorbed. It is represented by ϕ

$$\phi = \frac{Number of\ molecules reacting\ in\ a\ given time.}{Number of\ quanta of\ light\ absorbed\ in\ the same time.}$$

(Or)

$$\phi = \frac{Number of\ moles reacted\ in\ a\ given time.}{Number of\ Einstein of\ light\ absorbed\ in\ the same time.}$$

If stark –Einstein's law is strictly obeyed, then the ϕ value should be equal to unity. However this law is applicable only to the primary processes.

Number of moles React per unit time = Rate of the photochemical reaction.

$$\therefore \quad \phi = \frac{\text{Rate of photo Chemical reaction}}{\text{Number of Einstein absorbed.}}$$

Based on ϕ values photochemical reactions are classified as

i) Photochemical reaction with ϕ values of some small integers.

ii) Photochemical reaction with very low ϕ values 0.01 etc.

iii) Photochemical reaction with very high ϕ values $-10^3 - 10^6$ values

Energy transfer in photochemical reactions –photosensitization:

There are many substances which do not react directly when exposed to light. However, if another substance is added, the photochemical reaction starts. The substance thus added it self does not undergo any chemical change.

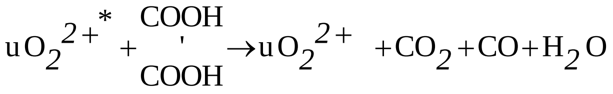
It merely absorbs the light energy and then passes it on to one of the reactants. Such a substance which when added to a reaction mixture helps to start the photochemical reaction but it self does not undergo any chemical change is called a photo sensitizer and the process is called photosensitization. Thus a photo sensitizer simply acts as a carrier of energy.

Examples:

1. Decomposition of oxalic acid in presence of uranyl sulphate:

The colored uranyl ions absorb the light and then pass it on to the colorless oxalic acid which then undergoes decomposition.

$$uO_2^{2+} + h\gamma \rightarrow uO_2^{2+*}$$



$$uO_2^{2+*} + \begin{array}{c}COOH\\ | \\ COOH\end{array} \rightarrow uO_2^{2+} + CO_2 + CO + H_2O$$

The uranyl ions thus act as photosensitizer.

2. Dissociation of H_2 molecules in presence of mercury vapor:

Hydrogen molecules do not dissociate which exposed to ultra violet. However when hydrogen gas is mixed with mercury vapour and then exposed to the UV light, hydrogen molecules dissociate to given hydrogen atoms.

$$Hg + h\gamma \rightarrow Hg^*$$

$$Hg^* + H_2 \rightarrow Hg + 2H$$

Here Hg acts as a photosensitizer.

3. Photosynthesis in plants:

Co_2 and water present in the air do not absorb the visible light emitted by the sun. However the chlorophyll present in the plants can absorb the visible light. After absorption it passes on the energy to the CO_2 and water molecules which then combine to form carbohydrates along with the evolution of O_2

$$CO_2 + H_2O + h\gamma \xrightarrow{Chlorophyll} (CH_2O)_n + O_2 \uparrow$$

Thus chlorophyll acts as a photosensitizer in the above reaction.

Chemiluminescence:

When a photochemical reaction takes place, light is absorbed. However, there are certain reaction in which light is produced. “The emission of light in chemical reactions at ordinary temperatures is called chemiluminescences. Thus chemiluminescence is just the reverse of a photochemical reaction.

Examples:

a) The light emitted by glow-worms is due to oxidation of the protein, Luciferin present in the glow worm.

b) The oxidation of yellow phosphorous in oxygen or air to give P_2O_5 at ordinary temperatures (-10 to 40^0C) is accompanied by the emission of visible greenish-white luminescence.

In the above cases, a part or whole of the energy emitted during the reaction, is used up for the excitation of electrons, when they jump back to the inner orbits, the emission of light takes place.

Fluorescence:

There are certain substances which when exposed to light or certain radiations absorb the energy and then immediately or instantaneously start re-emitting the energy. Such substances are called fluorescent substances and the phenomenon is called fluorescence. Obviously the absorption of energy results into the excitation of the electrons followed immediately by the jumping back of the excited electron to the lower levels. As a result, the absorbed energy is emitted back.

Fluorescence starts as soon as the substance is exposed to light and the fluorescence stops as soon as the light is cut off.

Examples:

i) Fluorite CaF_2

ii) Certain organic dyes such as eosin, fluorescein etc.,

iii) Certain inorganic compounds such as uranyl sulphate uo_2so_4

During fluorescence, the wave length of the emitted light is greater than that of the absorbed light. Thus the energy produced is smaller.

Phosphorescence:

There are certain substances which continue to glow for some time even after the external light is cut off. Such substances are called phosphors or phosphorescent substances and the phenomenon is called phosphorescence. It is found mostly in solids, because the molecules have least freedom of motion. The excited electrons thus keep on jumping back slowly for quite some time.

Examples:

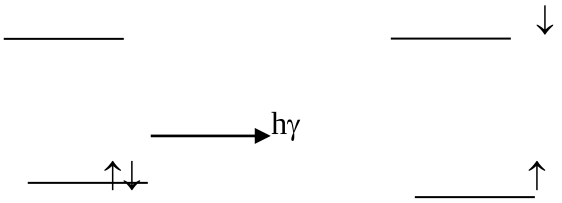
i) Zinc sulphide

ii) Sulphides of the alkaline earth metals.

It has been found that a fluorescent substance becomes phosphorescent by fusing it with other substances. For example many dyes which show fluorescence, when dissolved in fused boric acid or glycerol and cooled to rigid mass become phosphorescent.

Mechanism of fluorescence & phosphorescence (Jablonski diagram)

When energy in the form of light radiation falls on certain molecules, some of the electrons present in them absorb energy and jump t the outer orbital. The excitation of an electron occurs so rapidly that it is believed that there is not enough time for the orientation of the spin of the electron to change. I.e., the one which was clockwise remains clockwise and the one which is anti clockwise remains anti-clockwise after the excitation. Excitation of e^- can be representing as follows.

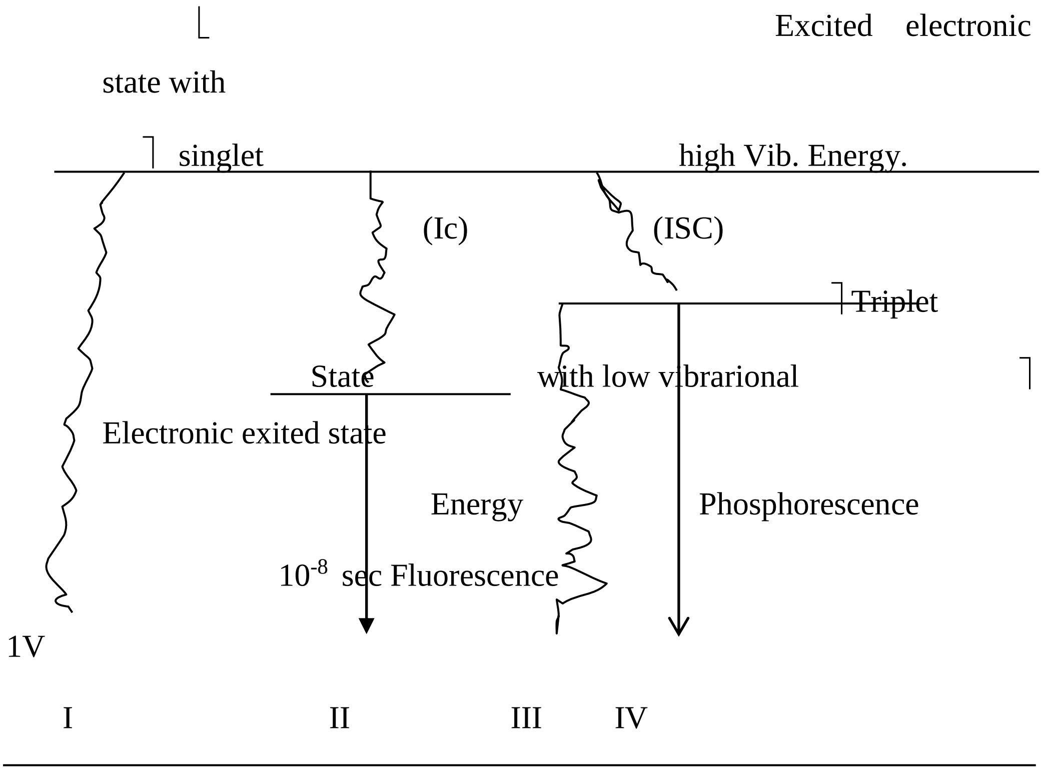


The excited electronic state having the 2 e^- with opposite spins is called a singlet state.

The excited e^- can return to the ground state by losing all of its excess energy in any one of the following 4 ways.

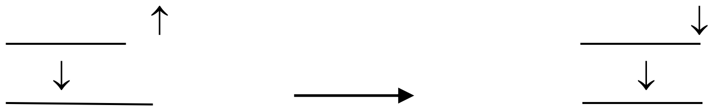
Route 1: The whole of the excess energy may be lost thro’ collision with other molecules & energy released appears as heat. Shown by wavy line.

Rout II: The excited species may lose a part of its energy in the form of heat because of collisions with other molecules. As a result it goes to an excited electronic state having a lower vibrational energy the new excited singlet state returns to the ground state by emitting light with in 10^{-8} secs called fluorescence.



Routes III & IV:

The initially formed excited state can undergo a change in spin orientation giving lower energy state having the 2 electrons in the two different orbitals but with the spin in the same direction. This state is called triplet state.

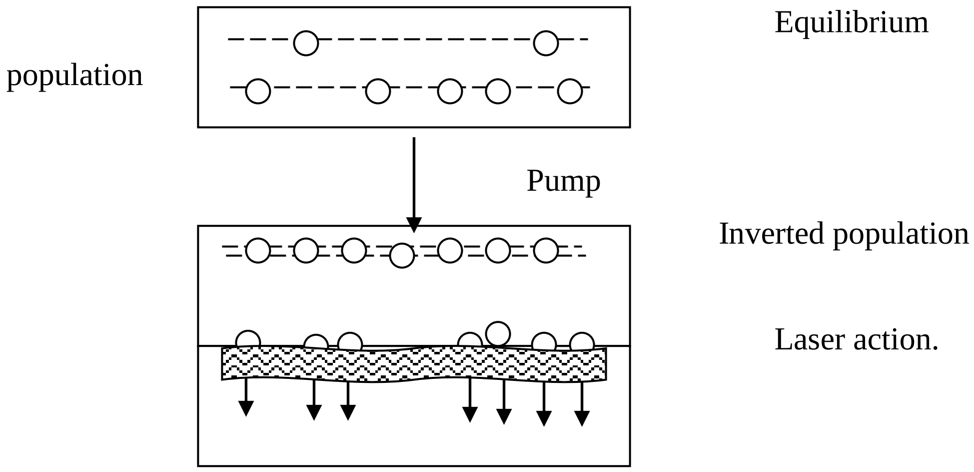


Exited singlet state exited triplet state.

The newly formed triplet can lose energy by collision or emit light, on returning to the ground state. This emission of light is called phosphorescence. Triplet excited states usually have much longer life times than singlet states- some as long as an hour. For this reason, phosphorescence persists even after removal of the absorbed radiation.

Lasers and uses of lasers:

The name laser comes from light amplification by stimulated emission of radiation. Normally a beam of light loses intensity as it passes through an absorbing material. However, if there are molecules in excited state, stimulated emission can occur, and the light beam can gain intensity. This action can be shown schematically in Figure.



In order to get a laser action it is necessary to get a population inversion in the absorber. In a population inversion there are more molecules in the upper state than in the lower state. This can not be achieved by simply using a high intensity of light source of proper frequency. By some means a majority of molecules in the samples are excited or pumped, in to the upper state. The sample is contained in a cavity between two mirrors and when a molecule emits spontaneously photon, it generates ricochets backwards and forwards. Its presence stimulates other molecules to emit: they add more photons of the same frequency to the cavity, and these photoms stimulate more molecules to emit.

Uses:

1. Study of fast reactions: Lasers can be used to initiate photochemical reaction, and the short pulses permit the study of very fast reactions.
2. Raman spectroscopy: Lasers have revolutionised Raman spectroscopy because exposures are greatly reduced, and even weak lines may be detected in experiments of short duration.
3. Separation of isotopes: A laser maybe used to ionize one isotopic species of a molecule, owing to the extreme monochromaticity associated with the excitation beam. The ionized molecules may be allowed to react with another substance so that the isotopes may be separated by a chemical method.

3.3 Kinetics of H_2 –Br_2 reactions:

The photo chemical reaction of moist H_2 and Br_2 vapour in visible light is chain reaction and it proceeds with measurable speed at 433-491 k. The primary process is the dissociation of molecule into atom.

$$i) \qquad Br_2 + h\delta \xrightarrow{K_1} + 2Br$$

The secondary reactions are

$$ii)\quad Br + H_2 \xrightarrow{K_2} HBr + H$$

$$iii)\quad H + Br_2 \xrightarrow{K_3} HBr + Br$$

$$iv)\quad H + HBr \xrightarrow{K_4} H_2 + Br$$

$$v)\quad Br + Br \xrightarrow{K_5} Br_2$$

The reaction (ii) is highly endothermic and takes place slowly. Reaction (IV) is reverse of (ii) which will be fast and hence formation of HBr decreases. As Br atom accumulates, hence these are not used up in reaction (ii) reaction (V) takes place readily. Hence the quantum yield of reaction is extremely low.

$$\frac{d[Br]}{dt} = K_1 \ I_{abs} \qquad \text{---------------} \ 1$$

The rate of formation of HBr

$$\frac{d[HBr]}{dt} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr] \ \text{--------} \ 2$$

Applying steady state principle to [H]

Rate formation of intermediate = Rate of its disappearance

$$K_2[H_2][Br] = K_3[H][Br_2] + K_4[H][HBr] \ \text{--------} \ 3$$

Apply Steady State Principle to [Br]

$$K_1 Iabo + K_3[H][Br] + K_4[H][HBr] = K_2[H_2][Br] + K_5[Br]^2 \ \text{------} \ 4$$

Sub tracking 3 from equation 4

$$k_1 Iabs = k_5[Br]^2$$

We get

$$[Br] = \sqrt{\frac{k_1}{k_5} Iabs}$$

Substituting the value of [Br] in 3

$$[H] = \frac{k_2[H_2]\sqrt{\frac{k_1 Iab}{k_5}}}{k_3 \ [Br_2] + k_4[HBr]}$$

Substitute the value of [H] & [Br] in equation in 2

$$\frac{d[HBr]}{dt}=\frac{2k_2\sqrt{\frac{k_1}{k_5}}\,.[H_2]\sqrt{Iabs}}{1+\frac{k_4}{k_3}[\frac{HBr}{Br_2}]}$$

$$=\frac{k\sqrt{Iabs}\,[H_2][Br_2]}{k^1[Br_2]+[HBr]}$$

Where k & k^1 are constant. The rate of the reaction varies as the square root of the intensity of light.

Decomposition of HI:

The photolysis of HI to give H_2 and I_2 has been studied in the wavelength 2070-2820A^0 and the quantum yield of this reaction has been found to be 2.

Mechanism:

a) Primary process

$$HI + h\gamma \rightarrow H + I^*$$

b) Secondary process: The products of the primary process then take part in the secondary processes as follows,

$$i)\ H+HI\rightarrow H_2+I$$

$$ii)\ I^*+HI\xrightarrow{endo}H+I_2$$

$$iii)\ H+H\xrightarrow{exo}H_2O$$

$$iv)\ I+I\rightarrow I_2$$

$$v)\ H+I\xrightarrow{Exo}HI$$

All the secondary processes are not important. The reaction (iii) and (iv) are highly exothermic and heat produced causes the dissociation of the products of these reaction, Reaction (ii) is endothermic and hence takes place slowly. Thus the only secondary processes of importance are i & iv Re writing the reaction of the primary process and two important reaction (i) and (iv) of the secondary processes, we have

$$HI+h\gamma\rightarrow H+I^*$$

$$H\ +HI\rightarrow H_2+I^*$$

$$I\ +I\ \rightarrow I_2.$$

$$\text{Overall reaction}\quad \overline{2HI+h\gamma\rightarrow H_2+I_2}$$

Thus for every one quantum of light absorbed, two molecules of HI are decomposed. Hence the quantum yield value of 2 is explained.

Photolysis of aldehydes

The photo dissociation of acetaldehyde on absorption of UV radiation ($\lambda < 3000A^0$) is an example of a photo chemical processes when the molecule is first excited then it breaks up into radicals which start chain reaction.

$$
\begin{aligned}
\text{Primary Process}: &\quad CH_3CHO + h\delta \rightarrow CH_3 + CHO. \\
\text{Secondary Process}: &\quad CH_3CHO + CH_3 \rightarrow CH + CH_3CO. \\
&\quad CH_3CO \rightarrow CO + CH_3. \\
&\quad CH_3 + CH_3 \rightarrow C_2H_6.
\end{aligned}
$$

ϕ = 1.5 at room temperature & high ϕ values are obtained at elevated temperature.

Photolysis of ketones:

$$
\underset{}{CH_3COCH_3} \xrightarrow{h\gamma} \underset{\text{ethane}}{C_2H_6} + \underset{\text{carbon monoxide.}}{CO}
$$

Small amounts of methane and appreciable amounts of diacetyl are also found to be present. The quantum yield of the reaction is found to be nearly unity.

Mechanism:

$$
\begin{aligned}
\text{Primary Process}: &\quad CH_3COCH_3 + h\gamma \rightarrow CH_3 + CHO. \\
\text{Secondary Process}: &\quad CH_3CO + CH_3 \rightarrow CH_4 + CO. \\
&\quad CH_3 + CH_3CO \rightarrow C_2H_6 + CO \\
&\quad CH_3CO + CH_3CO \rightarrow (CH_3CO)_2.
\end{aligned}
$$

Thus no chain reaction is setup. The free radicals formed in the primary process simply react with each other hence the quantum efficiency of the reaction is unity.

Phase Rule

Phase: (p) Phase is defined as homogenous, physically distinct and mechanically separable parts of a heterogeneous system.

Example: 1) Salt solution (or) sugar solution P=1

2) Ice water ↔ water vapor P =3

Component: (2)

The minimum number of atoms or molecules in terms of which composition and every phase can be expressed.

Example: 1) Ice ↔ water ↔ water vapor C =1

2) $CaCo_{3(s)} \leftrightarrow CaO_{(S)} + CO_{2\,(g)}$ C = 3.

There are three phases and three components but 2 components are enough to describe the composition of all the phases.

Degree of freedom (F):

The minimum number of variables such as pressure, temperature, composition etc., which must be arbitrarily fixed in order to define the system completely.

Example: Let us consider a system of 1 mole of an ideal gas. We know that PV=RT. If any two of three variables such as P, V & T is known the third variable can be easily determined. Hence the degree of freedom is 2.

Derivation of phase Rule:

Consider a heterogeneous system having p phases and c components. The degree of freedom is equal to the total number of variation minus the number of relation between them at equilibrium.

Total no. of variables:

i) Temperature: At equilibrium each phase has the same temperature, so there is one temperature variable for the whole system.

ii) Pressure: At equilibrium each phase has the same pressure, so there is one pressure variable for the whole system.

iii) Composition: suppose there are two components, A &B in a phase. If the molar concentration of A is 0.4 & that of b is known to be 1-0.4 (or) 0.6. Thus with 2 components concentration of one component is sufficient to define the system. Similarly with 3 components, concentration of two components is known, and then the system can be defined. Hence for c components the concentration of c-1 components must be known so p phases have total composition p(c-1)

Total no. of variables = p(c-1) +1+1

= p(c-1) +2

Number of relations at equilibrium:

According to thermodynamics the chemical potential of a component is same in all phases at equilibrium. This if there are three phases α, β & ∞ for a component c them

$$\propto_{\mu i} = \beta_{\mu i}$$

$$\beta_{\mu i} = \delta_{\mu i}$$

There are 2 equations (relation) for a component if there are 3 phases. So for p phases the number of such relation will be (p-1) for c components the number of relationship will be c (p-1)

Thus degree of freedom F = Total number of variables – total number of relations.

$$F = p(c-1) + 2 - C(p-1)$$

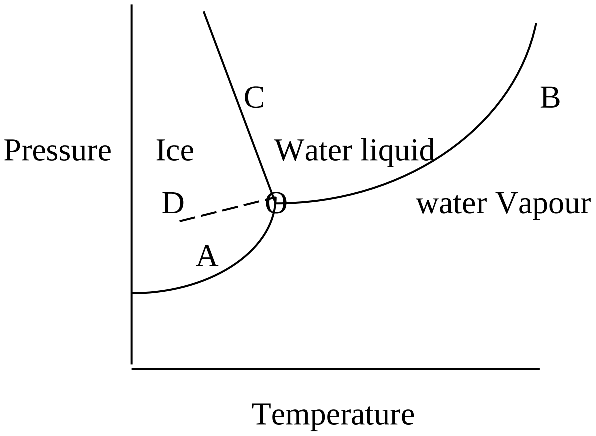
$$= PC - P + 2 - Cp + C$$

$F = C - p + 2$ this equation is called Gibb's phase rule.

One component systems:

Water system:

The phase diagram of water is shown in the following figure:



The Areas: There are three AOC COB, and AOB crease in the diagram. In each area only one phase is present.

Hence $F = 1-1+2 = 2$

Thus, it is necessary to specify 2 degrees of freedom such as temperature and pressure.

The lines:

AO is the sublimation curve of water. Along this curve ice and water vapor are in equilibrium.

OB is the vaporization curve of water. Along this curve liquid water and water vapor are in equilibrium.

OC is the fusion curve of ice. Along this curve ice and liquid water are in equilibrium. This curve shows the effect of pressure on the M.pt of ice. The curve OC point towards the pressure axis. Its means that increase pressure will decrease the M.pt of ice.

On each line 2 phases are in equilibrium. So

$$F = 1 - 2 + 2 = 1.$$

That is to define any point along a line it is required either temperature (or) pressure to define the system.

Triple point: 0

At this point ice, liquid water and water vapour are in equilibrium. So this is called a triple point. Then

$$F = 1 – 3 + 2.$$
$$= 0.$$

This is a non variant point. It means that it does not require any variable to describe the system.

Meta stable equilibrium:

Curve OD reproves the Meta stable equilibrium. When water is cooled slowly it can be cooled -9^{o}C without separation of ice. Such a water is called super cooled water and its stability is less (i.e.) if a bit of is added (or) the water is stirred immediately the whole mass become solid. Such equilibrium is called metal stable equilibrium.

Application of clapeyron equation:

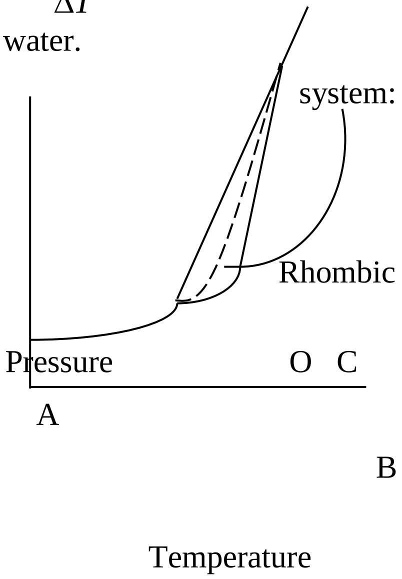
The slope of the fusion curve is negative (slopes towards the pressure axis). The molar volume of ice is greater than the molar volume liquid water so ΔV of water is negative.

From clapeyron equation $\frac{\Delta P}{\Delta T} = \frac{\Delta S}{\Delta V}$

ΔS is always positive. The slope the curve $\frac{\Delta P}{\Delta T}$ with depend upon the value of ΔV only and it is negative in the case of water.

Sulphur system:

Sulphur can exist in 4 phases. Since sulphur system is a one component system all the four phases can never co –exist in equilibrium. Only three phases can co-exist in equilibrium.



Areas:

ABCD - Vapour (sulphur)
ABEF - Rhombic sulphur
BEC - Monoclimic sulphur
DCEF - Liquid sulphur

Each area contains a single phase

$$F = C - P + 2.$$
$$= 1 - 1 + 2 = 2.$$

To define any point in the areas we have to mention 2 variable such as pressure and Temperature.

The Lines;

Line AB:

This is the sublimation curve of Rhombic Sulphur. Along AB two phases, namely, rhombic sulphur and vapor exist in equilibrium.

Line BC:

This is the sublimation curve of monoclinic sulphur. Along BC two phases, namely, rhombic sulphur. D vapour are in equilibrium.

Line CD:

This is the vapour pressure curve of liquid sulphur. Two phoses namely, liquid sulphur & sulphur vapour are in equilibrium.

Line BE:

This is the transition curve. Rhombic sulphur and monoclinic sulphur are in equilibrium. This curve indicates the effect of pressure on the transition temperature. As the curve slope away from pressure axis, the increase of presence will increase the transition temperature.

Line BF:

This is the melting curve or fusion curve of Rhombic sulphur. Along this line rhombic sulphur and liquid exist in equilibrium.

Line CE:

This is the melting curve or fusion curve of monoclinic sulphur. Along this line monoclinic sulphur and liquid sulphur are in equilibrium. The curve shows the effect of pressure on the melting point of monoclinic sulphur. As the curve slopes away from the pressure axis, the M.Pt. Increases with increase of pressure.

On each line two phases co-exist in equilibrium so F=1-2+2=1. To define any point along the line, it is enough to specify either temperature (or) pressure i.e., the curves are univarient.

Metastable equilibrium lines:

The dotted lines are metastable lines. If liquid sulphur is allowed to cool along the line DC,. the solid monoclinic phase may not separate out at c, unless cooling is slow. If cooling is fast the line extends as CO representing the Meta stable equilibrium between liquid and vapor sulphur.

Triple points:

There are three triple points. Three phases exist in equilibrium at each triple point. So

$$F = 1 - 3 + 2.$$
$$= 0.$$

The triple point is a non variant point.

Triple point B:

Rhombic, monoclinic and vapor sulphur are in equilibrium.

Triple point C;

Monoclinic, liquid and vapor sulphur and in equilibrium.

Triple point E:

Rhombic, monoclinic and liquid sulphur co-exist.

"O" is a Meta stable triple point where rhombic sulphur liquid sulphur and sulphur vapor are in equilibrium.

Application of clapeyron equation:

The slope of the fusion curves is positive (slopes away from the pressure axis). The ΔV of sulphur is positive.

From clapeyron $\dfrac{\Delta P}{\Delta T} = \dfrac{\Delta S}{\Delta V}$

ΔS is always positive. The slope of the curve $\dfrac{\Delta P}{\Delta T}$ will depend upon the value of ΔV only. It is positive in the case of sulphur system.

Two component system:

The minimum number of phases in equilibrium in any two components is one then

$$F = 2 - 1 + 2 = 3.$$

Degree of freedom is 3. For there pressure temperature and composition is necessary to define the system. This will lead to three dimensional diagrams.

It is not possible to draw on a paper or on a black board. To overcome this problem one of the variable is kept constant. In solid liquid equilibrium pressure does not have much influence. Hence the pressure variable sis kept constant.

Therefore the phase rule become

$$F = C - P + 1.$$

This equation is known as reduced (or) condensed form of phase rule. Therefore the phase diagram of two component systems is explained with the help of temperature and composition.

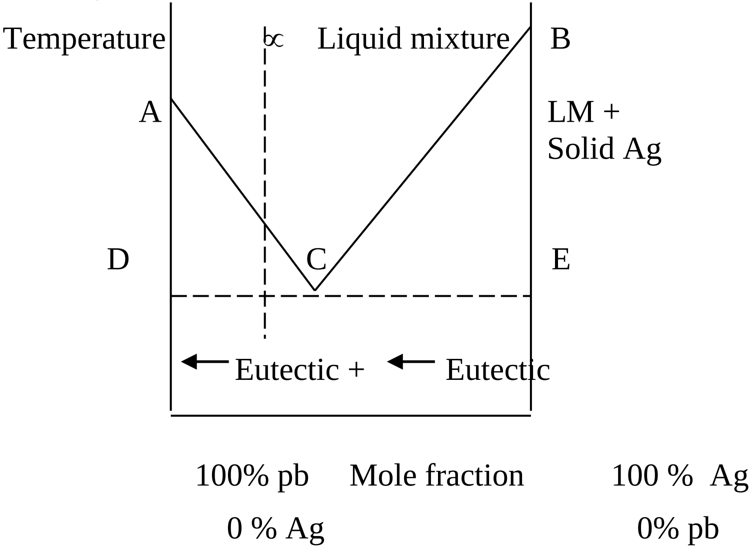
Simple eutectic system:

In this the two liquids are completely miscible in all proportion but there is no chemical combination between the two liquids. But on solidification the components lie closer to each other. i.e. simple eutectic is a intimate mixture of the two components. (In Greek simple eutectic means – easy melting).

Examples:

1. Lead – silver system
2. Antimony-lead system
3. Bismuth - Cd system

Lead – silver system:



In the phase diagram A represents the m.pt of 100% pb and B the m.p.t of 100% Ag. The curve Ac shows the variation of m.pt of pb on addition Ag. Similarly Bc Shows the variation of m.pt of Ag on the addition of pb. C is the point at which solid pb, solid Ag and liquid mixture are in equilibrium. This is called the eutectic point. This mixture is called the eutectic mixture. For this point

$$F = 2-3+1$$
$$= 0.$$

So the eutectic point is a non –variant point.

Above ACB only the liquid mixture can exist so

$$F = C-p+1$$
$$= 2-1+1 = 2$$

The system above ACB is bivariant. Below the line DCE no liquid can exist the two solid phases namely, pure Pb and Ag are present.

In the area ADC solid Pb and liquid mixture are in equilibrium and in BEC solid Ag and liquid mixture are in equilibrium and the system in monovariant.

Behaviour on cooling:

Let us consider liquid mixture of composition $\propto$ as the system cools solid pb appears at β, liquid composition moves along the curve βC. At γ the solution has the eutectic composition c and saturated with Ag. So silver begins to precipitate. Finally the liquid solidifies and the temperature decrease along $\gamma\,\delta$.

The eutectic point has the lowest m.pt. The eutectic mixture melts sharply at c to form a liquid of the same composition. Because of the sharp m.pt of the eutectic mixture originally thought to be a compound. Microscopic examination shows that it is a homogeneous mixture

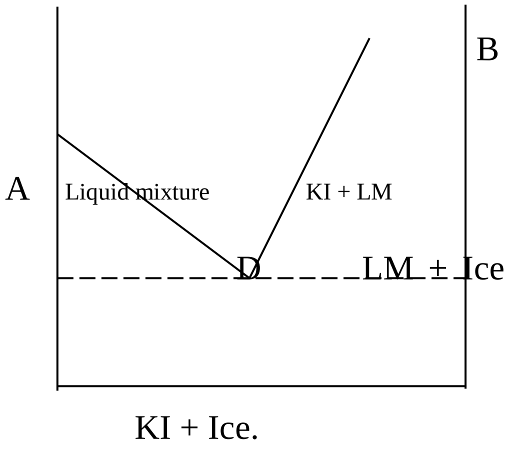
The m.pt of silver 961^0 c and leads in 327^0 C. the eutectic temperature is 303^0 & the eutectic composition 97.6 %Pb and 2.4% Ag.

Potassium Iodide-water system:

KI-H_2O system is an example of a two component system in which a simple eutectic mixture separates as a solid phases. Its phases diagram closely resembles that of lead silver system except that it is incomplete since one of the components is (H_2O) volatile at the m.pt of the other (KI)

The point A is the m.pt of ice. At 1 atm pressurem this temperature is 0^0C. On adding KI the freezing point is lowered till the point c is reached. Ac is the termed freezing point curve. Along the curve ice & liquid mixture are in equilibrium. Hence

$$F = C-p+1$$
$$= 2-2+1$$
$$=1$$



i.e. it is a monovariant system.

At the point KI separates as another solid phases. It is the eutectic point of the system ice; solid KI & liquid mixture are in equilibrium. It is the lowest temperature that can be attained in this system and as about -23^0C. The degree of freedom at this point is

$$F = C-p+1$$
$$= 2-3+1$$
$$= 0$$

It is a non variant point

If the system corresponding to the point c is heated, ice will melt and solid KI will pass into solution and temperature remains constant till the whole the ice melts. Addition of more and more of heat & excess KI. The curve CB is obtained. The curve CB is the solubility curve. Along this curve CB the system is monovariant. The steep rise of CB shows solubility of KI increase slowly with rise of temperature.

In the area ABC only liquid mixture exists. In the region ADC two phases such as ice and liquid mixture while in the region BCE solid KI & liquid mixture are in equilibrium. Below the eutectic line DCE, ice and solid KI with excess of ice to the left of a excess of solid KI to the right of C.

Systems with compound formation:

The system with compound formation can be classified into two types, namely,

1) Compound formation with congruent m.pt.
2) Compound formation with incongruent m.pt.

Compound formation with congruent m.pt:

The two components A &B enter into chemical combination and form a compound and it melts at a temperature without change in composition. This Temperature is called compound formation with congruent m.pt and system is called system with congruent m.pt.

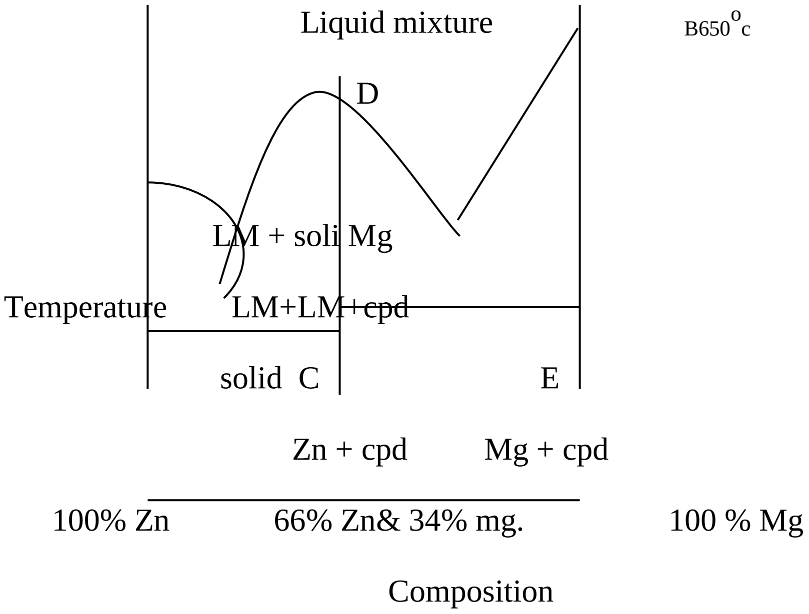
Examples

i) Zn-Mg system.

ii) Fe Cl_3 –H_2o system

iii) Sn-Mg system.

Zn-Mg system:



The point A&B represents the m.pt. of 100% Zn &100% Mg respectively. D represents the m.pt of the compound. $MgZn_2$. AC represents the variation of m.pt of Zn on the addition of mg. BE represents the variation of M.pt of Mg on the addition of Zn. Along this lines 2 phases are in equilibrium and the system is monovarient.

F = C – p+1

= 2-2+1

= 1

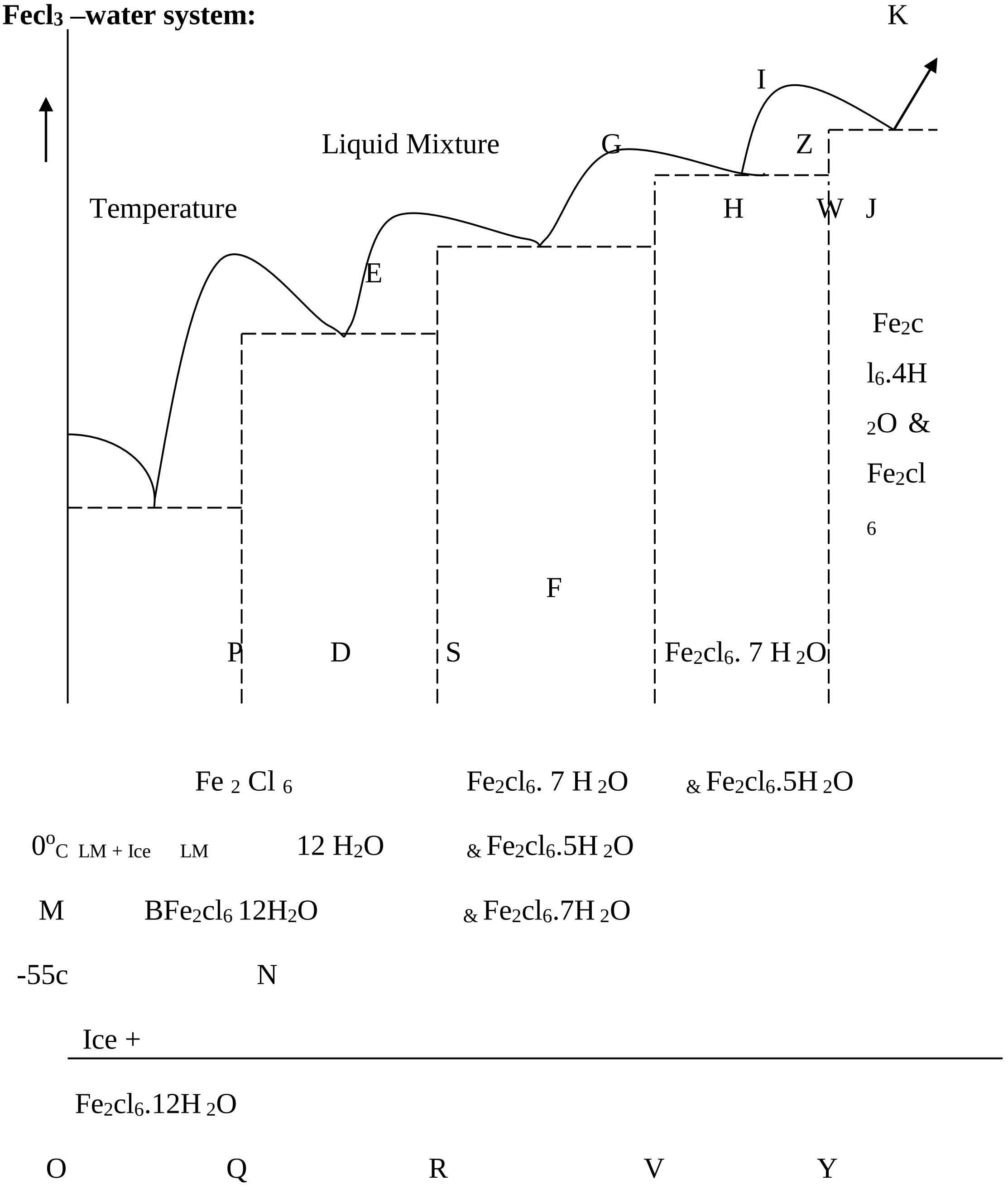
At the first eutectic point C solid Zn, solid compound and liquid mixture are in equilibrium. At the second eutectic point E, Solid Mg, solid compound and liquid mixture are in equilibrium. The degree of freedom at these eutectic points

F = 2-3+1

= 0

So they are non variant points. The curve CDE which has a maximum called congruent m.pt of the compound At this point compound melt sharply without charge in composition. The compound formed at D is 66.6% Zn and 33.3% Mg. So the formula of the compound is $MgZn_2$ and its m.pt. is 590^0C.

Fecl$_3$ –water system:



The curve AB shows the effect of adding ferric chloride to ice. It is the freezing point curve ferric chloride solution and B is the eutectic point -55^0C.

In addition to vapour, the other three phases in equilibrium are ice. & $Fe_2cl_6.12$ H_2O and liquid mixture. It is an invariant point.

$$\begin{aligned} F &= C-p+1 \\ &= 2-3+1 \\ &= 0. \end{aligned}$$

If the solution corresponding to the point B is allowed to warm and ferric chloride is added to keep the solution saturated, the curve BC is followed. This is the solubility curve of $Fe_2cl_6.12H_20$. At c the composition of liquid mixture and the solid Fe$Fe_2cl6.12H_20$ incontact with it is the same. Therefore c is the congruent m.pt of deca hydrate. Further addition of anhydrous $fecl_3$ results in the formation of another compound $Fe_2cl_6.12H_20$. The solubility curve falls until the point D is reached which is another eutectic, the phases in equilibrium being solution solid $Fe_2cl_6.12H_2O$, solid $Fe_2cl_6.7H_20$. By repeating the process three more maxima and 3 more minima are obtained. The maximum points are the congruent m.pt of compounds pentahydrate, tetrahedrate etc. While each minima represented eutectic point. Jk represents the solubility curve of anhydrous Fe_2cl_6.

Areas	No.of phases in equilibrium	Degree of freedom
AMB	Ice & LM	Monovarient
BCDPN	$Fe_2cl_6.12H_20$ & LM	Monovarient
APRS	$Fe_2cl_6.12H_20$ & Fe_2cl_6 $7H_20$	Monovarient
RTOV	$Fe_2cl_6.7H_20$& $Fe_2cl_6.5H_20$	Monovarient
VH'wy	$Fe_2cl_6.5H_20$& $Fe_2cl_6.4H_20$	”
To the riglet of zy	$Fe_2cl_6.4H_20$& Fe_2cl_6.	”
DEFTS	$Fe_2cl_6.7H_20$&LM	”
FGHH'U	$Fe_2cl_6.5H_20$& Fe_2cl_6.	”
HIJZW	$Fe_2cl_6.4H_20$& lM	”
Eutectic point	Ice. $Fe_2cl_6.12H_20$ LM	Non variant

B		
D	$Fe_2cl_6.12H_20$, Fe_2cl_6 7 H_20 LM	”
F	$Fe_2cl_6.7H_20$, Fe_2cl_6 5 H_20 LM	”
H	$Fe_2cl_6.5H_20$, Fe_2cl_6 4 H_20 LM	”
J	$Fe_2cl_6.4H_20$, Fe_2cl_6. LM	”

LM – Liquid Mixture

Peritectic change (or) Compound formation with in congruent M.Pt:

In these systems the compound formed undergoes decomposition before the actual M.Pt is reached. Such a change is called congruent in melting because the composition of the liquid differs from that of the solid.

Example

1) NaCl –H_2O system
2) Na-K system

Nacl –H_2O system

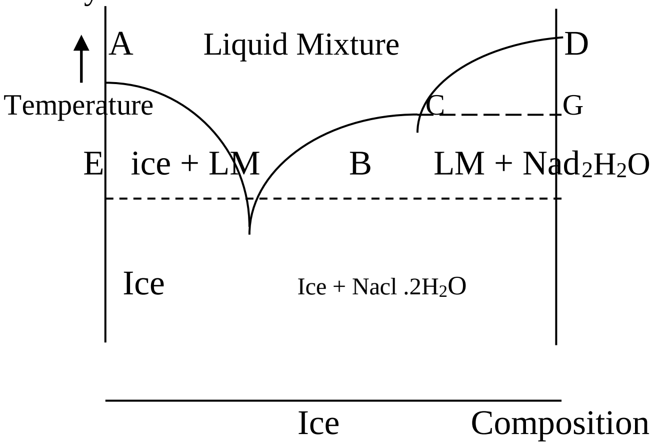
In the phase diagram A is the melting pt of ice. At 1 atm. Pressure this temperature is 0^0C. On adding Nacl to water freezing point is lowered till B is reached. AB is called the freezing point curve. Along this curve ice and liquid mixture are in equilibrium and the system is monovarient.

Ice F= C – P + 1

= 2 – 2 + 1

= 1.

F



NaCl

At the point B the solution becomes saturated and the compound dihydrate Nacl $2H_20$ separates. At this point ice, Nacl $2H_2O$ and liquid mixture are in equilibrium at -21^0C. It is the eutectic point of the system. The temperature at this point is the lowest temperature that can be attained in this system.

$$F = C - P + 1$$
$$= 2 - 3 + 1$$
$$= 0.$$

The point B is a non variant point.

With further addition of Nacl and heating, ice disappears the curve BC shows the effect of temperature on the solubility of the Nacl $2H_2O$ is termed solubility curve. Along this line the cpd and the solution are equilibrium and the degree of freedom is one.

$$F = 2 - 2 + 1$$
$$= 1.$$

The steep rise of the curve BC shows that the solubility of sodium chloride increases slowly with rise of temperature. The point C is the incongruent m.pt of the cpd. The curve CD is the solubility curve of anhydrous Nacl.

$$NaCl.\ 2\ H_2O \rightarrow NaCl + \text{Solution.}$$

In the area above ABCD only liquid mixture in exist in equilibrium. In the area CBFG Nacl $2H_2O$ and liquid mixture are in equilibrium. In the area DCGH Nacl and liquid mixture are in equilibrium. Below the eutectic line EBF ice & Nacl. $2H_2O$ are in equilibrium with excess of ice to the left of B and excess of salt to the right of B.

Efflorescence:-

When the vapour pressure of a salt hydrate is greater than that of water vapour in the air, given out their water of crystallization spontaneously and change into lower hydrates or even to anhydrous form.

Example: $Na_2So_4\ 10H_2O$, $Na_2CO_3\ 10H_2O$, $MgSO_4\ 7\ H_2O$ are exposed to atmosphere even at room temp → lower hydrates.

$Na_2So_4\ 10H_20 \rightarrow Na_2So_4\ H_20$

This can be explained as the dissociation pressure of hydrated crystal is higher than the partial vapour pressure of water vapour in the atmosphere at the room temperature.

Deliquescence:

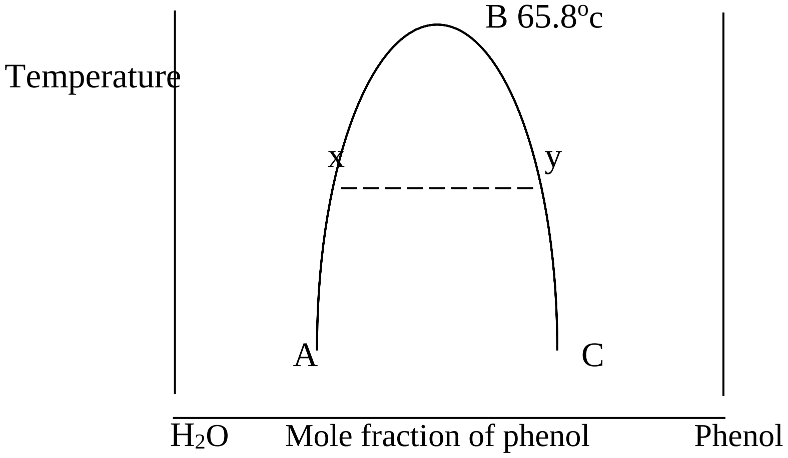
When a salt is exposed to water vapour at a pressure greater than that of the saturated solution of its highest hydrate at a given temperature, it will gradually take up water and finally form an solution. This phenomenon is known as deliquescence.

Example: $CaCl_2$, NaOH etc

Phenol- H_20 system:-

If a small quantity of phenol as added to water, it will dissolve completely. If the addition is continued, a stage is reached when no further dissolution takes place and two liquid layers separate out. Each layer is a saturated solution of one in the other. The two layers in equilibrium are called conjugate solution. The composition of the two layers depends on temperature and pressure.

If the temperature of the phenol-water systems is raised at constant pressure, the mutual solubilities(phenol in water, or water in phenol) the two liquids increase. At a particular temperature the two liquids become completely miscible.



The temperature at which two partially miscible liquids become completely miscible is called the critical solution temperature. (C.S.T) or the consulate temperature. We find two points X and Y on the curve representing the same temperature. They are called conjugate points. The area inside ABCD indicates the system in two layers. The area outside ABCD indicates the system is one layer. The C.S.T for phenol – water system is 65.85^{0}C. The C.S.T in this system corresponds to maximum miscibility temperature, is it called upper critical solution temperature.

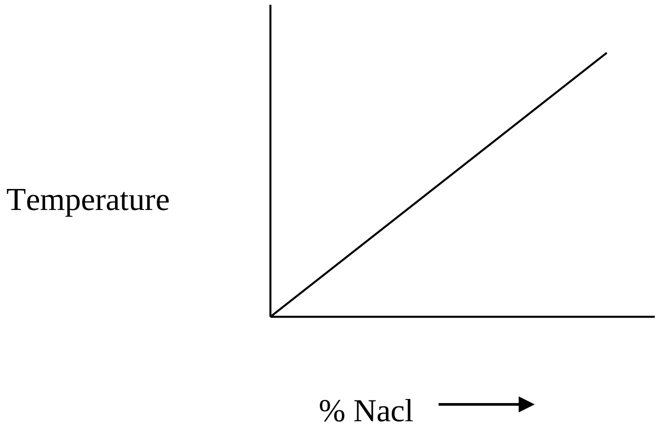
Effect of impurities:

The C.S.T of a system is a constant and it varies depending upon nature of the impurity and the amount of the impurity.

If the impurity is soluble in any one of the two liquids then C.S.T of the system increases. If the impurity is soluble in both the liquids then CST of the system decreases.

Examples:

1) If 0.1m naphthalene is present as impurity in phenol water system then CST is increased by 20^0 C.
2) If 1% H_2O is present as impurity in CH_3CooH- cyclohexane then CST is increased by 18^0C.
3) If 1% H_2O is present as impurity in C_2H_5OH-petroleum system CST is increased by 17^0C.
4) If soap is present as impurity in glycerol – water system then CST decreases.
5) If Nacl is present as impurity in phenol – H_2Osystem, the CST value increases as the % of Nacl increases.



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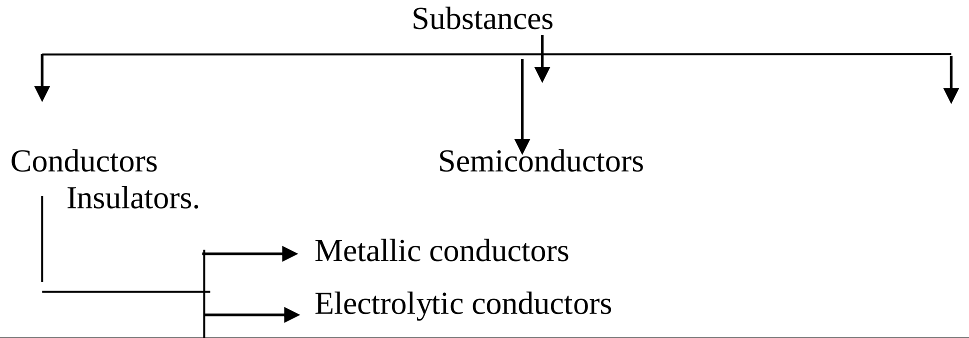
UNIT III

1) State & explain Stark – Einstain's Law of photochemical equivalence.
2) Distinguish between primary and secondary process in a photochemical process with examples.
3) Explain the photochemical decomposition of HI?
4) Draw the phase diagram of sulphur. Label & explain areas, lines and triple points.
5) Explain the following
   A) Phosphorescence
   B) fluorescence
6) Explain the photolysis of acetaldehde.
7) Sketch & explain the phase diagram of Mg-Zn system.
8) What do you understand by critical solution temperature of phenol and water? Explain the effect of impurity on the CST of the system.
9) Discuss the phase diagram of water system.
10) Explain with example
    1) Congruent M.pt.
    2) Peritectic point
    3) Eutectic point
11) Explain photosensitization with an examples.
12) Draw and explain the phase diagram of Pb Ag system.
13) Explain the phase diagram of phenol –water system.
14) Define the following
    1) Grotthus Drapper law
    2) Quantum yield.
15) Write a not on Fecl$_3$ water system.

UNIT IV Electrochemistry.

Electrochemistry is a branch of science deals with interconvertion of Electrical and chemical energy. Depending on conductance substances are classified as



Metallic Conductance	Electrolytic Conductance
1) Conductance is due to the movement of electron.	Conductance is due to the movement of ions.
2) It accompanies no transfer of matter and chemical change	It accompanies transfer of matter and chemical change. e.g. oxidation and Reduction
3) Increase of temperature will increase the resistance Examples, Metals, Graphite Pbs, Cds,	Increase of temperature will decrease the resistance. Examples: Acids, bases and Salt solutions.

Specific Conductance:

It is a conductance of a conductor when its length is l cm and area of cross section is 1cm^2 (or) it is reciprocal of specific resistance.

It is represented by the symbol k (kappa).

$$k = \frac{1}{R} \times \frac{l}{a}.$$

$$unit \quad = Mho\, cm^{-1}.$$

Equivallent conductance:

It is a conductance of solution containing 1 gram equivalent of any electrolytic solution (or) it is a product of specific conductance and solution volume of the solution contining 1 gm equivalent of a electrolyte.

$$\Lambda = \frac{k \times 1000}{C}.$$

$$C = in\,term\,of\ normality.$$

$$unit:\ Mho\,cm^2 / gram\,equivalent.$$

Molar conductance:

It is a conductance of a solution containing 1 gram mole of any electrolytic solution. (Or) it is a product of specific conductance and volume of the solution contining 1 gm mole of an electrolyte.

$$\Lambda = \frac{k \times 1000}{C}.$$

$$C = in\,term\,of\ normality.$$

$$unit:\ Mho\,cm^2 / gram\,mole.$$

Measurement of conductance:

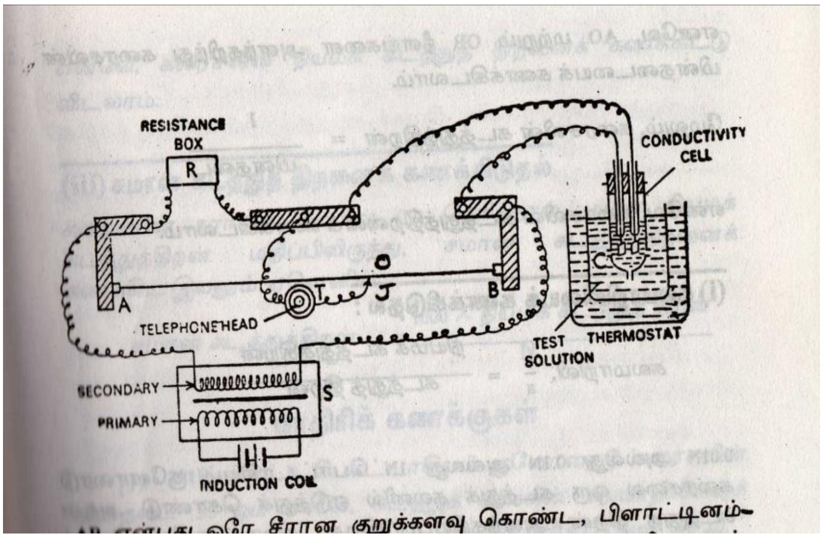
Determination of conductance involves 2 steps.

1. Determination of cell constant of the conductivity cell.
2. Determination of Resistance of the given solution.

Determination of cell constant:

It is a ratio of length the cell to area of cross section. Represent by l/a. It is a constant.Unit: Cm^{-1}. Determination is based on wheat stone bridge arrangement.

A solution of known specific conductance usually 0.1N kcl is taken in the conductivity cell and connection are made as shown in the diagram. A suitable Resistance is plugged out from the resistance box and Jockey wire is adjusted on the platinum- Iridium wire of uniform cross section till the Galvanometer shows null deflection. The distance AJ and JB are measured and let the distance be $l_1$and l_2



$$\frac{\text{Resistance of } kcl}{\text{Resistance from the Resistance box}} = \frac{AJ}{JB}$$

$$= \frac{l_1}{l_2}$$

$$\text{Resistance of } kcl = \frac{l_1}{l_2} \times \text{Resistance from the Resistance box}$$

We know that all constant

$$l/a = k \times R$$

$$= k \times R_{Kcl.}$$

ii) Determination of Resistance of the given solution:-

A solution to which conductance is to be determined is taken in the conductivity cell and its terminals are connected to the wheat stone bridge and the experiment is repeated as above.

$$\frac{\text{Resistance of Solution}}{\text{Resistance from the Resistance box}} = \frac{l_3}{l_4}$$

$$\text{Resistance of gived solution} = \frac{l_3}{l_4} \times \text{Resistance from the Resistance box}$$

We know that specific conductance

$$k = \frac{1}{R} \times \frac{l}{a}$$

$$= \frac{1}{R_{given}} \times cell\, constant.$$

Thus specific conductance is determined.

By knowing specific conductance and concentration we can determine equivalent conductance of the solution as.

$$\Lambda = \frac{k \times 1000}{C}.$$

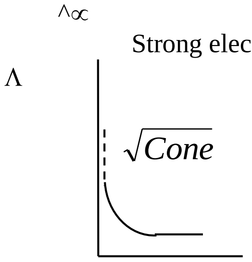
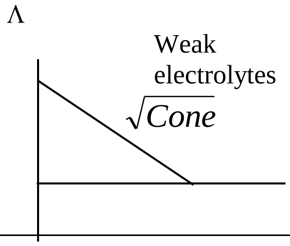
4.2 Variation of conductance with dilution

On dilution dissociation of an electrolyte increases. Therefore both the conductance should increases but on dilution specific conductance decreases and equivalent conductance increases.

On dilution the no. of ions as well as volume increases. Increase in volume is more compared to the no. of ions. Therefore number of ions per cc will decrease. Specific conductance depends upon the no. of ions per cc. Therefore specific conductance decreases.

Equivalent conductance depends upon the total number of ions present in the solution. Hence equivalent conductance increases on dilution.

Strong and weak electrolytes:

Strong electrolyte	**Weak Electrolyte**
1) The electrolyte which undergo complete dissociation on dilution is called strong electrolyte (E.g.) Hcl, NaoH, Nacl, Kcl etc.	The electrolyte which undergo poor dissociation on dilution is called weak electrolyte. (E.g.)CH_3COOH,NH_4OH,H_2CO_3 etc.
2) At normal concentrations equivalent conductance is high. As the dilution increases the increases in equivalent conductance is low.	At normal concentrations equivalent conductance is low. As the dilution increases the increases is more than strong electrolyte.
3) Equivalent conductance at infinite dilution Λ0(or) Λ∞ can be obtained from the graph Λ Vs $\sqrt{C}$.  	4) Equivalent conductance at infinite dilution can not be obtained from the graph Λ Vs $\sqrt{C}$.but it is determined using kohlrauseh's law. 

Migration of ions:

When two electrodes are placed in a solution of an electrolyte and on passing current, the ions present in the solution move towards the electrodes of opposite change. This kind of movement of ions is known as migration of ions.

Transport Number:

Fraction of current carried by each kind of ion to the total conductance of electrolyte is called its transport number.

Fraction of current carried by cation is called transport no. of cation and is represented by t_+

Fraction of current carried by anion is called transport no of anion and is represented as t-

Transport no. of an ion is always less than one …. i.e.,

$$t_+ + t_- = 1.$$

Determination of transport number:

Hitforf's method:

In this method transport no. is determined by measuring the change in concentration of the electrolyte at a particular compartment.

Hitforf's method consists of three compartments, namely catholic, anodic and middle compartments. Each compartment has a tap at the bottom for the removal of the solution.

To determine the transport number of Ag^+ in $AgNo_3$ the electrodes are then made either of Pt (or) pure Ag and the electrolyte is a dilute solution of Ag NO_3 then the electrolyte of known concentration is filled in the apparatus % connections are made on shown in the diagram.

Calculation:

When the electrodes are not attacked

Electrolysis of Ag NO_3 using Pt electrodes.

After electrolysis:

Weight of anodic solution = a gram.

Weight of $AgNO_3$ in anodic solution = b gram.

Weight water = (a-b) gm

(a-b) gm water contains = b gm of $AgNo_3$

$$= \frac{b}{170} \textit{ gm equivalent}$$

= y

Before electrolysis:

Weight of anodic solution = C gram

Weight $AgNo_3$ in anodic solution = d gram

Weight of water = (c-d) gram

(c-d) gm water contains d gm of $AgNo_3$

(a-b) gm water contains $= \frac{d}{c-d} \times \frac{(a-b)}{170.}$

= x.

During electrolysis:

$\left.\begin{array}{r}\text{The amount of copper deposited in the}\\ \text{copper coulometer}\end{array}\right\} = \text{W gram.}$

$\therefore$ total current passed = W/31.8 gm equivalent

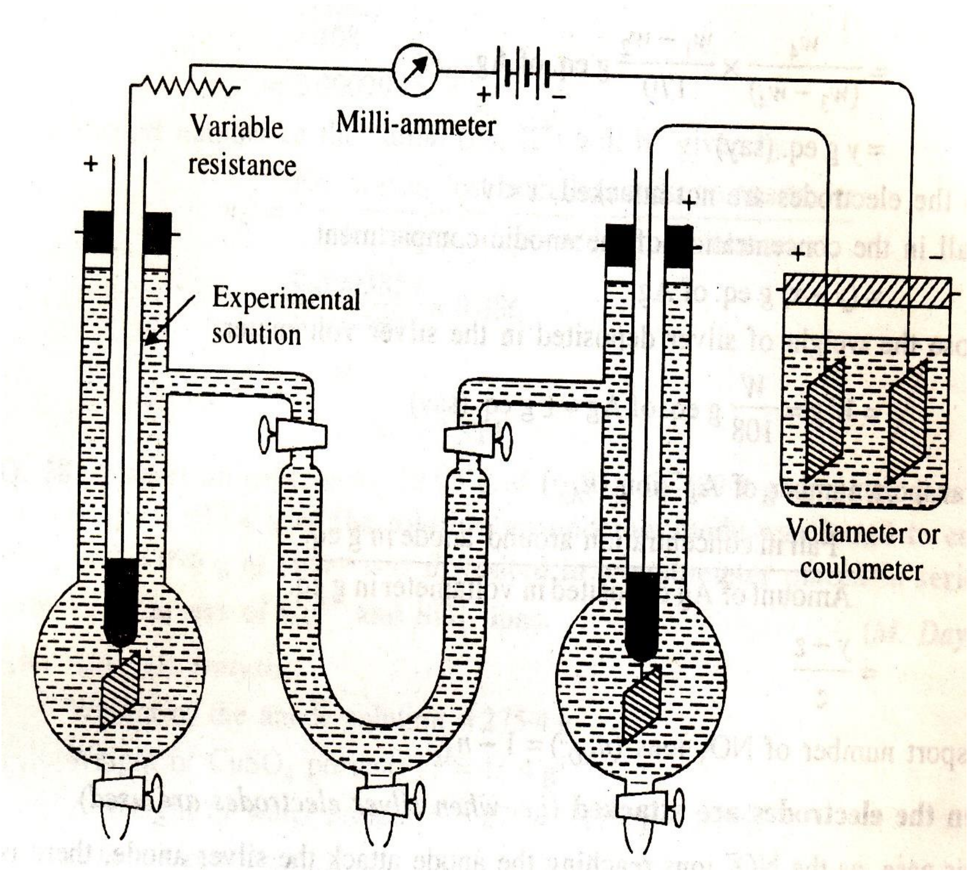
= Z.

As per Hittorf's rule

$t_+ = \frac{\text{Decrease in concentration at the anodic compartment}}{\text{Total Current parsed in Faraday}}$

$t_{Ag^+} = \frac{x-y}{Z}$

$t_{No3} = 1 - t_{Ag^+}$



A current of 10-20 milliampere is passed for about 2-3 hours so that an appreciable but not large change in concentration. The solution from the cathode (or) anode compartment is drained into a beaker and weight of the solution is noted. Solution is analyzed by titrating the $AgNo_3$ by NH_4CNS. From the amount of the electrolytes, in the same weight of water before & after electrolysis the loss in the electrode compartment is obtained. The total amount of electricity passed is found experimentally by means of a coulometer.

When the electrodes are attacked.

Example: Electrolysis of $AgNO_3$ using Ag electrodes

During electrolysis the nitrate ion that migrates from the cathodic to anodic compartment does not undergo discharge instead the silver electrode become activated and Ag+ ions goes into solution. Hence concentration of the anodic compartment increases. This increase in equal to the total current passed.

$\therefore$ The decreased in concentration of anodic compartment = (x+z) –y

$$\therefore t_{Ag^+} = \frac{(x+z)-y}{z}$$

$$\mathbf{t_{No3} = 1- t_{Ag^+}}$$

Moving boundary method

This method is more accurate than Hifforf's method. Speed of the ions are directly measured here. To find out the speed of ions 2 electrolytes are used

1) Primary electrolyte
2) Indicator electrolyte

Conditions for an electrolyte to be an Indicator electrolyte are

a) The cation of the primary electrolyte should have greater speed than the cation of secondary electrolyte.
b) Both the electrolyte must have common anion

For example let us consider thedetermination of transport number of H^+ ion. In this experiment $CdCl_2$ is used as an Indicator electrolyte. It satisfies the conditions of indicator electrolyte. Hcl and $Cdcl_2$ solutions are filled in a vertical tube of uniform cross section. The concentrations of the solution are so adjusted that Hcl float over $cdcl_2$. Platinum electrodes are placed at each ends of the vertical tube and connections are made as shown in the diagram. The boundary between Hcl and $cdcl_2$ marked as aa^1. On passing current H^+ ion move towards the cathode followed by Cd^{2+} ions. Therefore the boundary move to certain distance (bb')

Calculation

The distance moved by the boundary = lcm

Area of cross section of the vertical tube = Acm^2

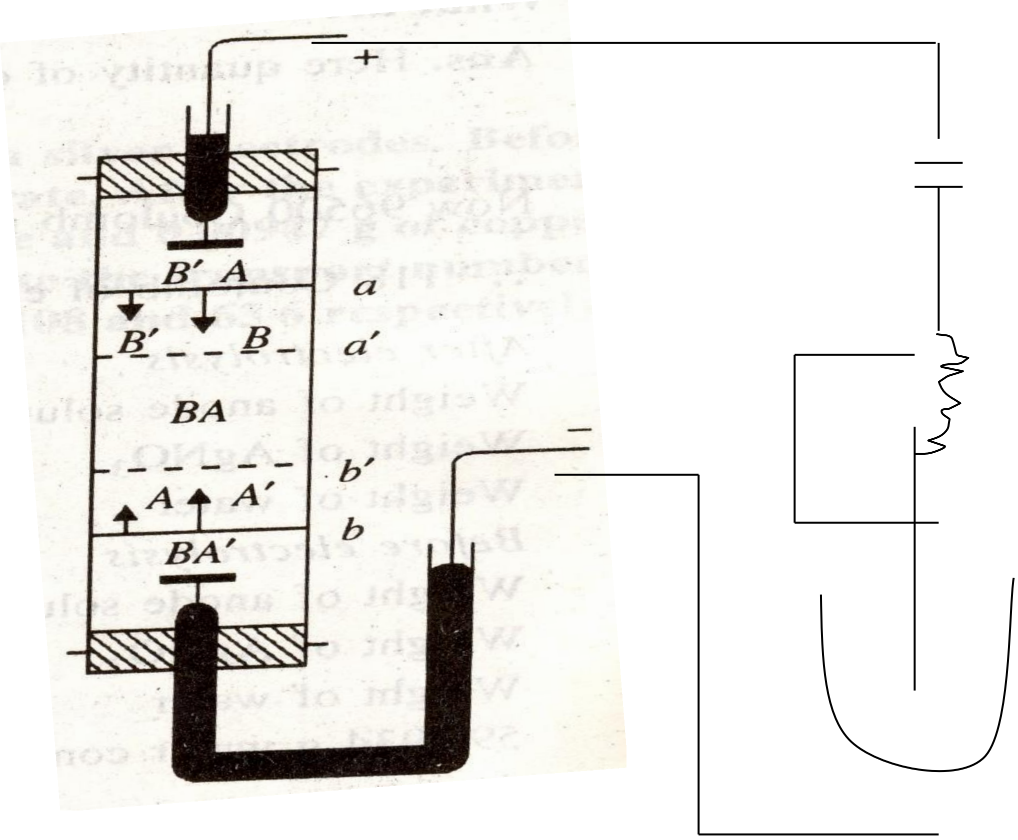
The volume swept away by the boundary = $lA\ cm^3$

The concentration of solution used for determination = c fram equivalent / litre

Current carried by the cation (H^+) = $\frac{lAc}{1000} gram equivalent.$

We know that

$$t_+ = \frac{Current\, carried\, by\, a\, cation}{Total\, current\, passed.}$$



Total current passed can be determined by coulometer and it is taken as Q Faraday

$$t_+ = \frac{lAc}{1000Q}$$

$$t - = 1 - t_{H+}$$

kohlrausch's law:

At infinite solution each ion contribute a definite amount to the total conductance of the electrolyte irrespective of the nature of other ion.

(or)

Equivalent conductance at infinite dicertion is equal to the sum of equivalent conductance of the cation and union.

$$\lambda_0 = \lambda^+ + \lambda^-$$

Application:

1) It is used to calculate the equivalent conductance at infinite dilution for a weak electrolyte. To determine the $^\wedge\infty$ value of a weak electrolyte we should know $\Lambda\propto$ values of three strong electrolyte. For example $\Lambda\propto$of

CH_3CooH is calculated using the $\wedge\alpha$ of Hcl and sodium acetate and Nacl

$$\lambda Hcl = \lambda_{H+} + \lambda_{cl-} \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (1)$$

$$\lambda CH_3CooNa = \lambda_{Na+} + \lambda_{CHacoo} \quad --(2)$$

$$\lambda Nacl = \quad \lambda_{Na+} + \lambda_{Cl^+} -----(3)$$

$$(1)+(2)-(3)$$

$$= \lambda_{H^+} + \lambda_{\bar{ci}+} + \lambda_{Na^+} \lambda_{CH_3Coo^-+} - \lambda_{Na^+} - \lambda_{cl\_}$$

$$= \lambda_{H^+} + \lambda_{CH3CO\bar{O}}$$

$$= \wedge cH_3CooH$$

$$iiirly \ \infty NH_4OH \text{ is calculated as}$$

$$\wedge NH_4oH = \lambda NH_4cl + \lambda NaoH - \lambda Nacl$$

Determination of transport number

We know that

$$t_+ = \frac{u}{u+v}$$

$$By \ Definition$$

$$\lambda C \infty u$$

$$\lambda a \infty V$$

$$u \,\&\, V are the ionic mobilities of cation and anion.$$

$$\therefore \ t_+ = \frac{\lambda_C}{\lambda_C + \lambda a}$$

$$\lambda_0 = \lambda c + \lambda a$$

$$\therefore t_+ = \frac{\lambda c}{\wedge 0}$$

By knowing $\lambda c \, and \wedge o$ we can calculate the transport number of an ion.

Ionic conductance and Ionic mobility.

Ionic conductance and Ionic mobility is not the same. However these are proportional to each other. If u & v are Ionic mobility of positive and negative ions of a given electron at infinite dilution

$$\lambda c = ku$$

$$\lambda a = kv$$

Where k is a constant Absolute ionic mobility of an ion is velocity in cm/sec under a potential gradient of 1 vol cm-^{1}. The value of K is 96500 coulombs (or) (1 Faraday)

Ionic mobility = $\frac{Ionic Conduc\tan ce}{96500}$

Diffusion and Ionic mobility:

Electrical conductance is due to motion of ions in an applied electric field. If the electric field is absent, the ions and the solvent molecules in solution move in a random manner as a result of thermal energy therefore concentration is higher at one region at a given temperature and pressure, then migration of ions takes place from the region of higher concentration to region of lower concentration.

An ion in a solution possesses a diffusion co efficient Di which measures the mobility of the ion due to its thermal energy kT. Ionic mobility ui of the ion, measures the mobility of ion due to kinetic energy imparted to it by applied electric field , E Di & ui are related by Nernst Einstein equation

Di = ui KT./ez

Where e is electronic charge and Z is charge of the ion.

Molar Ionic conductance and viscosity:

Consider a single ion immersed in a liquid and subjected to an electric field, E. As the ion moves through liquid, its motion is retarded by the viscosity of the liquid, the frictional force of acting on a spherical ion of radius, moving with a velocity v is given by stokes law.

F = $6\pi\eta rv$ = ZeE

When η is the co-efficient of viscosity of the liquid

This force is balanced by the electrical force acting on the in ZeE then

$6\pi\eta rv$ = ZeE z= charge on the ion

E = electronic charge

The ionic mobility, u of the ion is given by

$$u\pm = {}^{v}\!/_{E} = \frac{ze}{6\pi\eta r}$$

We know that

molar ionic conductance

$$\lambda\pm = ZuF$$

$$\lambda\pm = \frac{Z^2eF}{6\pi\eta r}$$

The terms on the right hand side are constant expect Therefore for a given ion in different solvent.

$$\lambda \pm {}^{0} \eta = constant$$

This is called Walden rule. Larger the viscosity of the medium, lesser would be the mobility of the ion Walden rule obeys only for large ions.

Applications of conductance measurements:

1) Degree of dissociation of weak electrolytes:

Degree of dissociation of $\propto$ represents the fraction of total number of molecules which are dissociated.

$$\alpha = \frac{Actual\ number\ of\ molecules}{Total\ number\ of\ molecules\ at\ \inf inite\ \ dilution}$$

$$or\ \alpha = \frac{equivalent\ conduc\tan ce\ at\ a\ particular\ dilution}{Equivalent\ conduc\tan ce\ at\ \inf inite\ \ dilution}$$

$$\alpha = \frac{\wedge}{\wedge\infty} ----(1)$$

$\wedge$ can be determined experimentally, $\Lambda\propto$ can be calculated using kohlrausch's law for weak electrolytes.

$$\wedge\infty = \lambda_{cation} + \lambda_{anion}$$

Thus the degree of dissociation α can be calculated using the equation. (1)

Determination of Ionic product of water:

Ionic product of water is defined as the product of concentration of H^+ and OH^- ions in water at constant temperature. It is a constant and represented by kw

$$K_w = [H^+][OH^-]$$

At 298k the specific conductivity of pure water is 5.51X 10^{-8}, ohm^{-1}, Cm^{-1}. The ionic conductance of H^+ and OH^- and 349.8 and 198.5 respectively.

$$\wedge = \frac{1000\,X\,k}{C}$$

$$= \frac{1000\,x\,5.51\,X\,10^{-8}}{c}$$

$$\wedge\infty = \lambda_{H+} + \lambda OH^-$$

$$= 349.8 + 198.5$$

$$= 548.3$$

Water is considered as a weak electrolyte and its conductance is equal to equivalent conductance at infinite dilution. Therefore $\wedge c\ will\ be\ taken\ as\ \wedge\alpha$

$$\therefore 548.3=\frac{1000 X\, 5.51 X\, 10^{-8}}{C}$$

$$=\frac{1000 X\, 5.51 X\, 10^{-8}}{548.3}$$

$$=1.005 X 10^{-7}$$

$$K \qquad =\left[H^{+}\right]\left[OH^{-}\right]$$

$$=1.005 X\, 10^{-7}\ X 1.005 X\, 10^{-7}$$

$$=1.01 X\, 10^{-14}$$

Ionic product of water depends on temperature.

Determination of solubility of sparingly soluble salts:

Substance such as Agcl, Ag_2Cr0_4, $BaSo_4$, $pbCro_4$ etc., are regarded as insoluble or sparingly soluble in water, the minute amount that is dissolved may be treated as present at infinite dilution. Hence the determined equivalent conductance may be taken as the equivalent conductance at infinite dilution.

Let us consider determination of the solubility of Agcl at 298k.

The salt is completely washed with conductivity water to remove soluble impurities. It is then warmed with conductivity water and cooled to 298k. On warming, a small quantity of the salt will dissolve and the rest will settle down. The conductance is determined by conductance measurements. The conductance of the conductivity water used is also determined and is subtracted from the conductance of Agcl solution.

K= 1/R X l/a

The above equation will give specific conductance of the solution.

Calculation

Let the solubility of AgCl = s gm equi / litre

Equivalent conductance of AgCl = $\wedge = \frac{kX1000}{s}$

Since $\wedge = \wedge\ \infty$ for sparingly soluble salts

$$\wedge\ \infty=\frac{\mathrm{k\,X1000}}{\mathrm{s}}$$

Equivalent conductance at infinite dilution may be calculated using kohlrausch’s law.

$$\wedge \infty Agcl = \lambda_{Ag+} + \lambda_{cl-}$$

$$= 61.92 + 76.34 = 138.26\, mhocm^{2}$$

$$138.26 \quad = \frac{K\, X\, 1000}{S}$$

$$S \quad = \frac{K\, X\, 1000}{138.6} \quad gm equi / lit$$

Conductometric titrations:

The principle involved in these titrations is that electrical conductance depends upon the number and mobility of the ions. Conductance of solution is measured during the course of titration and the values are plotted against the volume of the titrant added. Two straight lines are obtained. The point of intersection of the two straight lines gives the end point of the titration.

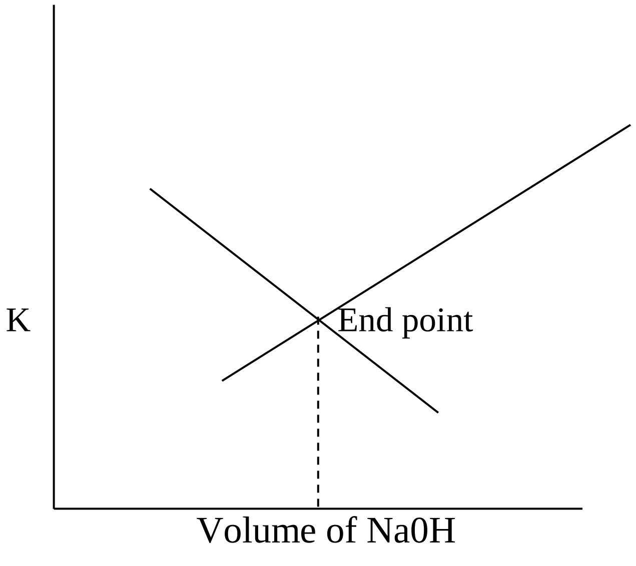
Type.1. Titration of strong acid vs strong base.

Example: HCl Vs NaoH.

A definite volume of the acid is taken in the conductivity cell and NaoH is taken in the burette. At the beginning of the titration the conductance is high since it is a strong electrolyte. When Na0H is added gradually from the burette, the fast moving H^+ ions are replaced by slow moving Na+ in the following way.

$H^+Cl^- + NaoH \rightarrow Na^+ Cl^- + H_2O$

Hence the conductance decreases till the neutralization is complete. After the neutralization, further addition of NaoH causes increase in conductance due to the fast moving OH^-. The plot of conductance Vs volume of Na0H gives two straight lines. The point of intersection of these two lines gives the end point of the titration.



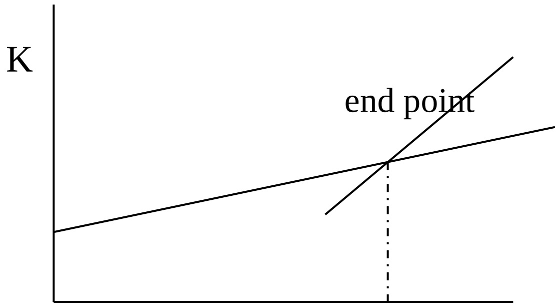
Type.II titration of weak acid Vs strong base:

Example: CH_3CooH Vs NaOH

Acetic acid is taken in the conductivity cell and Na0H is taken in the burette. At the beginning of the titration the conductance of the solution will be very low since it is a weak electrolyte. When Na0H is added gradually from the burette, the conductance increases due to the formation of highly ionized sodium acetate.

$$CH_3CooH + Na^+OH^- \rightarrow CH_3Coo^- + Na^+ + H_2O$$

After the complete neutralization of the acid, further addition of NaoH causes increase in the conductance value due to fast moving OH^- ions. The plot of conductance Vs vol. Of NaoH gives 2 straight lines. The point of intersection of these lines gives the end point of the titration.



Volume of NaoH

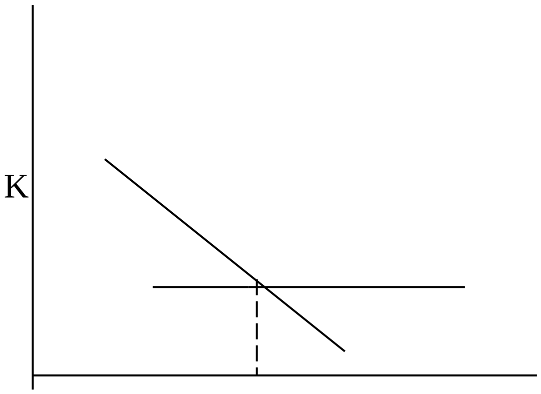
Type III Titration of strong acid Vs weak base:

Example: Hcl Vs NH_4OH

Hcl is taken in the conductivity cell and NH_4OHis taken in the burette. At the beginning of the titration the conductance of the solution will be very high since it is a strong electrolyte. When NH_4OH is added gradually from the burette, the conductance decreases due to the

$$H^+ Cl^- + NH_4OH \rightarrow NH_4^+ + cl^- + H_2o$$

replacement of fast moving H^+ions by NH_4^+ions. After the neutralization, further addition of NH_4^+ will cause no change in conductance as the weakly ionized NH_4OH has a very small conductivity. The plot of conductance vs volume of NH_4OH gives 2 straight lines. The point of intersection of these straight lines gives the end point of the titration.



Vol. Of NH_40H

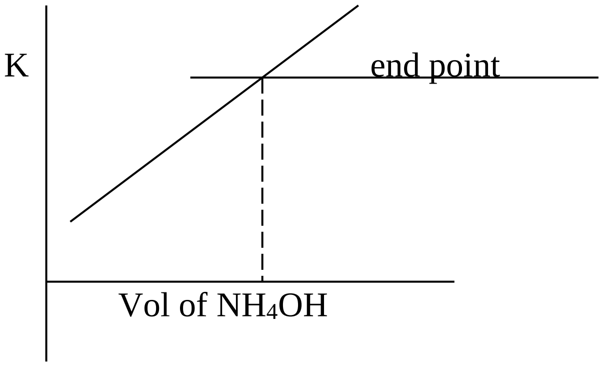
Type. IV Titration of weak acid Vs weak base

Example: CH_3COOH Vs NH_4OH

Acetic acid is taken in the conductivity cell and NH_4OH is taken in the burette. At the beginning of titration, the conductance of the solution will be very low since it is a weak electrolyte. When NH_4OH is added gradually from the burette. The conductance increases due to the formation of highly ionized ammonium acetate.

$CH_3CooH + NH_4OH \rightarrow CH_3Coo^- + Na^+ + H_2O$

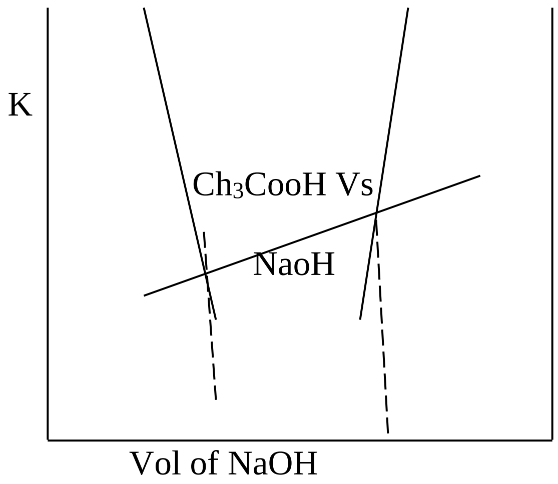
After the complete neutralization of the acid, further addition of NH_4OH no change in conductance since it is a weak electrolyte. The plot of conductance Vs volume of NH_4OH gives 2 straight lines. The point of intersection of these lines gives the end point of the titration.



Type V Mixture of acids Vs strong base

Example: Hcl and CH3CooH Vs NaOH.

When a mixture of acetic acid and hydrochloric acid is titrated against sodium hydroxide usually a combination of curves will be obtained.



In the type of titration, the strong acid (Hcl) will get titrated first and the titration of weak acid (Ch_3CooH) will commence only after the complete neutralization of strong acid. While the first point corresponds to the neutralization of Hcl, the second point corresponds to the neutralization of CH_3CooH.

Precipitation titration:

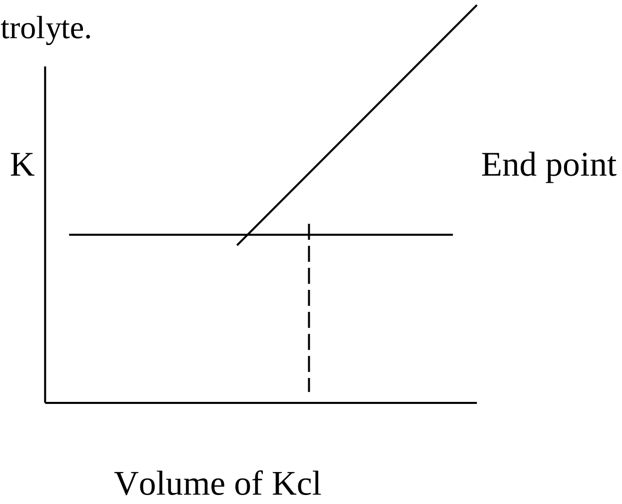
Example:$AgNo_3$Vs kcl.

The reaction involved may be treated as

$Ag+\ No_3^- + K^+cl \rightarrow k^+\ No_{3-} + Agcl \downarrow$

Potassium chloride is added to the $AgNo_3$ solution. The conductance upto the end point will remain more or less constant because the mobility of potassium ions is nearly the same as that of the Ag^+ ions. After the end point,

The conductance will begin to increase. Since kcl is a strong electrolyte.



Advantages of conductometric Titrations:

1. No special care is necessary near the end point as the end point is ascertained graphically.
2. Coloured solutions, where indicators can't be used can be titrated.
3. Very dilute solutions can also be titrated.
4. Titration of weak acid Vs weak base can be performed successfully.

Theory of strong electrolytes (or) Debye-Huckel-onsager theory (or) Interionic attraction theory

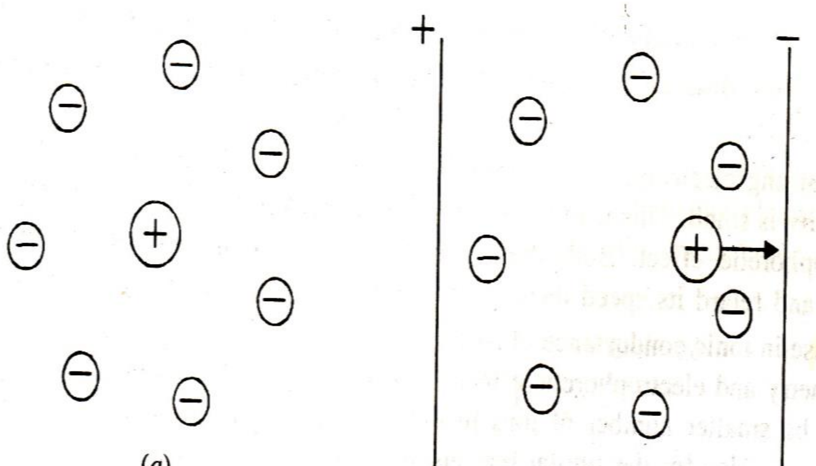
A strong electrolyte undergoes complete dissociation. Hence on dilution there is no change in the number of ions but equivalent conductance increases on dilution. This may be due to increase in the speed of ions. The scientists Debye and Huckel analysed about this and the scientist onsager gave mathematical expression. Hence this theory is called Debye Huckel onsager theory.

When 2 electrodes are placed in a solution of electrolyte and on passing current the ions present in the solution migrates to electrodes of opposite charge the speed of the ions depends upon the following factors.

1. Electromotive force, which attracts the ions towards charge of oppositely charged electrodes.
2. Viscosity of the medium controls the speed of the ions Greater the viscosity lesser the speed of the ions.
3. Asymmetric effect (or) Relaxation effect:

Due to attraction between the oppositely charged ions, a central ion is surrounded by ions of opposite charge and it is known as ionic atmosphere. i.e a central cation is surrounded by anionic atmosphere and central anion is surrounded by cationic atmosphere. In the absence of electric field these ionic atmosphere are spherical in shape. On passing current.

In the absence of electric field. In the presence of electric field.



(*a*) Symmetrical ionic atmosphere around a positive ion.

(*b*) Ionic atomosphere becoming asymmetric when central ion moves.

Fig. 10·1. Relaxation or asymmetry effect.

The central cation move towards cathode. Now the old ionic atmosphere decays and new ionic atmosphere is formed. There is time lag between the decay of old ionic atmosphere and the formation of newer one. Hence the ions around the cation is asymmetric ie., the number of anion at the back is greater than the anions at the front. Hence speed of the cation is reduced or retarded. This kind of effect is known as Relaxation effect (or) asymmetric effect.

4) Electrophoretic effect:

The central ion as well as the ionic atmosphere are solvated and carry with them their associated solvent molecules. Since the ionic atmosphere is comprised of more than one ion, more solvent molecules are carried in the direction opposite to the applied field. Thus the central ions are forced to move against a stream of solvent and, consequently, their velocities are reduced, this kind of effect of solvent molecules is known as electro phoretic effect.

On dilution the distance between central ion and the ionic atmosphere increases. Hence the effect of asymmetric effect and electro phoretic effect decreases. Therefore the speed of the central ion increases and the equivalent conductance increases. At infinite dilution the distance between the ions increases and the effects asymmetric & electro phoretic effect vanishes completely.

Based on De bye Huckel onsager theory an equation is derived for 1:1 electrolyte:

$$\lambda_c = \lambda_0 - \left[\frac{82.4}{(DT)^{1/2}\eta} + \frac{8.30\,X\,10^5}{(DT)^{3/2}}\lambda_0\right]\sqrt{c}$$

Where C = Concentration of the solution

D = Dielectric constant of the solvent

η = Viscosity Co-efficient

T = Temperature.

For a particular solvent at particular temperature the above equation can be rewritten as

$$\lambda_c = \lambda_0 - [A + B\lambda_0]\sqrt{c}$$

In water and at 298k

A= 60.2 B=0.229

Here A is constant due to electro phoretic effect and B is a constant due to asymmetric effect.

Verification of on sager equation:

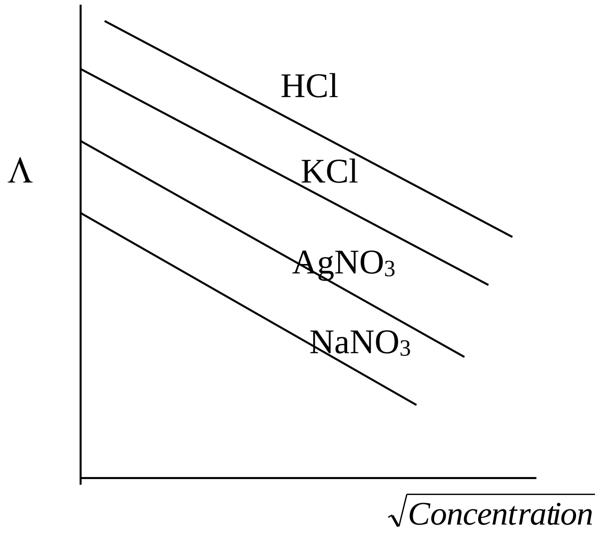
At a given temperature and for particular solvent onsager equation for a 1:1 electrolyte can be written as

$$\lambda_c = \lambda_0 - [A + B\lambda_0]\sqrt{c}$$

When the solvent is water and at 298k A=60.2; B=0.229 According to the above equation a plot of $\lambda c Vs \sqrt{c}$ gives a straight line. Slope of the straight line gives (A+B λ_0) value.

For different electrolytes like Hcl, Kcl, $AgNo_3$, Nacl λ_C values are measured at different concentrations and the plot of $\wedge c Vs \sqrt{c}$ gives straight lines. This confirms the on sager equation.

On Sager equation obeys upto the concentration of 0.02N. When the concentration increases above this value it deviates. This may be due to the various factors assumed for the derivation.



Wien effect (or) conductance under high potential gradient:

When 2 electrodes are placed in a solution of electrolyte and on passing current, the ions moves towards the oppositely charged electrodes. The speed of these ions depends upon the applied potential gradient. When potential gradient is 2000 Volt per cm, speed of ion will be 100cm/sec Due to high speed of ions, the ions not have enough time to form the ionic atmosphere. Hence there no role of assymetric and electro phoretic effect. Therefore conductance will be high. When the applied potential gradient is increased conductance increase upto certain limit. This kind of increased conductance under high potential gradient is known as wien effect.

Debye-Falkenhegan effect (or) conductance under high A.C frequency.

Debye-Falkenhagen developed a theory predicting that in an applied alternating electrical field of high frequency the ionic atmosphere will not be able to adopt an asymmetric structure corresponding to a moving central ion and thus will have no influence on the conductivity of the ion. Therefore, the conductance of a solution should vary with the frequency of alternating current used. The higher the frequency, the higher the conductance evidently. This effect is known as Debye falken Hager effect. Conductance remains independent of the frequency of alternating current upto 10^6 cycles per second but increase with further increase in frequency towards a certain limiting value.

Activity and activity co-efficient of strong electrolytes:

To determine the properties of solution, instead of concentration activity is utilized. It is defined as

$$a = Cf$$

$$\text{(or)} \quad a = m\gamma$$

Where

a = activity

f or γ = activity co-efficient

c = concentration in term of molarity

m = Concentration in term of molality

In dilute solution & there is less no of ions, for γ is equal to unity. Such a state is called ideals state of the solution. Therefore for such solutions.

$$a = c$$

$$\text{Or} \quad a = m.$$

For strong electrolytes (or) the no. of ions are more f or γ is vary from the value unity. Hence such solutions deviate from ideal state. For such solutions γ value decreases and then it begin to increase.

Mean ionic activity & Mean ionic activity co-efficient

An electrolytic solution consists of both cation and anion. Hence activity of a one ion is not enough to determine the properties. Therefore mean ionic activity is calculated.

Let us consider a 1:1 electrolyte AB which undergo ionization as follows

$$AB = A^{+} + B^{+}$$

Let the Activity of the cation is a_{+} and activity of anion is a_{-}

$$A = a_{+} \, . \, a_{-}$$

$$= (a\pm)^2$$

Where a± = Mean ionic activity.

For the electrolyte of the type A_x By

$$\text{Ax By} \quad \begin{matrix} \rightarrow \\ \leftarrow \end{matrix} \quad x A^{+} + y B^{-}$$

$$a \quad = a+^{x} . a-^{y}$$

$$= (a\pm)^{x+y}$$

If concentration is in terms of molality then. Molality of A^{+} is xm and molality of B^{-} is ym then

$$a = (xm\gamma_{+})^{x} \left(ym\gamma_{-}\right)^{y}$$

$$\therefore a = x^{x} y^{y} m^{x+y} \; .\infty_{+}{}^{x} \gamma - 4$$

$$a = x^{x} y^{y} \left(m\gamma \pm\right)^{x+y}$$

Where $\gamma \pm$ is mean ionic activity co-efficient and it is defined as

$(\gamma \pm)^{x+y} = \gamma_+^{x} . \gamma_-^{y}$

For 1:1 electrolytes x =1 y=1

Then $a = 1^1-1^1 (m\gamma \pm)^{1+1}$

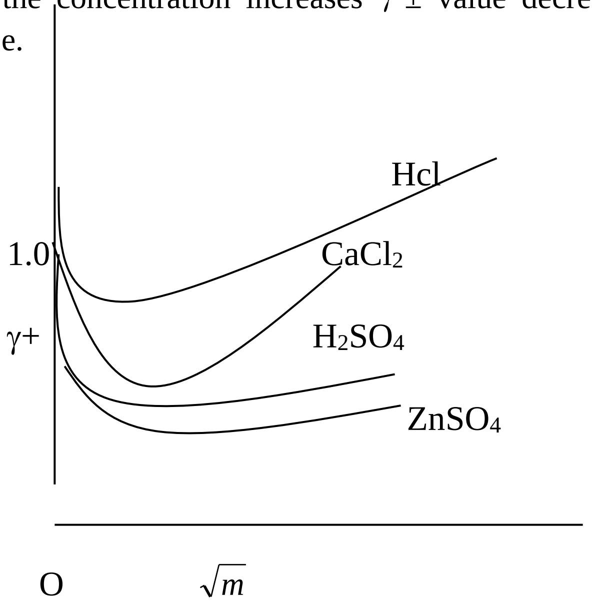
$= (m\gamma \pm)^2$

For 1:2 electrolytes x =2 y=1

Then $a = 2^2-1^1 (m\gamma\pm)^{2+1}$

$=4 (m\gamma \pm)^3$

For dilute solution mean ionic activity co-efficient is almost equal to unity. When the concentration increases $\gamma \pm$ value decrease and then it begins to increase.



Ionic strength:

Ionic strength is a measure of the intensity of the electrical field due to the ions in solution. It is represented by the symbol μ.

It is defined as half the sum of terms obtained by multiplying the concentration of each ion present in the solution by the square of its valency.

$\mu = \frac{1}{2} \Sigma m_1 Z_1^2$

or $= \frac{1}{2} (m_1 Z_1^2 + m_2 Z_2^2 + m_3 Z_3^2 + \ldots\ldots..)$

Where m_1, m_2, m_3 are concentration (or) molalities and Z_1, Z_2, Z_3 are the valencies of various ions present.

Ostwald's dilution law:-

According to Arrhenius theory, there exists a dynamic equilibrium between the ions and un-ionised molecules. The scientists applied Law of mass action to the weak electrolytes.

Consider 1 mole of the electrolyte AB dissolved in v litres. Let x be the degree of dissociation then

$$AB \leftrightarrow A^+ + B^-$$

Initial concentration	1	0	0
Equilibrium concentration	$c(1-\alpha)$	$c\alpha$	$c\alpha$

Applying law of mass action.

$$k = \frac{[A][B]}{[AB]}$$

$$= \frac{C \propto .C \propto}{c(1-\alpha)}$$

$$= \frac{C \propto^2}{(1- \propto)} ------(1)$$

The equation (1) is the mathematical representation of ostwald dilution law and k is called dissociation constant.

In case of weak electrolytes, the value of $\propto$ is comparatively small, hence it may be neglected in the denominator

$$\therefore \quad K = C\propto^2$$

Limitation: It is applicable only to weak electrolytes.

Determination of dissociation constants:

From ostwald's dilution law we know that the dissociation constant of the weak acid (or) weak base

$$K_a \text{ (or)} K_b = \frac{\alpha^2 c}{1-\alpha}$$

$$= \alpha^2 c \qquad Since\, \alpha <<< 1$$

By measuring the degree of dissociation $\propto$ and substituting the value of $\propto$ and concentration in Ka equation will given the dissociation constant of the acid (or) base.

P^H value

Definition: The P^H of a solution is defined as the negative logarithm to the base 10 of the hydrogen ion concentration

$$P^H = -\log_{10} [H^+]$$

It indicates whether a solution is acidic or basic or neutral. The concentration of $[H^+]$ in H_2O is $1X\ 10^{-7}$moles /line.

$$\therefore PH = -\log_{10} 10^{-7}$$
$$= -X - 7\log{}^{10}$$
$$P^{H} = 7$$
$$\therefore water\ \ is\ \ neutral.$$

Let us calculate the PH of decinormal Hcl.

$$\left[H^{+}\right] = 0.1(or)10^{-1} mole/line$$
$$\therefore PH = -\log{}_{10}10^{-1}$$
$$PH = -X - 1\log 10 = 1.$$

Similarly we can calculate P^H of decinormal. Solution of NaOH

P_{oH} = -log $_{10}$[OH]

= -log $_{10}$[10^{-1})

= 14-1 =13

We know that

PH+POH = 14.

PH = 14-POH

= 14-1 =13

Thus we find

	PH	= 7	=>	the solution is neutral
If	PH	< 7	=	the solution is acidic
If	PH	> 7	=	the solution is basic

Determination

The resistance of the given solution to which PH to be determined is measured by conductance measurements. From this ^c is calculated.

^ $\propto$ or $^{\wedge}{}_0$ can be determined by extra pollution of ^ Vs $\sqrt{c}$ graph for a strong electrolyte and using kolulrausch's law for a weak electrolyte.

Substitution of ^c & ^ $\propto$ in the equation

$$\propto = \frac{\wedge c}{\wedge \propto}$$

gives degree of dissociation

Substitution of α value and the concentration in the equation

$$\left[H^{+}\right] = C \propto$$

Gives hydrogen ion concentration.

Substitution of $\lfloor H^{+} \rfloor$ concentration in the PH equation.

$P^{H} = -\log_{10} [H^{+}]$

Gives the pH of the given solution.

Buffer solution:

A solution whose pH is not altered appreciably by the addition of small amounts of acids or bases is called the buffer solution.

Buffer solutions usually consists of mixture of weak acids and their salts or weak bases and their salts

Examples:

1) Acetic acid and sodium acetate
2) Ammonium hydroxide and ammonium chloride

Buffer action: the resistance to change the PH on the addition of acid or base is known as buffer action.

Henderson equation:

Consider the buffer solution contains a weak acid HA, and its highly ionized salt. A^{-}. the dissociation of weak acid HA occurs as

$$\text{HA} \overset{\rightarrow}{\leftarrow} H^{+} + A^{-} \downarrow$$

Applying law of mass action, the ionization constant Ka is given by

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

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

Taking logarithm & reversing the sign then

$$-\log[H^{+}] = -\log ka + \log\frac{[A^{-}]}{[HA]}$$

$$P^{H} \quad = \quad Pk_a + \log\frac{[A^{-}]}{[HA]}$$

$$in\ \ general\ \ P^{H} = pK_a + \log\frac{[Salt]}{[Acid]}$$

This equation is called Henderson's equation. This equation is used to calculate P^{H} of any buffer solution.

Uses of Buffer solution:

1) Buffers play an important role in respiration. The important buffers in blood are H_2Co_3–$NaHco_3$, NaH_2P_4-Na_2p04, protein and oxyhemoglobin, deoxy haemoglobin.
2) Buffer systems maintain the P^H of body fluids and tissues. The bicarbonae-carbonic and buffer is the most important.
3) Most biological fluids, blood and milk etc., have definite $P^{H.}$ For example, the P^H of human blood is about 7.35 and remains constant. Any changes from this value show pathological conditions such as diabetic coma in which the P^H of blood may drop to 6.82.
4) The P^H of gastric juice should be between 1.4-2. So there is any change vomiting takes place and ulcer results.
5) Control of the P^H of various parts of digestive enzymes is maximum only at specific P^H. Any change from these P^H values hinder or even stop the action of enzymes. For example the enzyme pepsin have maximum efficiency between 1.4-2.

Industrial application:

6) Buffers are used in the fermentation of alcohol at P^H equal to 6.
7) They are used in electroplating, tanning of leather and manufacture of sugar at constant P^H

Hydrolysis of Salts:

The interaction of cation or anion of the salt with water in known as hydrolysis. Because of hydrolysis of salts the solutions are either neutral or acidic or basic.

Hydrolysis of salt of weak acid and strong base:

Salts of this type like CH_3CooNa, Na_2Co_3etc undergo hydrolysis to given an alkaline solution.

For example CH_3CooNa, almost completely dissociates into Na^+ & CH_3Coo^-, ions.

$CH_3CooNa, \rightarrow CH_3Coo^- + Na^+$

The acetate ion reacts with water as follows.

$CH_3Coo^- + H_2O \rightarrow CH_3CooH + OH^-$

$\leftarrow$

$$k = \frac{[\mathrm{CH_3CooH}][\mathrm{OH^-}]}{[\mathrm{CH_3Coo^-}][H_2O]}$$

Applying law of mass action

Since [H_2o] remains constant, it may be combined with k equ to give a new constant k_h called hydrolysis constant

$$kh = \frac{[CH_3CooH][OH^-]}{[CH_3Coo^-]} \quad ------(1)$$

$$\text{we know that } k_w = [H^+][OH^-]$$

$$[OH^-] = \frac{kw}{[H^+]} \quad ------(2)$$

$$\text{The dissociation cons tan t of accetic acid}$$

$$ka = \frac{[CH_3Coo^-][H^+]}{[CH_3CooH]}$$

$$[CH_3Coo^-] = \frac{ka.[CH_3CooH]}{[H^+]} -----(3)$$

$$\text{subsituiting the equation } (2) \text{ and } (3) \text{ in } (1) \text{ gives}$$

$$kh = \frac{[CH_3CooH].kw.[H^{+-}]}{[H^+].ka.[CH_3CooH]}$$

$$kh = \frac{kw}{ka}$$

Thus the hydrolytes constant k_h varies inversely with dissociation constant ka of the acid. Weaker the acid greater is the hydrosis constant.

Degree of hydrolysis (x)

Fraction of the salt that has undergone hydrolysis at equilibrium is known as degree of hydrolysis.

Let us consider the Initial concentration of the salt is C moles/line. At equilibrium x moles undergo hydrolysis then.

$A^- + H_2O \rightarrow AH + OH^-$

At equilibrium C(1-x) ← cx Cx

$$\therefore kh = \frac{Cx \,.\, Cx}{C(1-x)}$$

$$\text{Since } x << 1 \,\&\, \text{it to neglected in the denominato r.}$$

$$kh = cx^2$$

$$\therefore x = \sqrt{\frac{kh}{c}}$$

PH of the solution:

The concentration of [OH^-] = Cx

$$\therefore \left[OH^-\right] = C\sqrt{\frac{kh}{c}}$$

$$= c\sqrt{\frac{kw.c}{ka.}}$$

$$we\ know\ that$$

$$\left[H^+\right] = \frac{kw}{\left[OH^-\right]}$$

$$\therefore \left[H^+\right] = \frac{kw}{c\sqrt{\frac{kw.c}{ka.}}} = \sqrt{\frac{kw.ka}{\sqrt{c}.}}$$

$$Take \log arithm on\ both sides\ \ and\ \ reverse the sign.$$

$$-\log\left[H^+\right] = -1/2\log kw - 1/2\log ka + 1/2\log c.$$

$$P^H \qquad = 1/2\,pkw + 1/2\,pka + 1/2\log c$$

using this equation p^H of the solution is determined

2. Hydrolysis of Salt of weak base and strong acid:

Salts like NH_4cl,$Alcl_3$,$Fecl_3$ undergo hydrolysis to give an acidic solution. For example NH_4cl dissociates as

$NH_4cl \rightarrow NH_4^+ + cl^-$

The ammonium ion reacts with water as follows

$NH_4^+ + H_2O \rightarrow NH_4OH^- + H^+$

Applying law of mass action:

$$kh = \frac{\left[NH_4OH\right]\left[H^+\right]}{\left[NH_4^+\right]}$$

$$we know that$$

$$kw = \left[H^+\right]\left[OH^-\right]$$

$$\left[H^+\right] = \frac{kw}{\left[OH^-\right]}$$

Let us consider weak base NH_4OH which dissociates or

$NH_4OH - \rightarrow NH_4^+ + OH^-$

$$\therefore kb = \frac{\left[NH_4^{+}\right]\left[OH^{-}\right]}{\left[NH_4OH\right]}$$

$$\left[NH_4^{+}\right] = \frac{kb\left[NH_4OH\right]}{\left[OH^{-}\right]}$$

$$Subsitutiting\ \ the\ valueof \left[H^{+}\right] and\ \ \left[NH_4^{+}\right] in\,(1)\,then$$

$$kh = \frac{\left[NH_4^{+}\right] kw \left[OH^{-}\right]}{\left[OH^{-}\right].kb\left[NH_4OH\right]}$$

The hydrolysis constant k_h varies inversely with the dissociation constant k_b of the base. Therefore weaker the base, the greater is the k_h value.

Degree of hydrolysis.

$$B+\ \ +H_2O \leftrightarrow BOH + H^{+}$$

$$C\ (1\text{-}x) \qquad\qquad cx \qquad\qquad cx$$

$$\therefore kh = \frac{c\propto .c\propto}{c(1-\propto)} = \frac{c\propto^2}{(1-\propto)}$$

$$\sin ce\ \ x <<< 1 it\ \ is\ \ neglected\ \ in\ the\ Dr.$$

$$kh = C\propto^2$$

$$\therefore x = \sqrt{\frac{kh}{c}}$$

PH of the solution

$$\left[H^{+}\right] = CX$$

$$\therefore \left[H^{+}\right] = c\sqrt{\frac{\lambda}{c}}$$

$$= c\sqrt{\frac{kw}{kb^{c}}} = \sqrt{\frac{kw.c}{kb.}}$$

Taking logarithm on both sides & reverses the sign.

$-\log [H^{+}] = -1/2 \log kw -1/2 \log c+1/2 \log kb.$

But $pH = -\log [H^{+}]$; $pkw = -\log kw$; $pkb =-\log kb$.

$\therefore$ PH = ½ pkw – ½ pkb - ½ log C.

Using this equation PH of the solution is determined.

3. Hydrolysis of salt of weak acid and w.Base:

Salts like ammonium acetate undergo hydrolyts to give a neutral solution. CH_3CooNH_4dissociates into NH_4^{+} and CH_3Coo^{-}

$CH_3CooNH_4 \rightarrow NH_4^+ + CH_3Coo^-$

NH_4^+& CH_3Coo^-ions interact with water as follows.

NH_4^+ $CH_3Coo^- + H_2O \rightarrow CH_3CooH + NH_4OH$

Applying law of mass action

$$kh = \frac{[CH_3cooH][\mathrm{NH_4OH}]}{[\mathrm{NH_4}^+][CH_3coo^-]}$$

For the dissociation of acetic acid we have

$$[CH_3coo^-] = \frac{ka.[CH_3cooH]}{[\mathrm{H}^+]}$$

For the dissociation of NH_4OH We have seen

$$[NH_4 +] = \frac{kb.[NH_4oH]}{[\mathrm{OH}^+]}$$

Subsitute $[NH_4+][CH_3Coo^-]$ in (1) then

$$kh = \frac{[CH_3cooH][\mathrm{NH_4OH}][H^+][oh^-]}{ka[CH_3cooH]kb[\mathrm{NH}_4OH]}$$

$$kh = \frac{[H^+][oH^-]}{ka.kb} = \frac{kw}{ka.kb.}$$

Degree of hydrolysis:

$B^+ + A^- + H_2O \rightarrow BOH + AH$

Cx cx

A+ equilibrium c(1-x)c(1-x)

$$\therefore kh = \frac{cx.\ cx}{C(1-x).c(1-x)}$$

$$= \frac{x^2}{(1-x)^2}$$

$since \quad x <<< 1 therefore\ it\ is\ neglected\ in\ the \quad Dr.$

$$kh = x^2$$

$$x = \sqrt{kh} = \sqrt{\frac{kw}{ka.kb}}$$

PH of the solution:

The Dissociation constant of the acid

$$Ka = \frac{\left[H^+\right]\left[A^-\right]}{\left[HA\ \right]}$$

$$\left[H^+\right] = \frac{ka.\left[HA\right]}{\left[A^-\right]}$$

$$but\left[HA\right] = cx; \left[A^-\right] = c\left(1-x\right).$$

$$\therefore \left[H^+\right] = ka.\frac{cx}{c\left(1-x\right)}$$

$$= \frac{ka.x}{\left(1-x\right)}$$

$$= kax.$$

$$Since\ X <<< 1\ it\ is\ \ neglected\ in\ the Dr$$

Taking logarithm on both sides & reverse the sign.

-log [H^+] = -1/2 log kw -1/2 logc+1/2 log kb.

But pH = -log [H^+]; pkw = -log kw; pkb =-log kb.

pH = ½ pkw + ½ pka - ½ pkb.

using this equation PH of the solution is determined

Hydrolysis of salt of strong acid & strong Base:

Salts like Nacl. Kcl,$NaNo_3$ does not undergo hydrolysis and the resulting solution is remain neutral in nature.

Determination of Degree of hydrolysis: Conductance (or) bredig's method

Conductance of a salt solution of weak acid or weak base depends upon ions due to hydrolysis and unionsed salt.

For example let as consider NH_4cl. The initial concentrations is 1 mole/litre and at equilibrium x moles undergo hydrolysis.

$NH_4cl+H_2O \rightarrow NH_4OH+H_2O$

At equilibrium (1-x) x x

The conductance of the solution λ is the sum of conductance due to (1-x) gm of unhydroysed salt and x gm Hcl.

$$\begin{aligned}
\lambda\ &=(1-x)\lambda s\ +\ \lambda\ Hcl.\\
&= \lambda s-\lambda ds+x\,\lambda\, Hcl\\
\lambda\ &= \lambda s-x\left(\lambda s+\lambda Hcl\right)\\
\lambda-\lambda \mathbf{s}&=-x\left(\lambda s+\lambda Hcl\right)\\
\lambda-\lambda \mathbf{s}&=-x\left(\lambda Hcl-\lambda s\right)\\
\therefore x&=\frac{\lambda-\lambda s}{\lambda Hcl-\lambda s}------(1)
\end{aligned}$$

Equivalent conductance of the solution is measured by conductance measurements Equivalent conductance of Hcl is obtained as $\lambda Hcl=\lambda_{H^+}+\lambda_{cl^-}$

On adding NH_4OH to NHcl solution hydrolysis is suppressed. Conductance of the resulting solution (λs) is determined Substitution of all these value in (1) gives degree of hydrolysis.

Distribution method:

If the acid or base obtained during hydrolysis is soluble in two solvents which are immiscible with each other, then this method can be employed to determine the degree of hydrolysis.

Example: Aniline hydrochloride on hydrolysis give the base aniline which is soluble in water & benzene. Hence on adding benzene to the reaction mixture Aniline is distributed between Aniline and water layers.

Benzene $C_6H_5NH_2$

⇅

H_20 $C_6\,H_5\,NH_2+H_2O$

$C_6\,H_5\,NH_3\,Cl \Leftrightarrow C_6\,H_5\,NH_3\,OH+HCl$

Concentration of aniline in the benzene layer is determined by experimental method concentration of aniline in the aqueous layer can be determined using the following formula.

$$\text{Distribution Co-efficient}=\frac{\text{Concentration aniline in organic layer}}{\text{Concentration of aniline in aqueous layer}}$$

Therefore the concentration of aniline obtained during hydrolysis is equal to concentration in aqueous layer + organic layer. This is equal to concentration of Hcl obtained during hydrolysis. By subtracting the concentration of Aniline of Hcl from the Initial concentration of salt solution gives the concentration of unhydrolysed salt

$$\therefore kh = \frac{[Hcl]\,[C_6H_5NH_2 in\, aqueous layer]}{concentration\, of\, unhydrosed\, salts.}$$

$$X = \sqrt{\frac{kh}{c}}$$

Hence x, the degree hydrolysis can be calculated.

Unit – IV

1) Define specific and equivalent conductance and write the relation between them.

2) Explain and give application of kholrausch's law.

3) Derive k_h for the hydrolysis fo sodium acetate

4) Explain the determination of transport number of Hittorf's method.

5) Discurss Debye-Huckel- on sager theory of strong electrolytes.

6) Define activity and activity co-efficient of electrolytes

7) Derive Henderson equation of buffer solution

8) Write short notes on

   a) wien effect

   b) De bye=Falkn hagen effect

9) Discuss the effect of conductance on dilution

10) Define the following

   (1) Ionic mobility

   (2) Ionic conductance

   (3) Walden rule

11) Describe the method of determination of solubiling product of sparingly soluble salt.

NOTES

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UNIT –V

Galvanic cells:

They are devices in which chemical energy is converted into electrical energy. All electrochemical cells are called galvanic cells.

A cell consists of two electrodes and a solution of an electrolyte. The two electrodes are called half cells. Thus a galvanic cells consists of two half cells.

E.g. Daniel cell.

It consists of Zinc electrode dipped in $ZnSO_4$ and cu electrode dipped in $CuSO_4$. It is represented by

$Zn/Zn^{2+}//Cu^{2+}/cu$.

The cell reaction is

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

The above redox reaction can be split into two half reactions as

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

$Cu^{2+} + 2e \rightarrow Cu$ (Reduction)

The Zinc electrode is called anode (+Ve electrode). The Copper electrode is called cathode (negative electrode)

The emf of this cell = 1.1V.

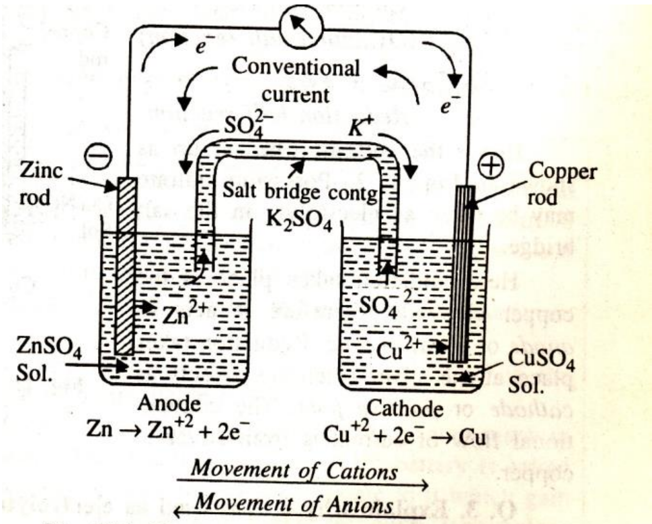


Fig. 11·1. Electrochemical cell based on the redox reaction $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$

Reversible or irreversible cells:

A cell is said to reversible if it satisfies the following three conditions.

1. If an opposing EMF equal to that of the cell is applied to the cell, no current flow in the circuit and hence no chemical reaction takes place (ex) Daniel cell.
2. If an opposing EMF infinitesimally smaller than that of the cell is applied an infinitesimally small current flow from the cell and reaction takes place in the forward direction.

   ie. $Zn + Cu^{2+} \rightarrow Zn^{2+} + zn$

3. If an opposing EmF infinitesimally greater than that of the cell is applied, an infinitesimally small current flow into the cell and the reaction takes place in the reverse direction

   $Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn$

Daniel cell obeys all these condition hence it is a reversible cells.

The cell which is not obeying the above three conditions are known as irreversible cells.

Example: A cell consists of Zn & Ag rod dipped in dil. H_2So_4

When the two electrodes are connected with a wire the following reaction takes place.

$Zn + H_2So_4 \rightarrow ZnSo_4 + H_2$

i.e. Zn is oxidized to Zn^{2+} ions are reduced to H^+ gas

Now if the cell is connected to the external EMF whose EMF is slightly greater than the emf of the cell then Ag dissolves at one electrode(ie oxidized) and H_2 gas is evolved at the other (Reduction).

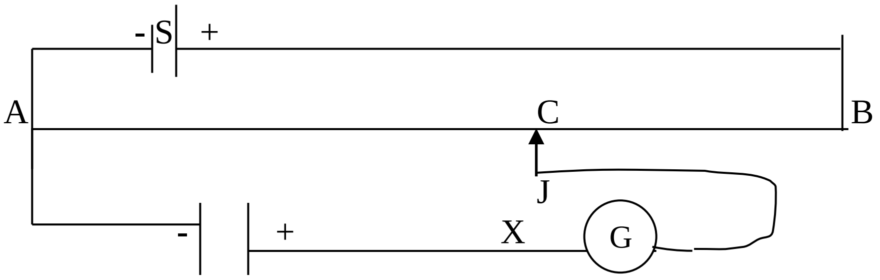
$2Ag + H_2So_4 \rightarrow Ag_2SO_4 + H_2$

Thus reversibility is not satisfied.

EMF and its measurement

It is defined as the potential difference between the two electrodes when no current is drawn from the external circuit is called Electromotive force.

It is determined by potentiometric method. Hence the unknown EMF is opposed by another known EMF until the two are equal. The general principle involved may be explained with the help of the following circuit



AB is a stretched wire of uniform thickness, S is a standard cell whose EMF is known. It is connected to the end A and B. X is a cell whose EMF is to be determined. One end of the cell x is connected to the end A and other to the sliding contact J through the galvanometer G in such a manner that it sends EMF in a direction opposite to that of the cell S. The sliding contact is moved along the wire AB till at a particular point, say c, no deflection is observed in the galvanometer. If E, represents the EMF of the standard cell S and EX that of the experimental cell, x then.

$$\frac{\text{Ex}}{\text{Es}} = \frac{\text{length Ac}}{\text{length AB}}$$

$$\text{Ex} = \frac{\text{length Ac}}{\text{length AB}} \text{ x Es}$$

Thus knowing Es, Ex can be calculated.

Weston – standard cell:

It is represented as

$$Cd(Hg)_{\Lambda} \left| \, Cd\,SO_4.8/3\underset{(S)}{H_2O} \right\| \underset{Cd\,SO_4}{Satd} \left| \, \underset{(S)}{Hg_2SO_4} \, , Hg \right.$$

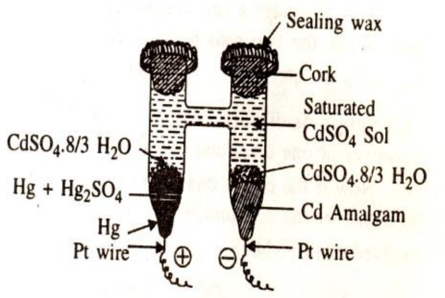


Fig. 11·5. Weston standard cell.

The cell reaction is

Cd +Hg_2So_4(s) → cd so_4(S) +2Hg.

Oxidation occurs at the cadmium electrode and Reduction at the Mercury electrode.

It consists of an H-shaped glass vessel. One of the limbs contain merury covered with a paste of mercurous sulphate and mercury, crystals of solid $cdso_4$ 8/3 H_2O and saturated solution of cadmium sulphate. This limb acts as the anode. The other limb which acts as the cathode contains cadmium amalgam covered with crystals of solid 8/3 H_2O and then saturated cdso4 solution. Short platinum wires are sealed into the bottoms of the limbs to make contact with the active materials. The limbs are finally closed with corks and sealing wax. The purpose of placing solid crystals of 8/3 H_2O is to keep the CdSO4 solution saturated at all temperatures.

This cell has a constant reproducible value of emf which does not change with time. Also the temperature co-efficient of emf is very low.

The EMF of the cell is 1.085 V at 15^0 C &

1.085 V at 25^0 C

Types of reversible single electrodes:

1) Gas –ion electrode

It consists of a gas bubbling about an inert metal immersed in a solution containing ions to which the gas in reversible

Example: Pt, H_2(gas) /H^+

The electrode reaction

$\frac{1}{2} H_2 \rightarrow H^+ + e^-$

The electrode potential is expressed by

$$E_{H2} = E^o_{H2} - RT/F \ln a_{H+}/a_H{}^{1/2}$$

$$E_{H2} = - RT/F \ln a_{H+}$$

2) Metal –metal ion electrode

In consists of a piece of metal dipped in a solution containing the metal ion

Example Zn/Zn^2

The electrode reaction is

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

The electrode potential in expressed by

$$E_{zn} = E0_{zn} - \frac{RT}{2F} \ln \frac{a_{zn\,2+}}{a_{zn}}$$

$$E_{zn} \quad - \frac{RT}{2F} \ln a_{zn\,2+}$$

3) Metal insoluble salt common anion electrode:

It consists of a metal ion contact with one of its sparingly soluble salts and a solution containing the ion present in the salt other than metal.

Example: Ag, Agcl, /$cl^-{}_{(soln)}$

The electrode reaction is

$Ag \rightarrow Ag^+ + e^-$

←

$Ag^{+} + cl^{-} \rightarrow Agcl$

$Ag + cl^{-} \rightarrow Agcl + e^{-}$

←

The electrode potential is given by

$E_{Ag\text{-}Agcl} = E^{0}\ Ag\text{-}Agcl - RT/F\ \ln a_{cl^{-}}$ a Ag =1

a Agcl =1.

4) Redox electrode:

Electrodes in which the potential results from the tendency of ion to pass from one state of oxidation into another more stable state.

Example :

$Pt, Fe^{2+} / Fe^{+3}$

Standard hydrogen electrode

The design of the hydrogen electrode is shown in the Figure. In the standard hydrogen electrode. Hydrogen gas 1 atmospheric pressures is passed into 1M Hcl in which foil of platinized platinum remains immersed.

It is represented as

Pt, H2(g) /Hcl

1 atm p a =1.

The std hydrogen electrode has em = o

ie $E^{0}H_{2} = 0$

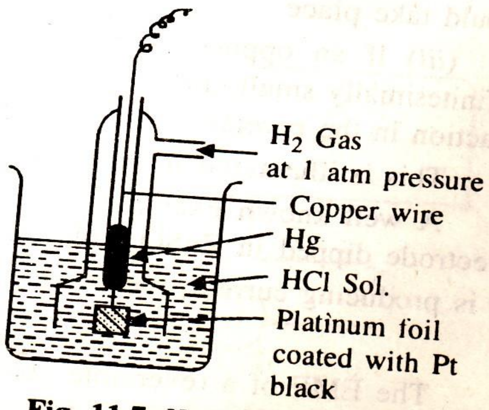


Fig. 11·7. Hydrogen electrode.

Calomel Releltrode:

Pure mercury is placed at the bottom of a tube. It is covered with a paste of mercurous chloride (calomel) and then filled with either decinormal (or) normal (or) saturated solution of kcl from the side tube A such that the side tube B is also filled with the kcl solution. A piece of platinum wire sealed at its end is fixed into the tube such that the pt wire remains dipped into the mercury.

It is represented as

Hg/ Hg_2Cl_2 (s), Hcl (solution)The electrode reaction is

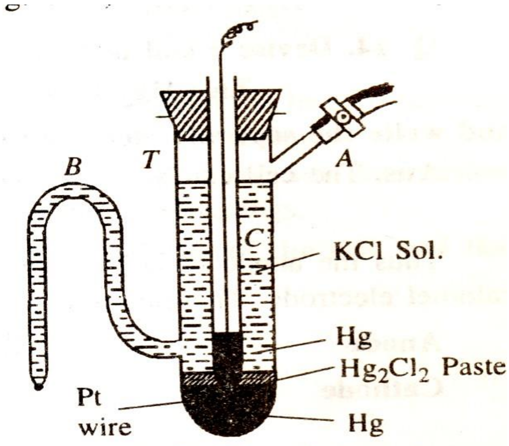


Fig. 11·8. Calomel electrode.

$2Hg \rightarrow Hg_2^{2+}+2c^-$

$Hg_2^{2+}+2cl^- \rightarrow Hg_2Cl_2$

$2Hg+ 2cl^- \rightarrow Hg_2Cl_2 + 2c^-$

The electrode potential is

$$E \text{ calomel} = E^o \text{ calomel} - \frac{RT}{2F}\, l\, \frac{aHg_2d_2}{(ahj)^2(a_{cl}-)^2}$$

$$a_{Hg_2Cl_2} = 1 \qquad a_{Hg} = 1$$

$$\therefore E_{Calomel} - E^o Calomel + \frac{RT}{2+} |n a_{Cl^-}$$

At 298 k the oxidation potential of calomel electrode

0.1 N kcl	-0.3338
1N kcl	-0.2800

Saturated kcl	-0.2415

Derivation of Nernst equation for emf of cells:

Let us consider a reversible reaction

$$A+B \longrightarrow C+D$$

The free energy charge of this reaction is given by

$$\Delta G = \Delta G^0 + RTin \frac{a_c \times a_D}{a_A \, . \, a_B} ---(1)$$

Where ΔG^0 represents std. Free energy and a_A, a_B, a_C,& a_D, are activities of A,B,C,D

If the cell reaction involves transfer of number Σ of electrons, this corresponds to the flow of nF Farday of electricity. If E is the EMF of the cell, then clerical energy produced in the cell = nFΣ. Since electrical energy produced is equal to the decrease in free energy of the cell reaction. We have

$-\Delta G = nFE$ --------- (2)

at std state $-\Delta G^0 = nFE^0$ ------- (3)

Where E^0 is the standard Emf of the cell, substituting the values of ΔG d

ΔG^o in (1) we get

$$-nF\Sigma = -nF\Sigma^o + RT \; in \; \frac{a_C \, .a_D}{a_A \, .a_B}$$

$$E = E^o - \frac{RT}{nF} \; in \; \frac{a \;\; products}{a \;\; reac\tan ts}$$

This equation is called nernst equation for the calculation of EMF of cell.

Nernst equation for single electrode potential:

In a Reversible cell the 2 electrodes are reversible in nature. Therefore nernst equation for electromotive force is applied to electrode potential. For any electrode.

Reduced state → Oxidixed state + ne^-

$$\therefore \Sigma \;= \Sigma^0 \;= \frac{2.303RT}{nF} \log \frac{a\, oxidised\, state}{a\,\mathrm{Re}\, duced\, state.}$$

Where E = electrode potential

E^0= std. Electrode potential

For example,

$Zn \rightarrow Zn^{+2}+2c^{-}$;   n=2

$$E_{zn/zn2+} = \Sigma^{0}_{zn/zn2+} - \frac{2.303k}{2F} \log a_{Zn^{+2}}$$

Where $a_{Zn} = 1$.

Nernst theory of electrode potentials:

Each cell is made up of two electrodes. At one electrode oxidation takes place i.e., electrons are evolved. At the other electrode reduction takes place i.e. electrons are taken up.

The tendency of an electrode to lose or gain electrons when it is in contact with its own ions in solution is called electrode potential. Since the tendency to gain electron means also the tendency to get reduced. This tendency is called reduction potential. Similarly the tendency, to loss electros means the tendency to get oxidized. This tendency in called oxidation potential. Oxidation potential is the reverse of reduction oxidation potential.

It is not possible to determine experimentally the potential of a single electrode. It is only the difference of potentials between two electrodes that we can measure by combining them to give a complete cell.

Standard electrode potential:

If the concentration of the ions is unity and the temperature is 25°c the potential of the electrode is termed as the std electrode potential. It is represented by E^{o}_{ele}.

Electro chemical series:

The various electrodes have been arranged in order of their decreasing value of standard reduction potentials. This arrangement is called electro chemical series.

For example.

Reduction half reaction	Std need potential E reduction
$Au_{+3}+3_{e-} \rightarrow Au$	1.50
$Cu_{+2}+2_{c-} \rightarrow Cu$	0.34
$2H^{+}+2_{c-} \rightarrow H_2$	0.00
$Ni^{2+}2_{c-} \rightarrow Ni$	-0.28

$Fe^{+2}+2^{e-} \rightarrow Fe$	-0.74
$Li + c^{-} \rightarrow Li$	-3.05

Applications:

1. To predict the relative ease of oxidation (or) reduction of various elements.

As by convention +ve sign is used to represent the reduction potential. Greater the reduction potential, more easily the element is reduced (or) strong oxidizing agent. Example F_2 has high reduction potential than Li. Hence F_2 strong oxidizing agent and Li is the weak oxidizing agent and vice versa.

2. To predict whether a metal reacts with acid to give hydrogen gas.

Metals lying below hydrogen (having negative reduction potential) in the electrochemical series react with the acid to give hydrogen gas. Further lower the reduction potential, higher is the reactivity.

3. To calculate the standard EMF of any electrochemical cell

In the representation of a cell, the electrode on which oxidation takes place is written on the left hand side and the electrode on which reduction takes place in written on the right hand side.

Emf of the cell = E cell = $E_{\text{Right electrode}} - E_{\text{left electrode}}$

4. To predict spontaneity of a reaction :

To find out whether a reaction is feasible or not. EMF of cell based upon the given redox reaction is calculated. If the EMF of the cell comes out to be positive, the reaction is feasible. If it comes out to be negative, the reaction is not feasible:

Application of EMF measurements:

It is used to calculate thermo dynamic quantities.

The decrease in free energy of a cell is equal to the electrical energy (nFE)

$$-\Delta G = nF\Sigma$$

$$or\ \Delta G = -nF\Sigma$$

$$then\ \Delta G^{O} = nF\Sigma^{o}$$

According Gibb's Helm holtz reaction

$$\Delta G = \Delta H + T\left(\partial \frac{\Delta G}{\rho T}\right) ---(2)$$

$$susbsitute\ (1)\ \ in\ (2)$$

$$-nF\Sigma\ = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)p$$

$$E\ = \frac{-\Delta H}{nF} + T\left(\frac{\partial E}{\partial T}\right)p$$

We know that

$$\Delta G = \Delta H - T\Delta S\ ---(3)$$

Compare equation (2) & (3)

$$\Delta s = \left(\frac{\partial \Delta G}{\partial T}\right)p$$

$$= -\left(\frac{\partial(-n\Sigma)}{\partial T}\right)p$$

$$\Delta s = nF\left(\frac{\partial E}{\partial T}\right)p$$

$$According\ \ to\ \ van't\ \ Hoff\ \ equilibrium$$

$$\Delta G^0 - RTin\,kequ.$$

$$-n\ F\Sigma^0\ = -RT\ in\ \ K.$$

$$RT\ \ in\,k\ \ = n\ F\Sigma^0$$

$$In\ K = \frac{nF\,\Sigma^0}{RT}$$

Thus it is used to calculate

Emf of cell, std emf of the cell, temperature co-efficient and $\Delta G, \Delta G^0, \Delta S, \Delta H$ equilibrium constant.

Determination of P^H of solution:

The various electrodes whose potentials depend upon the H+ ion concentration are hydrogen electrode, quinhydrone electrode and glass electrode. Using these electrodes against the reference calomel electrode, pH of the solution is determined.

1) **Using hydrogen electrode:**

The electrode reduction reaction is

$$H^+ + e^- \rightarrow 1/2\,H_2\ (1atm)$$

By Nernst equation, the potential of this electrode is given by,

$$E_{H^+,H_2} = E^o_{H^+,H_2} + \frac{Rl}{F}(\ln[H^*])$$

$$= E^o_{H^+,H_2} + \frac{2.303 \times 8.314 \times 298}{96500} \log[H^*]$$

Since, $E^o_{H^+,H_2}$ = 0.

$$= E^o_{H^+,H_2} + 0.0591 \log [H^*]$$

= - 0.0591 PH [- log [H*] = PH]

When the hydrogen electrode is combined with the calomel electrode, oxidation takes place at the hydrogen electrode and reduction at the calomel electrode, Hence by convention the cell may be written as.

$$pt, H_2(latm)/H^+{}_{(unknowncone)} // kcl(satd) / Hg_2cl_2(S)/Hg$$

EmF of this cell is given by

E = E $_{\text{Right electrode}}$ - E $_{\text{left electode}}$

= 0.245 – (-0.0591PH)

= 0.2415 + 0.0591 PH

$$PH = \frac{E - 0.2415}{0.0591}$$

Thus measuring the EMF of the cell potentiometrically the PH of the solution can be calculated.

Using the quinhydrone electrode:

Quinhydrone is a compound which contains equimolar amounts of quinone and hydroquinone. The working of the quin hydrone electrode is based upon the fact that quinone is reduced to hydroquinone ions.

$$c_6H_4O_2 + 2H^+ + 2c^- \;-->C_6H_6O_2$$

$$Q + 2H^+ + 2c^- --> QH_2$$

Thus if a Pt wire is dipped into a solution containing H$^+$and a pinch of quinhydrone. It can acts as a reversible electrode the electrode potential of the electrode is given by

$$\mathrm{Eq} = \mathrm{E}^0\mathrm{q} - \frac{\mathrm{RT}}{2\mathrm{F}}\,\mathrm{in}\,\frac{[QH_2]}{[Q]\,[H^+]^2} \qquad n = 2$$

$$[Q]\&[QH_2] = 1\,then$$

$$\mathrm{EQ} = \mathrm{E}^0\mathrm{Q} - \frac{\mathrm{RT}}{2\mathrm{F}}\,\mathrm{in}\,\frac{1}{[\mathrm{H}^+]^2}$$

$$= \mathrm{E}^0\mathrm{Q} - \frac{\mathrm{RT}}{2\mathrm{F}}\,\mathrm{in}\,[\mathrm{H}^+]$$

$$= \mathrm{E}^0\mathrm{Q} + \frac{2.303\mathrm{RT}}{\mathrm{F}}\log\,[\mathrm{H}^+]$$

$$= \mathrm{E}^0\mathrm{Q} + 0.0591og\,[\mathrm{H}^+]$$

$$E^0Q \text{ is found to be } 0.6996\,V.\ Hence$$

$$E = 0.6996 - 0.0591\,PH$$

When the quinhydrone electrode is combined with calomel electrode, oxidation takes place at the calomel electrode and reduction at the quinhydrone electrode, hence by convention.

$$\mathrm{E} = \mathrm{E}_{\text{Right electrode}} - \mathrm{E}_{\text{left electrode}}$$

$$= (0\text{-}6996 - 0.0591\ \mathrm{PH}) - 0.2415$$

$$= 0.4581 - 0.0591\ \mathrm{PH}$$

$$\mathrm{P^H} = \frac{0.4581 - \in}{0.0591.}$$

Thus by measuring the EMF of the cell potentio-metrically, the PH of the solution can be calculated.

Using glass electrode:

It has been found that if a thin glass membrane separates two solutions, a potential is developed across the membrane. The magnitude of this potential depends on the PH of the solution.

The glass electrode consists of thin walled glass bulb of relatively low melting and high electrical conductivity. A solution of constant PH (usually 0.1 m Hcl) is taken in the bulb. A pt wire is inserted to make the electrical contact.

The electrode potential is given by

$E_G = E^0G + 0.0591 \log [H^+]$

$E^0G - 0.0591\ pH$ -------- (1)

To determine the value of EMF of glass electrode it is combined with calomel electrode. The cell may be represented as

Glass electrode / Experimental solution/ Calomel electrode.

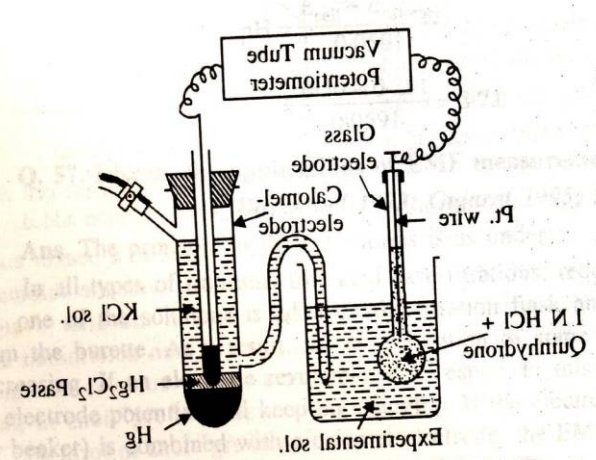


Fig. 11·18. Combination of a glass electrode with a calomel electrode.

EMF of this cell will be

$$E = E_{calomel} - E_{glass}$$

$$E_{glass} = E_{calomel} - E$$

Substituting the above equation in (1)

$$E_{calomel} - E = E^0_{Glass} - 0.0591\ PH$$

$$PH = \frac{E^0 G - E_{caloml} + E}{0.0591}$$

Potentiometric titrations:

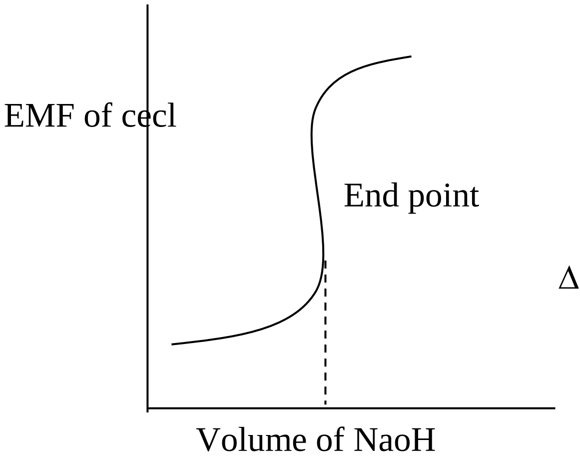
Principle:

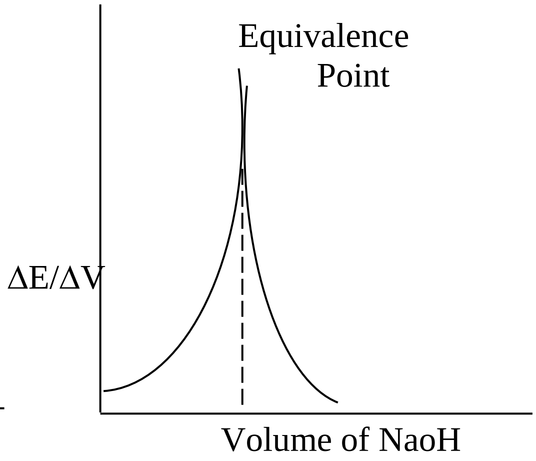
In this titration one of the solutions is taken in the titration flask and the other solution is added to it from the burette. As a result, the concentration of some is setup in the titration flask, keeps on decreasing

If an electrode reversible with respect to this ion is setup in the titration flask, its electrode potential will keep on changing. If the electrode thus set up in the titration flask is combined with a calomel electrode, the EMF of the cell will keep on changing and show a sudden change in value when the reaction is complete.

Acid Base titration:Hcl Vs NaoH

The acid solution is taken in a beaker and a hydrogen electrode is set up into it. This electrode is then coupled with the calomel electrode. A burette containing the NaoH solution is fitted over the beaker. NaoH solution is added to the beaker first in the larger amounts (Say 1ml or 0.5 ml at a time) and then in very small amounts (say0.1 ml) near the end point. Emf of the cell is noted after each addition. The EMF is then plotted against the volume of NaOH added when a curve of the following type is obtained. From this curve the volume of NaoH solution used corresponding to the equivalence point can be found.

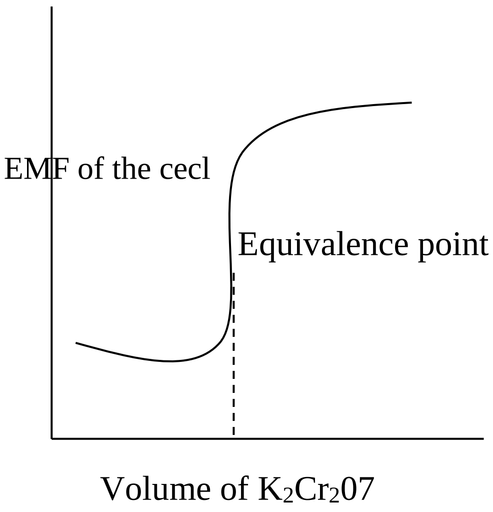


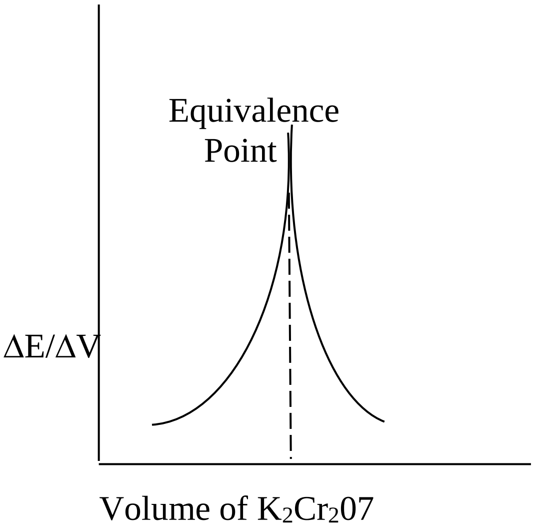


$\Delta E / \Delta V$ Vs NaoH is also gives the end point of the titration:

Redox titrations: Feso$_4$ Vs K$_2$Cr$_2$07

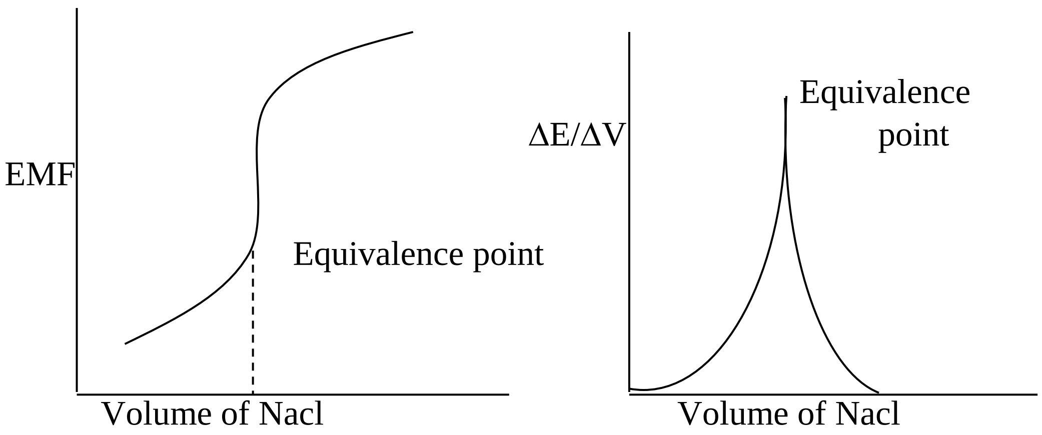
The FeSO$_4$ solution is taken into a beaker and a platinum wire is inserted into it. The electrode thus formed is combined with the calomel electrode. A burette containing K$_2$Cr$_2$O$_7$ is fixed over the beaker and after every addition of K$_2$Cr$_2$O$_7$ the EMF cell is noted. The EMF is then plotted against the volume of K$_2$Cr$_2$O$_7$ added when a curve of the following type is obtained. From this curve the volume ofk$_2$Cr$_2$O$_7$ used corresponding to the equivalence point can be found.





Precipitation titration: $AgNo_3$VsNacl

The $AgNo_3$ is taken in a beaker and a silver wire is inserted into it. The electrode thus formed is then combined with the calomel electrode. A burette containing the Nacl solution is fixed over the beaker and after ever addition of Nacl solution, the EMF of the cell is noted. During the titration EMF decreases. At the end point it decreases suddenly and further addition of Nacl causes EMF decreases slowly. The EMF is then plotted against the volume of Nacl added when a curve of following type is obtained. From this curve, the volume of Nacl used corresponding to the equivalence point can be found.



Advantages of potentiometric titration:

1) End point is determined accurately
2) Very dilute solutions can be determined accurately.
3) Coloured solutions can also be titrated.
4) It doesn't require any Indicator.
5) Weak acid Vs weak base can also be titrated.
6) By using proper electrodes mixture of substances in a given solution can also be titrated.

Concentration cells:

Cells in which the EMF produced is only due to difference in the concentrations of the electrodes (or) that of the solutions of the electrolytes with which they are in contact are called concentration cells.

When the difference is in the concentration of the electrodes, the cells are called electrode concentration cells.

When the difference is in the concentration of the electrolytes, the cells are called electrolyte concentration cells.

Derivation of EMF of electrode concentration cell without transference

There are 2 types of electrode concentration cells.

1) **Electrode concentration cell consisting of gas electrodes**

e.g pt, P_1 H_2/ H^+ / H_2,pt P_2

In the above cell both electrodes are hydrogen electrodes immersed in the same solution of H^+ions but H_2 gas passed in the two electrodes is at different pressures.

By convention. Oxidation takes place in the left hand electrodes

$\frac{1}{2} H_2\ P_1 \rightarrow H^+ + e^- (a_{H^+})$

To apply Nernst equation, this reaction may be written as reduction reaction.

$H^+ + e^- \rightarrow 1/2\ H_2$ (n=1) ----- (1)

(a_{H^+}) P_1

Electrode potential is

$$E_1 = E^o_{H^+,H_2} - \frac{RT}{F} \ln \frac{P_1^{1/2}}{a_{H^1}}$$

$[\because E^O_{H^+,H_2}] = 0.$

$$= -\frac{RT}{F} \ln \frac{P_1^{1/2}}{a_{H^+}} \quad --------(2)$$

Similarly by convention at the right electrode, reduction takes place

$$\underset{a_{H^+}}{H^+} + e^- \rightarrow 1/2\,\underset{(P_2)}{H_2} \quad (n=1) \quad ----(3)$$

The electrode potential of this electrode is

$$E_2 = -\frac{RT}{F} \ln \frac{P_2^{1/2}}{a_{H^+}} \quad --------------- (4)$$

The over all react ion taking place can be obtained by adding equations (1) &(3)

$$1/2\ \underset{(P_1)}{H_2} \rightarrow 1/2\ \underset{(P_2)}{H_2}$$

The EMF of the cell is given by

$$E \quad = \quad E_{\text{Right electrode}} - E_{\text{left electrode}}$$

$$= E_2 - E_1$$

$$= \frac{-RT}{F}\, ln \frac{P_2^{1/2}}{a_{H^+}} + \frac{RT}{F} ln \frac{P_1^{1/2}}{a_{H^+}}$$

$$= \frac{-RT}{F}(ln\ P_2^{1/2} - ln\ a_{H^+}) + \frac{RT}{F} ln\ P_1^{1/2}$$

$$= \frac{-RT}{F} ln\ P_2^{1/2} + \frac{-RT}{F}\ ln P_1^{1/2}$$

$$= \frac{-RT}{F} ln\ P_2 + \frac{RT}{2F} ln P_1$$

$$= \frac{-RT}{2F}\ [ln P_1 - ln P_2\ ]$$

$$E = \frac{RT}{2F} ln\ \frac{P_1}{P_2}$$

From this equation we came to know that there is no transference of electrolyte and EMF of the cell depends only upon the pressures P_1 & P_2 and does not depend upon the activity of the H^+ Ions.

2) Electrode concentration cell consisting of a amalgam electrodes

$$\underset{a_1}{Zn(Hg\ )} / \underset{a_{zn}{}^{+2}}{Zn^{2+}} \ /\ \underset{a_2}{Zn(Hg)}$$

For left hand electrode

The reaction is

$$\underset{a_1}{Zn(Hg)} \rightarrow Zn^{+2} + 2c^- ---------(5)$$

To use Nernst eqation, this reaction can be written as reduction reaction

$$\underset{a_{zn}{}^{2+}}{Zn^{+2}} + 2c^- \rightarrow \underset{a_1}{Zn(Hg)}\ (n = 2) \rightarrow$$

The electrode potential will be

$$E_1 = E^0{}_{zn^{+2}, zn} - \frac{RT}{2F}\ in \frac{a_1}{a_{zn^{+2}}}$$

For Right Electrode

The reaction is

$$\underset{a_{zn}^{2}}{Zn^{+2}} + 2c^{-} \rightarrow \underset{a_{2}}{Zn(Hg)} -------(6)$$

The Electrode potential will be

$$E_2 = E^0{}_{zn^{+2},zn} - \frac{RT}{2F}\, in \frac{a_2}{a_{Zn^{+2}}}$$

Overall reaction is obtained by adding equation (5) + (6) then

$$\underset{a_1}{Zn(Hg)} ----> \underset{a_2}{Zn(Hg)}$$

EMF of the cell is

$$E = E_2 - E_1$$

$$= -\frac{RT}{2F}\ln \frac{a2}{a_{zn}{}^{+2}} -+ \frac{RT}{2F}\ln \frac{a2}{a_{zn}{}^{+2}}$$

$$\frac{RT}{2F}\, In\, \frac{a_1}{a_2}$$

From this equation we came to know that there is no transference of electrolyte and EMF of the cell depends upon the activities of Zn in the two amalgams and not on the activity of Zn^{+2}

Further, in the final expression for EMF of the cell E^o does not appear. This is true for all concentration cells.

$\therefore$ In general EMF of the cell is given by

$$E_{cell} = \frac{RT}{nF}\ln \frac{a_1}{a_2}$$

Derivation of EMF of electrolyte concentration cells with out transference:

In this type of cells, the two electrodes are same, having different concentrations of the electrolytes and connected by a salt bridge

For example

$Pt, H_2 / \; H^+ \; // H^+ \; / H2, pt$

$(1atm.p)\; a_1 \quad a_2 \quad 1atm.p$

On the left hand electrode, by convention oxidation takes place. The electrode reaction is

$\frac{1}{2} H_2 \rightarrow H^+ e^-$ ---------- (1)

(1atm) (a$_1$)

To apply Nernst equation the above reaction may be written as reduction reaction.

$H^+ e^- \rightarrow 1/2 H_2$ (n=1)

a$_1$ (1atm.p)

Electrode potential will be

$$E_1 = E^0{}_{H_1+,H_2} - \frac{RT}{nF} \ln \frac{a_{H_2}}{a_1} \qquad \left[\because aH_2 = 1\right]$$

$$= E^0{}_{H_1+,H_2} + \frac{RT}{F} \ln a_1 \qquad \left[\because E^0{}_{H_1+,H_2} = 0\right]$$

$$= \frac{RT}{F} \ln a_1$$

On the right hand electrode, by convention reduction takes place the electrode reaction is

$H^+ + e^- \rightarrow \frac{1}{2} H2$ (1atm.p) --------- (2)

a$_2$

The EMF of this electrode will be

$$E_2 = \frac{RT}{F} \ln a_2$$

The overall reaction is obtained by adding the reactions

$$H^+(a_2) \;------> H^+(a_1)$$

The EMF of the cell is

$E = E_2 - E_1$

$$= \frac{-RT}{F} \ln a_2 - \frac{RT}{F} \ln a_1$$

$= RT/F \ln a_1/a_2$

For 1 faraday of electricity to be product, there is a transfer of 1 mol of H+ of activity a$_2$ to the solution having activity a$_1$. The transfer takes place through salt bridge secondly it is evident that for EMF to be positive a$_2$ must be greater than a$_1$.

Derivation of EMF of a concentration cell with transference:

In this type of cells the 2 electrodes are same having different electrolytes but the two solutions are directly in contact with each other. This can be done by putting the two solutions in a tube very carefully so that there is no mixing. The junction at which the two solutions meet is called liquid junction. Here there is direct transference of electrolyte from one solution to other through liquid junction. Hence these cells are called concentration cell with transference.

Example:

Pt_1, H2 / Hcl : Hcl (a_2) / H2, pt
(a_1) (1atm.p) 1atm

At electrodes by convention. Oxidation takes place on the left hand electrode

$\frac{1}{2} H_2$ ----------- > $H^+ + e^-$
(1atm.p) a_1

Reduction takes place on the right hand electrode

$H^+ + e^-$ ---------- > ½ H2
a_1 1 atm.

The overall reaction is

H^+ ------------- > H^+ ------------------ (1)
a_1 a_1

At the liquid junction:

Electrons flow in the external circuit from left to right. However as ions are produced in the left electrode and Cl^- ions are left in the right electrode, the inner circuit is completed by the transference of Cl^- ions from right to left and the transference of H^+ions from left to right across the liquid junction.

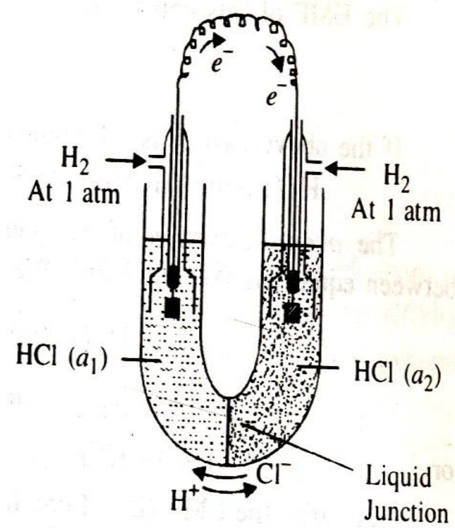


Fig. 11·17. Concentration cell with transference.

If the transport number Cl^- ions is represented by t-, then for one faraday of electricity passing through he cell, t-gram equivalents of the Cl^- ions will be transferred from right to left (i.e from solution of activity a_2 to solution of activity a_1)

t- cl^- -------------- > t-C l^- -------------- (2)

(a_2) (a_1)

Further, transport number of H^+ = 1-t . Therefore during the same time,

(1-t_) gram equivalents of the H^+ ions will be transferred from left to right i.e., (from solution of activity a_1 to solution of activity a_2) i.e

(1-t-) H^+ ------------- > (1-t-) H^+ ------- (3)

(a_1) (a_2)

Overall process:

To calculate the net transfer of material equation (1), (2), & (3) must be added.

$$H^{+}{}_{(a_2)} + t - cl^{-}(a_2) + (1 - t -)H^{+}{}_{(a_2)} = H^{+}{}_{(a_2)} + t - cl^{-}(a_1) + (1 - t -)H^{+}{}_{(a_2)}$$

$$t - H^{+}(a_2) + t - cl^{-}(a_2) \quad = t - H^{+}(a_1) + t - cl^{-}(a_1)$$

$$t - Hcl\ (a_2) \quad = t - Hcl\ (a_1)$$

It is clear from the equation that for one faraday of electricity passing through the cell t_ gram equivalents of Hcl from the activity a_2 are transformed to the Hcl of activity a_1.

Applying Nerust equation the EMF of the cell is

$$E = \frac{-RT}{F} \ln \frac{a_1^{t-}}{a_2^{t-}}$$

$$= \frac{t-RT}{F} \ln \frac{a_2}{a_1}$$

For EMF to be positive a_2 must be greater than a_1 we know that $a = (m\gamma)^2$

Then we have

$$E = \frac{t-RT}{F} \ln \frac{M_2^2 \gamma_2^2}{M_1^2 \gamma_1^2}$$

$$= \frac{2t\_RT}{F} \ln \frac{M_2 \ \gamma_2}{M_1 \gamma_1}$$

Thus EMF of a cell can be calculated if we know molalities, activity, co-efficient and transport number of the ions.

Liquid junction potential:

The potential set up at the junction of the two solution because of the difference in the speeds of the ions moving across the boundary is called liquid junction potential.

The EMF of cell E= $E_{oxid} + E_{\text{Re}\,d} + E_{junction}$

Liquid junction potential can be minimized by using salt bridge containing an electrolyte Kcl.

Expression for liquid junction potential:

Consider the following concentration cell with transference:

$$\begin{array}{l} Pt, H_2 / Hcl : Hcl / H_2 / Pt \\ \quad 1atm \quad a_1 : \ a_2 \qquad 1atm \end{array}$$

The sum of two electrode reaction gives

$$\begin{array}{ll} H^+ & \rightarrow H^+ \\ (a_2) & \ \ (a_1) \end{array}$$

The sum of 2 electrode potential $E_1 + E_2$ gives

$$E_1 + E_2 = \frac{-RT}{F} \ln \frac{(a_H{}^+)_1}{(a_H{}^+)_2}$$

$$= \frac{RT}{F} \ln \frac{(a_H{}^+)_2}{(a_H{}^+)_1}$$

$$= \frac{RT}{F} \ln \frac{(M_H{}^+ \gamma_H{}^+)_2}{(M_H{}^+ . \gamma_H{}^+)_1}$$

EMF of the cell in given by

$$E = \frac{2t - RT}{F} \ln \frac{M_2 \gamma_2}{M_1 \gamma_1}$$

We know that $Ej = E - (E_1 + E_2)$

$$= \frac{2t - RT}{F} \ln \frac{M_2 \gamma_2}{M_1 \gamma_1} - \frac{RT}{F} \ln \frac{(M_H{}^+ \gamma_H{}^+)_2}{M_H{}^+ \gamma_H{}^+} \qquad ----(1)$$

But $(M_H{}^+) = M_2$ $(M_H{}^+)_1 = M_1$ and $(\gamma_H{}^+)_2 = \gamma_2$ + $(\gamma_{H^+})_1 = \gamma_1$ then, equ 1 becomes

$$Ej = \frac{2t - RT}{F} \ln \frac{M_2 \gamma_2}{M_1 \gamma_1} - \frac{RT}{F} \frac{M_2 \gamma_2}{M_1 \gamma_1}$$

$$= (2t - 1) \frac{RT}{F} \ln \frac{M_2 \gamma_2}{M_1 \gamma_1}$$

Since ,

$$t_+ + t_- = 1$$

$$2t_- - 1 = t_- + (t_- - 1)$$

$$= t_- + (-t_+)$$

$$t_- - t_+$$

$$Ej = (t_- - t_+) \frac{RT}{F} \ln \frac{M_2 \gamma_2}{M_1 \gamma_1}$$

Application of concentration cells:

1) It is used to determine valency of ions:

The EMF of a concentration cell without transference is given by

$$E = \frac{RT}{nF} \ln \frac{a_2}{a_1}$$

$$= \frac{RT}{nF} \ln \frac{c_2}{c_1}$$

In this expression n is the valency of the ion involved. Thus knowing all other quantities n can be calculated.

For example:

$$\text{Hg / mercurous nitrate // } {}^{N}\!/_{2} \text{ mercurous nitrate / Hg}$$

$$E = \frac{0.0591}{n} \log {C_1}/{C_2} \qquad [\log \frac{C_2}{C_1} = \log 10 = 1]$$

$$n = \frac{0.0591}{E} = \frac{0.0591}{0.0295} = 2.$$

3) **It is used to determine transport number of the ions**

For a cell with transference

$$\begin{array}{l} H_2 \ / \ Hcl : Hcl \ \ / \ H_2 \\ 1atm \ \ (a_1) \ \ \ (a_2) \ 1atm. \end{array}$$

The EMF is given by

$$E = \frac{t - RT}{F} \ln \frac{a_2}{a_1}$$

By measuring the EMF of the cell & knowing the activities of the two solution, the transport number of the anion (t-can be calculated).

4) **It is used to determine solubility product of sparingly soluble salt.**

The cell is set up is that concentration of cell having higher concentration of Ag^+ in the left head side & low concentration of Ag^+ in the RHS electrode. The above cell may be written as

$$\text{Ag / Agcl } {}^{N}\!/_{10} \text{kcl // } 0.01 \text{N Ag No}_3 \text{ / Ag.}$$

$$[Ag+] = C \qquad\qquad [Ag+] = 0.01$$

EMF of the cell at 25°C.

$$E = 0.0591 \log \frac{0.01}{C}.$$

From the equation the value of C can be calculated thus in the solution of Ag Cl in N/10 kcl.

$[Ag^+]$ = C gram equivale / litre.

Ag in Ag Cl dissolves very little, the Cl^- ions produced from Agcl are negligible as compared to that produced from Kcl. Thus in the solution of AgCl in N/10 Kcl.

$\therefore$ the solbility product Ksp of Agcl.

$$Ksp = [Ag^+]\ [Cl^-]$$

$$= C \times 0.1.$$

If the solubility of Agcl is S moles/litre.

$[Ag^+][\ Cl^-]$ = S gram equivalent / litre.

$$Ksp = S \times S = S^2.$$

$$S \ = \ \sqrt{Ksp}$$

Determination of activity Co- efficient:

$$\begin{array}{l} K\ (Hg) \left| \ Kcl \ \right| Agcl \left| Ag \right| Agcl \left| Kcl \right| k \ \ Hg \\ \qquad\qquad\quad a_1 \quad (S) \qquad\quad (S) \end{array}$$

A cell with out transference

$$E = \frac{2.303RT}{F} \log \ \frac{a_2}{a_1}$$

If activity a=m γ then.

$$E \ = \ \frac{2.303RT}{F} \log \ \frac{(M_2\gamma_2)^2}{(M_1\gamma_1)^2}$$

$$= \ \frac{2.303RT \times 2}{F} \log \ \frac{M_2\gamma_2}{M_1\gamma_1}$$

$$= \ \frac{2.303RT \times 2}{F} \log \frac{M_2}{M_1} \quad \frac{2.303RT \times 2}{F} \log \frac{\gamma_2}{\gamma_1}$$

Since M_2/ M_1 of kcl solution is known, by measuring EmF_1 we can calculate $\frac{\gamma_2}{\gamma_1}$.

If second kcl solution very dilute then by de bye Hackle limiting law.

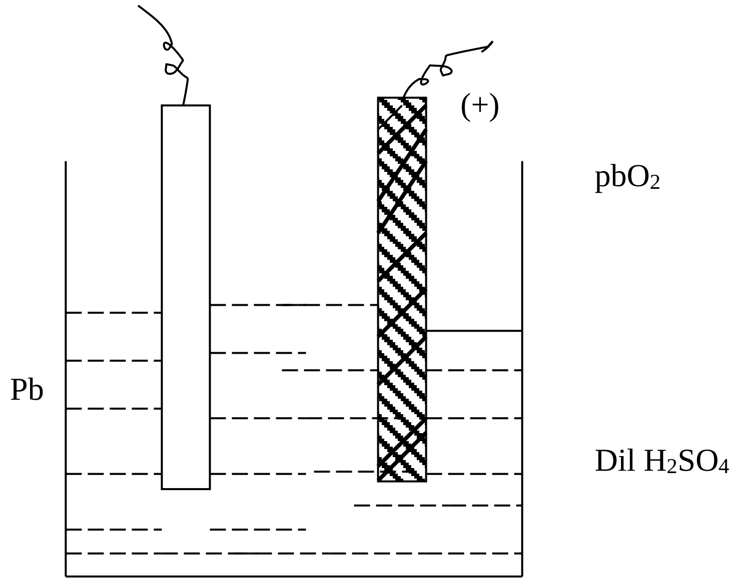
$$\log \ \gamma_{\pm} = 0.5 \ Z_{\pm} \ Z - \sqrt{\mu}.$$

We can calculate γ value. Thus the γ of given Kcl is calculated.

Storage cells:

When a voltaic cell supplies current, we obtain electrical energy at the expense of chemical reaction in the cell. If the cell is reversible, the direction of chemical reactions can be reversed and the original state of the cell can be restored by passing a current through the cell in the opposite direction. This can be down by some external source of emf and the cell can again be used as a source of electrical energy. These two processes, taking a current from a cell and passing a current in the opposite direction through the cell, are referred to as discharging and charging respectively, certain amount of electrical energy is stored in the cell by charging a reversible cell which is gained later in the discharge of the cell. Such a cell is called an accumulator or storage Battery.

Example Lead storage battery:



If consists of two lead electrodes, one of which is covered with lead oxide. It is to filled with $H_2\,SO_4$ of specific gravity 1.15 at 298 k. ie with 20% $H_2\,SO_4$.

The electrode reactions are

$$At\ Cathode:\ pb(S) + SO_4^{2-} \Leftrightarrow pbSO_4(S) + 2e^-$$

$$At\ \ anode:\ pbO_2\ (S) + 4H^+ + SO_4^{2-} \Leftrightarrow pbSO_4(S) + 2H_2O\ (l)$$

$$Net\,reaction:\ pb(S) + pbO_2\ (S) + 2H_2SO_4 \Leftrightarrow 2\,pbSO_4(S) + 2H_2O\ (l)$$

During discharge the concentration of H_2SO_4 diminishes and during the charge concentration of H_2SO_4 will increase.

Writing the emF expansion.

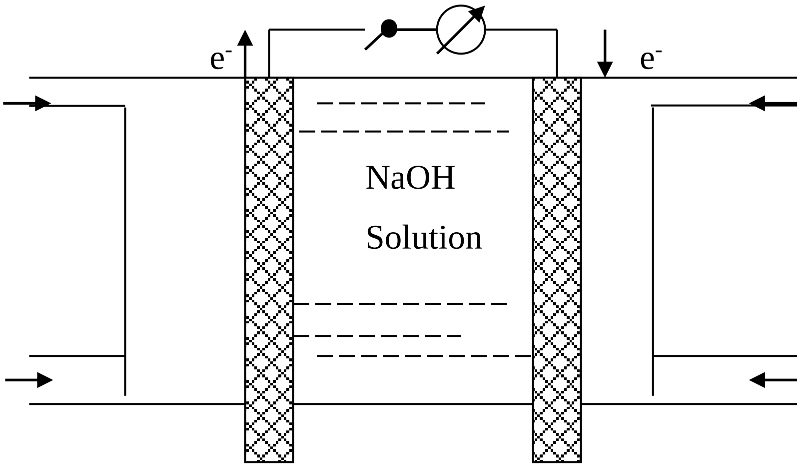
$$\begin{aligned} E &= E^o - \frac{RT}{2F}\ln\frac{a^4\ H_2O}{a^4\,H^+ . a^2\,So_4^{2-}} \\ &= E^o - \frac{RT}{F}\ln\ a\ H_2O + \frac{RT}{F}\ln\ (a^2\,H^+ ..a\,So_4^{2-}) \\ &= E^o - \frac{RT}{F}\ln\ (a^2\,H^+ ..a\,So_4^{2-}) \qquad\qquad \because\ a\,H_2O = 1. \end{aligned}$$

The lead storage battery loses a good deal of power under high loads. The Emf of pb storage battery is 2.07 volt.

Fuel cells:

Fuel cells are electrochemical devices in which chemical energy of the fuel is directly converted into electrical energy

Example: Hydrogen oxygen fuel cell.



This cell consists of 2 electrodes made of perforated carbon. Platinum is coated on the surface of electrodes to act as a catalyst. The electrodes are placed in an aqueous solution of NaOH or KOH. H_2 & 0_2 is bubbled into the cell under a pressure of 50 atmospheres. When the electrodes are connected, a flow of electric current takes place.

The cell reaction is

C. H_2 / KOH (or) NaOH / O_2, C.

The electrode reactions are,

$$\text{At the anode} \quad : \quad 2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$$
$$\text{At the cathods} : \quad O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

$$2H_2 + O_2 \rightarrow 2H_2O(l)$$

The emf of this cell is found to be 1.229 V & it does not depend on the composition of the electrolyte.

During the discharge of H_2 - O_2 fuel cell, the voltage is within 0,7-0.9V.

H_2 - O_2 fuel cells are used in space crafts. Here the electrolyte used is Ion exchange membrane instead of KOH (or) NaOH.

Polarisation:

When 2 electrodes are placed in a electrolyte and on electrolysis, the emf passed is slightly greater than the emf of the cell the electrodes are reversible. If applied emf is larger than the emf of the cell the electrodes became irreversible. Because of irreversibility electrolytes causes a voltaic cell in the solution which opposes the applied emf. This opposing tendency is called polarization.

For example let us consider electrolysis of $AgNo_3$ using silver electrodes. At cathode discharge of Ag^+ takes place hence concentration of Ag^+ ions decreases. At the same time activation of Ag takes at the anode and Ag^+ ions goes into solution. Hence a voltaic cell is developed in the electrolyte Emf of this voltaic cell opposes the applied emf causes polorisation.

The amount of polarization depends upon the nature of the solution, nature of electrodes and the amount of current passed.

Methods to prevent polarsation:

1. Continuous stirring of the electrolyte during electrolysis prevents polarization.
2. By using Rough electrodes & continuous removal of gas adhering on the electrodes prevents polarization.
3. By using depolarisers like H_2cro_4, HNo_3 & MnO_2 prevents polarization.
4. By using 2 solutions during electrolysis we can prevent polarization.

Over voltage

The excess voltage over the voltage of the cell that is required to reverse the reaction is termed over voltage.

(or)

The difference between the potential of the electrode when H_2(or) o_2 gas evolution is actually observed & the theoretical value for the same is called H_2 over voltage (or) O_2 over voltage.

The value of over voltage depends on the nature of the metal, current strength and temperature.

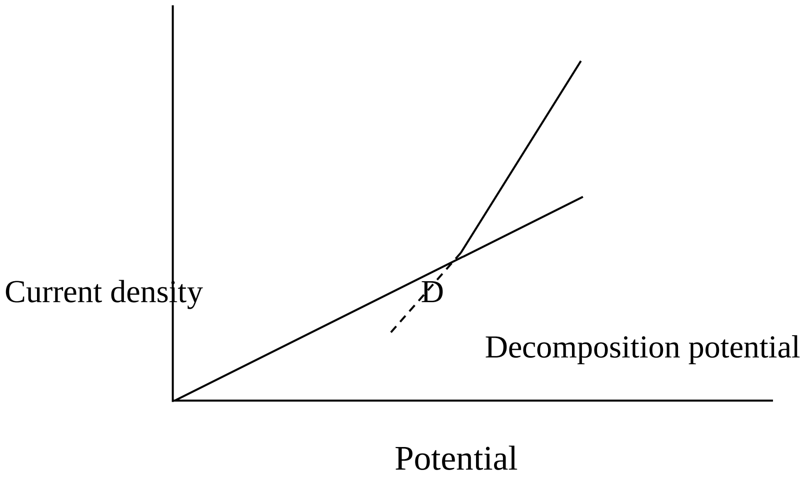
Significance over voltage:

1. Electro deposition of Na at mercury cathode from an aqueous solution of Nacl is made feasible due to H_2 over voltage.
2. The electrodes with high over voltage (Pb) is used instead of costly pt electrodes in Redction of nitrobenzene.
3. Due to hydrogen over voltage, it is possible to deposit metals like Zn,cd from an acid solution having move negative potential than hydrogen.
4. $O_{2\ over}$ voltage explains why halogens are liberated at the anode instead of O_2during electrolysis of halides & halogen acids.
5. While charging a lead accumulator, instead of the hydrogen being evolved, lead is deposited on the cathode. This is due to high over voltage of lead.

Decomposition voltage:

The minimum potential to be applied in order to bring about continuous electrolysis.

When the applied potential reaches certain value, the current suddenly increases with increases in applied potential as in figure.



Importance of Decomposition voltage:

1. Decomposition potential is of extensive use in electro refining and elecro metallurgy of metals. For example Cu and Zn can be separated electrically since the decomposition potentials $CUSO_4$ $ZnSO_4$ are 1.5 & 2.55 volts.
2. This is of great importance in the controlled deposition of metals in a given mixture.
3. In the preparation of brass by electrolytic method, the decomposition potential is taken into account.
4. The controlled voltage to playing a vital role in electroplating.

Unit –V

1) Describe Weston standard cell
2) Define polarization and overvoltage. Discuss the applications of over voltage.
3) Discuss reversible and irreversible process of galvanic cells.
4) Write a short note on fuel cell.
5) Define liquid junction potential Explain concentration cell with & without transference.
6) Describe a method of determination of valency of ion.
7) Write a note on lead storage battery
8) Describe a potentiometric method of determination of PH of a solution.
9) Explain the method of measurement of emf of a cell
10) Write a short note on fuel cells.
11) Describe the structure & function of calomel electrode.
12) Derive Gibbs-Helm holtz equation and relate emf with various thermodynamic quantities.
13) Explain he various types of single electrodes.

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