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Unit I

Q.1. Derive an expression for the variation of free energy with temperature and pressure for a process.

Ans. **Variation of Free Energy Change with Temperature and Pressure:-** (2017)

The variation of free energy change with variation of temperature and pressure may now be considered. According to Eq. 67,

$$G = H - TS$$

Since $H = U + PV$, hence $G = U + PV - TS$

Upon differentiation, $dG = dU + PdV + VdP - TdS - SdT$ (i)

The First law equation for an infinitesimal change may be written as (ii)

$$dq = dU - dw$$

If the work done is only due to expansion, then, $-dw = PdV$ (iii)

$$\therefore dq = dU + PdV$$

For a reversible process. (iv)

$$dS = dq/T \text{ or } TdS = dq = dU + PdV$$

Combining Eqs.(ii) and (v) we have (v)

$$dG = VdP - SdT$$

..... (vi)

This equation gives change of free energy when a system undergoes, reversibly, a change of pressure as well as change of temperature.

If pressure remains constant, i.e., $dP = 0$, then, from eq.(vi)

$$dG = -SdT \text{ or } \left(\frac{\partial G}{\partial T} \right)_P = -S$$

..... (vii)

On the other hand, if temperature remains constant, i.e., $dT = 0$, then, from Eq. (vi).

$$dG = VdP \text{ or } \left(\frac{\partial G}{\partial P} \right)_T = V$$

..... (viii)

Let the free energy of a system be G_1 in the initial state and G_2 in the final state when an appreciable change in pressure has taken place, at constant temperature. Then, integrating Eq. (viii), the free energy change, ΔG , is given by

$$\Delta G = G_2 - G_1 = \int_{P_1}^{P_2} VdP$$

..... (ix)

where P_1 and P_2 are the initial and final pressures, respectively.

If one mole of an ideal gas is under consideration, then $PV = RT$.

$$\Delta G = RT \int_{P_1}^{P_2} \frac{dP}{P} = RT \ln \frac{P_2}{P_1} = RT \ln \frac{V_1}{V_2}$$

..... (x)

Where V_1 and V_2 are the initial and final volumes, respectively

For n moles of the gas,

$$\Delta G = nRT \ln (P_2 / P_1) = nRT \ln (V_1 / V_2)$$

(2017)

Q.2. Define entropy and mention its physical significance.

Other Related Questions -

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- Q. Write short note on entropy and its physical significance. (2017)
 Q. What is physical significance of entropy? Show that for ideal gas

$$\Delta s = C_v \ln T_2 / T_1 + R \ln V_2 / V_1 \quad (2011)$$

All terms have their usual meaning.

- Q. Deduce an expression for change of entropy for an ideal gas with temperature and volume.

- Q. Derive an expression for entropy change associated with the change in temperature and pressure of an ideal gas. (2012, 09)

- Q. Derive expression showing variation of entropy with pressure and volume. (2016)

Ans. **Concept of Entropy:-**

$$q_1/T_1 = q_2/T_2 \quad \dots\dots(i)$$

Eq.(i) has been derived by giving positive sign to the heat absorbed (q_2) and negative sign to the heat lost (q_1) by the system. Describing q_1 and q_2 merely as heats exchanged (may be evolved or absorbed), Eq. (i) may be written as

$$q_1/T_1 + q_2/T_2 = 0 \quad \dots\dots(ii)$$

Thus, when the isothermal and adiabatic processes in a Carnot cycle are carried out infinitesimally slowly (i.e., reversibly), the summation of q/T terms is equal to zero.

Any cyclic process, if carried out reversibly, can be shown to consist of a series of Carnot cycles. Consider a cyclic process in which the change from the state A to state B and back to the state A (Fig.) is carried out reversibly. The path ABA may be considered to comprise of a number of small Carnot cycles, i.e., of a series of isothermals and adiabatics, as shown in the figure.

The lines slanting horizontally stand for a diabatics and those slanting vertically stand for isothermals of the small carnot cycles.

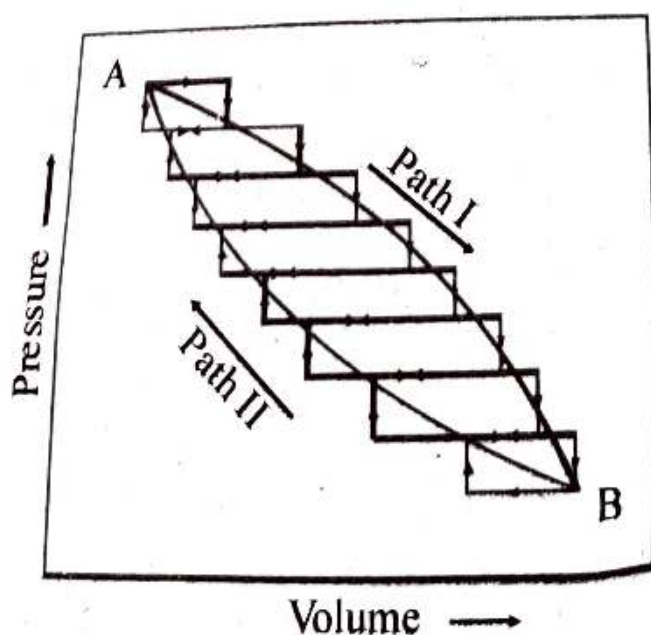


Fig. - Entropy change in a reversible cyclic process

If each isothermal and adiabatic change is made extremely minute, i.e., each Carnot cycle is made extremely small by increasing their number, the

paths inside the loop cancel one another and the cycle corresponds to the continuous isothermal curve ABA. Thus, any reversible cycle can be regarded as being made up of infinite number of small Carnot cycles.

Knowing that for each Carnot cycle, $q_1/T_1 + q_2/T_2 = 0$, it follows that in the case of the reversible cycle ABA, comprising of a series of Carnot cycles, the summation term takes the form

$$\sum q/T = 0 \quad \text{.....(iii)}$$

i.e., the sum of all the q/T terms of the Carnot cycles involved is zero. When the changes are infinitesimal, the above equation may be put as

$$\sum dq/T = 0 \quad \text{.....(iv)}$$

Since the cycle is performed in two steps, viz., from A to B and back from B to A, it follows that

$$\sum \frac{dq}{T} = \int_A^B \frac{dq}{T} + \int_B^A \frac{dq}{T} = 0 \quad \text{.....(v)}$$

The integral $\int_A^B \frac{dq}{T}$ is the summation of all the $\frac{dq}{T}$ terms when the system changes from A to B along path I and $\int_B^A \frac{dq}{T}$ is the similar summation when the system returns from state B to the original state A along path II.
From Eq.(v),

$$\int_A^B \frac{dq}{T} = - \int_B^A \frac{dq}{T}$$

$$\text{Or} \quad \int_A^B \frac{dq}{T} (\text{path I}) = \int_A^B \frac{dq}{T} (\text{path II}) \quad \text{.....(vi)}$$

It follows from above that $\int_A^B \frac{dq}{T}$ is a definite quantity independent of the path followed for the change and depends only upon the initial and final states of the system. This quantity, therefore, like ΔU and ΔH , should represent the change in some single-valued function of the states A and B of the system. This function is called **entropy** and is denoted by the symbol, S . If S_A is the entropy in the initial state A and S_B is the entropy in the final state B, then the change in entropy, ΔS , is given by the equation

$$\Delta S = S_B - S_A = \int_A^B \frac{dq}{T} \quad \text{.....(vii)}$$

For each infinitesimally small change,

$$dS = dq/T \quad \text{.....(viii)}$$

At constant temperature, for a finite change, dS becomes ΔS and dq becomes q .

$$\Delta S = q/T \quad \text{.....(ix)}$$

It may be emphasised that since entropy is a function of the state only, the change of entropy (ΔS) for the change of state from A and B will invariably be the same whether the change is reversible or not. However, mathematically, it will be given by the equation

$$\Delta S = \int_A^B \frac{dq}{T} \quad \dots\dots (x)$$

only when the change has been brought about reversibly. This is because the above equation has been derived from Carnot cycle in which all the changes are brought about reversibly.

Thus, the entropy change for a finite change of state of a system at constant temperature is given by

$$\Delta S = q_{rev}/T \quad \dots\dots (xi)$$

Unit of entropy :-

Since entropy change is expressed by a heat term divided by the absolute temperature, entropy is expressed in terms of joules per degree Kelvin ($J K^{-1}$). This is known as **entropy unit, e.u.**

Entropy is an extensive property. Its value, therefore, depends upon the amount of the substance involved. It is necessary, therefore, to make a mention of the quantity of the substance taken. This quantity is usually taken as one mole.

Calculation of Entropy Change of an Ideal Gas with Change in P, V and T :-

Since entropy of a system varies with the state of the system, its value for a pure gaseous substance will depend upon any two of the three variables T, P and V. Since T is taken generally as one of the variables, the second variable to be considered may be V or P. Thus, the two variables to be considered are either T and V or T and P.

When T and V are the two variables: -

The increase in entropy of the gas for an infinitesimally small change is given by the expression

$$dS = dq_{rev}/T \quad \dots\dots (xii)$$

where dq_{rev} is the small amount of heat absorbed by the gas (system) reversibly from the surroundings at temperature T.

According to the equation of the First law of thermodynamics, viz., $\Delta U = q + w$, we have

$$dq_{rev} = dU - dw \quad \dots\dots (xiii)$$

If the work involved is due to expansion of the gas, then, for an infinitesimal increase in volume dV against a pressure P,

$$-dw = PdV \quad \dots\dots (xiv)$$

Substituting the value of dU from $C_v = (\partial U / \partial T)_v$ and $-dw$ from eq. (xiv), we have

$$dq_{rev} = C_v dT + PdV \quad \dots\dots (xv)$$

For one mole of an ideal gas,

$$dq_{rev} = C_v dT + RT dV/V$$

$$\therefore dq_{rev}/T = dS = C_v dT/T + R dV/V \quad \text{..... (xvi)}$$

For a finite change of state of a system, the entropy change (ΔS) is obtained by integrating the above equation between the limits of the initial state 1 and the final state 2. Assuming C_v to be constant within the temperature range T_1 and T_2 , for one mole of the gas we have

$$\Delta S = S_2 - S_1 = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V} \quad \text{..... (xvii)}$$

$$\text{Thus, } \Delta S = C_v \ln T_2/T_1 + R \ln V_2/V_1 \quad \text{..... (xviii)}$$

For n moles of the ideal gas, the above equation may be written as

$$\Delta S = nC_v \ln (T_2/T_1) + nR \ln (V_2/V_1) \quad \text{..... (xix)}$$

It is evident that the entropy change for the change of state of an ideal gas depends upon the initial and final volumes as well as on the initial and final temperatures.

When T and P are the two variables: -

If P_1 is the pressure of the ideal gas in the initial state and P_2 in the final state, then

$$P_1 V_1 = RT_1 \text{ for one mole of the gas in the initial state}$$

$$P_2 V_2 = RT_2 \text{ for one mole of the gas in the final state.}$$

$$\therefore V_2/V_1 = P_1 T_2 / (P_2 T_1) \quad \text{..... (i)}$$

Substituting in $\Delta S = C_v \ln T_2/T_1 + R \ln V_2/V_1$ for one mole of the gas, we have

$$\Delta S = C_v \ln T_2/T_1 + R \ln T_2/T_1 - R \ln P_2/P_1 \quad \text{..... (ii)}$$

Remembering that $C_p - C_v = R$

$$\Delta S = C_p \ln T_2/T_1 - R \ln P_2/P_1 \quad \text{..... (iii)}$$

For n moles of the ideal gas,

$$\Delta S = nC_p \ln (T_2/T_1) - nR \ln (P_2/P_1) \quad \text{..... (iv)}$$

It is evident from the above equations that the entropy change for the change of state of an ideal gas depends on the initial and final pressure as well as on the initial and final temperature.

Physical Significance of Entropy: -

1. Entropy as a Measure of the Disorder of the System - It has already been shown that all spontaneous processes, such as flow of heat from a hot end to a cold end of a conductor, flow of electricity from a point at a higher potential to a point at a lower potential, expansion of a gas in vacuum, diffusion of a solute from a concentrated to a dilute solution, are accompanied by increase in the 'disorder' of the system. Spontaneous processes are accompanied by increase in entropy as well as increase in the disorder of the system.

It has also been shown that melting of a solid or evaporation of a liquid is accompanied by increase of entropy. At the same time, it is known that a solid has a definite crystal lattice, i.e., the atoms or ions or molecules in a solid are arranged in a definite order. The order is much less in a liquid and least in a

gas. Thus, increase of entropy implies increase in disorder.

Thus, entropy is regarded as a measure of the disorder of a system. The great thermodynamicist Gibbs described entropy as a measure of the "mixed up - ness" of a system.

2. Entropy as Measure of Probability - All spontaneous processes lead to increase in entropy and also to increase in disorder. A little consideration will show that when a process is spontaneous it means that it is proceeding from a less probable to a more probable state. It appears, therefore, that there is a close relation between entropy S and the thermodynamic probability W of the state of the system both of which increase at the same time. This relationship was expressed by Boltzmann as

$$S = k \ln W + \text{constant} \quad \text{.....(xx)}$$

where k is Boltzmann constant, i.e. gas constant per single molecule ($= R/N_A$). Boltzmann defined thermodynamic probability of a system as the ratio of the probability of the actual state to the probability of the state in which there is complete order for the same energy and volume.

According to Planck, the constant in Eq.(xx) is zero. Hence,

$$S = k \ln W \quad \text{.....(xxi)}$$

Eq.(xxi) is called **the Boltzmann entropy equation**. A solid at absolute zero temperature is considered to be in a most ordered state. In this case, evidently, W is unity and hence $S_0 = 0$. The entropy of crystalline solids at absolute zero is, therefore, taken as zero.

Q.3 Derive the concept of entropy from the second law of thermodynamics and show that change in entropy is a state functions. (2010)

Ans. The second law of thermodynamics states that the total entropy of an isolated system can never decrease over time. The total entropy can remain constant in ideal gases where the system is in a steady state (equilibrium), or is undergoing a reversible process. In all spontaneous processes, the total entropy always increases and the process is irreversible. The increase in entropy accounts for the irreversibility of natural processes, and the asymmetry between future and past.

The second law has been expressed in many ways. Its first formulation is credited to the French scientist Sadi Carnot, who in 1824 showed that there is an upper limit to the efficiency of conversion of heat to work, in a heat engine.

The first law of thermodynamics provides the basic definition of internal energy, associated with all thermodynamic systems, and states the rule of conservation of energy. The second law is concerned with the direction of natural processes. It asserts that a natural process runs only in one sense, and is not reversible. For example, heat always flows spontaneously from hotter to colder bodies, and never the reverse, unless external work is performed on the system. The explanation of the phenomena was given in terms of entropy. Total entropy (S) can never decrease over time for an isolated system because

the entropy of an isolated system spontaneously evolves toward thermodynamic equilibrium: the entropy should stay the same or increase.

In a fictive reversible process, an infinitesimal increment in the entropy (dS) of a system is defined to result from an infinitesimal transfer of heat (dQ) to a closed system (which allows the entry or exit of energy - but not matter) divided by the common temperature (T) of the system and the surroundings which supply the heat:

$$dS = \frac{\delta Q}{T} \quad (\text{Closed system, idealized fictive reversible process})$$

Different notations are used for infinitesimal amounts of heat and infinitesimal amounts of entropy because entropy is a function of state, while heat, like work, is not. For an actually possible infinitesimal process without exchange of matter with the surroundings, the second law requires that the increment in system entropy be greater than that:

$$dS > \frac{\delta Q}{T} \quad (\text{Closed system, actually possible, irreversible process}).$$

This is because a general process for this case may include work being done on the system by its surroundings, which must have frictional or viscous effects inside the system, and because heat transfer actually occurs only irreversibly, driven by a finite temperature difference. Introducing a set of internal variables ξ to describe the deviation of a thermodynamic system from the equilibrium state, one can record the equality

$$dS = \frac{\delta Q}{T} - \frac{1}{T} \sum_j \Xi_j \delta \xi_j \quad (\text{Closed system, actually possible, irre-}$$

versible process)

The second term represents work of internal variables that can be perturbed by external influences, but the system cannot perform any positive work via internal variables. This statement introduces the impossibility of the reversion of evolution of the thermodynamic system in time and can be considered as a formulation of the second principle of thermodynamics - the formulation, which is, of course, equivalent to the formulation of the principle in terms of entropy.

The zeroth law of thermodynamics in its usual short statement allows recognition that two bodies in a relation of thermal equilibrium have the same temperature, especially that a test body has the same temperature as a reference thermometric body. For a body in thermal equilibrium with another, there are indefinitely many empirical temperature scales, in general respectively depending on the properties of a particular reference thermometric body. The second law allows a distinguished temperature scale, which defines an absolute, thermodynamic temperature, independent of the properties of any particular reference thermometric body.

State function -

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Go through Q.2

Q.4 Derive thermodynamically the Nernst distribution law and enumerate its limitations and application. (2017)

Other Related Question -

- Q. Write short note on Nernst distribution law. (2016)
- Q. State Nernst distribution law. Derive this law thermodynamically. Mention two important application of the law. (2011)
- Q. What are limitation of Nernst distribution law. (2012)
- Q. Explain Nernst distribution law. (2009)
- Q. Derive the distribution law thermodynamically. (2013)
- Q. State distribution law and describe its applications. Discuss the limitation of this law. (2014)

Ans. Nernst Distribution law: -

In 1872, Berthelot and Jungfleisch found that when solutions of iodine in carbon disulphide, of different concentrations, were shaken with distilled water, the iodine distributed itself between the two solvents in such a way that, at a given temperature, the ratio of its concentrations in the two layers was constant, irrespective of the amount of iodine. In other words ,

$$\frac{[I_2]_{CS_2}}{[I]_{H_2O}} = c_1 / c_2 = K_D \quad \dots\dots\dots(i)$$

The constant K_D is termed as the **partition coefficient or distribution coefficient**.

Nernst, however, showed that the ratio c_1/c_2 is constant only when the solute has the same molecular conditions , i.e., the same molar mass in the two solvents. If a solute partly associates to form double molecules in one solvent but not in the other, the law is valid only if the ratio of concentrations of single molecules in the two phases is taken into consideration.

The distribution of benzoic acid between water and benzene may be taken as a typical example. In water, the acid exists mostly as single molecules, i.e., as C_6H_5COOH . In benzene, however, benzoic acid exists as associated molecules, i.e., as $(C_6H_5COOH)_2$, along with only a small proportion of single molecules. The Nernst distribution law is valid only for concentrations of single molecules in the two phases. Therefore, if total concentration of benzoic acid in benzene is taken, the law will not hold good.

The Nernst distribution law may thus be stated as follows:

When a solute distributes itself between two immiscible solvents in contact with each other, there exists, for similar molecular species, at a given temperature, a constant ratio of distribution between the two solvents irrespective of the total amount of the solute and irrespective of any other molecular species which may be present.

Conditions for the validity of the distribution law: - The two essential prereq

quisites for the validity of the distribution law are:

1. Constant temperature and
2. Existence of similar molecular species in the two phases in contact with each other.

In addition, the following conditions are also necessary :

1. The solutions are dilute. The departures usually set in at higher concentrations. Generally speaking, the higher the concentration, the larger is the deviation. In an extreme case, both the solvents may be saturated with respect to the solute. Then, the partition coefficient, K_D , is given by

$$K_D = s_1/s_2 \quad \text{..... (ii)}$$

where s_1 and s_2 are the solubilities of the solute in the two solvent layers. The above equation will be strictly valid only if s_1 and s_2 are not large, i.e., if the solute is sparingly soluble in each solvent.

2. The two liquids are mutually immiscible or only very sparingly miscible (e.g., benzene and water) and their mutual miscibility is not altered by the presence of the solute.

Thermodynamic Derivation: - Suppose a solute A is present in two immiscible solvents 1 and 2 in contact with each other, Suppose further that its chemical potential in solvent 1 is μ_1 and in solvent 2 is μ_2 . When two phases are in equilibrium, their chemical potentials will be equal to one another, i.e.,

$$\mu_1 = \mu_2 \quad \text{..... (iii)}$$

$$\text{Since } \mu = \mu^\circ + RT \ln a, \quad \text{..... (iv)}$$

$$\text{therefore, } \mu_1 = \mu_1^\circ + RT \ln a_1 \text{ for Phase 1} \quad \text{..... (v)}$$

$$\text{and } \mu_2 = \mu_2^\circ + RT \ln a_2 \text{ for Phase 2} \quad \text{..... (vi)}$$

$$\text{Hence, } \mu_1^\circ + RT \ln a_1 = \mu_2^\circ + RT \ln a_2 \quad \text{..... (vii)}$$

$$\text{Or } RT \ln(a_1/a_2) = \mu_2^\circ - \mu_1^\circ \quad \text{..... (vii)}$$

Now, at constant temperature, the standard chemical potentials μ_1° and μ_2° are constant. Since R is also a constant (being the gas constant), it follows that

$$a_1/a_2 = \text{constant (at constant temperature)} \quad \text{..... (viii)}$$

Since the solutions are dilute, they behave ideally and hence Henry's law, according to which activity is proportional to mole fraction, is obeyed in each phase.

$$\therefore a_1/a_2 = k_1 x_1/k_2 x_2 = \text{constant (at constant temperature)} \quad \text{..... (ix)}$$

where x_1 and x_2 are the mole fractions of the solute in the two phases and k_1 and k_2 are the Henry's law constants for the solute in the two phases.

$$x_1/x_2 = \text{constant (at constant temperature)} \quad \text{..... (x)}$$

Further, since the solutions are dilute, the ratio of the mole fractions is almost the same as the ratio of the concentrations. Hence,

$$\therefore x_1/x_2 = c_1/c_2 = \text{constant (at constant temperature)} \quad \text{..... (xi)}$$

Thus, if a substance is present in two phases in contact with each other, then, at equilibrium,

$$\therefore c_1/c_2 = \text{constant (at constant temperature)} = K_D$$

This is the Nernst distribution law.

Let us consider cases in which a solute may associate or dissociate or enter into chemical combination with one of the solvents.

1. Association of the solute in one of the solvents: -

Let X represent the molecular formula of the solute. Let it remain as such in the first phase marked I (Fig. 1) in which its concentration is c_1 . Suppose it is largely associated to give the molecules $(X)_n$ in the second phase marked II. The associated molecules will exist in equilibrium with single molecules as shown. Let c_2 be the total concentration of the solute in this phase.

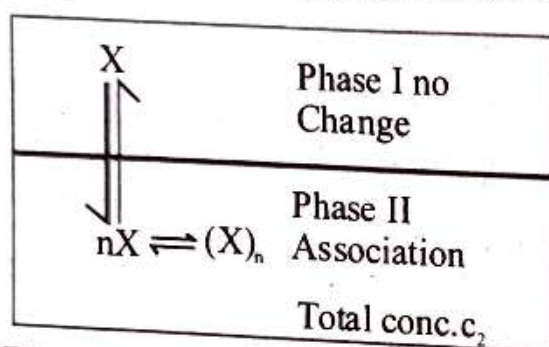


Fig. Association in one of the phases.

Applying the law of chemical equilibrium to the equilibrium between the associated and single molecules, viz., $(X)_n \rightleftharpoons nX$, in the second phase, we have

$$K = [X]^n / [(X)_n] \quad \dots\dots\dots(xii)$$

$$\text{or } [X] = \sqrt[n]{K \times [(X)_n]} = \text{constant} \times \sqrt[n]{[(X)_n]} \quad \dots\dots\dots(xiii)$$

If the solute exists largely as associated molecules, which is generally true except at large dilutions, the concentration of the associated molecules, $[(X)_n]$ may be taken as equal to c_2 , the total concentration, i.e.,

$$[(X)_n] = c_2 \quad \dots\dots\dots(xiv)$$

$$\text{From Eqs. (xiii) and (xiv), } [X] = \text{constant} \times \sqrt[n]{c_2} \quad \dots\dots\dots(xv)$$

Since the distribution law is valid only for concentrations of similar molecular species in the two phases, hence,

$$c_1 / [X] = \text{constant} \quad \dots\dots\dots(xvi)$$

$$\text{From Eqs. (xv) and (xvi), } c_1 / \sqrt[n]{c_2} = \text{constant} = K_D \quad \dots\dots\dots(xvii)$$

Eq. (xvii) has been checked by studying the distribution of benzoic acid between water and benzene.

The acid exists almost entirely as $(C_6H_5COOH)_2$ in benzene but in normal state in water.

2. Dissociation of the solute in one of the solvents: -

Let X, as before, represent the normal formula of the solute. Suppose it does not dissociate in the solvent marked I (Fig. 2) but dissociates into A and B in the solvent marked II. Let c_1 be its concentration in the first solvent and c_2 the total concentration in the second solvent. The distribution law is valid only

for the ratio of concentrations of similar molecular species in the two solvents.

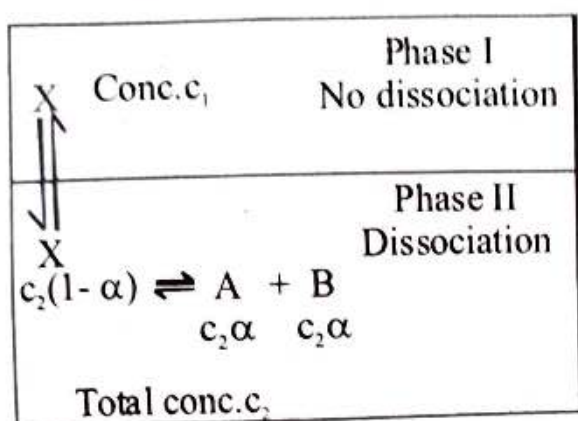


Fig. Dissociation in one of the phases.

Suppose, α is the degree of dissociation of the solute X in phase II. Then, the concentrations of the various species would be as shown below:



Therefore, according to the distribution law,

$$c_1 / [c_2(1-\alpha)] = K_D \quad \dots\dots\dots(\text{xviii})$$

3. Solute enters into chemical combination with one of the solvents. When the solute enters into chemical combination with one of the solvents, there is no change in the general equation of the Nernst distribution law, as shown below.

Let c_1 be the concentration of the solute X in one of the solvents in which it does not undergo any chemical change (Fig.3) and c_2 its total concentration in the second solvent with which it enters into chemical combination forming complex molecules, as represented by the equation

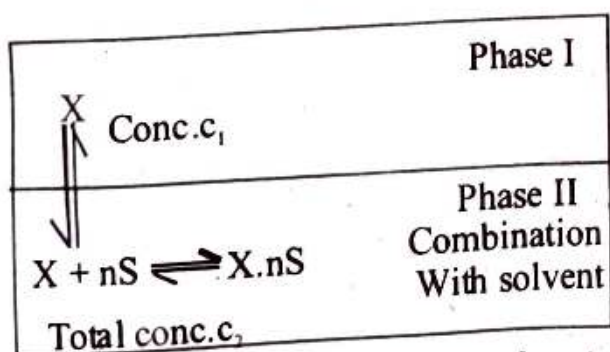
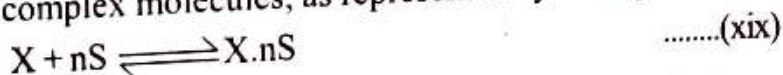


Fig. Combination with the solvent.

If α is the fraction of the solute that enters into chemical combination with the solvent, then the concentration of the various molecular species would be as follows:

Concentration of uncombined solute molecules = $c_2(1-\alpha)$

Concentration of the complex molecules formed = $c_2\alpha$

Applying the law of chemical equilibrium to the equilibrium represented by Eq. (xix), we have

$$K = \frac{c_2 \alpha}{c_2 (1 - \alpha) [\text{solvent}]^n} \quad \dots\dots (xx)$$

Since the solvent is in large excess, its concentration may be taken as constant

$$c_2 \alpha / [c_2 (1 - \alpha)] = \text{constant} \quad \dots\dots (xxi)$$

Since the distribution law is valid only for concentrations of similar molecular species, i.e., single molecules of X, in both the solvents, hence,

$$c_1 / [c_2 (1 - \alpha)] = \text{constant} \quad \dots\dots (xxii)$$

Dividing Eq.(xxii) by Eq. (xxi), we have

$$c_1 / c_2 \alpha = \text{constant} \quad \dots\dots (xxiii)$$

Now, α , the fraction of the solute that combines with the same solvent, is also constant at a given temperature. Eq. (xxiii) may, therefore, be written as

$$c_1 / c_2 = \text{constant} \quad \dots\dots (xxiv)$$

Thus, the combination of the solute with one of the solvents does not make any change in the fundamental equation of the distribution law except in changing the numerical value of the partition coefficient.

Applications of Nernst Distribution Law: -

1. Study of Association of a Solute - As shown above, if a solute associates in one of the solvents in which its concentration is c_2 but not in the other in which its concentration is c_1 , then

$$c_1 / \sqrt[n]{c_2} = K_D$$

n being the number of simple molecules which combine to form one associated molecule. It has thus been possible to show by studying distribution of acetic acid and benzoic acid between water and benzene that these substances exist in benzene as double molecules (or dimers), the value of n being 2.

2. Study of Dissociation of a Solute - As has been shown earlier, if a solute undergoes dissociation in one of the solvents in which its concentration is c_2 but not in the other in which its concentration is c_1 , then,

$$c_1 / [c_2 (1 - \alpha)] = K_D$$

Thus, if the degree of dissociation (α) of a solute is known at one concentration, its value at any other concentration can be obtained, since K_D is constant.

3. Distribution Indicators - It is a common experience that iodine distributes itself considerably more in carbon disulphide than in water when both the solvents are in contact with each other. Therefore, an extremely dilute solution of iodine in water can be successfully titrated by adding a drop or two of carbon disulphide. The concentration in the carbon disulphide layer becomes large enough to give a distinct violet colour.

4. Study of Complex Ions - The Nernst distribution law has been successfully applied in determining the formula of the complex ions formed between bromine and bromide ion as well as between iodine and iodide ion. The following example will illustrate the method.

On shaking a solution of iodine in carbon disulphide with water, the iodine distributes itself between the two solvents in accordance with the distribution law.

bution law. Knowing the concentrations of iodine in the two layers, the partition coefficient, K_p , can be determined. Now, suppose a solution of iodine in carbon disulphide containing X moles of iodine per litre is shaken with an aqueous solution of potassium iodide containing A moles of potassium iodide per litre (Fig.4). The total concentration of iodine in the aqueous layer will now be much higher due to formation of the soluble complex KI_3 . Let this concentration be B moles per litre. Evidently, the concentration of iodine in carbon disulphide layer will fall to (X - B) moles per litre. The concentration of free iodine (as I_2) in aqueous solution, according to the Nernst distribution law, should be $= K_p (X - B) = D$ moles per litre (say)

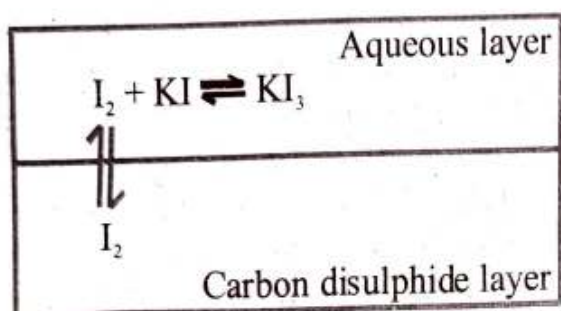


Figure - study of complex ions

Suppose the complex ion formed is I_3^- . Then, the following equilibrium will exist in aqueous solution:



Evidently, B - D moles of iodine must have combined with B - D moles of iodide ions (assuming that potassium iodide is completely ionised) to give B - D moles of iodide ions (assuming that potassium iodide is completely ionised) to give B - D moles of the complex ion I_3^- .

Therefore, the equilibrium constant will be given by

$$K = [I_3^-] / ([I_2][I^-])$$

The concentrations of the various species in the aqueous layer will be as follows:

$$[I_3^-] = B - D \text{ mol dm}^{-3}; [I_2] = D \text{ mol dm}^{-3}; [I^-] = A - (B - D) \text{ mol dm}^{-3}$$

The results of determinations carried out at 30°C are given in Table.

Study of Complex Ions

A (Mol dm ⁻³)	B (Mol dm ⁻³)	D (Mol dm ⁻³)	K (dm ³ mol ⁻¹)
0.250	0.1111	0.0261	19.72
0.125	0.0686	0.0259	20.04
0.0625	0.0625	0.0257	20.40

The fact that K is reasonably constant, in spite of variations in A and B, shows that the formula of the complex ion is I_3^- .

5. Solvent Extraction: -The most important application of the distribution law

is in the process of extraction, in the laboratory as well as in industry. In the laboratory, for instance, it is frequently used for the removal of a dissolved organic substance from aqueous solution with solvents such as benzene, ether, chloroform, carbon tetrachloride, etc. The advantage is taken of the fact that the partition coefficient of most of the organic compounds is very largely in favour of organic solvents.

The same principle applies in the desilverization of lead by **Parke's process**. The argentiferous lead is melted and heated to 800°C . Molten zinc is then added. Molten lead and molten zinc behave as two immiscible liquids in contact with each other and silver behaves as a solute which is more soluble in zinc than in lead, the partition coefficient being of the order of 300 at 800°C . Silver, therefore, passes readily from the heavier lead layer into the lighter zinc layer which is separated. By repeating the process three or four times, almost the entire amount of silver passes into the zinc layer.

We can derive a general formula which enables the calculation of the amount of the solute that is left unextracted after a given number of operations. Let V ml of a solution containing W gram of solute be repeatedly extracted with v ml of another solvent which is immiscible with the first. Let w_1 be the mass of the solute that remains unextracted at the end of the first operation. Then, K_D will be given by

$$\frac{w_1 / V}{(W - w_1) / v} = K_D \quad \Rightarrow \quad w_1 = W \frac{K_D V}{K_D V + v}$$

Similarly, at the end of the second extraction, the amount w_2 that remains unextracted is given by

$$w_2 = w_1 \frac{K_D V}{K_D V + v} = W \left(\frac{K_D V}{K_D V + v} \right)^2$$

In general, the amount that remains unextracted at the end of n operations, w_n , will be given by

$$w_n = W \left(\frac{K_D V}{K_D V + v} \right)^n$$

It is evident that in order to make w_n as small as possible, for a given value of K_D , n should be as large as possible. But $n \times v$ is equal to the total volume of the extracting liquid available, i.e., it is constant. Therefore, it is better to keep n large and v small, rather than the reverse. In other words, the efficiency of extraction increases by increasing the number of extractions using only a small amount of the extracting solvent each time.

For the same reason, in the washing of precipitates it is more effective to use a small quantity of water at a time and to repeat the process a number of times.

Q. 5. Derive Gibbs - Helmholtz equation. With the help of this equation show that in the case of galvanic cells evolved ($-\Delta H$) only when $(\partial E/\partial T)_p = 0$. (2016)

Other related question -

Q. Write short note on Gibbs and Helmholtz free energies. (2014)

Q. What is the concept of free energy. Deduce the Gibbs - Helmholtz equation. (2011)

Q. Write notes on Gibbs - Helmholtz equation work. (2011)

Ans. Work and Free Energy Functions: -

The sum total of the entropy change of the system and the surroundings (viz., $\Delta S_{\text{sys}} + \Delta S_{\text{sur}}$) serves as a criterion of spontaneity or feasibility of a process. If the total entropy change is positive, the process is feasible. If it is zero, the system remains in a state of equilibrium. However, in order to decide about the feasibility of a process, we shall have to know the entropy change of the system as well as that of the surroundings. This is not always convenient. We, therefore, consider entropy change in terms of other state functions which can be determined more conveniently. Two such functions are the **work function** and the **free energy function** represented by A and G , respectively. These are defined by the equations

$$A = U - TS \quad \text{.....(i)}$$

$$G = H - TS \quad \text{.....(ii)}$$

Since, U , H and S depend only upon the state of a system (the temperature is included in the state), it is evident that the functions A and G also depend upon the state of the system only. Let the three functions in Eq.(i) at constant T , be A_1 , U_1 and S_1 so that

$$A_1 = U_1 - TS_1 \quad \text{.....(iii)}$$

Let an appreciable change take place at the same temperature T so that the three functions in another state of the system become A_2 , U_2 and S_2 . Then,

$$A_2 = U_2 - TS_2 \quad \text{.....(iv)}$$

Subtracting Eq. (iii) from Eq. (iv), we have

$$A_2 - A_1 = (U_2 - U_1) - T(S_2 - S_1)$$

$$\text{or } \Delta A = \Delta U - T\Delta S \quad \text{.....(v)}$$

where ΔA is the change in the function A . ΔU is the corresponding change in internal energy and ΔS is the change in entropy of the system.

Suppose the change under reference is brought about reversibly at the constant temperature T and that the heat absorbed is equal to q_{rev} .

Since $\Delta S = q_{\text{rev}}/T$, hence, substituting in Eq. (v), we have

$$\Delta A = \Delta U - q_{\text{rev}} \quad \text{.....(vi)}$$

From the equation of the First law of thermodynamics, viz., $\Delta U = q + w$, it follows that

$$w_{\text{rev}} = \Delta U - q_{\text{rev}} \quad \text{.....(vii)}$$

If work is done by the system, it is negative so that

$$-w_{\text{rev}} = \Delta U - q_{\text{rev}} \quad \text{.....(viii)}$$

Comparing Eq.(vi) with Eq. (viii),

$$-\Delta A = w_{\text{rev}} \quad \text{.....(ix)}$$

Since the process is carried out reversibly, w represents the maximum work. It is thus clear that decrease in the function A (i.e., $-\Delta A$) gives the maximum work that can be done by the system during the given change. The function A is, therefore, termed as the work function. This is also referred to as

Helmholtz free energy or Helmholtz function: -

The German physicist Hermann von Helmholtz (1821 - 1894) was a versatile scientist who made contributions to optics, thermodynamics, acoustics and physiology.

If G_1 , H_1 and S_1 represent the thermodynamic functions in the initial state and G_2 , H_2 and S_2 in the final state, the temperature remaining constant at T , we have from Eq. (ii),

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1) \text{ or } \Delta G = \Delta H - T\Delta S \quad \text{.....(x)}$$

But at constant pressure

$$\Delta H = \Delta U + P\Delta V$$

$$\therefore \Delta G = \Delta U + P\Delta V - T\Delta S \quad \text{.....(xi)}$$

Comparing with Eq.(v),

$$\Delta G = \Delta A + P\Delta V \quad \text{.....(xii)}$$

Since ΔA is equal to $-w$ Eq. (ix), hence

$$\Delta G = -w + P\Delta V$$

$$\text{or } -\Delta G = w - P\Delta V \quad \text{.....(xiii)}$$

The quantity $P\Delta V$ is the work done by the gas on expansion against the constant external pressure P . Therefore, $-\Delta G$ gives the maximum work obtainable from a system other than that due to change of volume, at constant temperature and pressure. The work other than that due to change of volume is called the net work. Thus,

$$\text{Net work} = w - P\Delta V = -\Delta G \quad \text{.....(xiv)}$$

Hence, $-\Delta G$ is a measure of the net work that can be obtained from a system at constant temperature and pressure. The quantity G is called the **Gibbs function** or **Gibbs free energy** or merely free energy. Thus, ΔG is measure of the decrease in free energy. The net work that it measures may be electrical work or chemical work. This quantity is of great importance in physical chemistry; it is named in honour of the great American physicist, J.W. Gibbs (1839-1903).

The Gibbs-Helmholtz Equation: -

Let G_1 represent the free energy of a system in its initial state at temperature T . Suppose the temperature rises to $T + dT$ where dT is infinitesimally small. Let the free energy at the new temperature be $G_1 + dG_1$.

Now suppose that when the system is in its final state, its free energy is given by G_2 at the temperature T and by $G_2 + dG_2$ at the temperature $T + dT$. If the pressure remains constant all along, $dG = -SdT$ is applicable, i.e.,

$$dG_1 = -S_1 dT \quad \text{.....(xv)}$$

$$\text{and } dG_2 = -S_2 dT \quad \text{.....(xvi)}$$

where S_1 and S_2 are the entropies of the system in the initial and final states of the system, respectively.

Subtracting Eq.(xv), from Eq. (xvi), we have

$$d(G_2 - G_1) = -(S_2 - S_1) dT$$

$$d(\Delta G) = -\Delta S dT \quad \text{.....(xvii)}$$

As the pressure is constant, therefore,

$$(\partial(\Delta G)/\partial T)_p = -\Delta S \quad \text{.....(xviii)}$$

Also, since from Eq. (x), $-\Delta S = (\Delta G - \Delta H)/T$, hence, Eq. (xviii) becomes

$$(\Delta G - \Delta H)/T = (\partial(\Delta G)/\partial T)_p \quad \text{.....(xix)}$$

$$\text{Or } \Delta G = \Delta H + T(\partial(\Delta G)/\partial T)_p \quad \text{.....(xx)}$$

This equation is known as the **Gibbs - Helmholtz equation**. It is applicable to all Processes occurring at constant pressure. It has been used for calculating the enthalpy change ΔH for a process or a reaction provided the values of free energy changes at two different temperatures are known.

For a reaction at constant volume, the corresponding equation will be

$$\Delta A = \Delta U + T(\partial(\Delta A)/\partial T)_v$$

Q.6. Write short note on entropy of mixing of ideal gases. (2014)

Ans. Entropy of mixing of Ideal Gases: -

In order to calculate the entropy of mixtures we can first calculate the entropies of the pure components of the mixture and then add the entropy change of mixing to the sum of these. Entropy of mixing is most easily calculated for ideal gas mixtures. Because ideal gas molecules do not interact, their mixing is at constant temperature. Probably the simplest way of thinking about mixing two ideal gases is to have them in separate containers at the same pressure and then open a valve connecting two containers. In this case, we are mixing the components from their partial molar volumes in the final mixture to the total volume of the mixture. Because this process involves no heat, we might think that it has no entropy change. However, this is not correct, because this "mixing at constant pressure" is not reversible and the entropy change for this process cannot be directly calculated.

Q.7. Derive clausius clapeyron equation. How this equation is verified? (2014, 16)

Other related question

Q. Derive clausius clapeyron equation. (2011)

Q. Derive the integrated form of clapeyron clausius equation for liquid $\rightleftharpoons$ vapour and solid $\rightleftharpoons$ liquid equilibrium. (2010)

Ans. Integrated form of Clapeyron Equation for Liquid $\rightleftharpoons$ vapour Equilibrium: -

Clapeyron Clausius Equation:-

The Clapeyron equation

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{T(V_g - V_l)} \quad \text{.....(i)}$$

as applied to liquid $\rightleftharpoons$ vapour equilibrium, can be easily integrated. The molar volume of a substance in the vapour state is considerably greater than that in the liquid state. In the case of water, for example, the value of V_g at 100°C is $18 \times 1670 = 30060$ ml while that of V_l is only a little more than 18 ml. Thus, $V_g - V_l$ can be taken as V_g without introducing any serious error. The Clapeyron equation (i), therefore, may be written as

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{TV_g} \quad \text{..... (ii)}$$

Assuming that the ideal gas law is applicable, i.e., $PV = RT$ (per mole), $V_g = RT/P$. Hence,

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{T} \times \frac{P}{RT} = P \frac{\Delta H_{\text{vap}}}{RT^2} \quad \text{..... (iii)}$$

$$\text{or} \quad \frac{1}{P} \times \frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2} \quad \text{or} \quad \frac{d(\ln P)}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2} \quad \text{..... (iv)}$$

Assuming that ΔH_v remains constant over a small range of temperature, we have

$$\int d(\ln P) = \frac{\Delta H_{\text{vap}}}{R} \int \frac{dT}{T^2} \quad \text{or} \quad P = -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} \right) + C \quad \text{.....(v)}$$

where C is integration constant.

Eq. (v) is, evidently, the equation of a straight line. Hence, the plot of $\ln P$ against $1/T$ should yield a straight line with slope = $-\Delta H_{\text{vap}}/R$ and intercept = C. This enables evaluation of ΔH_{vap} . Eq. (iv) can also be integrated between limits of pressures P_1 and P_2 corresponding to temperatures T_1 and T_2 . Thus,

$$\int_{P_1}^{P_2} d(\ln p) = \frac{\Delta H_{\text{vap}}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \quad \text{.....(vi)}$$

$$\begin{aligned} \therefore \ln \frac{P_2}{P_1} &= -\frac{\Delta H_{\text{vap}}}{R} \left[\frac{1}{T} \right]_{T_1}^{T_2} = \frac{\Delta H_{\text{vap}}}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \\ &= \frac{\Delta H_{\text{vap}}}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad \text{.....(vii)} \end{aligned}$$

The integrated form of Clapeyron equation is known as Clapeyron - Clausius equation.

Applications of Clapeyron - Clausius Equation for Liquid $\rightleftharpoons$ vapour Equilib-

ria:-

Eq. (vii) can be used for calculating the molar heat of vapourisation, ΔH_{vap} , of a liquid if we know the vapour pressure at two temperatures. Further, if ΔH_{vap} is known, vapour pressures at a desired temperature can be calculated from the knowledge of a single value of vapour pressure at a given temperature.

The Clapeyron - Clausius Equation for Solid $\rightleftharpoons$ Vapour Equilibria:-

The Clapeyron equation for solid $\rightleftharpoons$ vapour equilibrium may be put as

$$\frac{dP}{dT} = \frac{\Delta H_{\text{sub}}}{T(V_g - V_s)} \quad \text{.....(viii)}$$

where ΔH_{sub} stands for the molar heat of sublimation of the substance. Since the molar volume of a substance in the gaseous state is very much greater than that in the solid state, $V_g - V_s$ can be safely taken as V_g . Eq. (viii) can thus be easily integrated, as before, to give the following expression:

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{sub}}}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad \text{.....(ix)}$$

Eq. (ix) can be put to the same use for solid $\rightleftharpoons$ vapour equilibria as Eq. (vii) for liquid $\rightleftharpoons$ vapour equilibria.

Application of Clapeyron - Clausius Equation for Solid $\rightleftharpoons$ Liquid Equilibria:-

The Clapeyron equation $\frac{dP}{dT} = \frac{\Delta H_{\text{gas}}}{T(V_l - V_s)}$ for solid $\rightleftharpoons$ liquid equilibrium cannot be integrated easily since V_s cannot be ignored in comparison with V_l . Also the laws of liquid state are not so simple as those for gaseous state. However, this equation as such can be used for calculating the effect of pressure on the melting point of a solid and also for calculating heats of fusion from vapour pressure data obtained at different temperatures.

Q.8. Write short note on Maxwell's relations.

(2014)

Ans. The Maxwell Relations:-

The various expressions connecting internal energy (U), enthalpy (H), Helmholtz free energy (A) and Gibbs free energy (G), with relevant parameters such as entropy,

Pressure, temperature and volume, may be put as

(i) $dU = TdS - PdV$

(ii) $dH = TdS + VdP$

(iii) $dA = -SdT - PdV$

(iv) $dG = -SdT + VdP$

If V is constant so that dV is zero, then, Eq. (1) yields the result

$$(\partial U / \partial S)_V = T \quad \dots\dots\dots(1)$$

If S constant so that dS is zero, then Eq. (1) yields the result

$$(\partial U / \partial V)_S = -P \quad \dots\dots\dots(2)$$

Differentiating Eq. (1) with respect to V keeping S constant and differentiating Eq. (2) with respect to S keeping V constant, we get

$$\partial^2 U / (\partial S)(\partial V) = (\partial T / \partial V)_S \quad \dots\dots\dots(3)$$

$$\text{and } \partial^2 U / (\partial V)(\partial S) = -(\partial P / \partial S)_V \quad \dots\dots\dots(4)$$

It follows from Eqs.(3) and (4) that

$$(\partial T / \partial V)_S = -(\partial P / \partial S)_V \quad \dots\dots\dots(5)$$

Following the same mathematical procedure as above, the following expressions can be easily derived:

$$(\partial T / \partial P)_S = (\partial V / \partial S)_P \quad \text{from (ii)} \quad \dots\dots\dots(6)$$

$$(\partial S / \partial V)_T = (\partial P / \partial T)_V \quad \text{from (iii)} \quad \dots\dots\dots(7)$$

$$(\partial S / \partial P)_T = -(\partial V / \partial T)_P \quad \text{from (iv)} \quad \dots\dots\dots(8)$$

Eqs. (5) and (8) known as Maxwell's relations.

Another set of Maxwell's relationship, which can also be derived from (i) to (iv), are as follows :

$$(\partial U / \partial S)_V = (\partial H / \partial S)_P \quad \text{from (i) and (ii)} \quad \dots\dots\dots(9)$$

$$(\partial U / \partial V)_S = (\partial A / \partial V)_T \quad \text{from (i) and (iii)} \quad \dots\dots\dots(10)$$

$$(\partial H / \partial P)_S = (\partial G / \partial P)_T \quad \text{from (ii) and (iv)} \quad \dots\dots\dots(11)$$

$$(\partial A / \partial T)_V = (\partial G / \partial T)_P \quad \text{from (iii) and (iv)} \quad \dots\dots\dots(12)$$

Q.9. What are the limitations of first law of thermodynamics. (2011)

Ans. Limitations of the First law:-

The First law of thermodynamics, though exact, has certain limitations-

1. The First law establishes definite relationship between the heat absorbed and the work performed by a system in a given process. But it puts no restriction on the direction of flow of heat. According to the first law, for example, it is not impossible to extract heat from ice by cooling it to a low temperature and then use it for warming water. But it is known from experience that such a transfer of heat from a lower to a higher temperature is not possible without expenditure of energy, i.e., without doing some external work. It is known, on the other hand, that heat flows spontaneously, i.e., of its own accord, from a higher to a lower temperature.
2. According to the First law, the energy of an isolated system remains constant during a specified change of state. But it does not tell whether a specified change or a process including a chemical reaction can occur spontaneously, i.e., whether it is feasible.
3. The First law states that energy of one form can be converted into an

equivalent amount of energy of another form. But it does not tell that heat energy cannot be completely converted into an equivalent amount of work. There is thus need for another law, viz., the Second law of thermodynamics.

The Second law helps us to determine the direction in which energy can be transferred. It also helps us to predict whether a given process or a chemical reaction can occur spontaneously. It introduces a new concept of entropy. It also helps us to know the equilibrium conditions.

It is known from experience that although various forms of energy can be completely transformed into one another, yet heat is a typical form of energy which cannot be completely transformed into work. The Second law helps us to calculate the maximum fraction of heat that can be converted into work in a given process. Entropy can be thought of as arising from the dispersal or degradation of the total energy of an isolated system.

Q .10. Show that

(2013)

$$(i) \quad \left(\frac{\partial G}{\partial T} \right)_P = -S$$

$$(ii) \quad \left(\frac{\partial G}{\partial P} \right)_T = V$$

Ans. We know that

$$dG = -SdT + VdP$$

Dividing by dT , keeping P constant, we get

$$\left(\frac{\partial G}{\partial T} \right)_P = -S$$

And dividing by dP keeping T constant

$$\left(\frac{\partial G}{\partial P} \right)_T = V$$

Q .11. Show that decrease in Helmholtz free energy gives maximum work obtained from the system.

(2013)

Ans. Helmholtz Free Energy Function $A = E - TS$:-

Helmholtz free energy function (A) is sometimes called work function or maximum work content of the system. At a constant temperature, the maximum work obtainable from a system is at the expense of decrease in Helmholtz free energy of the system.

$$\Delta A = \Delta E - T \Delta S \quad \text{or} \quad \Delta A = \Delta E - T \frac{q_{rev}}{T}$$

$$\Delta A = \Delta E - q_{rev} \quad \therefore \quad \Delta E = q + W$$

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$$\therefore w_{\text{rev}} = \Delta E - q_{\text{rev}}$$

In case of work is done by the system, then sign is - ve

$$-w_{\text{rev}} = \Delta E - q_{\text{rev}}$$

$$-\Delta A = w_{\text{rev}}$$

where w_{rev} represents maximum useful work done during the reversible process. Hence, decrease in

Helmholtz free energy gives the maximum work obtained from the system.

Q.12. Describe the working of carnot cycle. Show that the thermodynamic efficiency η of the cycle is given by.

$$\eta = \frac{T_2 - T_1}{T_2}$$

(2012)

Ans. Carnot cycle: -

Carnot employed a reversible cycle to demonstrate the maximum convertibility of heat into work.

The system consists of one mole of an ideal gas which is subjected to a series of four successive operations, commonly termed as **four strokes**, as given below.

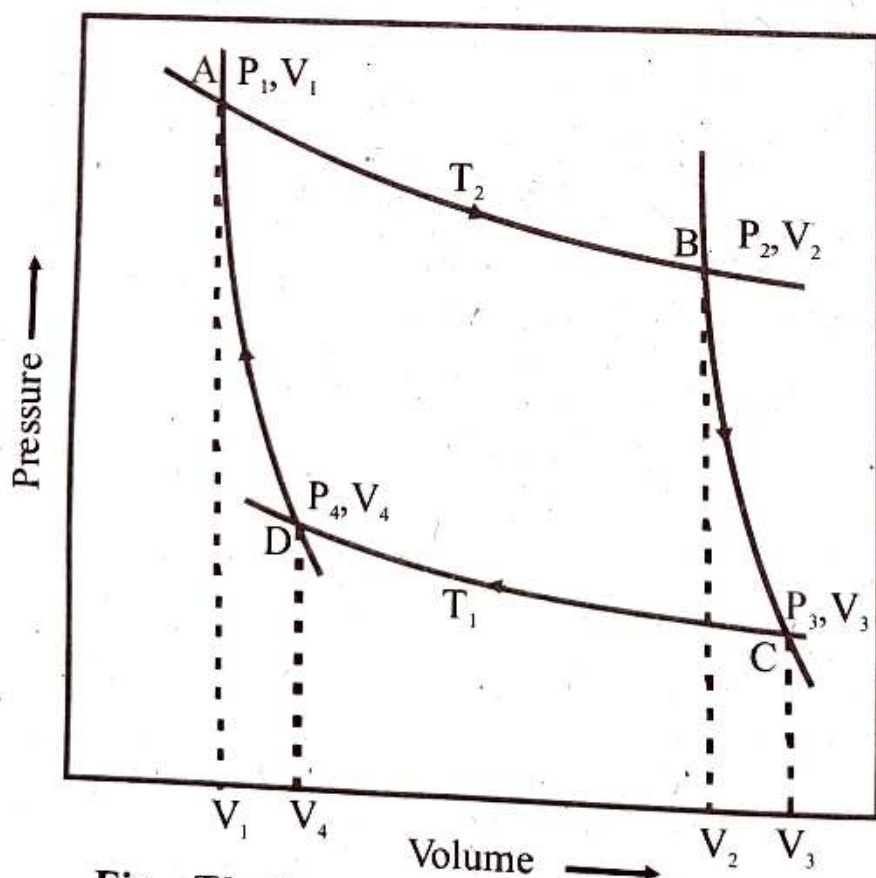


Fig. - The four operations in Carnot cycle

I. Stroke 1. Isothermal Expansion: -

The gas is allowed to expand reversibly and isothermally at the temperature T_2 so that the volume increases from V_1 , represented by the point A, to V_2 represented by the point B (Fig.). Since in the isothermal expansion of an

ideal gas $\Delta U = 0$, it follows from the First law equation (viz., $\Delta U = q + w$) that $q = -w$, i.e., the heat absorbed is equal to the work done by the system on the surroundings. Let q_2 be the heat absorbed by the system at the temperature T_2 and w_1 be the work done by the system on the surroundings. Then

$$q_2 = -w_1 = RT_2 \ln(V_2/V_1) \quad \dots (i)$$

II. Stroke 2. Adiabatic Expansion: -

The gas is then allowed to expand reversibly and adiabatically from the volume V_2 to V_3 , i.e., from the point B to C.

Since work is done by the system adiabatically, it is not in a position to absorb heat. The temperature of the system, therefore, falls from T_2 to say, T_1 . As q is equal to zero in this case, it follows from the First law equation (viz., $\Delta U = q + w$) that $\Delta U = w$. Since the process involves expansion of the gas, therefore, work is done by the system on the surroundings. Hence, by convention, w is negative so that $\Delta U = -w$.

$$\text{Now, by definition, } C_v = (\partial U / \partial T)_v \quad \dots (ii)$$

$$\therefore \Delta U = C_v \Delta T = C_v (T_1 - T_2) = -w \quad \dots (iii)$$

(change in temperature, ΔT = final temperature - initial temperature)

$$\text{or } -w = C_v (T_1 - T_2) = -C_v (T_2 - T_1) \quad \dots (iv)$$

If the work done in this stage is denoted by w_2 , then

$$\therefore -w_2 = -C_v (T_2 - T_1) \quad \dots (v)$$

III. Stroke 3. Isothermal Compression: -

After this, the gas is subjected to a reversible and isothermal compression at the lower temperature T_1 so that the volume decreases from V_3 to V_4 (i.e., from the point C to D). In this case, evidently work is done on the system. Hence, heat will be produced and given up to the surroundings. Since compression takes place isothermally and reversibly, $\Delta U = 0$. Therefore, if q_1 is the heat given out to the surroundings at the temperature T_1 and w_3 is the work done on the system in this process, then remembering signs of q and w ,

$$-q_1 = w_3 = RT_1 \ln(V_4/V_3) \quad \dots (vi)$$

IV. Stroke 4. Adiabatic Compression: -

Finally, by an adiabatic and reversible compression, the gas is restored to its original volume V_1 and temperature T_2 . Thus, the gas is compressed adiabatically from D to A. In this case, work is done on the system. Hence, w is positive. According to the First law, $\Delta U = q + w$

Since in adiabatic process, $q = 0$. Hence,

$$\Delta U = w = C_v \Delta T = C_v (T_2 - T_1)$$

Let w_4 be the work done in this stage. Then,

$$w_4 = C_v (T_2 - T_1) \quad \dots (vii)$$

where $T_2 - T_1$ is the increase in temperature produced by the adiabatic compression.

The net heat absorbed (q) by the ideal gas in the whole cycle is given by

$$q = q_2 + (-q_1) = RT_2 \ln(V_2/V_1) + RT_1 \ln(V_4/V_3) \\ = RT_2 \ln(V_2/V_1) - RT_1 \ln(V_3/V_4) \quad \dots(\text{viii})$$

In the light of adiabatic expansion of an ideal gas, the following equations can be written:

$$C_v \ln(T_2/T_1) = R \ln(V_3/V_2) \quad (\text{For stage II})$$

$$C_v \ln(T_2/T_1) = R \ln(V_4/V_1) \quad (\text{For stage IV})$$

$$\text{or } V_3/V_2 = V_4/V_1 \text{ or } V_2/V_1 = V_3/V_4 \quad \dots(\text{ix})$$

Hence, the net heat absorbed, according to Eq(viii), may be put as

$$q = q_2 - q_1 = R(T_2 - T_1) \ln(V_2/V_1) \quad \dots(\text{x})$$

Similarly, the net work done by the gas is given by

$$w = -w_1 + (-w_2) + w_3 + w_4 \\ = RT_2 \ln V_2/V_1 - C_v(T_2 - T_1) + RT_1 \ln(V_4/V_3) + C_v(T_2 - T_1) \\ = RT_2 \ln(V_2/V_1) - RT_1 \ln(V_3/V_4) \quad \dots(\text{xi})$$

$$\text{since } V_2/V_1 = V_3/V_4$$

$$\text{Hence, } w = R(T_2 - T_1) \ln(V_2/V_1) \quad \dots(\text{xii})$$

It follows from Eqs. (x) and (xii) that $q = w$. Thus, the essential condition for a cyclic process that the net work done is equal to the net heat absorbed is fully satisfied.

The relationship between w , the net work done by the system and q_2 , the quantity of heat absorbed at the higher temperature T_2 , in Carnot cycle, can be obtained from the following two equations :

$$w = R(T_2 - T_1) \ln(V_2/V_1) \quad (\text{Eq. xii})$$

$$\text{and } q_2 = RT_2 \ln(V_2/V_1) \quad (\text{Eq. i})$$

Hence, dividing Eq. (xii) by Eq. (i),

$$w = q_2 (T_2 - T_1) / T_2 \quad \dots(\text{xiii})$$

Since $(T_2 - T_1)/T_2 < 1$, it follows that $w < q_2$, i.e., work done is less than the heat absorbed. This means that only a part of the heat absorbed by the system at the higher temperature T_2 is transformed into work. The rest of the heat q_1 is given out by the system to the surroundings which is at the lower temperature T_1 .

Thus, Kelvin stated the second law of thermodynamics as follows : It is impossible to use cyclic process to extract heat from a reservoir and to convert it into work without transferring at the same time a certain amount of heat from a hotter to a colder part of the system.

Efficiency of a Heat Engine: -

The fraction of the heat absorbed by an engine which it can convert into work gives the efficiency (η) of the engine.

From Eq. (xiii), it is seen that

$$\text{Efficiency, } \eta = w/q_2 = (T_2 - T_1)/T_2 \quad \dots(\text{xiv})$$

Since $(T_2 - T_1)/T_2$ is invariably less than 1, the efficiency of a heat engine is always less than 1. No heat engine has yet been constructed which has an efficiency equal to unity. Mathematically, however, if $T_1 = 0$, efficiency = 1.

It follows from Eq. (xiv) that the efficiency depends upon the difference between T_2 and T_1 . Thus, the greater the difference between the temperature of

the 'source' and the 'sink', the greater is the efficiency. This explains why superheated steam is used in a steam engine.

The net heat absorbed by the system, q , is equal to $q_2 - q_1$ and according to the First law of thermodynamics, this must be equivalent to the net work done by the system. Thus,

$$w = q_2 - q_1$$

Combining this with eq.(xiv) we get

$$(q_2 - q_1)/q_2 = (T_2 - T_1)/T_2 \quad \dots(xv)$$

$$\text{Thus, efficiency, } \eta = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \quad \dots(xvi)$$

Eq. (xvi) has been arrived at by assuming that the series of changes in the cycle are brought about in a thermodynamically reversible manner so as to obtain maximum possible work. But, in actual practice, it is not possible to carry out the process infinitesimally slowly so that the efficiency is even less than that given by the above equation.

Carnot Theorem: -

According to Eq. (xvi), the efficiency of a machine working reversibly depends only on the temperature of the source and the sink. It is independent of the nature of the substance or substances used for operations. The same idea may be expressed by saying that all periodic machines working reversibly between the same two temperatures have the same efficiency. This statement is commonly known as the **Carnot theorem**, in honour of S. Carnot (1796-1832), the brilliant French physicist, known for important contributions to thermodynamics.

It may be noted that while the First law states that when one form of energy is transformed into another, the amount of energy that disappears is exactly equivalent to the amount of energy that is produced, it is silent about the extent to which such conversion can take place. The Second law of thermodynamics gives information about this point. It tells us that while all other forms of energy can be completely converted into heat, the complete conversion of heat into any other form of energy cannot take place without leaving some lasting change in the system. This has led to the following enunciation of the Second law of thermodynamics :

It is impossible to convert heat into work without compensation.

Q.13. Write short note on thermodynamic potential. (2012)

Ans. A thermodynamic potential (in fact, rather energy than potential) is a scalar quantity used to represent the thermodynamic state of a system. The concept of thermodynamic potentials was introduced by Pierre Duhem in 1886. Josiah Willard Gibbs in his papers used the term fundamental functions. One main thermodynamic potential that has a physical interpretation is the internal energy U . It is the energy of configuration of a given system of conservative forces (that is why it is called potential) and only has meaning

with respect to a defined set of references (or data). Expressions for all other thermodynamic energy potentials are derivable via Legendre transforms from an expression for U . In thermodynamics, external forces, such as gravity, are typically disregarded when formulating expressions for potentials. For example, while all the working fluid in a steam engine may have higher energy due to gravity while sitting on top of Mount Everest than it would at the bottom of the Mariana Trench, the gravitational potential energy term in the formula for the internal energy would usually be ignored because changes in gravitational potential within the engine during operation would be negligible. In a large system under even homogeneous external force, like the earth atmosphere under gravity, the intensive parameters should be studied locally having even in equilibrium different values in different places far from each other.

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Unit II

Q.1. Write short note on phase rule and its application to sulphur system. (2011)

Other Related Question -

Q. Discuss phase rule application to sulphur system. (2007)

Ans. Sulphur System: -

Sulphur exists in two crystalline forms, rhombic and monoclinic, with 95.6°C as the transition temperature at one atm pressure at which they can be transformed into one another. Below 95.6°C , rhombic is the stable form while above it, monoclinic is the stable variety. At 95.6°C , both forms are in equilibrium with each other. Each form has its own characteristic melting point. Thus, under a pressure of one atm, melting point of rhombic sulphur (S_R) is 114°C while that of monoclinic sulphur (S_M) is 120°C . The liquid form of sulphur (S_L) undergoes notable changes in colour and viscosity when heated and ultimately boils at 444.7°C . Thus, sulphur can exist in four possible phases, two solids (S_R and S_M), one liquid (S_L) and one vapour (S_V) phase. However, all the four phases cannot coexist at the same time since the number of phases coexisting in a one - component system cannot exceed three.

The phase diagram of sulphur system is represented in Figure.

The curve AO is the **sublimation curve of rhombic sulphur** and gives the vapour pressure of rhombic sulphur at different temperatures. The two phases in equilibrium are rhombic sulphur and the vapour. The equilibrium ($S_R \rightleftharpoons S_V$) is monovariant. Therefore, at one temperature, there can be one vapour pressure only.

The point O is the transition temperature (95.6°C) at which rhombic sulphur changes into monoclinic sulphur. O is thus a triple point at which three phases, two solids and the vapour (S_R - S_M - S_V) coexist in equilibrium. This is a non - variant point.

The curve OB is the sublimation curve of monoclinic sulphur. It gives vapour pressure of monoclinic sulphur at different temperatures. As the number of phases is 2, the system is monovariant.

The Clapeyron - Clausius equation can be used to study quantitatively the variation of vapour pressure of solid sulphur (S_R Or S_M) with temperature.

The point B is the melting point (120°C) of monoclinic sulphur. This is another triple point at which three phases, viz., sulphur monoclinic, liquid and vapour (S_M - S_L - S_V) are in equilibrium. This is a non - variant point.

The curve BE is the vapour pressure curve for liquid sulphur. The two - phase equilibrium ($S_L \rightleftharpoons S_V$) is monovariant.

The curve OC is the transition curve which gives the effect of pressure on the transition temperature of rhombic sulphur into monoclinic sulphur.

The equilibrium involved along the curve is $S_R \rightleftharpoons S_M$. Both the phases are solid. The system is monovariant. Since transformation of rhombic into monoclinic sulphur is accompanied by increase of volume, the increase of pressure causes a rise in the transition temperature. This can be predicted with the help of Clapeyron equation which, when applied to $S_R \rightleftharpoons S_M$ equilibrium, may be put

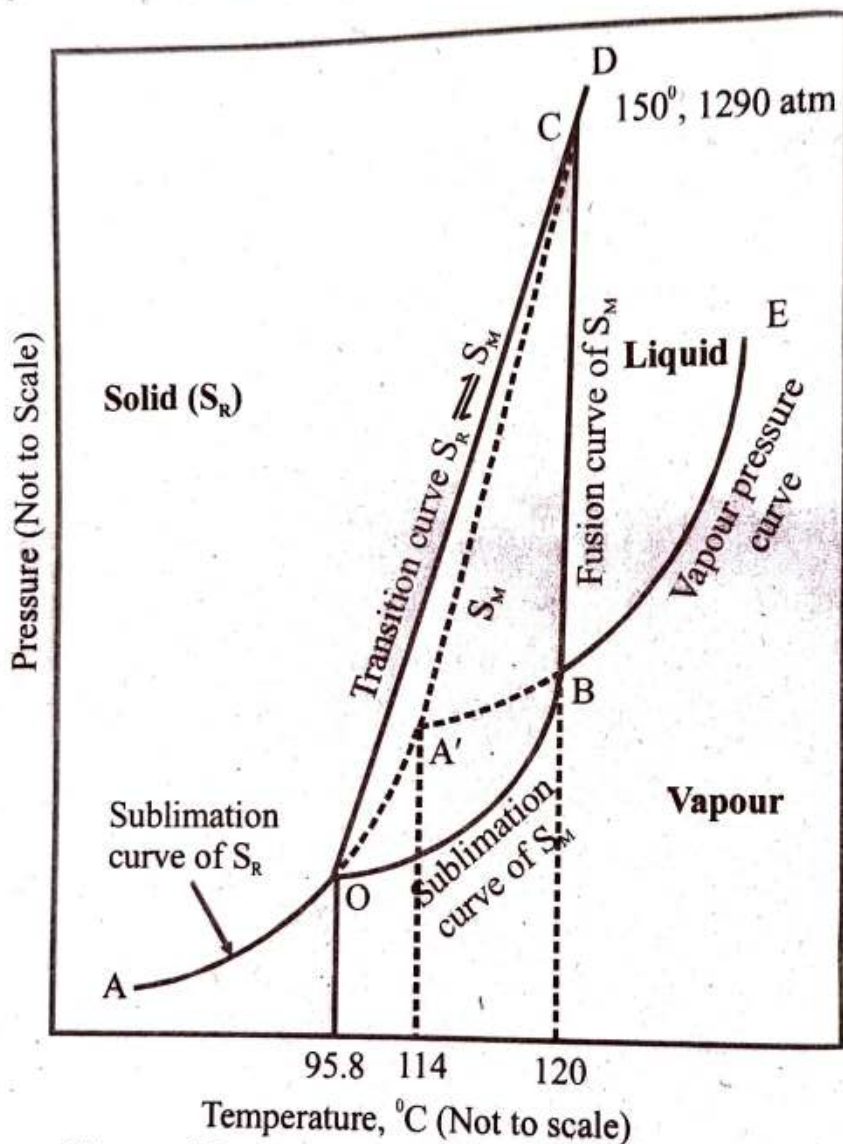


Figure - The phase diagram for the sulphur system

$$\frac{dP}{dT} = \frac{\Delta H_{trs}}{T(V_B - V_A)}$$

where ΔH_{trs} is the molar heat of transition. Since density of monoclinic sulphur (1.95 g cm^{-3}) is less than that of rhombic sulphur (2.05 g cm^{-3}), V_B is larger than V_A . The right hand side of the above equation is, therefore, positive. Hence, dP/dT should also have a positive sign. This means that increase of pressure raises the transition temperature. The curve OC, therefore, slopes away from the pressure axis.

The curve BC is the fusion curve for monoclinic sulphur. This gives the effect of pressure on the melting point of monoclinic sulphur. The two -phase

equilibrium ($S_M \rightleftharpoons S_L$) along the curve BC is univariant. As the melting of monoclinic sulphur is accompanied by a slight increase of volume, it follows from Clapeyron - Clausius equation that the melting point will rise slightly by the increase of pressure. The curve BC, therefore, slopes slightly away from the pressure axis. As the slope of this curve is much less than that of the curve OC, the two curves meet at the point C. Thus, C is another triple point where three phases, viz., rhombic sulphur, monoclinic sulphur and liquid sulphur ($S_R - S_M - S_L$) are the equilibrium and the system is non - variant. At C, the temperature is 151°C and the pressure is 1290 atm.

The curve CD is the fusion curve for rhombic sulphur. The equilibrium along this curve is $S_R \rightleftharpoons S_L$. As the number of phases is 2, the system is monovariant.

Metastable Equilibria: -

In addition to the stable equilibria discussed above, there are also some metastable equilibria indicated by the dotted lines in Fig. 4. Since the conversion of one solid into another solid, as that of rhombic sulphur into monoclinic sulphur, at the point O (95.6°C) involves molecular rearrangement necessary for bringing about the change in the crystalline form, the process is naturally slow. Therefore, unless heating is done extremely slowly, there is a possibility that the first solid may not change into the second solid at the normal transition point. The first solid, therefore, will exist in metastable equilibrium with its vapour.

The possibility in sulphur system is represented by the dotted line OA'. If the temperature of rhombic sulphur is allowed to rise rather quickly at about 95.6°C , it will persist in equilibrium with its vapour phase without changing into monoclinic sulphur for several degrees above the normal transition temperature. Thus, along the dotted curve OA' which is the extension of the curve AO, the metastable equilibrium, $S_R \rightleftharpoons S_V$ exists. The vapour pressure at each temperature, as can be seen, is higher than the vapour pressure of monoclinic sulphur which is the stable phase in this range.

Similarly, if liquid sulphur is allowed to cool along the curve EB, the solid phase (monoclinic sulphur) may not separate out at B unless cooling is extremely slow. The line BA' in this case represents the metastable equilibrium between liquid sulphur and its vapour (i.e., $S_L \rightleftharpoons S_V$). The point A', therefore, represents the melting point of the metastable rhombic sulphur. This is another triple point where the three phases, $S_R - S_L - S_V$, coexist in metastable equilibrium. The temperature A' has been found to be about 114°C .

The curve A'C, evidently, gives the effect of pressure on the melting point of metastable rhombic sulphur. In other words, this is the fusion curve of metastable rhombic sulphur along which rhombic sulphur is in metastable equilibrium with the liquid.

Areas: -

As the curves AO and OC both involve rhombic sulphur in equilibrium with the vapour phase in one case and solid monoclinic sulphur in the other, it can be shown that the area bounded by these lines towards the left represents conditions for the stable existence of rhombic sulphur alone. Similarly, as the curves BE and BC both have liquid phase as common, in equilibrium with vapour in the first case and with solid monoclinic sulphur in the second case, the area bounded by these lines represents liquid sulphur as the stable phase. Similarly, as the curves AO, OB and BE have the vapour phase as common, the area lying below these lines represents only vapour as the stable phase. Lastly, as the lines OC, OB and BC have monoclinic sulphur as the common phase, the triangular area bounded by these lines represents monoclinic sulphur as the stable phase. The existence of this form of sulphur, evidently, is limited on all sides.

Q.2. Calculate number of phases components and degree of freedom for



Ans. The number of components will depend upon the method used to prepare the system and the final status of the system. Thus, if we are given a mixture of three species, $C = 3$. Since $P = 3$, hence $F = C - P + 2 = 3 - 3 + 2 = 2$.

Thus, we need to specify two variables such as T and P .

If we are dealing with a mixture produced by the decomposition of CaCO_3 , only two components need to be specified since the third can be calculated from the stoichiometry of the reaction. Thus, $C = 2$ and since $P = 3$, therefore, $F = C - P + 2 = 2 - 3 + 2 = 1$ so that only T or P need to be specified.

Q.3. Discuss and apply phase rule to potassium iodide - water system. (2013)

Ans. Potassium iodide - water system:-

The potassium iodide - water system is a typical example of a binary system involving a salt and water which form a eutectic mixture.

One essential feature of a salt - water system is that the melting point of the salt is usually very high, even higher than the critical temperature of water. It is, therefore, not possible to represent melting points of both the components in the equilibrium diagram as has been done in the case of the binary systems involving metals.

The equilibrium diagram of potassium iodide - water system is shown in Fig. Its resemblance with the general diagram for binary systems forming eutectics is quite evident. However, the melting point of potassium iodide, as expected, is not realised in practice, as explained above.

A is the melting point of ice (or freezing point of water). At a pressure of 1 atm and in the presence of dissolved air, this temperature is 0°C . As potassium iodide is added, some of it dissolves in the water which was in contact with ice. The number of components rises to two. As the experiments are generally conducted at atmospheric pressure, the vapour pressure of water can be neglected in comparison and hence the vapour phase can be ignored. The

system, therefore, may be considered to have two phases, viz., ice and solution. Accordingly, the degree of freedom of the system at constant pressure, will be 1. Thus, corresponding to each temperature, there will be a definite composition of the solution. In other words, if the temperature changes, there will have to be a change in composition (concentration) of the solution and if the composition of the solution changes, there will have to be a corresponding change in temperature.

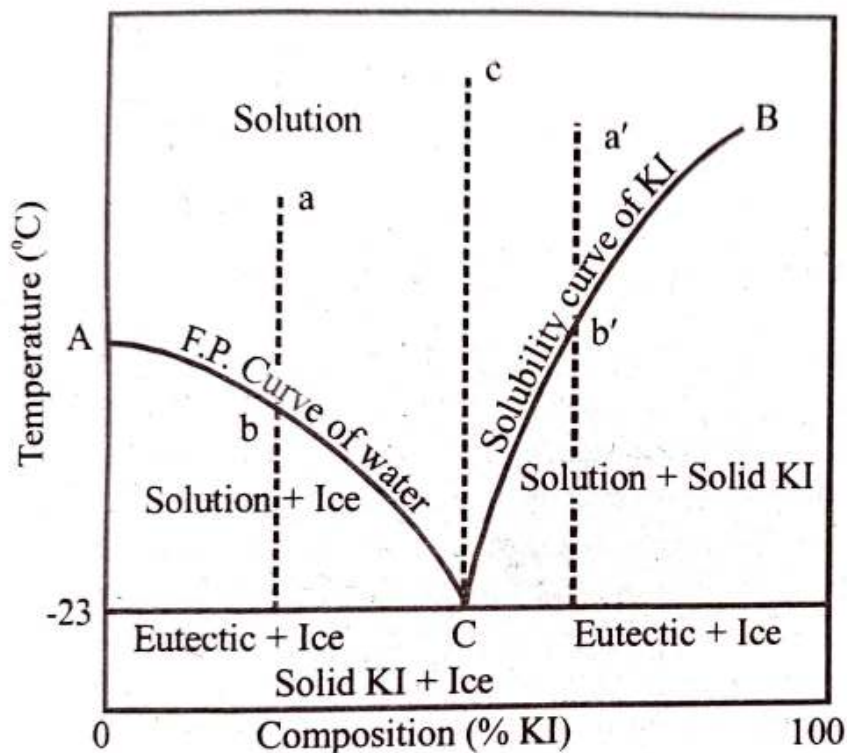


Figure - The phase diagram for the potassium iodide - water system

If the addition of potassium iodide is continued, there will be a change in the concentration of the solution and there will be a corresponding change in the temperature of the system. This is represented by the curve AC which is known as the **freezing point curve of water** (or **fusion curve of ice**). Along this line, the solution (containing potassium iodide in water) is in contact with ice. At the point C, the solution becomes saturated and, therefore, potassium iodide also separates out as another solid phase. The system now consists of three phases (solid ice, solid KI and solution) in equilibrium. The point C, therefore, is invariant at a constant pressure. This is the eutectic point of the system. The temperature at this point is -23°C which is the lowest temperature that can be attained in this system.

If the system at C is heated, ice will melt and solid potassium iodide will pass into solution in the same ratio in which it is already present in the solution so that composition of the solution remains unchanged. The temperature of the system does not rise so long as the number of phases is 3. The heat supplied to the system is utilised in bringing about the change of state of ice

into water. If heat continues to be supplied to the system and if potassium iodide is present in excess, ultimately ice will disappear. The system will be left with two phases (solid KI and solution) and will become univariant. The temperature will now rise but there will be a corresponding change in composition. The curve CB will be traced out. Since solid potassium iodide is in contact with its solution in water along the curve CB, this is known as the solubility curve of potassium iodide. The steep rise of the curve shows that the solubility of potassium iodide increases slowly with rise of temperature.

It may be noted that along both the curves AC and CB, the solutions of potassium iodide of varying compositions are in equilibrium with a solid phase, the solid being ice along AC and potassium iodide along CB. The two curves meet at the eutectic point C, which has been discussed above. In the area lying above the curves AC and CB, only solution phase can exist.

The existence of various phases in different regions of the equilibrium diagram is shown in the figure.

If a solution represented by the point a is cooled, the temperature will fall along ab without any change of composition as the system is bivariant. On reaching b, ice will separate out. The system will now become univariant. Therefore, the composition of the solution will change with temperature. Accordingly, on continued cooling, the composition of the solution will move along the freezing point curve AC until the eutectic point C is reached when potassium iodide will also separate out. The number of phases now rises to 3 and the degree of freedom at constant pressure falls to zero. Ultimately, the whole of the solution will freeze to give the eutectic mixture at a constant temperature. If a solution of composition, say, a', lying on the right of the eutectic point, is cooled, potassium iodide will begin to crystallise out as soon as the point b' is reached. The composition will henceforth change with the temperature along b' C and more of potassium iodide will continue to separate out until at the eutectic point C, ice also begins to deposit. Ultimately, as before, the whole of the solution will freeze to give the eutectic mixture consisting of 52% potassium iodide and 48% ice at a constant temperature.

Finally, consider a solution of composition represented by c which lies vertically above the eutectic point. When such a solution is cooled, the temperature will continue to fall along cC without any change in composition until the eutectic point C is reached when ice and potassium iodide both begin to separate out simultaneously. It will be seen from the above discussion that all solutions on cooling ultimately show an arrest or halt in temperature at the eutectic point. Further, when a solid mixture of the same composition as the eutectic mixture is heated, it melts sharply at the eutectic temperature. Hence, the mixture of potassium iodide and ice deposited at the eutectic point was at one time considered to be a definite compound of the form of a salt hydrate. This was given the name cryohydrate. However, a closer examination showed that physical properties such as density and heat of solution of the eutectic

solid were almost exactly equal to the mean values of the two constituents, namely, potassium iodide and ice, indicating that it is a mixture. Further, when the solid was examined under a powerful microscope, both the constituents were seen to lie as separate crystals. There is hardly any doubt, therefore, that the eutectic solid is a mixture and not a compound. The constancy of composition and melting point alone cannot establish a chemical compound.

Freezing Mixtures: -

The well known observation that the addition of salt to crushed ice produces an appreciable fall in temperature can readily be explained by means of a phase diagram of the kind shown in Fig.. Suppose, some salt, such as potassium iodide or sodium chloride, is added to ice in contact with a small amount of water at 0°C (point A). As some of the salt will dissolve in the water, there will be three phases, viz., salt, ice and solution in contact with one another. Now three phases can coexist in stable equilibrium only at the eutectic temperature. This temperature, in most cases, is considerably below the normal melting point of ice. Hence, ice will melt and the salt will dissolve in the water thus produced so that the composition varies along the line AC. Now, melting

Eutectic Temperatures and Eutectic Compositions of Some Common System

System	Composition (% salt in the eutectic)	Eutectic Temperature (°C)
NH ₄ Cl and Ice	20.1	-16.0
NH ₄ NO ₃ and Ice	43.0	-18.0
NaNO ₃ and Ice	33.3	-18.1
NaCl.2H ₂ O and Ice	23.0	-22.0
KI and Ice	52.0	-23.0
CaCl ₂ .6H ₂ O and Ice	15.2	-55.9

of the ice as well as dissolution of the salt are accompanied by absorption of heat. If the system is not in a position to absorb heat from the surroundings, its temperature will fall. This fall, which takes place along the line AC, will continue until the eutectic point is reached or until either salt or ice is used up completely. The lowest temperature that can be attained in the presence of excess of a salt and ice depends upon the eutectic temperature of the system.

The eutectic temperatures and eutectic compositions of some of the common systems are given in table.

Aceton -Dry Ice Freezing Mixture: -

Another freezing mixture, based on an entirely different principle, is the acetone - dry ice freezing mixture.

Dry ice, viz., solid carbon dioxide, changes directly to the gaseous state under atmospheric pressure. When dry ice is added to acetone contained

in a Dewar flask, it sublimes rapidly producing intense cold since the heat required for sublimation is taken from acetone. If sufficient amount of dry ice is added, the temperature of acetone can, theoretically, go down to approaching -95°C , the freezing point of acetone. This exceedingly low temperature can be maintained as long as sufficient amount of dry ice is present in acetone. However, due to radiation factors, etc., the temperature actually attained remains around -60°C which is a sufficiently low temperature indeed.

Q.4. State Gibb's phase rule. Draw and discuss the phase diagram of water system. Can all the three phase solid, liquid and gas coexist. (2017)

Other Related Questions -

Q. Discuss phase diagram of water system. (2019)

Q. State phase rule and discuss its application to water system. Draw the phase diagram. (2012)

Q. Define the term involved in phase rule. (2015)

Q. Explain with examples, phase component and degree of freedom. Discuss the application of phase rule to water system. (2014)

Ans. The phase rule is an important tool used for the quantitative treatment of systems in equilibrium. It enables us to predict the conditions that must be specified for a system to exhibit equilibrium. J.W. Gibbs enunciated the phase rule in 1876 while investigating heterogeneous equilibria. According to the phase rule, for systems in complete internal equilibrium.

$$F = C - P + 2, \quad \dots(i)$$

where C is the number of components ; p is the number of phases and F is the number of degrees of freedom.

Phase:-

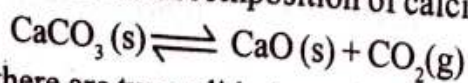
A phase is defined as any homogeneous and physically distinct part of a system which is bounded by a surface and is mechanically separable from other parts of the system. Examples of various types of phases are:

(i) A gas mixture constitutes a single phase since gases are completely miscible.

(ii) Immiscible liquids constitute different phases. Thus, carbon tetrachloride (CCl_4) and water (H_2O), which do not mix with each other, form two phases.

(iii) Completely miscible liquids such as water and alcohol and benzene and chloroform constitute one - phase systems.

(iv) Consider the decomposition of calcium carbonate into CO_2 and CaO .



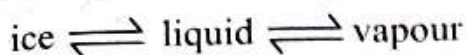
Here there are two solid phases and one gaseous phase. So it is a three - phase system.

Components :-

The number of components of a system at equilibrium is defined as the smallest number of independently variable constituents by means of which the composition of each phase can be expressed either directly or in terms of

chemical equations. We may consider a few examples:

(i) Water exists in three phases, viz.,



However, the composition of each phase can be expressed in terms of H_2O . Hence, it is a one component system.

(ii) Sulphur exists in four phases, viz., rhombic sulphur, monoclinic sulphur, liquid and vapour. But since the composition of each phase can be expressed in terms of sulphur only, it is a one component system.

(iii) Consider an aqueous sucrose solution. The composition of the solution phase can be expressed by specifying the amounts of sugar and water. Hence, it is a two - component system.

In a chemically reactive system, the number of components is given by

$$C = N - m - n - R \quad \dots(\text{ii})$$

where N is the number of chemical species, m is the number of independent equilibrium conditions, n is the number of relations between concentrations due to initial conditions and R is the number of independent chemical reactions. We can also write

$$C = N - E \quad \dots(\text{iii})$$

where E is the number of independent equations relating the concentrations of the N species. Each independent chemical equilibrium involving the constituents counts as one equation. The condition that a solution be electrically neutral also counts as one equation if ions are considered as constituents.

Degree of Freedom (F): -

The degree of freedom of a system is defined as the number of independent variables such as temperature, pressure and concentration (or composition) which must be specified in order to define the system completely. Thus , the state of a pure gas can be specified by two variables P and T or P and V , since the third variable can be calculated from the equation of state. This means that a pure gas has two degrees of freedom.

Consider now a one - component system having two phases. The example is furnished by water (liquid) in equilibrium with its vapour. The system will have only one degree of freedom because at a given temperature, the equilibrium vapour pressure of water can have only one fixed value. Thus, if temperature is specified, pressure becomes known automatically and vice-versa. We have to mention only one variable, either temperature or pressure. The system is, therefore, monovariant.

Finally, consider a one - component system having three phases. The example is furnished by ice, liquid water and vapour coexisting at the freezing point of water. This system will have no degree of freedom. The reason is that these three phases can coexist only at one particular temperature under one particular pressure. The mere statement that these three phases coexist defines the system completely.

Thus, if $F = 0$, the system is called invariant; if $F = 1$, univariant

(monovariant), if $F = 2$, bivariant and if $F = 3$, trivariant, etc.

We thus conclude that

1. The greater the number of components in a system, the greater is the number of degrees of freedom for a given number of phases.
2. The greater the number of phases, the smaller is the number of degrees of freedom, such as T , P and composition, required to specify the system completely.
3. For a given number of components, the number of phases is maximum when the number of degrees of freedom is zero. Thus, for a one - component system, the maximum number of phases is three and for a two - component system, the maximum number of phases is four.

Water System: -

Water can exist in three phases, namely, solid, liquid and vapour. Hence, there can be three forms of equilibria, viz.,

1- Liquid $\rightleftharpoons$ Vapour 2. Solid $\rightleftharpoons$ Vapour 3. Solid $\rightleftharpoons$ Liquid.

Each equilibrium involves two phases. The phase diagram for the water system is shown in Fig.

The curve OA represents the equilibrium between liquid water and vapour at different temperatures. It is called the vapour pressure curve of water as it gives the vapour pressure of water at different temperatures. It can be seen that, for any given temperature, there exists one and only one vapour pressure. Similarly, for each vapour pressure, only one temperature can be maintained. Thus, the degree of freedom of the system is one, i.e., the system is univariant:

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

At 100°C , the vapour pressure of water equals the pressure of the atmosphere (1atm = 760 mm Hg). This is, therefore, the boiling point of water. The curve OA extends as for the critical temperature of water (374°C) since above this temperature liquid water cannot exist.

The variation of vapour pressure with temperature is quantitatively given by Clapeyron equation or Clapeyron - Clausius equation, viz.,

$$\frac{dP}{dT} = \frac{\Delta H_{\text{vap}}}{T(V_g - V_l)} \text{ or } \ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{R} \left\{ \frac{T_2 - T_1}{T_1 T_2} \right\}$$

The curve OB represents the equilibrium between ice and vapour. It is called the vapour pressure curve of ice or sublimation curve of ice. Its lower end B extends to absolute zero. Again, as can be seen, for each temperature there can be one and only one pressure and similarly for each pressure, one and only one temperature can be maintained. In other words, the degree of freedom is 1.

The variation of vapour pressure of ice with temperature, is quantitatively given by Clapeyron or Clapeyron - Clausius equation, viz.,

$$\frac{dP}{dT} = \frac{\Delta H_{\text{sub}}}{T(V_g - V_s)} \text{ or } \ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{sub}}}{R} \left\{ \frac{T_2 - T_1}{T_1 T_2} \right\}$$

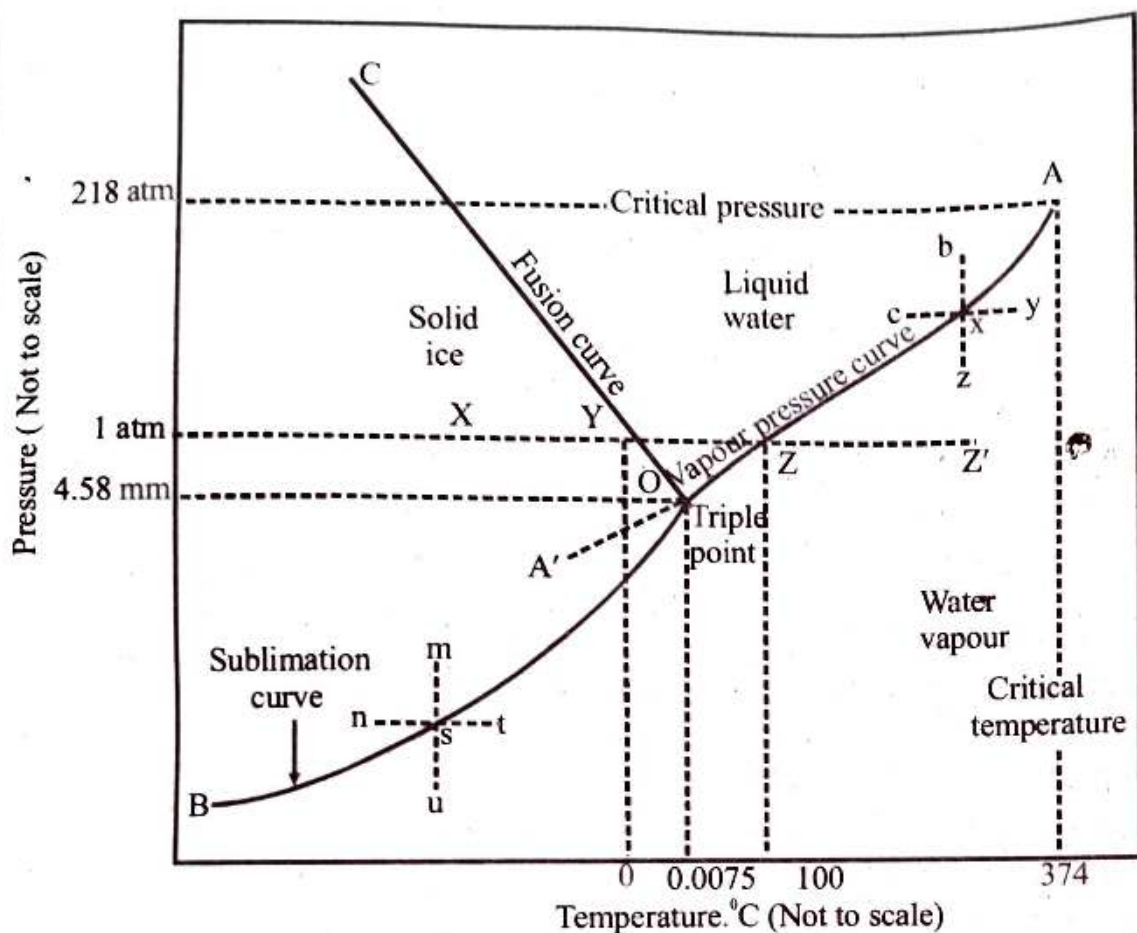


Fig. The phase diagram for the water system.

Since, along OA, the two phases are liquid and vapour and along OB, the two phases are solid and vapour, at the point O, where the two curves meet, three phases, namely, solid, liquid and vapour, will coexist. Such a point is known as the triple point. The temperature and pressure at the triple point of water are 0.0075°C and 4.58 mm of Hg, respectively. According to the phase rule, O is an invariant point:

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

The curve OC represents the equilibrium between ice and water. It is called the fusion curve of ice as it indicates the temperatures and pressures at which the solid (ice) and liquid (water) can coexist in equilibrium. In other words, this curve shows the effect of pressure on the melting point of ice. As can be seen, the line OC is inclined towards the pressure axis which indicates that the melting point of ice is lowered by increase of pressure. This follows from

Clapeyron equation, viz.,
$$\frac{dP}{dT} = \frac{\Delta H_{\text{fus}}}{T(V_l - V_s)} \text{ or } \frac{dT}{dP} = \frac{T(V_l - V_s)}{\Delta H_{\text{fus}}}$$

Since density of ice is less than that of water, V_s is greater than V_l . In other words, the expression on the right hand side of the above equation is negative. Hence, dT/dP should also have a negative sign. This means that the increase of pressure must lower and decrease of pressure must raise the freezing point

of water. It can be easily shown with the help of the above equation that freezing point of water is lowered by 0.0075°C by 1 atm increase in pressure. Thus, while the freezing point of water at a pressure of 4.58 mm is $+0.0075^{\circ}\text{C}$, at a higher pressure of 760 mm (i.e. 1 atm) it is reduced to 0°C .

Q.5. Define cooling curves in a two component system forming a eutectic.

Other Related Question -

Q. Define reduced phase rule equation and with the help of a general phase diagram discuss simple eutectic in a two component system. (2019)

Q. State the phase rule and discuss all the terms involved in it. Apply phase rule to lead silver system. (2010)

Ans. Two - Component Systems :-

For a two - component system, the phase rule becomes $F = 4 - P$

Since the minimum number of phases, P , in any system is 1, the maximum number of degrees of freedom, F , is 3. Thus, three variables would be necessary to describe a system. Since three variables are difficult to graph, it is customary to hold one of them say, the pressure, constant on a diagram of temperature plotted versus concentration. This reduces the degree of freedom of the system by one and the phase rule equation is then written as $F' = 3 - P$.

This is known as the **reduced phase rule equation**.

For the two - component solid - liquid equilibria, we come across the following cases: 1. The two components are miscible in the liquid state. 2 -The two components are only partially miscible in the liquid state. We shall restrict ourselves to the former case. Under this category, we shall discuss the following cases:

A- The two components are not miscible in the solid state and form a eutectic mixture.

B - The two components form a stable compound with congruent melting point.

C - The two components form a compound with incongruent melting point.

Some of these systems are -

Type A. Simple Eutectic Systems :-

The general phase diagram of such a system is presented in Fig.(a).

The points A and B represent the melting points of the components A and B. As increasing quantities of B are added to A, the freezing point of A falls along the curve AC. Similarly, as increasing quantities of A are added to B, the freezing point of B falls along the curve BC. Thus, along the curve AC, the solid A is in equilibrium with the solution (liquid) of the component B in A. This is called the freezing point curve of the component A. Similarly, along the curve BC, the solid B is in equilibrium with the solution (liquid) of the component A in B. This represent the freezing point curve of the component B. The number of phases along AC, as well as along BC, is two. Since measurements are made at atmospheric pressure (i.e., at constant pressure), we may apply the reduced

phase rule equation. Thus, we have $F' = C - P + 1 = 2 - 2 + 1 = 1$. Hence, the system is monovariant. The composition varies with temperature along AC or BC, as the case may be. The two curves intersect at some point C where both the solids A and B must be in equilibrium with the liquid phase (i.e., the liquid solution of the two components). The number of phases is 3. Applying the reduced phase rule equation, $F' = 0$. Thus, the system at C has no degree of freedom. It is invariant. This means that under a given pressure, the system consisting of two solids and their liquid solution, i.e., A - B - L, can exist only at a definite temperature and that the composition of the liquid (solution) phase also is definite. The point C, as can be seen, is the lowest temperature at which liquid can exist in equilibrium with the solids A and B. Since the mixture of A and B of composition corresponding to point C, has the lowest melting point, the point C is known as the eutectic point (eutectic means easy melting).

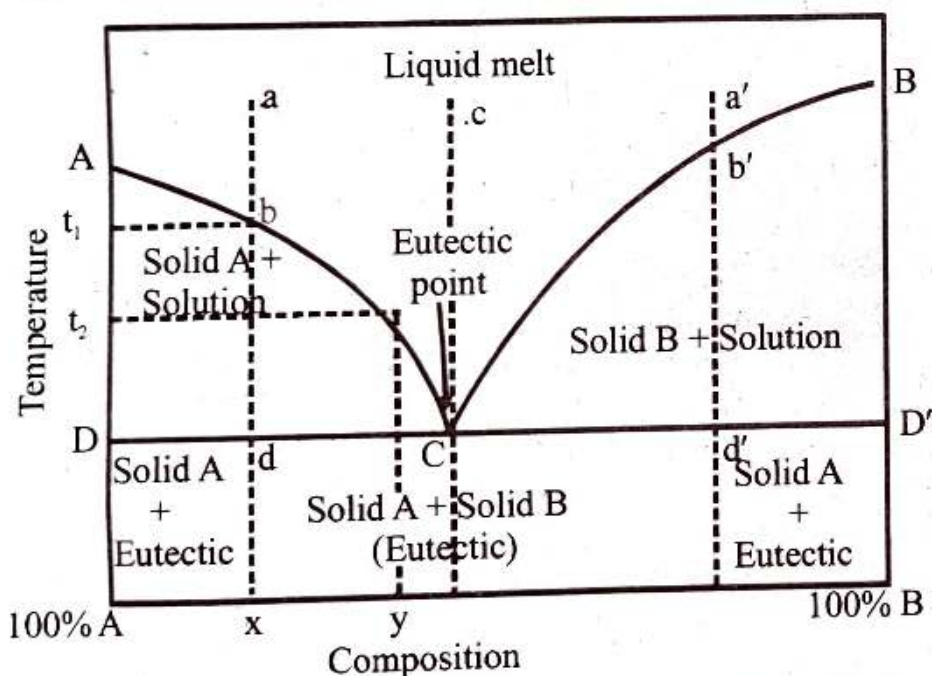


Fig.(a) - A simple eutectic system at constant pressure.

In the area above the line AC and BC, the two components are present only as a homogeneous liquid solution. As the system consists of only one phase in this area, it is bivariant. Therefore, in order to define any point in this area, it is necessary to specify the temperature as well as the composition. It is understood that the pressure has been kept constant.

Suppose, a liquid mixture of composition represented by point a is cooled at a constant pressure. The temperature will fall without any change of composition until the point b on the freezing point curve AC is reached. At this temperature, which corresponds to t_1 , the solid A separates out. The system now consists of two phases and is, therefore, monovariant (assuming pressure to be constant). The temperature will fall only with change in composition of the liquid phase. Therefore, as cooling continues, the component A keeps on separating out and the solution becomes relatively richer in B. The temperature

and the solution composition both change along the curve bC. Thus, at temperature t_1 , solid A is in equilibrium with solution of composition x and at temperature t_2 it is in equilibrium with solution of composition y. It is evident, therefore, that in area ACD, solid A is in equilibrium with solutions of varying composition given by the curve AC depending upon the temperature.

When the eutectic temperature is reached at d, the second solid B also begins to crystallise out. The system now has 3 phases and, therefore, at constant pressure, it becomes invariant. On further cooling the system, solid A and solid B separate out together in a fixed ratio so that the composition of the solution remains constant as indicated by the point C. The temperature also remains constant. When the solution phase has been completely solidified and the system consists only of a mixture of solid A and solid B, it becomes monovariant and continued cooling results in fall of temperature below the line DD' into the area within which only the two solids coexist, as shown.

Similarly, if the composition of the original liquid is on the right side of the eutectic point, as represented, say, by the point a', similar series of changes will be observed on cooling. In this case, however, on reaching the point b' on the freezing point curve BC, the solid B will separate out. As cooling continues, B keeps on separating and the solution becomes now richer and richer in A. The temperature and the composition both change along the curve b' C. Thus, in the area BCD', solid B is in equilibrium with solutions of varying composition. Again, when the eutectic temperature is reached at the point d', A also begins to separate out. The system now becomes invariant. On withdrawing heat further from the system, the temperature remains constant and solid A and solid B continue to separate in the same ratio so that the solution composition also remains constant. Ultimately, the solution phase solidifies completely as before and thereafter the temperature of the system can fall below the line DD' into the area of coexistence of two solids A and B.

Consider a special case when the liquid has the same composition as that of the eutectic. This is represented by the point c. On cooling, no solid will separate out until the eutectic temperature is reached. At this temperature, both the solids A and B crystallise out simultaneously. The temperature and composition of the solution remain constant until the system gets completely solidified.

Thermal Analysis. Cooling Curves: -

It can be seen on reference to Fig.(a) that when a liquid mixture (or melt) consisting of A and B is allowed to cool, solid A (or solid B) begins to separate out as soon as the temperature falls to a point on the line AC (or BC), as the case may be. The number of phases is now two, viz., the liquid mixture and the solid A or B. If cooling is continued thereafter, the given solid continues to deposit with the corresponding fall in temperature till the eutectic temperature (point C) is reached. At this point both the solids separate out and the number of phases rises from two to three. The system now becomes invariant and, therefore, the temperature remains constant.

One important point to be remembered in this connection is that the separation of the solid A (or B) from the liquid solution is an exothermic process. The heat evolved in the process is similar to the heat given out when the same substance changes from liquid to solid state at its freezing point. As a result of this, the rate of cooling is diminished as soon as the separation of solid A or B commences to take place. The rate of cooling is, therefore, slower than that before till the eutectic point is reached. After this, temperature remains unchanged.

The above facts can be represented by plotting fall of temperature with time as in Fig.(b). Such a graph is called a cooling curve. In the figure, the rate of cooling along ab is quite rapid. This is when separation of a solid has not yet commenced. At b one of the solids begins to separate. The rate of cooling along bd, therefore, slows down. The cooling curve thus shows a distinct break at the point b. At d, the eutectic point is reached. The temperature, therefore, remains constant along dd' until the solidification has taken place completely. With the disappearance of the liquid phase, the system now consisting only of solid phase, becomes univariant and further cooling results in fall of temperature along d'e. Thus, there are three breaks in the cooling curve. The first one occurs at the freezing point of the mixture where the solid first commences to form. The second break occurs at the eutectic point and the third one occurs when the mixture gets completely solidified.

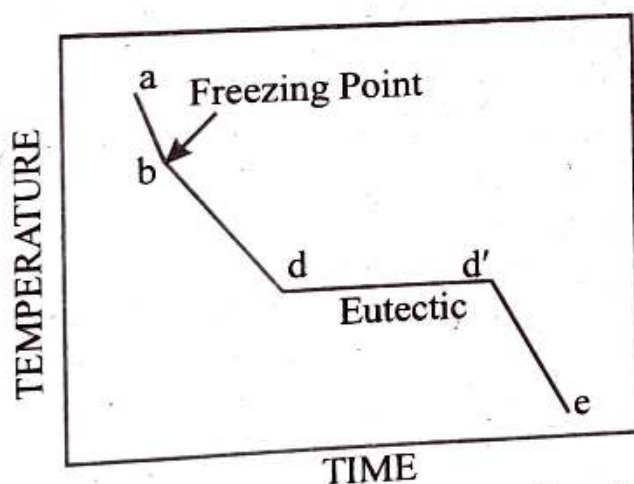


Fig.(b) - A cooling curve in a two component system forming a eutectic

The above discussion provides a basis for the principle on which the method of thermal analysis used in the study of solid - liquid phase equilibria involving metals, is based. In actual practice, a number of mixtures of metals A and B of different compositions lying between 100% A and 100% B are prepared. These are heated above their respective melting points so that there is only one phase (i.e., liquid phase) in every case. Each liquid is then allowed to cool slowly and the temperature is recorded after small intervals of time. In this way several cooling curves are obtained, as shown in Fig.(c). The first break in each curve occurs at the freezing point, that is, at the commencement of

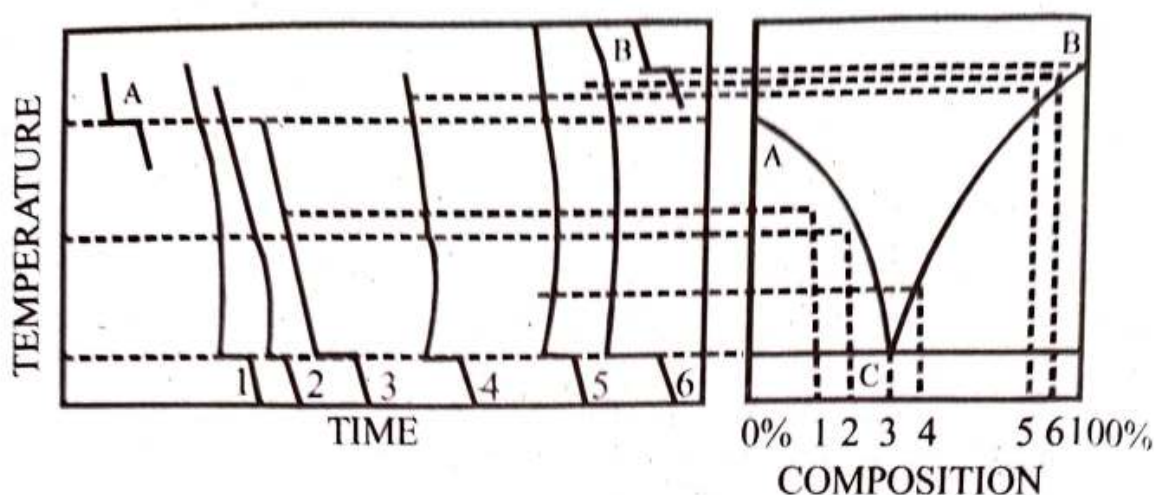


Fig. (c) Cooling curves for different composition in a two-component system forming a eutectic.

the freezing of the mixture of that particular composition. As the mixtures differ in the compositions, their freezing will commence at different temperatures. The second break occurs at the point at which the temperature remains constant. This gives the eutectic temperature which will be the same in all the mixtures irrespective of their initial compositions. The freezing points of pure A and pure B (i.e., 100% A and 100% B) are also determined in a similar manner. The equilibrium diagram for the system of two metals (A and B) under examination is thus determined. This is illustrated in Fig.(c).

There are many two - component systems which follow the general behaviour as depicted in Fig.(a). They include pairs of metals, metallic alloys, organic compounds and a number of salts and water. Two representative cases, one involving metals and the other involving a salt and water will be discussed here.

Lead - Silver System: -

These metals are completely miscible in liquid state and do not give rise to any compound formation. The equilibrium diagram, therefore, is similar to that shown in Fig.(a). The various features are illustrated in Fig.(d).

Pure lead melts at 327°C and the addition of silver lowers its melting point along AC. Thus, AC is the freezing point curve of lead containing varying amounts of silver. Pure silver melts at 961°C and the addition of lead lowers its melting point along BC. Thus, BC is the freezing point curve of silver. Along AC, solid lead and solution (melt) coexist while along BC, solid silver and solution (melt) coexist. The system, at constant pressure, is monovariant along AC as well as along BC.

C is the **eutectic point** where the three phases, solid lead, solid silver and their liquid solution (melt), coexist. It is an invariant point. The temperature of the eutectic is 303°C and the composition of the solution phase is 2.6 per cent silver, as shown in the figure. The phases coexisting in the various areas or regions are also shown in the fig.(d).

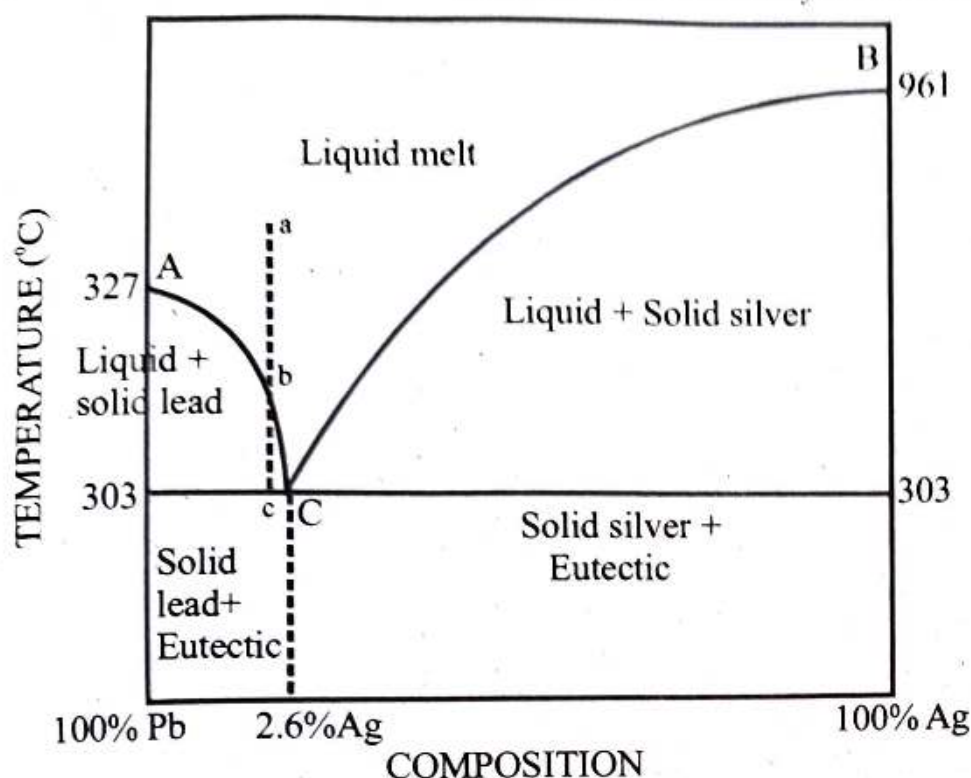


Fig.(d) - The phase diagram for lead-silver caption system

The phase diagram of lead -silver system has a special significance in connection with the desilverisation of lead. The argentiferous lead consisting of a very small percentage of silver is first heated to a temperature well above its melting point so that the system consists only of the liquid phase represented, say, by the point a, in the fig.(d). It is then allowed to cool. The temperature of the melt will fall along the line ab. As soon as the point b is reached, lead will begin to crystallise out and the solution will contain relatively increasing amounts of silver. Further cooling will shift the system along the line bC. Lead continues to separate out and is constantly removed by means of ladels. The melt continues to be richer and richer in silver until the point C is reached where the percentage of silver rises to 2.6. Thus, the original argentiferous lead which might have contained 0.1 percent (or even less) of silver, can now contain up to 2.6 percent of this metal. The process of raising the relative proportion of silver in the alloy is known as **Pattinson's process**.

Type B. Systems in which two components form a stable compound :-

There are again numerous systems including metals, organic compounds and inorganic salts dissolved in water, which fall under this category. The two components of the system at a certain stage enter into chemical combination with one another forming stable compounds. Thus, a number of intermetallic compounds when the two components are metals, are formed. Similarly, several double compounds are formed when the two components are organic compounds. In the case of system involving salt and water, a number of salt hydrates are formed.

Such systems are of two kinds depending upon whether the compound formed has a congruent or an incongruent melting point.

Class I. Formation of Compounds with Congruent Melting Points: -

A compound which melts sharply at a constant temperature into a liquid of the same composition as the solid, is said to possess a **congruent melting point**. To take a general case, let A and B be the two components and AB a stable solid compound formed by their chemical combination. The phase diagram will be of the type shown in Fig.(e). In this system there are three different solid phases, namely A, B and the compound AB. Accordingly, there will be three fusion or freezing point curves AC, BE and CDE. While along AC, the solid A is in equilibrium with the liquid phase and along BE, the solid B is in equilibrium with the liquid phase, along the central portion CDE, the solid compound AB is in equilibrium with the liquid phase, at different temperatures. The maximum point D of the curve is the congruent melting point of the compound because the solid and liquid phases now have the same composition. Evidently, at this temperature, the two - component system has become a one - component system because both solid and liquid phases contain only the compound AB. Therefore, according to the phase rule, D is a non - variant point. This represents a definite temperature just like the melting points A and B of the pure components. The congruent melting point D of compound AB has been shown to lie above the melting points of the pure components A and B. But, it is not necessarily so always. There are different types of systems known in which the congruent melting point of the compound formed lies above, below or in - between the melting points of the pure components.

In the fig.(e), the compound has been shown to contain equimolar amounts of A and B. This is not necessarily so in every system.

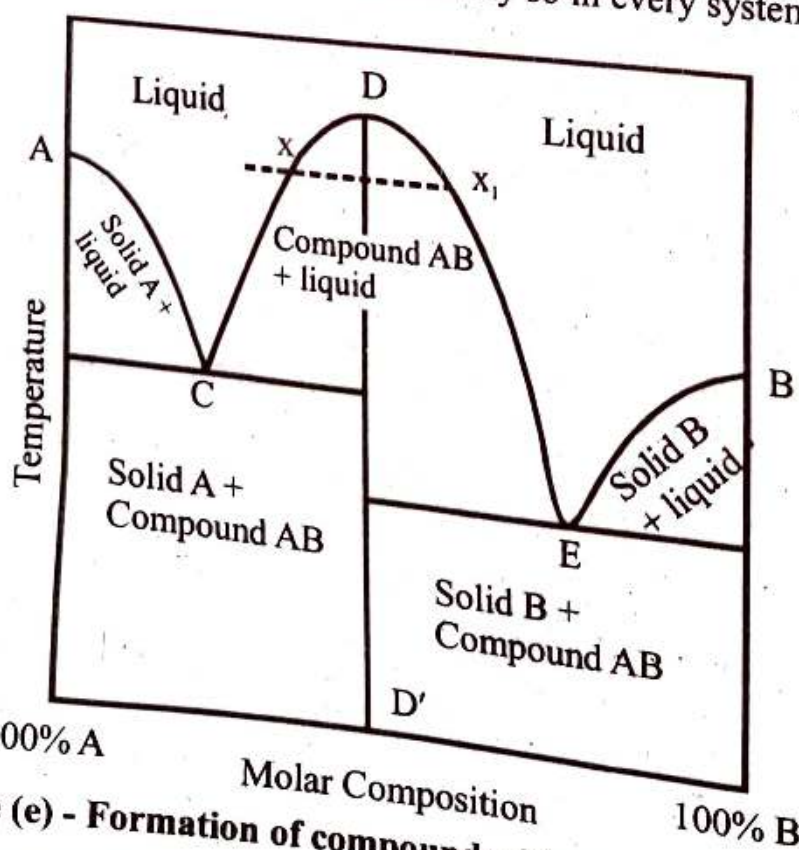


Figure (e) - Formation of compound with congruent melting point.

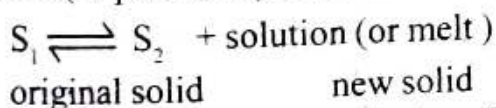
There are two eutectic points in such a system as represented by C and E in the fig.(e). At C, the solids A and AB are in equilibrium with the liquid phase while at E, the solids B and AB are in equilibrium with the liquid phase.

It can be seen that at a certain temperature, say, t , the liquid phase can have two compositions, x and x_1 in equilibrium with the same solid AB. In other words, the compound AB can have two solubilities at the same temperature. This paradox can readily be explained if the diagram is looked upon as made up of two parts with DD' as the dividing line. The left half of the diagram shows two-component system: A and AB while the right half shows the two - component system: B and AB. On the left hand side, the curve DC represents the usual depression in freezing point of the compound AB on the addition of A while on the right hand side, the curve DE represents the usual depression in freezing point of the compound AB on the addition of B.

The names of the various phases in different areas of the diagram are represented in the fig.(e). The two component systems which form one or more compounds with congruent melting points include zinc - magnesium, aluminium - magnesium, mercury - thallium, gold - tin and phenol - aniline systems. Amongst the salt hydrates, $\text{FeCl}_3 - \text{H}_2\text{O}$ system falls into this category.

Case II. Formation of Compounds with Incongruent Melting Points: -

In many systems, the compounds formed by the combination of two components, instead of melting congruently, decompose when heated giving a new solid phase and a solution with a composition different from that of the solid phase. Such a compound is said to have an **incongruent melting point**. Its decomposition at this temperature is known as transition reaction or meritectic (or peritectic) reaction and may be represented by the equation.



The incongruent melting point is, therefore, also known as transition temperature or meritectic or **peritectic temperature**.

The incongruent melting point is, therefore, also known as **transition temperature** or **meritectic** or **peritectic temperature**.

Since during the peritectic reaction, as represented by the above equation, the number of phases is 3 (two solids and one liquid), the system is invariant (i.e., $F' = 0$) as the pressure is fixed. Hence, the temperature as well as the composition of all the phases remain fixed.

The general phase diagram for this type of systems may be represented graphically as in Fig.(f). Let A and B be the two components which combine to form a compound AB_2 . The points A and B represent the respective melting points of the two pure components while D represents the incongruent melting point (or transition temperature) of the compound AB_2 . Here this compound breaks down to give a new compound. This point lies below E which may be taken as the hypothetical congruent melting point of the compound AB_2 . AC is the fusion curve of A along which the solid is in equilibrium with the liquid. BD

is the fusion curve of B along which the solid B is in equilibrium with the liquid

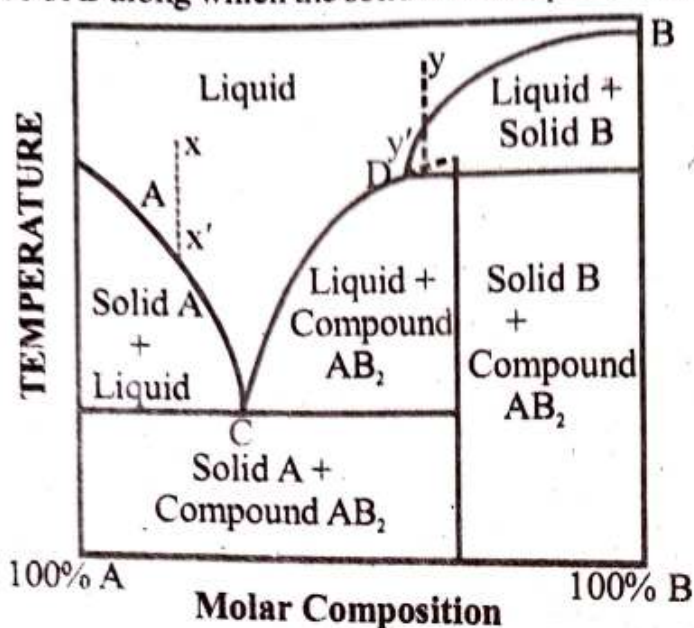
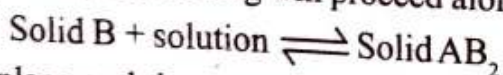


Fig.(f) - Formation of compound with incongruent melting point

On cooling a liquid of composition x , A is the first solid to separate out at the point x' . Further cooling then proceeds with change of composition along $x'C$. At C the compound AB_2 commences to form. Since the system now consists of two solids and one liquid phase (excluding the vapour phase), applying the reduced phase rule the system at C is non-variant. If a liquid of composition y is cooled down, the first solid to separate out will be solid B at point y' . Further cooling will proceed along $y'D$. At D, the peritectic reaction



takes place and the compound AB_2 separates out. Since the system will now have three phases, it will again become non-variant. The transition of solid AB_2 into compound AB_2 will take place at constant temperature till the whole of solid B disappears. Point D is, thus, the peritectic point.

Picric acid - benzene, gold - antimony and sodium - potassium are some examples of two - component systems which give rise to compounds with incongruent melting points. Amongst the salt hydrates, mention may be made of sodium sulphate - water system.

Calculation of Eutectic Point and Eutectic Composition: -

When a two - component solution is cooled to a low temperature, a component which is present in excess separates out as solid at the freezing point of the solution. The variation of the freezing point with composition is given by the following expressions:

$$d \ln x_A = (\Delta H_{\text{fus}A} / RT^2) dT \quad \dots\dots(i)$$

$$d \ln x_B = (\Delta H_{\text{fus}B} / RT^2) dT \quad \dots\dots(ii)$$

where the ΔH_{fus} s are the enthalpies of fusion of the two components and

and x_B are their mole fractions. Assuming that the components A and B behave ideally and ΔH_{fus} is independent of temperature, we can integrate Eq.(i) and (ii) for the limits $T = T_{\text{fus}}$, the melting point and $T = T_e$, the eutectic point, to obtain

$$-\ln(x_A)_e = \frac{\Delta H_{\text{fus},A}}{R} \left(\frac{1}{T_e} - \frac{1}{T_{m,A}} \right) \quad \text{.....(iii)}$$

$$\text{and } -\ln(x_B)_e = \frac{\Delta H_{\text{fus},B}}{R} \left(\frac{1}{T_e} - \frac{1}{T_{\text{fus},B}} \right) \quad \text{.....(iv)}$$

Using Eq. (iii) and (iv), we can calculate T_e , the eutectic point as well as the eutectic composition, viz., $(x_A)_e$ and $(x_B)_e$.

Q.6. Write short note on Eutectic mixture.

Ans. A eutectic mixture is defined as a mixture of two or more components which usually do not interact to form a new chemical compound but, which at certain ratios, inhibit the crystallization process of one another resulting in a system having a lower melting point than either of the components. Eutectic mixtures, can be formed between Active Pharmaceutical Ingredients (APIs), between APIs and excipient or between excipient; thereby providing a vast scope for its applications in pharmaceutical industry. Eutectic mixture formation is usually, governed by following factors: (a) the components must be miscible in liquid state and mostly immiscible in solid state, (b) Intimate contact between eutectic forming materials is necessary for contact induced melting point depression, (c) the components should have chemical groups that can interact to form physical bonds such as intermolecular hydrogen bonding etc., (d) the molecules which are in accordance to modified VantHoff's equation can form eutectic mixtures.

Q.7. Define reduced phase rule equation.

Ans. Reduced Phase Rule Equation: -

In the study of two-component system, usually, one of the three variables is kept constant and therefore, the degree of freedom is reduced by one.

Hence, the phase rule equation for two components reduces to $F = C - P + 1$, and called reduced phase rule equation.

This condensed phase rule has two variables, namely temperature and concentration (or composition) of the constituents. Therefore, the solid-liquid equilibria are represented on temperature composition diagram.

Unit III

Q.1. What do you mean by reversible electrodes? How are they classified? Give their example. (2017)

Other Related Questions -

Q. Write short note on reversible and irreversible electrodes. (2016)

Ans. Electrode Composition: -

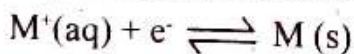
Electrodes are composed of variety of metals. While silver and gold have been traditionally used, a variety of other metals are used. Electrodes are reversible or irreversible. Reversible electrodes include the typical silver chloride electrodes. Reversible electrodes have easy bidirectional chemical reactions accounting for the movement of charge. Non-reversible electrodes have difficulty with electron flow in one direction, essentially conducting electric charge mainly in one direction well, and the opposite direction less well. A junction potential can be developed across interfaces, which can create electrode pops and distort the frequency response of the recording system.

Reversible Electrodes :-

1- Metal - Metal Ion Electrodes: -

An electrode of this type consists of a metal rod dipping in a solution containing its own ions, as, for example, zinc rod dipping in zinc sulphate solution or a copper rod dipping in copper sulphate solution, as in the Daniell cell.

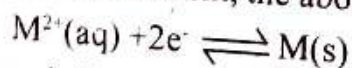
If the metal is univalent, the electrode reaction may be represented as



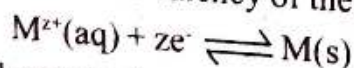
If the metal rod behaves as positive electrode (i.e., the reaction at the electrode involves reduction), the equilibrium will shift towards the right. The concentration of M^+ ions in solution will, therefore, decrease.

If, on the other hand, the metal rod behaves as negative electrode (i.e., the electrode reaction involves oxidation), the above equilibrium will shift towards the left. The concentration of the M^+ ions in solution will, therefore, increase. The electrode is thus reversible with respect to M^+ ions.

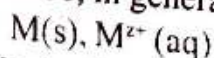
If the metal is bivalent, the above equilibrium may be represented as



In general, if the valency of the metal is z , the equilibrium is represented as



The electrode, in general, is represented as

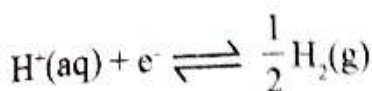


2. Gas Electrodes:-

a. Hydrogen Electrode -

Hydrogen gas bubbling in a 1M solution of an acid (say, hydrochloric acid) forms an electrode of this type. The equilibrium in this case is represented as

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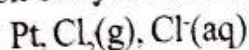


The electrode is reversible with respect to hydrogen ion.

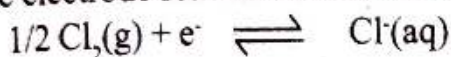
Since hydrogen gas is nonconducting, platinum or some other metal which is not attacked by the acid and easily comes into equilibrium with hydrogen, is used for making electrical contact in the circuit (Fig.1) The electrode is represented as $\text{Pt}; \text{H}_2(\text{g}), \text{H}^+$. It is called **standard hydrogen electrode (SHE)**.

b. Chlorine Electrode -

In this electrode, chlorine gas at a given pressure is bubbled into a solution of hydrochloric acid. The electrode, is represented as



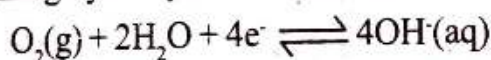
and the electrode reaction is written as



The electrode is evidently reversible with respect to chloride ion.

c. Oxygen Electrode -

In this electrode, oxygen gas at a given pressure is bubbled through a solution containing hydroxyl, OH^- , ions. The electrode reaction is written as



But, since equilibrium between oxygen gas and hydroxyl ions in solution cannot be established quickly, oxygen electrode does not behave as a truly reversible electrode.

3. Metal - Insoluble Metal Salt Electrodes: -

These electrodes consist of a metal and a sparingly soluble salt of the same metal dipping in a solution of a soluble salt having the same anion. An important electrode of this type is the calomel electrode.

Calomel Electrode :-

Calomel electrode consists of mercury, solid mercurous chloride and a solution of potassium chloride. The electrode is represented as $\text{Hg}, \text{Hg}_2\text{Cl}_2(\text{s}); \text{KCl}(\text{solution})$.

It can be easily set up in the laboratory as follows: Mercury of high grade purity is placed at the bottom of a glass tube having a side tube on each side (Fig.2.) Mercury is covered by a paste of mercurous chloride (calomel), as shown. A solution of potassium chloride is introduced above the paste through the side tube shown

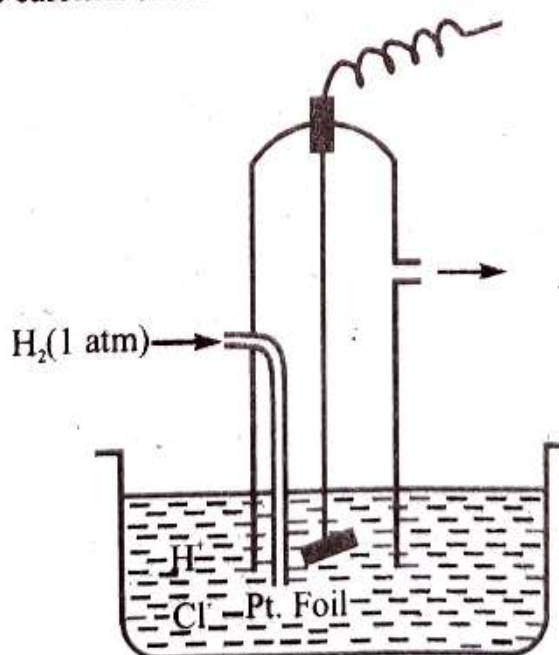
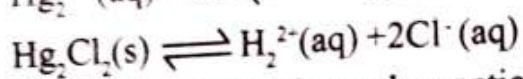
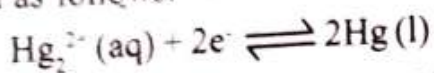


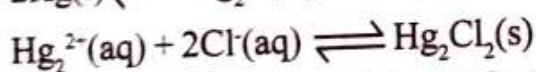
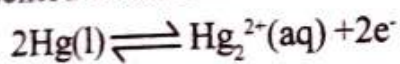
Figure - The hydrogen electrode

on the right. The concentration of the solution is either decinormal, nor else the solution is fully saturated. The solution also fills the side tube in a jet on the left. A platinum wire sealed into a glass tube serves to electrical contact of the electrode with the circuit.

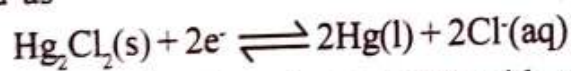
If the electrode reaction involves reduction, the Hg_2^{2+} ions furnish the sparingly soluble mercurous chloride would be discharged at the electrode. Hence, more and more of calomel would pass into solution. The result is an increase in the concentration of chloride ions. The reactions may be represented as follows:



If, on the other hand, the electrode reaction involves oxidation, it would liberate electrons and send Hg_2^{2+} ions into solution. The Hg_2^{2+} ions would combine with Cl^- ions (furnished by KCl) forming sparingly soluble Hg_2Cl_2 . The result is a fall in the concentration of chloride ions in the solution. The reactions may be represented as follows :



Thus, in the case of the calomel electrode, the electrode reaction may be represented as



The electrode, therefore, is reversible with respect to chloride ion.

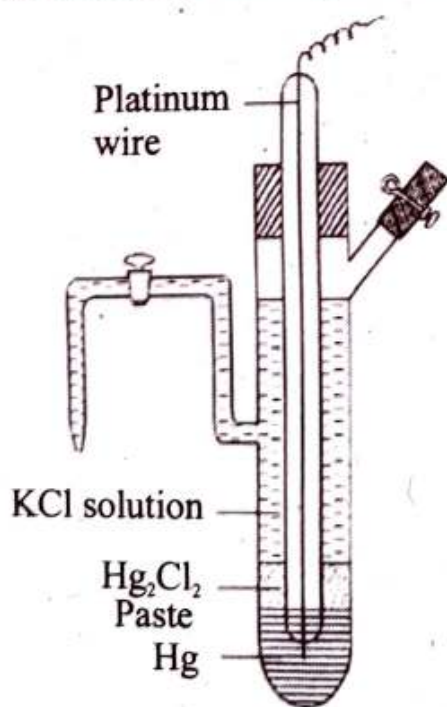
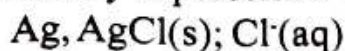


Figure - The calomel electrode

Another common electrode of this type is the silver-silver chloride electrode which consists of a silver wire coated with a layer of silver chloride inserted in a solution of KCl or HCl of a known concentration. The electrode reaction is

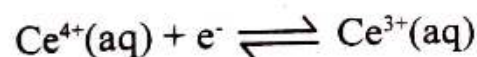
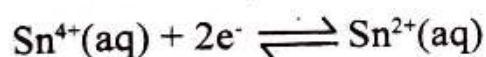
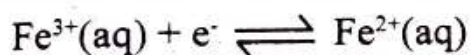
schematically represented as



The electrode is reversible with respect to Cl^- ion.

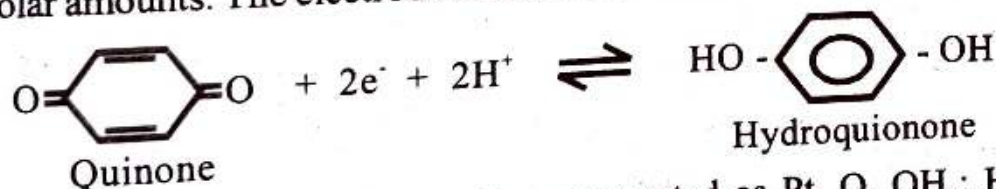
4. Oxidation -Reduction Electrodes: -

The term oxidation -reduction electrode is used for those electrodes in which the potential is developed due to the presence of ions of the same substance in two different valence (i.e., oxidation) states. Such an electrode is set up by inserting an unattackable metal (e.g., platinum) in an appropriate solution. Thus, when a platinum wire is inserted in a solution containing Fe^{2+} and Fe^{3+} ions, it is found that the wire acquires a potential. The same thing happens when a platinum wire is inserted in a solution containing Sn^{2+} and Sn^{4+} ions or Ce^{3+} and Ce^{4+} ions. The potential at the electrode arises from the tendency of the ions in one oxidation state to change into the other more stable oxidation state. The electrode reactions may be represented as follows :



The function of the platinum wire is to 'pick up' the electrons and to provide electrical contact to the electrode.

Another important but a slightly different type of oxidation - reduction electrode is the so called quinhydrone electrode which consists of a platinum wire placed in a solution containing hydroquinone (QH_2) and quinone (Q) in equimolar amounts. The electrode reaction in this case is represented as follows:



This electrode, which may be represented as $\text{Pt}, \text{Q}, \text{QH}_2; \text{H}^+(\text{aq})$, is evidently reversible with respect to H^+ ions.

Q.2. Show how the solubility and solubility product of sparingly soluble salt can be determined with the help of EMF of the cell. (2015)

Ans. Determination of solubility of sparingly soluble salts:-

The solubility and solubility product of sparingly soluble salts like AgCl , PbSO_4 , AgI , etc., can be calculated by measuring the EMF of a suitable concentration cell composed of salt under investigation. For example, if it is required to determine the solubility and solubility product of AgCl the following cell may be constructed

$\text{Ag}|\text{AgCl}; 0.01\text{N KCl}|\text{Saturated } \text{NH}_4\text{NO}_3|| 0.01\text{N AgNO}_3|\text{Ag}$
by placing one Ag electrode in contact with AgNO_3 of known concentration (say, 0.01N) and the other in contact with 0.01N KCl solution containing a drop of AgNO_3 . The added AgNO_3 drop will produce a small amount of AgCl which

will be sufficient to give its saturated solution. The two solutions are connected through a saturated NH_4NO_2 salt bridge in order to avoid liquid junction potential. The EMF of the above concentration cell is given by

$$E = \frac{2.303RT}{1 \times F} \log \frac{0.01}{C}$$

where C = concentration of Ag^+ ions furnished by AgCl in KCl solution. By measuring EMF, E , of the cell the value of C can be calculated. If 0.01KCl is assumed to be completely ionised, then $[\text{Cl}^-] = 0.01$.

$$\therefore K_s, \text{ the solubility product of } \text{AgCl} = [\text{Ag}^+][\text{Cl}^-] \\ = C \times 0.01$$

$$\text{Then solubility of } \text{AgCl}, S = \sqrt{K_s} \\ = \sqrt{C \times 0.01} \text{ g mole/litre}$$

Q.3. Show that equilibrium constant K_c can be calculated if standard emf of the cell is known. (2015)

Ans. Standard EMF and Equilibrium Constant :-

If the standard EMF (E^0) of a particular cell is known, the equilibrium constant of the cell reaction can be calculated straightaway by making use of the relation

$$-\Delta G^0 = RT \ln K = nFE^0 \text{ whence } \ln K = \frac{nFE^0}{RT}$$

$$\text{or } \log K = \frac{nFE^0}{2.303RT}$$

Q.4. Show that equilibrium constant of the cell reaction can be calculated by knowing EMF of the cell and concentration of the reactants and products of the cell reaction. (2013)

Ans. EMF of the cell and equilibrium constant of a cell reaction:-

Consider, the general electrochemical cell reaction



The decrease in free energy - ΔG for the process is given by thermodynamic equation,

$$-\Delta G = -\Delta G^0 - RT \ln Q$$

where $-\Delta G^0$ = decrease in free energy of system when the substances are in their standard states of unit activity, ...(i)

Q = Reaction quotient

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The electrical energy produced during the reaction by the cell in nFE volt.

$$-\Delta G = nFE$$

$$nFE = -\Delta G^\circ - RT \ln Q \quad \dots(ii)$$

we know that $-\Delta G^\circ = RT \ln K$

where K is the equilibrium constant for the cell reaction.

Substituting in eqn. (ii), we get

$$nFE = RT \ln K - RT \ln Q$$

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

Changing $\ln$ to $\log 10$, we get

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log K - \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \dots(iii)$$

At 25°C , the value of $\frac{2.303RT}{nF}$ is

$$= \frac{2.303 \times 8.313 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{(n) \times 96500 \text{ C mol}^{-1}} = \frac{0.0591}{n} \text{ volt}$$

Putting value in eq.(iii)

$$E_{\text{cell}} = \frac{0.0591}{n} \log K - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

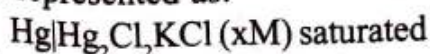
The equilibrium constant of the cell can be calculated from this equation if we know the Emf of the cell and the concentration of reactants and products of the cell reaction.

Q.5. Write short note on calomel electrode. (2013)

Ans. A calomel electrode is a reference electrode that is based on reactions between mercury (I) chloride (calomel) and elemental mercury. The aqueous phase in contact with both the calomel and the mercury is a saturated solution of water and potassium chloride. The linking of the electrode is through a porous frit to the solution that contains the other electrode.

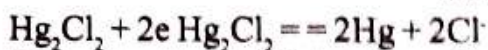
Its structure consists of an outer glass tube that is fitted with a frit at the bottom. This permits electrical contact with the solution on the outside. Another tube is fitted on the inside of the first tube. The bottom of this inner tube has glass wool at the bottom to allow for further connection of electricity between the contents of both tubes.

In calomel electrodes, mercury paste is packed on the inner tube, with mercurous chloride being dispersed in a saturated potassium chloride solution. This can be represented as:



The electrode reaction is:

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When the electrode is immersed in a solution, there is an electric contact made between the electrolyte and the sample at a certain opening located near the end of the electrode. This forms a conductive bridge between the sample, the reference electrode and the indicating electrode.

The glass body liquid-filled types include the porous ceramic junctions used for routine applications. Cracked bead junctions are used for samples that require slow electrolyte flow, while sleeve junctions require fast electrolyte flow. The polymer-bodied types of electrodes include electrodes such as the liquid-filled with a junction, ceramic junction and the gel-filled with porous polymer junction. The permanent gel-filled type do not require a lot of maintenance and can be applied to numerous routine applications.

The electrode potential is reported with the concentration of potassium chloride, because the electrode potential depends on the potassium chloride concentration. The common reference voltage for a saturated calomel electrode is +0.244 V. Mercurous chloride can disproportionate to mercury and mercuric chloride if supplied with a temperature of above 80°C, thus restricting the operation of the calomel electrode below 80°C. Its design and thermal characteristics make the rate of change of progress slow. They can be used in pH measurements and general aqueous electrochemistry.

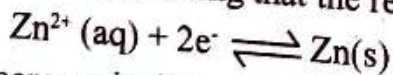
Q.6. Derive Nernst equation for emf of a cell involving reversible chemical reaction. (2009)

Other related question -

Q. Derive the Nernst equation for the cell emf. What is the emf at equilibrium.

Ans. Effect of Electrolyte Concentration on Electrode Potential: Nernst Equation: - (2012)

Consider an electrode consisting of a metal in contact with a solution of its own cations. As an example, we may consider a zinc rod in contact with solution of zinc sulphate furnishing Zn^{2+} ions. The following equilibrium will be established considering that the reaction from left to right involves reduction:



The decrease in free energy accompanying the electrode reaction is given

$$nFE_{\text{el}} = nFE_{\text{el}}^{\circ} - RT \ln \frac{a_{\text{Zn}}}{a_{\text{Zn}^{2+}}}$$

$$E_{\text{el}} = E_{\text{el}}^{\circ} - \frac{RT}{2F} \ln \frac{a_{\text{Zn}}}{a_{\text{Zn}^{2+}}} = E_{\text{el}}^{\circ} + \frac{RT}{2F} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Zn}}}$$

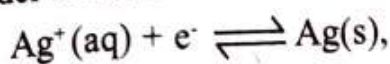
$$= E_{\text{el}}^{\circ} - \frac{RT}{2F} \ln a_{\text{Zn}^{2+}}$$

($\because$ for solids, $a = 1$)

.....(i)

$$= E_{el}^{\circ} - \frac{RT}{2F} \ln [Zn^{2+}] \text{ as an approximation.} \quad \text{.....(ii)}$$

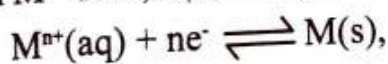
where E_{el} is the electrode potential of zinc electrode under the operating conditions and E_{el}° is the **standard electrode potential** of zinc electrode i.e., the potential developed on the zinc rod when it is in contact with a solution of Zn^{2+} ions of unit activity (or to be approximate, unit molar concentration).
Consider the half - cell reaction



the electrode potential of which is given by

$$\begin{aligned} E_{el} &= E_{el}^{\circ} - \frac{RT}{F} \ln \frac{1}{[Ag^{+}]} \quad \{ \because [Ag(s)] \text{ taken as unity} \} \\ &= E_{el}^{\circ} + \frac{RT}{F} \ln [Ag^{+}] \quad \text{.....(iii)} \end{aligned}$$

Hence, the general expression for the electrode potential of a metal M in contact with M^{n+} ions, involving the electrode reaction

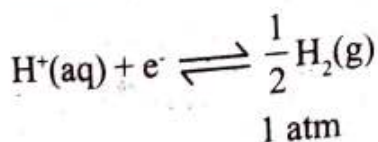


may be written as

$$\begin{aligned} E_{el} &= E_{el}^{\circ} - \frac{RT}{F} \ln \frac{1}{[M^{n+}]} \quad \{ \because [M] \text{ is taken as unity} \} \\ &= E_{el}^{\circ} + \frac{RT}{nF} \ln [M^{n+}] \quad \text{.....(iv)} \end{aligned}$$

$$= E_{el}^{\circ} + \frac{0.0591}{n} \log [M^{n+}] \text{ at } 25^{\circ}C \quad \text{.....(v)}$$

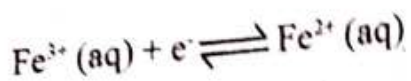
Eq. (v) which gives the effect of the concentration of M^{n+} ion on the potential of M^{n+}/M electrode, is known as the **Nernst equation**.
In the case of hydrogen electrode, the equilibrium is represented as



Hence,
$$E_{el} = E_{el}^{\circ} - \frac{RT}{F} \ln \frac{1}{[H^{+}]} \quad (\because \text{activity of } H_2 \text{ gas at 1 atm pressure is taken as unity})$$

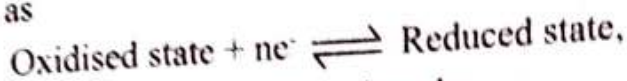
$$= E_{el}^{\circ} + \frac{RT}{F} \ln [H^{+}] = \frac{RT}{F} \ln [H^{+}] \quad \text{.....(vi)}$$

because E_{el}° for hydrogen electrode is arbitrarily taken as zero.
In the case of Fe^{3+}/Fe^{2+} electrode, the equilibrium is represented as



$$\text{Hence, } E_{\text{el}} = E_{\text{el}}^0 - \frac{RT}{F} \ln \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = E_{\text{el}}^0 + \frac{RT}{F} \ln \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \dots\dots(\text{vii})$$

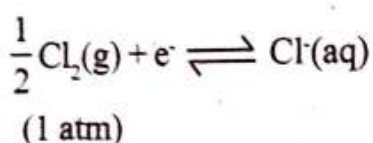
It follows from the above discussion that if we write the electrode reaction, in general, as



the potential of the electrode is given by

$$E_{\text{el}} = E_{\text{el}}^0 - \frac{RT}{F} \ln \frac{[\text{Reduced state}]}{[\text{Oxidised state}]} = E_{\text{el}}^0 + \frac{RT}{F} \ln \frac{[\text{Oxidised state}]}{[\text{Reduced state}]} \dots\dots(\text{viii})$$

In the case of a chlorine electrode, in which chlorine gas is bubbled at a pressure of 1 atmosphere through a solution containing Cl^- ions, the equilibrium is represented as

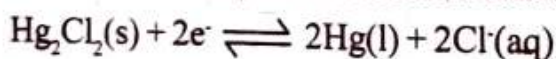


The potential of the electrode is given by

$$E_{\text{el}} = E_{\text{el}}^0 - \frac{RT}{F} \ln \frac{[\text{Cl}^-]}{[\text{Cl}_2]} = E_{\text{el}}^0 - \frac{RT}{F} \ln [\text{Cl}^-] \dots\dots(\text{ix})$$

(since activity of chlorine gas at 1 atm pressure is taken as unity)

For the calomel electrode, the electrode reaction is



The potential of the calomel electrode is given by

$$\begin{aligned} E_{\text{el}} &= E_{\text{el}}^0 - \frac{RT}{2F} \ln \frac{[\text{Cl}^-]^2 [\text{Hg}]^2}{[\text{Hg}_2\text{Cl}_2]} \\ &= E_{\text{el}}^0 - \frac{RT}{2F} \ln [\text{Cl}^-]^2 = E_{\text{el}}^0 - \frac{RT}{F} \ln [\text{Cl}^-] \end{aligned}$$

{[(Hg(l)) and $[\text{Hg}_2\text{Cl}_2(\text{s})]$ is also taken as unity each}

Q.7. Write short note on Kopp's law.

(2012)

Ans. Kopp's law can refer to either of two relationships discovered by the German chemist Hermann Franz Moritz Kopp (1817–1892).

1. Kopp found "that the molecular heat capacity of a solid compound is the sum of the atomic heat capacities of the elements composing it; the elements having atomic heat capacities lower than those required by the Dulong–Petit law retain these lower values in their compounds."
2. In studying organic compounds, Kopp found a regular relationship between

tween boiling points and the number of CH_2 groups present.

Kopp – Neumann law: -

The Kopp – Neumann law, named for Kopp and Franz Ernst Neumann, states that the specific heat C per unit mass (in $\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) for alloys can be calculated from the following equation:

$$C = \sum_{i=1}^N (C_i f_i)$$

where N is the total number of alloy constituents, and C_i and f_i denote the specific heat and mass fraction of the i -th constituent.

Q.8. What are concentration cell? Discuss and describe a concentration cell without transference. (2010)

Other related questions -

Q. Write short note on concentration cell. (2012)

Q. Discuss and describe concentration cell without transference. (2017)

Ans. Concentration Cells:-

In the case of galvanic cells, the electrical energy arises from the chemical reactions which take place in the cells. There is, however, another category of cells in which the EMF arises not due to any chemical reaction but due to transfer of matter from one half-cell to the other because of a difference in the concentrations of the species involved. These are called concentration cells.

Concentration cells are of two types, viz.,

1. Electrode- Concentration Cells and 2. Electrolyte- Concentration Cells.

1. Electrode - Concentration Cells: -

In these cells, two like electrodes at different concentration are dipping in the same solution. Two hydrogen electrodes at unequal gas pressures immersed in the same solution of hydrogen ions constitute an electrode-concentration cell. This may be represented as follows:

$\text{Pt}; \text{H}_2(p_1) \mid \text{Solution of } \text{H}^+ \text{ ions, say, HCL solution} \mid \text{H}_2(p_2); \text{Pt}$

The reactions occurring are:

R.H.E.: $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2(p_2)$ (Reduction)

L.H.E.: $\text{H}_2(p_1) \rightleftharpoons 2\text{H}^+ + 2\text{e}^-$ (Oxidation)

Overall reaction: $\text{H}_2(p_1) \rightleftharpoons \text{H}_2(p_2)$

This reaction is evidently independent of the concentration of the electrolyte.

At moderate pressures, H_2 can be considered to an ideal gas so that the ratio of the activities can be considered to be equal to the ratio of the gas pressures. Hence, the Nernst equation may be written as

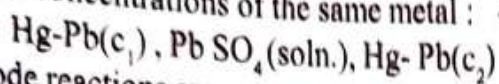
$$E = E^0 - \frac{0.0591}{2} \log \left(\frac{p_2}{p_1} \right) \text{ at } 25^\circ \text{C}$$

Since, by definition, $E^0 = 0$, we have

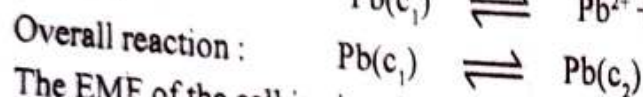
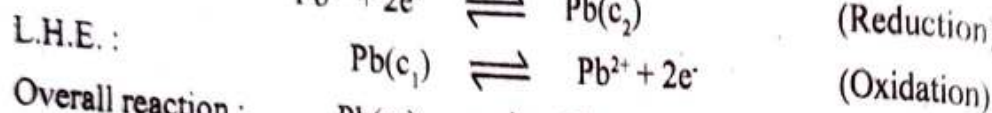
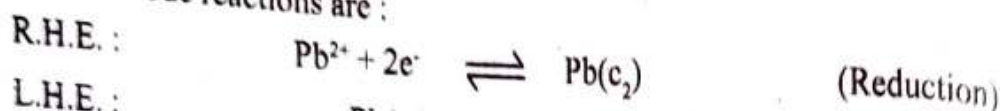
$$E = -0.02955 \log (p_2/p_1) = 0.02955 \log (p_2/p_1)$$

When $p_2 < p_1$ the EMF is positive so that the whole process is spontaneous, being equivalent to the expansion of H_2 gas.

Another example of the electrode-concentration cell is that of an amalgam with two different concentrations of the same metal :



The electrode reactions are :



The EMF of the cell is given by

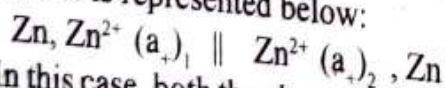
$$E = E_R - E_L = \left(E_{pb}^0 - \frac{0.0591}{2} \log c_2 \right) - \left(E_{pb}^0 - \frac{0.0591}{2} \log c_1 \right)$$

$$= \frac{0.0591}{2} \log \frac{c_1}{c_2} = 0.02955 \log \frac{c_1}{c_2}$$

Here, too, if $c_2 < c_1$, the EMF is positive so that the whole process is spontaneous, i.e., lead will go spontaneously from the higher concentration amalgam to the lower concentration amalgam.

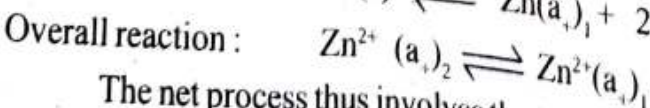
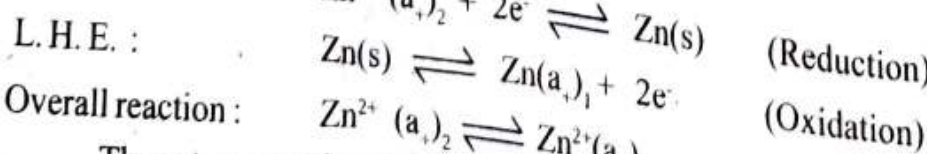
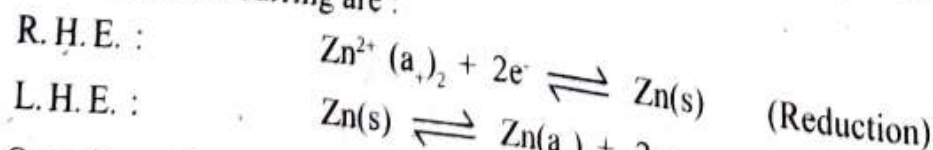
2. Electrolyte - Concentration Cells: -

In these cells, the two electrodes of the same metal are dipping in solutions of metal ions of different concentration and hence of different activities. One such cell is represented below:



In this case, both the electrodes are of the same metal (Zn) and these are in contact with solutions of the same ions (Zn^{2+}). The concentrations and hence activities of the ions are, however, different. Let $(a_+)_1$ and $(a_+)_2$ be the activities of zinc ions in the two electrolytes surrounding the electrodes. The two electrolytes, which are generally $ZnSO_4$ solutions, are separated from each other by a bridge. This is represented by the double line put in between the half-cells.

The reactions occurring are :



The net process thus involves the transfer of 1 mole of Zn^{2+} ions from the solution in which the activity is $(a_+)_2$ to the solution in which the activity is $(a_+)_1$.

According to Nernst equation, the reduction potentials of R.H.E. and L.H.E. are given by

9

Overall reaction : $H^+(a_2) + Cl^-(a_2) \rightleftharpoons H^+(a_1) + Cl^-(a_1)$
 Thus, the overall reaction involves no chemical change. It consists only of the transfer of HCl from solution of activity a_2 to solution of activity a_1 .
 The EMF of the cell is given by

$$\begin{aligned} E_{\text{cell}} &\equiv E = E_R - E_L \\ &= E_{\text{el}}^0 - \frac{RT}{F} \ln \frac{1}{(a_{H^+})_2 (a_{Cl^-})_2} - \left(E_{\text{el}}^0 - \frac{RT}{F} \ln \frac{1}{(a_{H^+})_1 (a_{Cl^-})_1} \right) \\ &= \frac{RT}{F} \ln \frac{(a_{H^+})_2 (a_{Cl^-})_2}{(a_{H^+})_1 (a_{Cl^-})_1} = \frac{RT}{F} \ln \frac{(a_{\pm})_2^2}{(a_{\pm})_1^2} \\ &= \frac{2RT}{F} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1} = 0.1182 \log \frac{(a_{\pm})_2}{(a_{\pm})_1} \text{ at } 25^\circ \text{C} \end{aligned}$$

where $(a_{\pm})_1$ and $(a_{\pm})_2$ are the mean ionic activities of the HCl solutions in the two cells.

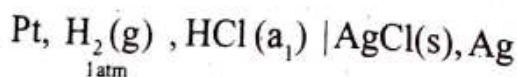
Here, too, we see that when $a_2 > a_1$, E is positive so that the process is spontaneous from right to left and consists in the dilution of HCl from activity a_2 to activity a_1 even though the two solutions are not in contact with each other.

Types of Electrolyte-Concentration Cells: -

Electrolyte - concentration cells in which solutions of the same electrolyte of different concentrations are used are of two types. In one of the types, the two electrolytic solutions are not in direct contact with each other and the transference of ions from one solution to the other does not take place directly. These are called concentration cells without transference. The two solutions are separated from each other by means of a salt bridge or by some other means to be considered shortly. In the second type, the two solutions are in direct contact with each other. The transference of ions from one solution to the other takes place directly. Such cells are called concentration cells with transference. We shall consider here both the types of concentration cells.

Concentration Cells Without Transference; -

The two concentration cells discussed above in which the two solutions are separated from each other through a salt bridge fall in this category. But, more often some other means are employed to keep the solutions apart and bring about the transference of ions indirectly. In order to understand the setting up of such a cell, consider a simple electrochemical cell such as



Let the activity of H^+ ions in the solution be $(a_+)_1$ and that of Cl^- ions be $(a_-)_1$.

$$\text{AgCl(s)} + \text{e}^- \rightleftharpoons \text{Cl}^-(\text{aq}) + \text{Ag(s)} \quad \text{.....(i)}$$
$$\frac{1}{2} \text{H}_2(\text{g}) \rightleftharpoons \text{H}^+(\text{a}_+)_1 + \text{e}^- \quad \dots\dots\dots(\text{ii})$$
$$\frac{1}{2} \text{H}_2(\text{g}) + \text{AgCl}(\text{s}) \rightleftharpoons \text{H}^+(\text{a}_+)_1 + \text{Cl}^-(\text{a}_-)_1 + \text{Ag}(\text{s}) \dots\dots(\text{iii})$$
$$\text{Pt, H}_2(\text{g}), \text{HCl}(\text{a}_2) \mid \text{AgCl}(\text{s}), \text{Ag}$$
$$1/2 \text{H}_2(\text{g}) + \text{AgCl}(\text{s}) \rightleftharpoons \text{H}^+(\text{a}_{+})_2 + \text{Cl}^-(\text{a}_{-})_2 + \text{Ag}(\text{s}) \dots\dots(\text{iv})$$
$$\text{Pt}, \underset{1 \text{ atm}}{\text{H}_2(\text{g})}, \text{HCl}(\text{a}_1), \text{AgCl}(\text{s}), \text{Ag} \mid \text{Ag}, \text{AgCl}(\text{s}), \text{HCl}(\text{a}_2), \underset{1 \text{ atm}}{\text{H}_2(\text{g})}, \text{Pt}$$
$$\text{H}^+(\text{a}_+)_2 + \text{Cl}^-(\text{a}_-)_2 \rightleftharpoons \text{H}^+(\text{a}_+)_1 + \text{Cl}^-(\text{a}_-)_1$$

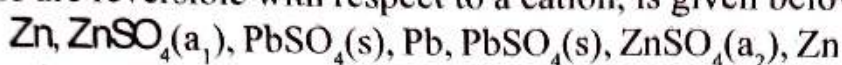
Hence, EMF of such a cell would be given by

$$E_{w.o.t} = \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} + \frac{RT}{F} \ln \frac{(a_-)_2}{(a_-)_1} = \frac{RT}{F} \ln \frac{(a_{\pm})_2^2}{(a_{\pm})_1^2}$$

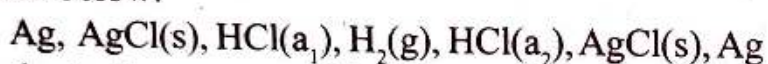
$$E_{\text{w.o.t.}} = (RT/F) \ln(a_2/a_1) \quad [\because a = (a_{\pm})^2]$$

where a_1 and a_2 are the activities of hydrochloric acid in the two solutions. It will be observed that the cell reaction does not involve transfer of electrolyte from one solution to the other directly. It takes place indirectly. The cell is, therefore a concentration cell without transference. If the middle electrode, viz., Ag, AgCl(s), is withdrawn, the two solu-

tions of HCl will be in direct contact with each other. The cell will then become a concentration cell with transference. A little reflection shows that a concentration cell with transference in which the two electrodes are reversible with respect to cations (H^+ ions in the present case) can be converted into a concentration cell without transference by interposing in between another electrode which is reversible with respect to anions (Cl^- ions in the present case). Another example of a concentration cell without transference, in which the electrodes are reversible with respect to a cation, is given below:



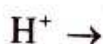
Concentration cells without transference in which the end electrodes are reversible with respect to an anion and in which an electrode reversible with respect to a cation is inserted in between, are also known. One such cell is as represented below:



The end electrodes are reversible with respect to Cl^- ions while the intermediate electrode is reversible with respect to H^+ ions.

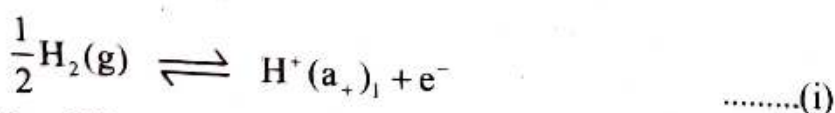
Concentration cells with transference:-

Now consider a concentration cell formed by combining two hydrogen gas electrodes in contact with HCl solutions of different concentrations. The two solutions are in direct contact with each other, as shown:

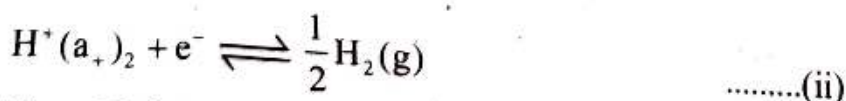


The reaction on the left involves oxidation and that on the right involves reduction, as usual. The following change are involved for the flow of one faraday of electricity:

Left Hand Electrode:

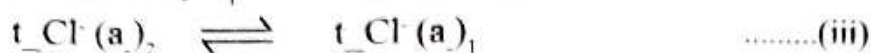


Right Hand Electrode :

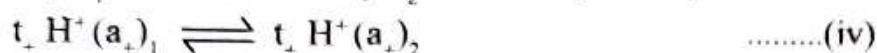


Thus, H^+ ions are generated at the left hand electrode and consumed at the right hand electrode as the current flows. Since the solutions are in direct contact with each other, the ions are free to move from one solution to the other when current flows through the cell. In the present case, evidently, H^+ ions move from the solution on the left hand side to that on the right hand side. Since anions move in direction opposite to that in which cations move, Cl^- ions migrate from right to left, as shown in the cell above.

Let t_- be the transport number of Cl^- ion and $t_+ (= 1 - t_-)$ that of H^+ ion in HCl . Then, for one faraday of electricity passing through, t_- faraday will be carried by Cl^- ions and t_+ faraday by H^+ ions. According to Faraday's second law, t_- equivalent of Cl^- ions will be transferred from the solution of activity a_2 to the solution of activity a_1 . This may be represented as



At the same time, t_+ equivalent of H^+ ions will be transferred from the solution of activity a_1 to that of activity a_2 which may be represented as



The net result for the flow of one faraday of electricity is summed up below:

Left Hand Electrode:- The Following operations occur at this electrode:

Gain of 1 gram equivalent of H^+ ions by process (i)

Loss of t_+ gram equivalent of H^+ ions by process (iv)

$\therefore$ Net gain of H^+ ions = $(1 - t_+)$ gram equivalent = t_- gram equivalent

At the same time,

Net gain of Cl^- ions = t_- gram equivalent by process (iii)

Right Hand Electrode:- The following operations occur at this electrode:

Loss of 1 gram equivalent of H^+ ions by process (ii)

Gain of t_+ gram equivalent of H^+ ions by process (iv)

$\therefore$ Net loss of H^+ ions = $(1 - t_+)$ gram equivalent = t_- gram equivalent

At the same time,

Net loss of Cl^- ions = t_- gram equivalent by process (iii)

Thus, for every one faraday of electricity, there is net transfer of t_- gram equivalent of H^+ ions and t_- gram equivalent of Cl^- ions from right to left, i.e., from the solution in which activity of HCl is a_2 to that in which activity of HCl is a_1 .

These changes are represented as



The EMF of concentration cell with transport is given by

$$E_{\text{w.t.}} = t_- \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} + t_+ \frac{RT}{F} \ln \frac{(a_-)_2}{(a_-)_1} \quad \text{.....(v)}$$

If $(a_{\pm})_1$ and $(a_{\pm})_2$ are the mean ionic activities of the two hydrochloric acid solutions

$$(a_{\pm})_1^2 = (a_+)_1 (a_-)_1 \text{ and } (a_{\pm})_2^2 = (a_+)_2 (a_-)_2 \quad \left[\because (a_{\pm})^2 = a_+ a_- \right]$$

Eq.(v), therefore may be put as

$$E_{\text{w.t.}} = t_- \frac{RT}{f} \ln \frac{(a_{\pm})_2^2}{(a_{\pm})_1^2} \quad \text{.....(vi)}$$

knowing that the activity of a uni-univalent electrolyte is given by $a = (a_{\pm})^2$,

Eq.(vi) may also be written as

$$E_{w.t.} = t_- \frac{RT}{F} \ln \frac{a_2}{a_1} \quad \dots\dots\dots(vii)$$

where a_2 and a_1 , as already stated, are activities of HCl solutions of the right and the left hand electrode, respectively.

Eq.(vii) is used for calculating activity of an electrolyte at a given concentration from the experimental value of $E_{w.t.}$. One of the solutions used should be of known activity.

Q.9. Describe the application of EMF measurement for the determination of solubility product and dissociation constant of an acid. (2010)

Other related question -

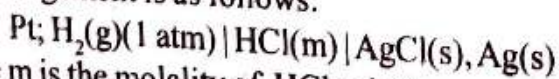
Q. Write short note on application of e.m.f. measurements. (2009,19)

Ans. Applications of EMF measurements:-

The EMF measurements find a number of useful applications. Some of these are given below.

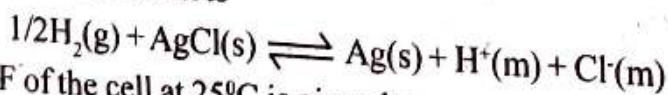
1. Determination of Activity Coefficients of Electrolytes: -

Suppose we want to determine the activity coefficient of hydrochloric acid. Consider a cell without liquid junction containing HCl. The two electrodes are so chosen that one is reversible with respect to the cation of the electrolyte (in this case, the H^+ ion) and the other is reversible with respect to the anion (i.e., the Cl^- ion). Evidently, the first electrode is the hydrogen electrode and the other can be the silver-silver chloride electrode. Accordingly, the cell arrangement is as follows:



where m is the molality of HCl solution.

The cell reaction is



The EMF of the cell at $25^\circ C$ is given by

$$E = E^0 - 0.0591 \log \frac{a_H + a_{Cl^-}}{(a_{H_2})^{1/2}} \quad \dots\dots(i)$$

$$= E^0 - 0.0591 \log a_H + a_{Cl^-} \quad \dots\dots(ii)$$

because activity of each of $Ag(s)$, $AgCl(s)$ and $H_2(g)$ at 1 atm pressure is taken as unity.

As we know,

$$a_H \cdot a_{Cl^-} = (a_{\pm})^2 = (\gamma_{\pm} m)^2 = \lambda_{\pm}^2 m^2$$

where $\gamma_{\pm}$ and m are the mean ionic activity coefficient and the molality of HCl, respectively. Substituting in Eq. (ii), we get

$$E = E^0 - 0.0591 \log \gamma_{\pm}^2 m^2 \quad \text{.....(iii)}$$

$$= E^0 - 0.1182 \log \gamma_{\pm} - 0.1182 \log m \quad \text{.....(iv)}$$

Rearranging,

$$E + 0.1182 \log m = E^0 - 0.1182 \log \gamma_{\pm} \quad \text{.....(v)}$$

The two unknowns E^0 and $\gamma_{\pm}$ in Eq. (v) can be determined by measuring the EMFs of the cell over various concentrations of HCl, including dilute concentrations. At infinite dilution, $m = 0$ and $\gamma_{\pm} = 1$ So that $\log \gamma_{\pm} = 0$. Thus, a plot of $E + 0.1182 \log m$ versus m , extrapolated to $m = 0$ gives E^0 as the y - intercept. Knowing the value of E^0 , the mean ionic activity coefficient $\gamma_{\pm}$ of HCl at any other concentration can be determined from the EMF data of the cell at that concentration.

Alternatively, we can use the Debye - Huckel limiting law (DHLL) equation, viz.,

$$\log \gamma_{\pm} = -0.509 |z_{+} z_{-}| I^{1/2} \quad \text{.....(vi)}$$

to substitute for the $\log \gamma_{\pm}$ term in Eq. (v) giving

$$E + 0.1182 \log m = E^0 + 0.0602 \quad \text{.....(vii)}$$

Thus, a plot of $E + 0.1182 \log m$ versus $I^{1/2}$ will give a straight line at low concentrations where the limiting law is valid. The extrapolation of this plot to $I^{1/2} = 0$ gives E^0 as the y - intercept of the line..

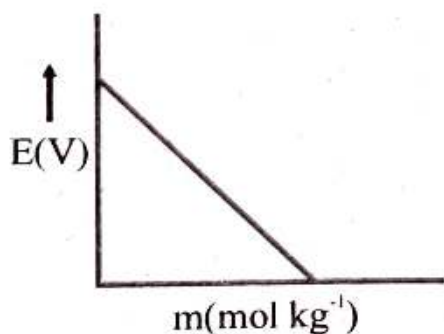


Figure - Determination of E^0

In practice, however, an extension of the DHLL is needed to make a satisfactory linear extrapolation. For a uni-univalent electrolyte in dilute aqueous solution at 25°C, an empirical extension of Eq.(vi) is

$$\log \gamma_{\pm} = -0.509 m^{1/2} + bm \quad \text{.....(viii)}$$

where b is an empirical constant.

Substituting this equation in Eq.(v) and rearranging the terms, we obtain

$$E + 0.1182 \log m - 0.0602 m^{1/2} = E' = E^0 - (0.1182b)m \quad \text{.....(ix)}$$

This equation shows that the left hand side (which we have designated as E'), when plotted against m , will give a straight line whose intercept at $m = 0$, is E^0 (Fig.).

2. Determination of Transport Numbers: -

The EMF of a concentration cell with transference, represented by $E_{w.t.}$, in which the end electrodes are reversible with respect to cation, is given by,

$$E_{w.t.} = t_+ (RT/F) \ln (a_2/a_1) \quad \dots\dots(x)$$

The EMF of the same cell with the same solutions but without transference, denoted by $E_{w.o.t.}$ is given by,

$$E_{w.o.t.} = (RT/F) \ln (a_2/a_1) \quad \dots\dots(xi)$$

Dividing (x) by (xi), we have

$$t_+ = E_{w.t.} / E_{w.o.t.} \quad \dots\dots(xii)$$

Thus, the ratio of the EMFs of the two concentration cells, one with transference and the other without transference, gives the transference number of the anion, if the end electrodes are reversible with respect to the cation.

If the end electrodes are reversible with respect to the anion, then the ratio of the two EMFs will give the transference number of the cation of the electrolyte.

3. Determination of Valency of Ions in Doubtful Cases: -

The valency of mercurous ions was in doubt for a considerable time. It was finally established by determining the EMF of a concentration cell of the type given below:

Mercury, Mercurous nitrate solution (c_1) || Mercurous nitrate solution (c_2), Mercury

The salt bridge represented by the two vertical lines connecting the two solutions contains saturated solution of ammonium nitrate.

The EMF of the cell, E , assuming the activity coefficients to be equal to unity, is given by the expression

$$E = (RT/nF) \ln (c_2/c_1)$$

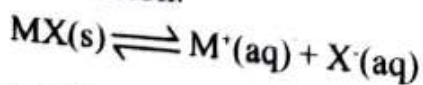
where n is the valency of mercurous ion and c_2 is greater than c_1 . Thus,

$$E = \frac{0.0591}{n} \log \frac{c_2}{c_1} \quad (\text{at } 25^\circ\text{C})$$

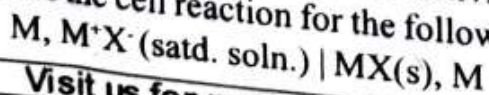
It was found that when c_2/c_1 was 10, the EMF was 0.0295 volt. Therefore, the valency of mercurous ion is 2 and it should be represented as Hg_2^{2+} .

4. Determination of the Solubility Product Constants: -

The solubility product constant of a sparingly soluble salt is a kind of equilibrium constant. Consider the salt MX in equilibrium with its ions in a saturated solution.

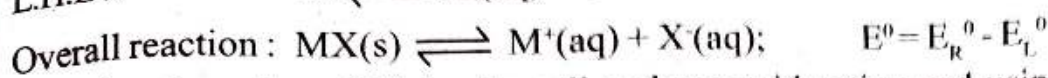
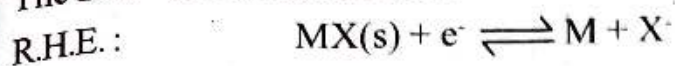


The solubility product of the salt is given by $K_{sp} = a_{\text{M}^+} \times a_{\text{X}^-} = [\text{M}^+][\text{X}^-]$, assuming an ideal solution so that activities equal concentrations. The above reaction is the cell reaction for the following cell:



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The half - cell reactions are :



Knowing the value of E^0 for the cell under consideration and using the relations: $\Delta G^0 = nFE^0$ and $-\Delta G^0 = 2.303RT \log k_{sp}$, we get

$$\log K_{sp} = \frac{nFE^0}{2.303RT}$$

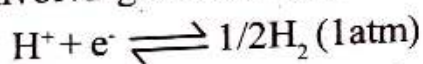
$$\text{i.e., } E^0 = \frac{2.303RT}{nF} \log K_{sp} = \frac{0.0591}{n} \log K_{sp} \text{ at } 25^\circ\text{C}$$

Thus, K_{sp} can be calculated from the known value of E^0 .

5. Determination of pH:-

a. By using hydrogen electrode:-

a. By using hydrogen electrode:-
The potential of a hydrogen electrode in contact with a solution of H^+ ions involving the reaction.



is given by Nernst equation, viz.,

$$E_{el} = E_{el}^0 + 2.303(RT/F) \log [H^+] \quad \text{.....(xii)}$$

By convention, $E_{\text{el}}^0 = E_{(\text{cl})}^0$, i.e., the standard electrode potential of hydrogen electrode, is zero

$$E_{el} = \frac{2.303RT}{F} \log [H^+] = -0.0591 \text{pH (at } 25^\circ\text{C)} \quad \text{.....(xiv)}$$

Thus, the potential of a hydrogen electrode depends upon the pH of the solution with which it is in contact. This can be determined by combining the hydrogen electrode with a reference electrode, say, calomel electrode. The complete cell is represented as

$$\text{Pt}(\text{H}_2, \text{H}^+(\text{unknown})) \parallel \text{KCl}(\text{sat. soln.}), \text{Hg}_2\text{Cl}_2(\text{s}), \text{Hg}.$$

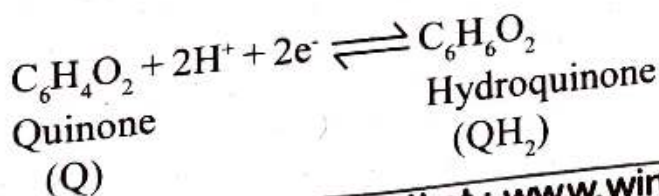
complete cell is represented as
 $\text{Pt, H}_2 (1 \text{ atm}), \text{H}^+ (c = \text{unknown}) \parallel \text{KCl (sat. soln.)}, \text{Hg}_2\text{Cl}_2 (\text{s}), \text{Hg}.$
 The EMF of the cell is determined potentiometrically. This is given by
 $E = 0.2422 - (-0.0591 \text{ pH})$

or $E = E_R - E_L = 0.2422 - (-0.0591 \text{ pH})$
 $0.0591 \text{ pH} = E - 0.2422$

or $\text{pH} = \frac{E - 0.2422}{0.0591}$

b. By using quinhydrone electrode:-

b. By using quinhydrone electrode:-
The quinone - hydroquinone system involves the following equilibrium:



For the reduction reaction given above, the potential developed on a platinum electrode immersed in this system is given by the Nernst equation as

$$E_{el} = E_{el}^0 - \frac{2.303RT}{2F} \log \frac{[QH_2]}{[Q][H^+]^2} \quad \text{.....(xv)}$$

$$= E_{el}^0 + \frac{2.303RT}{2F} \log \frac{[Q][H^+]^2}{[QH_2]} \quad \text{.....(xvi)}$$

$$= E_{el}^0 + \frac{2.303RT}{2F} \log \frac{[Q]}{[QH_2]} + \frac{2.303RT}{F} \log H^+ \quad \text{.....(xvii)}$$

Instead of taking quinone and hydroquinone, a small amount of quinhydrone, which is an equimolar compound of quinone (Q) and hydroquinone $[QH_2]$, is taken. Since hydroquinone (QH_2) is a weak acid, its ionisation is very small particularly if the pH of the solution is less than 7. Therefore, the concentration of hydroquinone $[QH_2]$ is the same as that of quinone [Q], i.e., the quantity $[Q]/[QH_2]$ is unity. The middle term in Eq.(xvii) therefore, reduces to zero. Hence,

$$E_{el} = E_{el}^0 + \frac{2.303RT}{2F} [H^+] = E_{el}^0 + 0.0591 \log [H^+] \text{ at } 25^\circ\text{C}$$

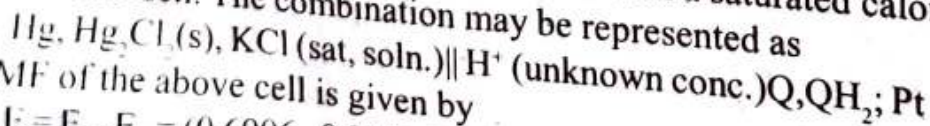
$$= E_{el}^0 - 0.0591 \text{pH} \quad \text{.....(xviii)}$$

The standard electrode potential of the quinhydrone electrode, $E_{el}^0 = +0.06996\text{V}$

$\therefore E_{el} = +0.6996 - 0.0591 \text{pH}$ (xix)

Thus, the potential of the quinhydrone electrode, just as that of the hydrogen electrode, depends upon the pH of the solution with which it is in contact, i.e., the quinhydrone electrode behaves as a reversible hydrogen electrode. Consequently, this electrode can be used for measuring pH values of solutions. This electrode is preferred to the hydrogen electrode as it can be set up easily by merely adding a pinch of quinhydrone to the solution under examination and inserting a clean platinum electrode for making electrical connection. The electrode gives accurate results even in the presence of oxidising ions which usually interfere with the working of the hydrogen electrode.

The quinhydrone electrode is combined with a saturated calomel electrode to form a cell. The combination may be represented as



The EMF of the above cell is given by

$$E = E_R - E_I = (0.6996 - 0.0591 \text{pH}) - 0.2422 \text{ at } 25^\circ\text{C}$$

or $0.0591 \text{pH} = 0.6996 - 0.2422 - E$

$$\therefore \text{pH} = \frac{0.6996 - 0.2422 - E}{0.0591}$$

Unit IV

Q.1. Write short note on Gibbs adsorption equation. (2011)

Other Related Question -

Q. Differentiate between physical and chemical adsorption. (2010,15)

Q. Differentiate between chemical and physical adsorption. Derive Gibbs's adsorption equation. (2009,16)

Ans. Adsorption: -

Adsorption is to be carefully distinguished from absorption. The latter term implies that a substance is uniformly distributed throughout the body of a solid or a liquid. Thus, while water vapours are absorbed by anhydrous calcium chloride, these are adsorbed by silica gel. Similarly, while ammonia is absorbed in water, it is adsorbed by charcoal. When a hot crucible is cooled in atmosphere, a film of moisture collects at its surface. This is a case of adsorption of water vapour on the material of the crucible. Charcoal when mixed with a coloured solution of sugar, adsorbs the colouring matter and is used as a decoloriser. McBain suggested the use of the term **sorption** to describe a process in which both absorption and adsorption take place simultaneously.

Adsorption is not necessarily a physical phenomenon always. It may as well be a chemical process involving chemical interaction between the surface atoms of the adsorbent and the atoms of the adsorbate. This type of adsorption is known as chemisorption. For example, oxygen is chemisorbed by carbon and hydrogen is chemisorbed by nickel under suitable conditions. In each case, a stable surface compound, frequently referred to as surface complex, results. Chemisorption differs from physical adsorption (or physisorption) in the following respects:

1. Physical adsorption occurs appreciably only at very low temperatures falling below the boiling point of the adsorbate. Chemisorption can occur at all temperatures.
2. The magnitude of chemisorption increases with rise in temperature. This is just as the magnitude of a chemical reaction in a given time increases with rise in temperature. Physisorption, on the other hand, decreases with rise in temperature.
3. The heat evolved in chemisorption is very high, varying generally between $40 - 400 \text{ kJ mol}^{-1}$, as in many chemical reactions. The heat evolved in physisorption, on the other hand, is quite low, varying generally between $4 - 40 \text{ kJ mol}^{-1}$.
4. Chemisorption is irreversible as the gas adsorbed cannot be recovered from the adsorbent as such on lowering the pressure of the system at the same temperature. Physisorption is, however, reversible as the gas adsorbed can be recovered from the adsorbent easily on lowering the pressure of the system at the same temperature.

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5. Since chemical forces operate within short distances only, chemisorption does not extend beyond a monolayer of gas molecules or atoms on the surface of the solid. Physisorption may extend beyond a monolayer also.
6. In physisorption, the adsorbate molecules are held by comparatively weak van der Waals forces. Hence, the activation energy of desorption, in this category, is very low. In chemisorption, the adsorbate molecules are held by comparatively strong valence forces. Hence, the activation energy of desorption is very high.

The Gibbs Adsorption Isotherm for Adsorption From Solutions: -

The concentration of a solute at the surface of a solution is, in general, markedly different from that in the bulk. If the surface tension of the solute is lower than that of the liquid, it tends to accumulate at the surface of the liquid thereby decreasing the surface tension (or the surface free energy per unit area) of the liquid. A quantitative treatment of the thermodynamics of adsorption of a solute at the surface of a liquid was given in 1878 by J.W. Gibbs (1839 - 1903), the greatest 19th century American mathematical physicist.

For a system containing two components, the Gibbs free energy can be written as

$$G = n_1 \mu_1 + n_2 \mu_2 \quad \text{..... (i)}$$

Where n_1 and n_2 are the amounts (number of moles) and μ_1 and μ_2 are the chemical potentials (i.e., partial molar Gibbs free energies) of the two components, respectively. Since we are dealing with the adsorption of one of the components on the surface which results in changing the surface free energy, Eq. (i) is modified to

$$G = n_1 \mu_1 + n_2 \mu_2 + \gamma \sigma \quad \text{.....(ii)}$$

Where γ is the surface energy which is numerically the same as the surface tension and σ is the surface area.

The complete differential of Eq. (ii) is written as

$$dG = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2 + \gamma d\sigma + \sigma d\gamma \quad \text{.....(iii)}$$

We see that free energy G now depends upon five independent variables, viz., T , P , n_1 , n_2 and σ .

Thus.

$$G = f(T, P, n_1, n_2, \sigma) \quad \text{.....(iv)}$$

$$\therefore dG = \left(\frac{\partial G}{\partial T} \right)_{P, n_1, n_2, \sigma} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_1, n_2, \sigma} dP + \left(\frac{\partial G}{\partial n_1} \right)_{T, P, n_2, \sigma} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{T, P, n_1, \sigma} dn_2 + \left(\frac{\partial G}{\partial \sigma} \right)_{T, P, n_1, n_2} d\sigma \quad \text{.....(v)}$$

According to thermodynamics, the partial derivatives

$$-\left(\frac{\partial G}{\partial T} \right)_{P, n_1, n_2, \sigma}, \left(\frac{\partial G}{\partial P} \right)_{T, n_1, n_2, \sigma}, \left(\frac{\partial G}{\partial n_1} \right)_{T, P, n_2, \sigma} \text{ and } \left(\frac{\partial G}{\partial \sigma} \right)_{T, P, n_1, n_2} \text{ in Eq.(v)}$$

are, respectively, equal to S, V, μ_1, μ_2 and γ .

$$\text{Hence, } dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma \quad \text{.....(vi)}$$

At constant temperature, $dT = 0$ and at constant pressure, $dP = 0$. Hence, Eq. (vi) reduces to

$$(dG)_{T,P} = \mu_1 dn_1 + \mu_2 dn_2 + \gamma d\sigma \quad \text{.....(vii)}$$

From Eqs. (iii) and (iv),

$$n_1 d\mu_1 + n_2 d\mu_2 + \sigma d\gamma = 0 \quad \text{.....(viii)}$$

The corresponding expression for the bulk of the liquid is

$$n_1^0 d\mu_1 + n_2^0 d\mu_2 = 0 \quad \text{.....(ix)}$$

where n_1^0 and n_2^0 are the amounts (number of moles) of the liquid and the solute, respectively, in the bulk phase.

Since the system is in equilibrium, the chemical potential of each component in the bulk and the surface phase must be the same. The system, on being disturbed, attains a new equilibrium so that the changes in the chemical potentials must be identical in both the phases, i.e., $d\mu_1$ and $d\mu_2$ in Eqs. (viii) and (ix) must be identical. Elimination of $d\mu_2$ from these equations gives

$$n_1 [-(n_2^0/n_1^0) d\mu_2] + n_2 d\mu_2 + \sigma d\gamma = 0 \quad \text{.....(x)}$$

$$\text{or } (n_2 - n_1 n_2^0/n_1^0) d\mu_2 + \sigma d\gamma = 0$$

$$\text{or } -\frac{d\gamma}{d\mu_2} = \frac{n_2 - (n_1 n_2^0/n_1^0)}{\sigma} \quad \text{.....(xi)}$$

The quantity within parenthesis of Eq. (xi) gives the amount n_2^0 of solute 2 associated with the amount n_1^0 of liquid 1 in the bulk phase. On the other hand, n_2 is the amount of the solute associated with the amount n_1 of the liquid at the surface. Thus, the numerator on the right hand side of Eq. (xi) gives the excess amount of the solute present in the surface of the liquid. Evidently, the right hand side of Eq. (xi) gives the surface excess, i.e., the excess concentration of the solute per unit area of the surface, designated as Γ_2 , i.e., $[n_2 - (n_1 n_2^0/n_1^0)]/\sigma = \Gamma_2$.

Thus, from Eq. (xi),

$$\Gamma_2 = -d\gamma/d\mu_2 \quad \text{.....(xii)}$$

The chemical potential of solute 2 is given by

$$\mu_2 = \mu_2^*(l) + RT \ln a_2 \quad \text{.....(xiii)}$$

where $\mu_2^*(l)$ is the chemical potential of the pure solute in the liquid phase.

Hence,

$$d\mu_2 = RT d \ln a_2 \quad [\because d\mu_2^*(l) = 0] \quad \text{.....(xiv)}$$

Substituting for $d\mu_2$ in Eq. (xii), we obtain

$$\Gamma_2 = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln a_2} \right)_T = -\frac{a_2}{RT} \left(\frac{\partial \gamma}{\partial a_2} \right)_T \quad \text{.....(xv)}$$

When the solution is very dilute, it behaves ideally so that the activity a_2 of the solute can be replaced by its concentration c_2 . Thus,

$$\Gamma_2 = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln c_2} \right)_T = -\frac{c_2}{RT} \left(\frac{\partial \gamma}{\partial c_2} \right)_T \quad \text{.....(xvi)}$$

S.No.	Physical adsorption	Chemical adsorption
1.	Force of attraction are weak vander Waal's forces.	The forces of attraction involved are similar to those of a chemical bond.
2.	Low enthalpy of adsorption usually in the range of 20-40 kJ mol ⁻¹ .	High enthalpy of adsorption in the range of 80-240 kJ mol ⁻¹ .
3.	Reversible.	Irreversible.
4.	Physisorption usually takes place at low temperature and decreases with increase in temperature.	It takes place at high temperature.
5.	It is quite general phenomenon.	It is highly specific.
6.	It does not require any activation energy.	It requires activation energy.
7.	It forms multimolecular layers of gas molecules on the surface.	It forms unimolecular layer.

Eq. (xvi) is called the Gibbs adsorption isotherm. Knowing the concentration - dependence of γ , Γ_2 can be calculated.

For a solute that lowers the surface tension, the surface excess concentration Γ_2 is positive and for a solute that raises the surface tension, Γ_2 is negative. Soaps have a higher concentration in the neighbourhood of the surface than in the bulk aqueous phase whereas inorganic salts have lower concentrations in the neighbourhood of the surface than in the bulk aqueous phase.

Solutes are classified as capillary - active or capillary - inactive on the basis of their effect on surface tension. For the aqueous solution-air interface, **capillary - active** solutes are organic acids, alcohols, ethers, esters, amines, ketones, etc., and **capillary - inactive** solutes are inorganic electrolytes, salts of organic acids and bases of lower molar mass and certain nonvolatile compounds such as sugar and glycerol.

Q.2. Derive Langmuir's adsorption theorem. Discuss its applicability at:
 (i) Low pressure (ii) High pressure (iii) Intermediate pressure. (2017)

Other Related Question -

Q. List the assumption on which Langmuir's theory of adsorption is based

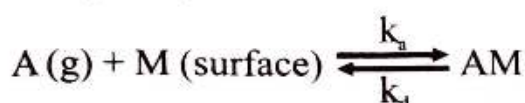
and derive the Langmuir's adsorption Isotherm.

(2010)

Q. Write note on Langmuir theory of adsorption.

Ans. The Langmuir Theory of Adsorption: -

In 1916 Langmuir proposed his theory of adsorption of a gas on the surface of a solid. He considered the surface of the solid to be made up of elementary sites each of which could adsorb one gas molecule. It is assumed that all adsorption sites are equivalent and the ability of the gas molecule to get bound to any one site is independent of whether or not the neighbouring sites are occupied. It is further assumed that a dynamic equilibrium exists between the adsorbed molecules and the free molecules. If A is the gas molecule and M is the surface site, then



where k_a and k_d are the rate constants for adsorption and desorption, respectively. The rate of adsorption is proportional to the pressure of A, viz., p_A and the number of vacant sites on the surface, viz., $N(1 - \theta)$ where N is the total number of sites and θ is the fraction of surface sites occupied by the gas molecules, i.e.,

$$\theta = \frac{\text{Number of adsorption sites occupied}}{\text{Number of adsorption sites available}}$$

Thus, the rate of adsorption = $k_a p_A N(1 - \theta)$ (i)

The rate of desorption is proportional to the number of adsorbed molecules, $N\theta$.

Thus, the rate of desorption = $k_d N\theta$ (ii)

Since at equilibrium, the rate of adsorption is equal to the rate of desorption, we can write from Eqs. (i) and (ii),

$$k_a p_A N(1 - \theta) = k_d N\theta \quad \text{.....(iii)}$$

$$\text{or } K p_A (1 - \theta) = \theta \quad \text{.....(iv)}$$

where $K = k_a/k_d$.

Eq.(iv) may, thus, be written as

$$\frac{1 - \theta}{\theta} = \frac{1}{K p_A}$$

$$\text{or } \frac{1}{\theta} - 1 = \frac{1}{K p_A} \quad \text{.....(v)}$$

$$\frac{1}{\theta} = \frac{1}{K p_A} + 1 = \frac{1 + K p_A}{K p_A} \quad \text{.....(vi)}$$

Hence, $\theta = \frac{Kp_A}{1 + Kp_A}$ (vii)

Eq. (vii) is called the Langmuir adsorption isotherm.

The following assumptions are involved in the derivation of the Langmuir adsorption isotherm:

1. The adsorbed gas behaves ideally in the vapour phase.
2. Only a monolayer is formed by the adsorbed gas.
3. The surface of the solid is homogeneous so that each binding site has the same affinity for the gas molecules.
4. There is no lateral interaction between the adsorbate molecules.
5. The adsorbed gas molecules are localized, i.e., they do not move around on the surface.

The first assumption holds at low pressure; the second assumption breaks down when the pressure of the gas is increased. The third assumption is not strictly true because the real surfaces are quite heterogeneous so that affinity for gas molecules is different at different sites. Crystal imperfections and cracks lead to the creation of different sites on the surface. The fourth and fifth assumptions, too, are not strictly valid.

Now, let us consider Eq. (vii). At low pressures, $Kp_A \ll 1$ so that

$$\theta = Kp_A \quad \text{.....(viii)}$$

i.e., the fraction of the surface covered is directly proportional to the partial pressure of the gas molecules. This behaviour corresponds to first - order reaction and is depicted by the initial steep rise of the isotherm (Fig.).

At high pressure, $Kp_A \gg 1$ So that Eq.(vii) reduces to

$$\theta = 1 \quad \text{.....(ix)}$$

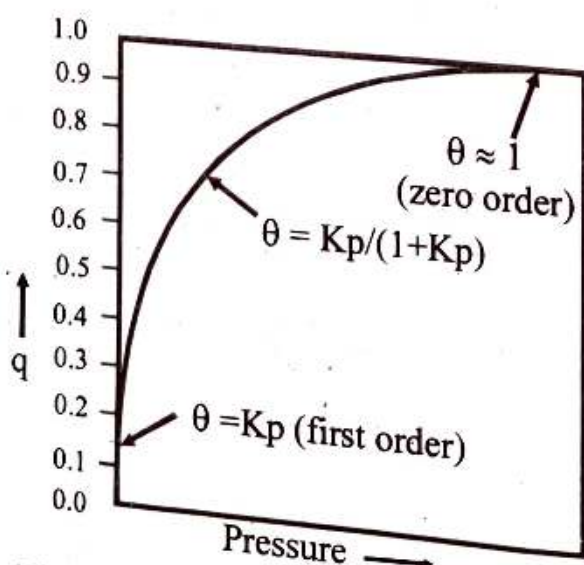


Fig. - The Langmuir plot. The kinetics of a gaseous reaction on solid surface.

Thus, at high pressures, the value of θ tends to become unity, i.e., the entire surface gets covered by a monomolecular layer of the gas thereby mak-

ing the reaction rate independent of the pressure. Thus, the reaction is of the zero order (Fig.).

Combining the results of Eqs. (viii) and (ix), it is evident that according to this theory, the magnitude of adsorption at a given temperature should first increase in proportion to increase of pressure and finally tend to attain a certain limiting value.

Since at low pressures, adsorption is proportional to pressure, i.e.,

$$\theta = K (p_A)^1 \quad (\text{from Eq.viii})$$

and, at high pressures, $\theta = 1 = (p_A)^0$ (from Eq.ix)

it follows that, at intermediate pressures, the following expression should hold good:

$$\theta = K(p_A)^n \text{ where } n \text{ lies between } 0 \text{ and } 1. \quad \dots(x)$$

Since, according to Langmuir's theory, only a single layer of molecules is adsorbed on the surface of the adsorbent, the fraction θ gives the amount of the gas adsorbed per unit mass of the adsorbent, that is, $a \propto \theta$ or $a = k_1 \theta$ where k_1 is another constant. Thus,

$$a = k_1 \theta = k_1 K (p_A)^n = k (p_A)^n \quad \dots(x_i)$$

Eq. (xi) is the same as the Freundlich empirical equation. This agreement was taken as a proof for the theory of monomolecular adsorption advanced by Langmuir. Irving Langmuir (1881 - 1957), the American chemist, was awarded the 1932 Chemistry Nobel Prize for his contributions to surface chemistry. Research in surface science has now acquired tremendous importance and a research journal called Langmuir is exclusively devoted to contributions in all areas of surface science.

Q.3. Discuss BET theory of multilayer adsorption. (2011)

Other related questions -

Q. Explain BET theory of multilayer adsorption. With the help of BET equation show how surface area of adsorbent and area of cross section of a molecule can be determined. (2016,19)

Q. Write short note on BET Theory. (2010)

Ans. BET Theory of Multilayer Adsorption :-

The Langmuir theory of adsorption is restricted to the formation of a monomolecular layer of the gas molecules on the solid surface and disregards the possibility that multilayer adsorption may also take place. The theory of the possibility that multilayer adsorption may also take place. The theory of adsorption proposed in 1938 by Brunauer, Emmett and Teller (known as the **BET theory**, after the initials of these scientists) assumes that physical adsorption resulting in the formation of multilayers, is the true picture of adsorption. In the BET theory, it is assumed that the solid surface possesses uniform, localized sites and that adsorption at one site does not affect adsorption at neighbouring sites, as was assumed in the Langmuir theory. It is further assumed that molecules can be adsorbed in second, third, ... and n^{th} layers, the

surface area available for the n th layer being equal to the coverage of the $(n - 1)$ th layer. The energy of adsorption in the first layer, E_1 , is assumed to be constant and the energy of adsorption in succeeding layers is assumed to be the same as E_1 , the energy of liquefaction of the gas. Based on the above assumptions, Brunauer, Emmett and Teller derived the following equation, known after them as the **BET equation**:

$$\frac{p}{v_{\text{total}}(p_0 - p)} = \frac{1}{v_{\text{mono}}c} + \frac{c - 1}{v_{\text{mono}}c} \left(\frac{p}{p_0} \right) \quad \dots\dots(i)$$

where v_{total} is the volume of the gas adsorbed at the pressure p , v_{mono} is the volume adsorbed when the surface of the solid is covered completely with a monolayer of the adsorbed molecules of the gas and c is a constant depending upon the nature of the gas. Its numerical value is given approximately by the expression $c = \exp(E_1 - E_L)/RT$ in which E_1 is the heat of adsorption in the first layer and E_L is the heat of liquefaction of the gas. Since c is a constant for a given gas and v_{mono} is a constant for a given gas - solid system, the plot of $p/v_{\text{total}}(p_0 - p)$ against p/p_0 should give a straight line. This has been checked in the case of adsorption of a number of gases on various solid adsorbents. The results obtained in the case of adsorption of nitrogen on silica gel at -183°C are shown in Fig. As can be seen, the plot obtained is a good straight line. Fairly satisfactory straight lines are obtained in most cases as long as pressure p does not exceed one - third of the saturation pressure p_0 , i.e., the pressure required to condense the gas into the liquid state at the prevailing temperature. At higher pressures, however, deviations set in.

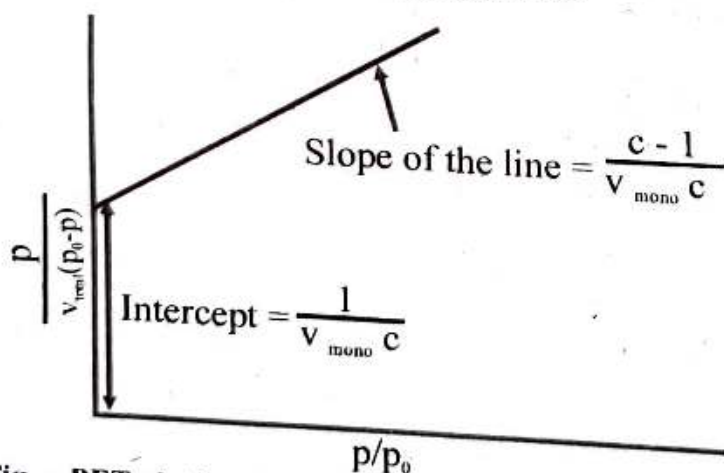


Fig. - BET plot for the adsorption of N_2 on silica gel at -183°C

The slope of the linear plot, evidently, gives the value of $(c - 1)/(v_{\text{mono}}c)$ while the intercept yields the value of $1/(v_{\text{mono}}c)$. Thus, from the slope and the intercept, both v_{mono} and c can be evaluated.

Determination of Surface Area: -

Knowing v_{mono} , the surface area of the adsorbent can be easily calculated, as shown in the following example. The assumption is that the molecules of the gas adsorbed in the first layer are closely packed on the surface.

Determination of Area of Cross - Section of a Molecule:-

The area of cross-section a of the molecule can be determined from the density of the liquefied or solidified adsorbate. Thus, if ρ is the density and M_m is the molar mass of the adsorbate, then the volume v occupied by a single molecule, assuming the adsorbate to be closely packed with no void volume, is obtained as follows:

$$\rho = M_m/V = M/(N_A v)$$

$$v = M_m/(N_A \rho)$$

Assuming the molecule to be spherical with radius r , we have

$$v = (4/3) \pi r^3 = M_m/(N_A \rho) \quad \text{.....(ii)}$$

$$r = \left[\frac{3M_m}{4\pi N_A \rho} \right]^{1/3} \quad \text{.....(iii)}$$

$$\text{Hence, } a = \pi r^2 = \pi \left[\frac{3M_m}{4\pi N_A \rho} \right]^{2/3} \quad \text{.....(iv)}$$

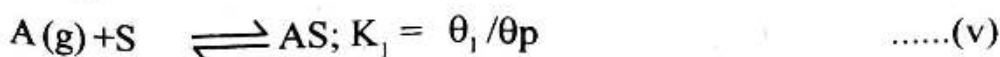
Eq. (iv) is only approximate for calculating the area of cross - section of a molecule since it does not take into account the nature of packing at the surface of the adsorbent. Also, the presence of void volumes in the crystal lattice has been ignored. The areas of cross-section of some common molecules are given in Table.

Areas of Cross-section of Some Common Molecules

Molecules	Temperature(⁰ C)	Liquid Density (ρ) (g cm) ⁻³	$a(\text{nm})^2$
Ar	-183	1.374	0.144
N ₂	-196	0.808	0.162
O ₂	-183	1.140	0.141
CO	-183	0.763	0.168
CO ₂	-57	1.179	0.170
CH ₄	-140	0.392	0.181
NH ₃	-36	0.688	0.129

Derivation of the BET equation: -

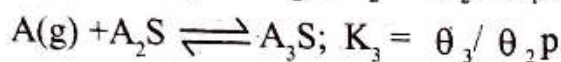
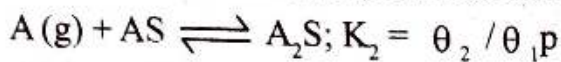
In 1938, Brunauer, Emmett and Teller proposed a model, known as the BET isotherm, for multilayer adsorption. According to them, the first step in adsorption is



where A is the gaseous adsorbate, S is a vacant site on the surface, AS repre-

sents an adsorbed molecule of A or an occupied site on the surface, K_1 is the equilibrium constant, θ_1 is the fraction of the surface sites covered by single molecules θ_v is the fraction of vacant sites and p is the pressure of the gas.

They further assumed that additional molecules sit on top of one another to form a variety of multilayers. This process was interpreted as a sequence of chemical reactions, each with an appropriate equilibrium constant:



where the symbol A_nS indicates a surface site that has a stack of n A molecules piled up on it. The θ_i is the fraction of sites on which the stack of A molecules is i layers deep. The interaction between the first A molecule and the surface site is unique, depending on the nature of the particular A molecule and the surface. However, when the second A molecule sits on the first A molecule, the interaction cannot be very different from the interaction of two A molecules in the liquid. The same is true when the third molecule sits on the second. All of these processes except the first can be regarded as being essentially equivalent to liquefaction. Hence, they should have the same equilibrium constant, K . Thus, the BET treatment assumes that

$$K_2 = K_3 = K_4 = \dots = K_n = K \quad \dots\dots(vi)$$

where K is the equilibrium constant for the reaction $A(g) \rightleftharpoons A(liq)$. Obviously,

$$K = 1/p^0 \quad \dots\dots(vii)$$

where p^0 is the equilibrium vapour pressure of the liquid.

we can use the equilibrium conditions to calculate the values of the various θ_i . We have

$$\theta_2 = \theta_1 Kp, \theta_3 = \theta_2 Kp, \theta_4 = \theta_3 Kp, \dots\dots \quad \dots\dots(viii)$$

Combining the first two, we have, $\theta_3 = \theta_1 (Kp)^2$

Repeating the operation, we find that

$$\theta_i = \theta_1 (Kp)^{i-1} \quad \dots\dots(ix)$$

The sum of all these fractions must be equal to unity:

$$1 = \theta_v + \sum_{i=1} \theta_i = \theta_v + \sum_{i=1} \theta_1 (Kp)^{i-1} \quad \dots\dots(x)$$

where we have used Eq.(ix) for θ_i . Let $Kp = x$, then Eq.(x) becomes

$$1 = \theta_v + \theta_1 (1 + x + x^2 + x^3 + \dots\dots)$$

Assuming that the process can go on indefinitely, then $n \rightarrow \infty$ and the series is simply the expansion of $1/(1-x) = 1 + x + x^2 + \dots$. Thus,

$$1 = \theta_v + \theta_1 / (1 - x) \quad \dots\dots(xi)$$

Using the equilibrium condition for the first adsorption, we find that $\theta_v = \theta_1 / K_1 p$. Defining a new constant, $c = K_1 / K$, we have $\theta_v = \theta_1 / (cx)$ and Eq.(xi)

becomes

$$1 = \theta_1 \left(\frac{1}{cx} + \frac{1}{1-x} \right) \text{ or } \theta_1 = \frac{cx(1-x)}{1+(c-1)x} \quad \text{.....(xii)}$$

Let N be the total number of molecules adsorbed per unit mass of adsorbent and c_s be the total number of surface sites per unit mass. Then $c_s \theta_1$ is the number of sites carrying one molecule, $c_s \theta_2$ is the number of sites carrying two molecules, and so on. Accordingly,

$$N = c_s (1\theta_1 + 2\theta_2 + 3\theta_3 + \dots) = c_s \sum_i i\theta_i \quad \text{.....(xiii)}$$

From Eq.(ix) we have $\theta_i = \theta_1 x^{i-1}$ so that

$$N = c_s \theta_1 \sum_{i=1}^{\infty} ix^{i-1} = c_s \theta_1 (1+2x+3x^2+\dots) \quad \text{.....(xiv)}$$

This series is the derivative of the earlier one. Thus,

$$1+2x+3x^2+\dots = \frac{d}{dx} (1+x+x^2+x^3+\dots) = \frac{d}{dx} \left(\frac{1}{1-x} \right) = \frac{1}{(1-x)^2} \quad \text{.....(xv)}$$

Using this result, the expression for N becomes

$$N = c_s \theta_1 / (1-x)^2 \quad \text{.....(xvi)}$$

If the entire surface is covered with a monolayer, then N_m molecules would be adsorbed so that $N_{\text{mono}} = c_s$ and

$$N = N_m \theta_1 / (1-x)^2 \quad \text{.....(xvii)}$$

Substituting the value of θ_1 from Eq(xii), we have

$$N = \frac{N_m cx}{(1-x)[1+(c-1)x]} \quad \text{.....(xviii)}$$

The amount adsorbed is usually reported as the volume of the gas adsorbed measured at STP. The volume is, of course, proportional to N so that we have $N/N_{\text{mono}} = v/v_{\text{mono}}$.

$$\text{or } v_{\text{total}} = \frac{v_m cx}{(1-x)[1+(c-1)x]} \quad \text{.....(xix)}$$

where v_m stands for v_{mono}

Recalling that $x = Kp$ and that $K = 1/p^0$, we obtain the BET isotherm:

$$v_{\text{total}} \equiv v = \frac{v_m cp}{(p^0 - p)[1+(c-1)(p/p^0)]} \quad \text{.....(xx)}$$

The volume v_{total} is measured as a function of p . From the data we can obtain the value of v_{mono} and c . Note that when $p = p^0$, the equation has a singularity and $v \rightarrow \infty$. This accounts for the steep rise of the isotherm (Fig.) as the pressure approaches p^0 .

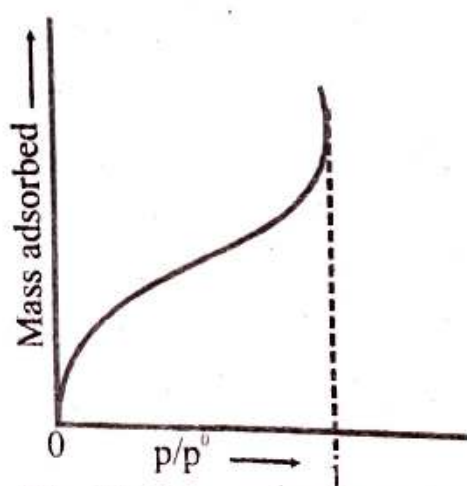


Fig. Multilayer physisorption.

To obtain the constants c and v_m , we multiply both sides of Eq. (xx) by $(p^0 - p)/p$:

$$\frac{v(p^0 - p)}{p} = \frac{v_m c}{1 + (c - 1)(p/p^0)} \quad \text{.....(xxi)}$$

Taking the reciprocal of both sides, we have

$$\frac{p}{v(p^0 - p)} = \frac{1}{v_m c} + \left(\frac{c - 1}{v_m c} \right) \left(\frac{p}{p^0} \right) \quad \text{.....(xxii)}$$

This is the well known BET equation.

The left - hand side of this equation is experimentally measured. The plot of $p/[v(p^0 - p)]$ versus p gives a straight line. From the intercept, $(1/v_m c)$ and the slope, $(c - 1)/(v_m c p^0)$, we can calculate the value of v_m , i.e., v_{mono} . From the value of v_{mono} at STP, N_{mono} can be calculated:

$$N_{\text{mono}} = \frac{N_A v_{\text{mono}}}{0.022414 \text{ m}^3 \text{ mol}^{-1}} \quad \text{.....(xxiii)}$$

Since N_{mono} is the number of molecules required to cover a unit mass of the adsorbent with a monolayer, then if we know the area, a , covered by a molecule, we can calculate the area of unit mass of material:

$$\text{Area/unit mass} = N_{\text{mono}} a \quad \text{.....(xxiv)}$$

In this way the surface area of a finely divided solid can be determined.

Q.4. Write short note on Freundlich adsorption isotherm. (2009, 14)

Ans. In 1909, Freundlich gave an empirical expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure. This equation is known as Freundlich Adsorption Isotherm or Freundlich Adsorption equation.

$$\frac{x}{m} = kP^{1/n}$$

Where x is the mass of the gas adsorbed on mass m of the adsorbent at

pressure P and k, n are constants whose values depend upon adsorbent and gas at particular temperature.

Explanation of Freundlich Adsorption equation: -

At low pressure, extent of adsorption is directly proportional to pressure (raised to power one).

$$\frac{x}{m} \propto P^1$$

At high pressure, extent of adsorption is independent of pressure (raised to power zero)

$$\frac{x}{m} \propto P^0$$

Therefore at intermediate value of pressure, adsorption is directly proportional to pressure raised to power $1/n$. Here n is a variable whose value is greater than one.

$$\therefore \frac{x}{m} \propto P^{1/n}$$

Using constant of proportionality, k also known as adsorption constant we get

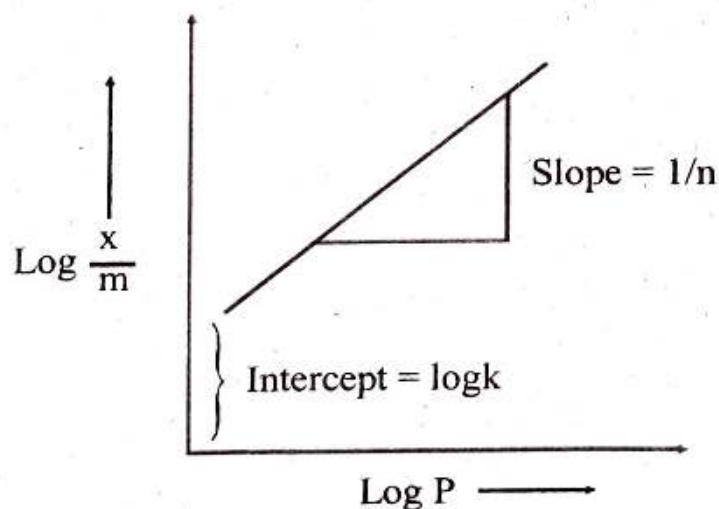
$$\frac{x}{m} = kP^{1/n}$$

The above equation is known as Freundlich adsorption equation.

Plotting of Freundlich Adsorption Isotherm:-

As per Freundlich adsorption equation

$$\frac{x}{m} = kP^{1/n}$$



Taking log both sides of equation, we get,

$$\log \left(\frac{x}{m} \right) = \log k + \frac{1}{n} \log P$$

The equation above equation is comparable with comparable with equation of straight line, $y = m x + c$ where, m represents slope of the line and c represents intercept on y axis.

Plotting a graph between $\log(x/m)$ and $\log p$, we will get a straight line with value of slope equal to $1/n$ and $\log k$ as y -axis intercept.

Limitation of Freundlich Adsorption Isotherm: -

Experimentally it was determined that extent of adsorption varies directly with pressure till saturation pressure P_s is reached. Beyond that point rate of adsorption saturates even after applying higher pressure. Thus Freundlich Adsorption Isotherm failed at higher pressure.

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Unit V

Q.1 Write note on clausius - Mossotti equation. (2017)

Other related question

Q. Explain clausius - Mossotti equation. (2009)

Q. Derive Clausius - Mossotti equation for molar polarization. (2014)

Ans. Clausius - Mossotti Equation: -

Suppose that several molecules of a substance in the solid, liquid or gaseous state are introduced into the space between the plates of a condenser which is charged by applying a constant electrostatic field. The substance is called a dielectric and is assumed to be an insulator. The charges on the condenser plates are partially compensated by the induced charges on the boundary of the dielectric (Fig.). The electric field strength in the dielectric is, therefore, reduced to a value E from its value E_0 in vacuum, the two quantities being related by the expression

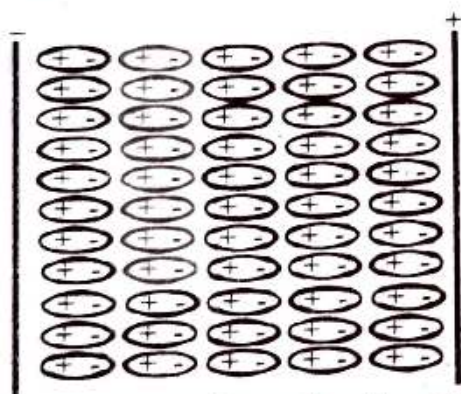


Fig. - Orientation of polar molecules in an electric field.

$$E_0 = E + 4\pi P \quad \dots\dots(i)$$

where P , called the dielectric polarization, is the induced dipole moment per unit volume of the dielectric. Thus, $p = N \mu_{ind}$ where N is the number of molecules per unit volume of the dielectric.

From Eq. (i). $E_0/E = 1 + 4\pi (P/E) = 1 + 4\pi (N \mu_{ind}/E) \quad \dots\dots(ii)$

or $\epsilon_r = 1 + 4\pi N \alpha_d \quad \dots\dots(iii)$

where the quantity $\epsilon_r (= E_0/E)$ is called the dielectric constant or relative permittivity. Here we have made use of the fact that $\alpha_d = \mu_{ind}/E$ where α_d is the distortion polarizability. The relative permittivity of the medium can be measured experimentally by using the relation

$$\epsilon_r = C/C_0 \quad \dots\dots(iv)$$

where C and C_0 are the capacitances of the condenser with the medium and the vacuum, respectively, as the dielectric between the plates.

Suppose that one mole of a substance of molar volume V_m , density ρ and molar mass M is used as a dielectric. Then,

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$$N = N_A / V_m = N_A \rho / M$$

Where N_A is the Avogadro number. Hence, Eq. (iii) can be written as

$$(\epsilon_r - 1)M / \rho = 4\pi N_A \alpha_d \quad \dots\dots(v)$$

Evidently, the ratio $(\epsilon_r - 1) / \rho$ is independent of ρ since α_d is a constant for a substance.

Eq. (v) holds for gases at very low pressures when the interaction of the dipole moments between the neighbouring molecules is negligible since the molecules are far apart. However, at high pressures and for condensed phases (solids or liquids), this relation does not hold since now interactions between induced moments have to be taken into consideration. Clausius and Mosotti, taking into consideration these interactions for condensed phases, introduced the following relation:

$$P_m = \frac{\epsilon_r - 1}{\epsilon_r + 2} V_m = (4\pi/3) N_A \alpha_d \quad \dots\dots(vi)$$

where the quantity P_m is called **molar polarization**. Eq. (vi) is known as the **Clausius - Mosotti equation**.

Relative permittivity, ϵ_r , is also defined as $\epsilon_r = \epsilon / \epsilon_0$ where ϵ is the permittivity of the medium and ϵ_0 is the permittivity of free space. In SI system, the Clausius - Mosotti equation is written as

$$P_m = \frac{\epsilon_r - 1}{\epsilon_r + 2} V_m = (N_A / 3\epsilon_0) \alpha_d \quad \dots\dots(vii)$$

Since α_d (viz., distortion polarizability) is a characteristic constant of molecule, hence P_m , according to Eq. (vi), should be a constant, independent of density or temperature. This has been verified experimentally for non - polar molecules such as H_2 , CO_2 , CH_4 , CCl_4 etc., which do not have a permanent dipole moment. The Clausius - Mosotti equation is not obeyed by polar molecules such as HCl , H_2O , NH_3 , etc., which possess a permanent dipole moment.

Q.2. Define molar refraction and explain its role in determining the chemical constitution. (2010)

Other Related Question -

Q. Define molar refraction and its additive and constitutional nature.

Ans. Molar Refraction: - (2015)

The refractive index of a fluid varies with temperature and pressure, as these factors alter the number of molecules in the path of the light. Hence, it cannot be used to compare refractive powers of different fluids in relation to their molecular structures.

To eliminate the effect of these factors, H.A. Lorenz (1880) from the electromagnetic theory of light, and L.V. Lorenz (1880) from the wave theory of light, independently deduced the following theoretical relationship between

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refractive index and density, which should be constant all temperatures:

$$R = \frac{\mu^2 - 1}{\mu^2 - 2} \times \frac{1}{d} \quad \text{.....(i)}$$

where μ is the refractive index of a liquid and 'd' its density, R is a constant called the specific refraction or refractivity. Multiplying the above equation by, the molecular weight of the liquid on both sides we get,

$$R \times M = \frac{\mu^2 - 1}{\mu^2 - 2} \cdot \frac{M}{d} = R_m \quad \text{.....(ii)}$$

The product $R \times M$ is denoted by R_m and is called the molar refraction or molar refractivity. R_m is characteristic of the liquid and remains constant at the given temperature.

The molar refraction is independent of temperature and pressure, but as is the case with refractive index it varies with the wave-length of the light used. Generally, the D-line of sodium is the light source. If any other source is employed (e.g., the D-line in the hydrogen spectrum) it should be specifically mentioned.

The molar refractivity of a solute, solvent and solution can be determined as follows:

A known weight of the solid is dissolved in a known weight of a suitable solvent. The refractive index and density of the solution are determined in the usual way. If R' is molar refractivity of the solution, it is given by,

$$R' = \frac{\mu^2 - 1}{\mu^2 - 2} \left[\frac{N_1 M_1 + N_2 M_2}{d} \right] \quad \text{.....(iii)}$$

where μ is the refractive index of the solution N_1, N_2 the mole fractions of the solute and solvent respectively, M_1 and M_2 are their molecular weights and 'd' and density of the solution. The molar refractivity of the solution R' , is related to the molar refractivities of the solute and solvent respectively as N_1 and N_2 have the same meaning as before.

The refractive index and density of the solvent are now determined and its molar refractivity R_2 is calculated with the help of equation (ii). Substituting this value in equation (4), R_1 the molar refractivity of the solutes is calculated.

Molar refraction or refractivity as an additive and constitutive property: -

It was found by comparing the R_m values for different substances that it is both additive and constitutive property, i.e., it depends upon both the number and arrangement of atoms in the molecule. Thus from a study of molar refractions of a large number of compounds the constants for different atoms and types of linkages were determined. For example, in a homologous series of aliphatic compounds of difference of CH_2 in composition makes a difference of 4.618 in molecular refractivity. The contribution of other atoms and structures can be calculated like molar volume as follows:

$$R_m \text{ for } \text{C}_7\text{H}_{16} = 34.54 \text{ cm}^3 \text{ mol}^{-1}$$

$$R_M \text{ for } C_6H_{14} = 29.92 \text{ cm}^3 \text{ mol}^{-1}$$

$$\text{Difference } (=CH_2) = 4.62 \text{ cm}^3 \text{ mol}^{-1}$$

$$\text{Thus, } C_6H_{14} = 6CH_2 + 2H$$

$$29.92 = 6 \times 4.62 + 2H$$

$$\therefore R_M \text{ for H atom} = 1.1 \text{ cm}^3/\text{atom}$$

$$C \text{ atom} = 4.62 - 2 \times 1.10$$

$$= 2.42 \text{ cm}^3/\text{g atom}$$

The molar refraction values for some elements and groups based of the refractive indices measured with the D-line of sodium have been included in table.

With the help of molar refraction contributions, given in Table the molar refraction of a compound O the basis of its assumed structure is calculated and compared with the value obtained experimentally. This can be understood from the following examples.

Table: Molar refraction contributions of atoms and bonds (Vogel 1948)

Atom or structure	$R_M(\text{cm}^3)$	Atom or structure	$R_M(\text{cm}^3)$
H	1.028	C - O	4.601
C	2.591	- OH	1.546
Cl	5.844	- COOH	7.226
Br	8.741	- NO ₂	6.713
I	13.954		1.575
O (>C=O)	2.573		1.977
O(R-O-R)	1.764	6 membered ring	- 0.15
O(-OH)	1.518	5 membered ring	- 9.89
C ₃ radical	5.653	4 membered ring	0.317
C ₂ H ₅ radical	10.300		

1. Structure of benzene - Kekule's formula for benzene is:

There are six carbon atoms, 6 hydrogen atoms, 3 double bonds and one six carbon atom ring.

$$\therefore \text{Molar refraction due to 6 C atoms} = 6 \times 2.591 = 15.546$$

$$\text{Molar refraction due to 6 H atoms} = 6 \times 1.028 = 6.168$$

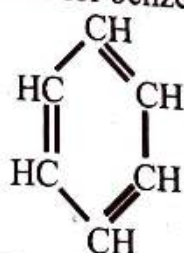
$$\text{Molar refraction due to 3 double bonds} = 3 \times 1.575 = 4.725$$

$$\text{Molar refraction due to one six membered ring} = 1 \times (-0.15) = -0.15$$

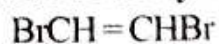
Total

$$= 25.289$$

The experimental value 25.95 is fairly close to the above calculated value. Hence the Kekule's structure for benzene is correct.



2. Structure of acetylene dibromide - The structure of acetylene dibromide is



$$2\text{C} = 2 \times 2.591 = 5.182$$

$$2\text{H} = 2 \times 1.028 = 2.056$$

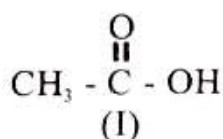
$$2\text{Br} = 2 \times 8.741 = 17.482$$

$$\text{One double bond} = 1 \times 1.575 = 1.575$$

$$\text{Total} = 26.295$$

The observed value is 26.30. Hence the formula of acetylene dibromide is verified. Thus molecular refractivities have been useful in deciding between the alternate structure of the various isomeric compounds.

3. Structure of acetic acid - The correct structure of acetic acid can be either (I) or (II).



$$2\text{C} \quad 3 \times 2.591 = 5.182$$

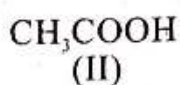
$$4\text{H} \quad 4 \times 1.028 = 4.112$$

$$\text{O}(\text{C}=\text{O}) \quad 1 \times 2.573 = 2.573$$

$$-\text{OH} \quad 1 \times 1.518 = 1.518$$

$$\text{Total} = 13.385$$

$$\text{Observed value of } R_M = 13.021.$$



$$\text{CH}_3 \text{ radical} = 5.653$$

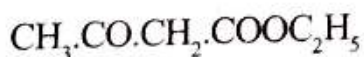
$$-\text{COOH} = 7.226$$

$$\text{Total} = 12.879$$

As the calculated value of R_M of structure I has been found to be very close to observed value of R_M , the structure I is the correct structure of acetic acid.

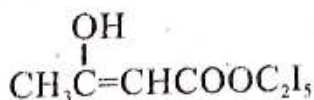
4. Keto-enol tautomerism - Molar refraction can give an approximate indication whether one or the other form in keto-enol tautomerism of a compound predominates in its normal state.

The enol form is having double bond and therefore two forms should possess different values of R_M . The calculated molar refractions of the keto and enol forms of acetoacetic ester are 31.57 and 32.62, respectively, hence



$$31.57$$

Keto



$$32.62$$

enol

The enolic form is having conjugated double bond and therefore, an optical exaltation equal to 1.8 is found. The molar refraction of the enolic form should be 34.42. The measured molar refraction of the acetoacetic ester in its normal state is 32. The proportion of enolic form should be given as follows:

$$\frac{32.00 - 31.57}{34.42 - 31.57} \times 100 = 15\%$$

Molecular refraction values such as parachor can be used for elucidation the chemical constitution. Even though the calculated and observed val-

ues of molecular refraction closely tally in many cases but anomalous results are also obtained. This is ascribed to the optical exaltation.

Q.3. Write short note on parachor.

(2016)

Other Related Question -

Q. Define parachor.

(2017,10)

Q. Explain the meaning of parachor.

(2012)

Ans. A numerical quantity (found empirically to be constant over a wide range of temperature) equal to the molecular weight of a liquid multiplied by the fourth root of its surface tension and divided by the difference between the density of the liquid and that of its vapour.

$$P = \gamma^{1/4} M / d$$

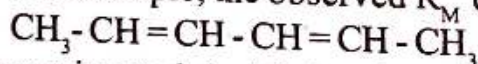
Q.4. Write short note on optical exaltation.

(2017)

Ans. Optical Exaltation:-

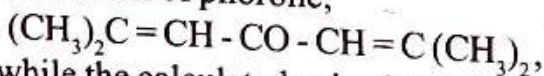
It is observed that when a compound contains more than one double bond, the molecular refractivity depends not only on the number of double bonds but on their position also. Thus in case of conjugated system of double bonds i.e., alternate double bonds there is a marked increase in the value of the observed molecular refractivity than the value calculated from the atomic and the structural constants. This behaviour is known as optical exaltation.

For example, the observed R_M of isodially,



having conjugated double bonds, is 1.76 units higher than the calculated R_M whereas for the isomeric dually, $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH} = \text{CH}_2$, in which the double linkages are not conjugated, the observed value of R_M is smaller by about 0.12 unit.

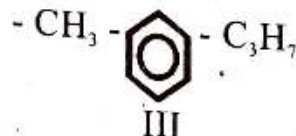
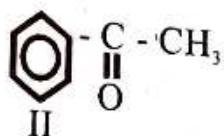
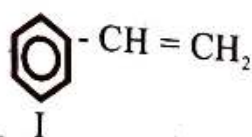
It has also been found that a carbonyl group, if present along with a double or triple bond, causes optical exaltation. Hence, the experimental value of molar refraction of phorone,



is 45.39 while the calculated value is 42.85.

$$\text{Optical exaltation} = 45.39 - 42.85 = 2.45$$

If the conjugated double linkages constitute a closed ring as in benzene and cyclo-octatetrene, the optical exaltation is observed but if the conjugated system is partly within the ring and partly in a side chain as in styrene I and acetophenone (II) the positive optical exaltation is observed.



If there exists a gap in the ring as in α -phellandrene (III), the optical exaltation is present.

Q.5. Write short note on dipole moment.

Other Related Questions -

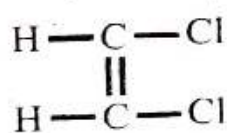
Q. Explain the meaning of dipole moment. What is its unit? Write down the Debye equation for the dipole moment and explain the meaning of each term. How dipole moment is determined? (2012)

Ans. Dipole Moments and Molecular Structure: -

The linear triatomic molecules of the type B - A - B (e.g., CO_2) have no dipole moment, not because the individual C = O bonds are non - polar but because the two bond moments cancel being equal and opposite. Again, angular triatomic molecules (such as H_2O) and linear asymmetric molecules (such as N_2O) have dipole moments because their bond moments do not cancel. For polyatomic molecules, the situation becomes increasingly complicated. For instance, in the case of the planar symmetrical molecule like AB_3 , the three bond moments cancel to give a zero dipole moment. BF_3 belongs to this category.

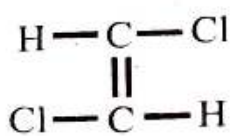
On the other hand, the vector sum of bond moments of NH_3 does not cancel so that the molecule possesses a dipole moment. This indicates that the three hydrogen atoms do not lie symmetrically with respect to the nitrogen atom. The high value (1.40D) of the dipole moment of NH_3 can be explained by assigning a triangular pyramidal structure to the molecule in which the nitrogen atom is situated at the apex of the pyramid and the three hydrogens lie at the three corners of the base.

Symmetrical polyatomic polar molecules do not show dipole moment if the vector sum of the bond moments cancels out. Examples are CH_4 , CCl_4 , SF_6 , C_6H_6 and $[\text{Ni}(\text{CN})_4]^{2-}$.



cis form

$$(\mu = 1.86 \text{ D})$$



trans form

$$(\mu = 0)$$

Dipole moments are helpful in distinguishing between the cis and trans isomers. Thus, the cis isomer of 1,2-dichloroethane has a dipole moment whereas the trans isomer does not. The zero dipole moment of the trans isomer is due to the fact that the vector sum of the bond moments of the two C - Cl bonds cancels and the dipole moment data can also help in the identification of cis and trans isomers of square planar PtA_2B_2 complexes. The trans isomer should have a very small dipole moment whereas the cis isomer should possess a fairly large moment. This fact is corroborated experimentally.

It may also be noted that the experimental measurement can yield only the magnitude, not the direction, of the dipole moment. In most cases it is possible to have a fairly good idea of the direction of the dipole moment by considering the difference in electronegativities and by making comparison with similar molecules. However, in several cases, it is difficult to predict the direction of the dipole moment. A well known example is furnished by carbon

monoxide, CO, which has a small value of $\mu = 0.10D$.

Debye Equation: -

In 1912, Debye considered the behaviour of polar molecules placed between the plates of a condenser. In the absence of the electric field, as a result of thermal motion, the molecules are randomly oriented so that there is no net dipole moment in any direction (Fig.(a)) However, on the application of the electric field across the plates of the condenser, the molecules under the combined influence of the electric field and the thermal motion orient themselves as shown in Fig.(b).

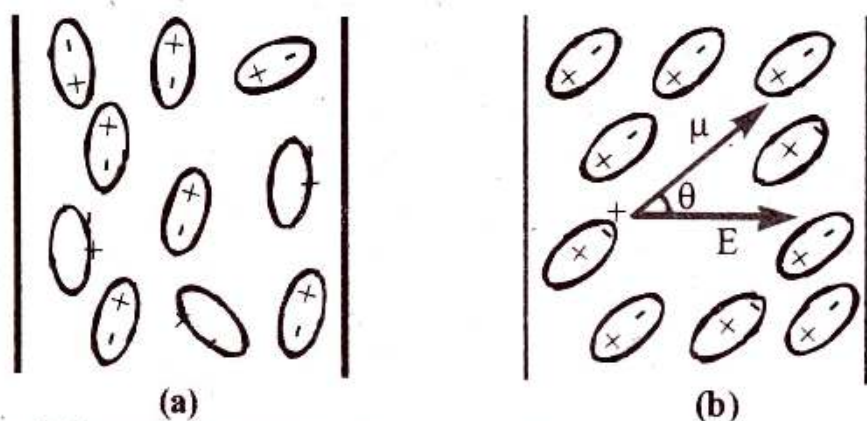


Fig. Orientation of molecules : (a) in the absence of an electric field (b) in the presence of an electric field.

Debye calculated the average component of the permanent dipole moment μ of a molecule in the direction of the electric field as a function of temperature.

For a randomly oriented dipole in the absence of electric field, all orientations are equally probable. This means that the number of dipole moments directed within a solid angle $d\omega$ is $A d\omega$, where A is a constant which depends on the number of molecules under observation.

The potential energy, U , of a polar molecule with molecular dipole moment μ oriented at an angle θ to the electric field of strength E is given by

$$U = -\mu E \cos \theta \quad \text{.....(i)}$$

According to the Boltzmann distribution, the number of molecules oriented within the solid angle $d\omega$ is given by

$$dN = A \exp(-U/kT) d\omega \quad \text{.....(ii)}$$

$$= A \exp(\mu E \cos \theta / kT) d\omega \quad \text{.....(iii)}$$

Hence, the average value of the dipole moment in the direction of the field is given by

$$\bar{\mu}_{ind} = \frac{\int A \exp(\mu E \cos \theta / kT) \mu \cos \theta d\omega}{\int A \exp(\mu E \cos \theta / kT) d\omega} \quad \text{.....(iv)}$$

where the integrals are taken over all the possible orientations. Putting $\mu E/kT = x$ and $\cos \theta = y$ (so that $dy = -\sin \theta d\theta$), we have

$$d\omega = 2\pi \sin \theta d\theta = 2\pi dy \quad \text{.....(v)}$$

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Thus, Eq. (iv) takes the form,

$$\frac{\bar{\mu}_{\text{ind}}}{\mu} = \frac{\int_{-1}^{+1} e^{xy} y dy}{\int_{-1}^{+1} e^{xy} dy} \quad \text{.....(vi)}$$

Using the standard integrals,

$$\int_{-1}^{+1} e^{xy} dy = (e^x - e^{-x}) / x \quad \text{.....(vii)}$$

$$\text{and } \int_{-1}^{+1} e^{xy} y dy = (e^x - e^{-x}) / x - (e^x + e^{-x}) / x^2 \quad \text{.....(viii)}$$

$$\text{we find that } \frac{\bar{\mu}_{\text{ind}}}{\mu} = \frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} = \coth x - \frac{1}{x} = L(x) \quad \text{.....(ix)}$$

where $L(x)$ is called the **Langevin function**. The Langevin function is plotted in fig. At room temperature, $x \ll 1$ so that on expanding $L(x)$ as a power series, only the first term needs to be retained, giving $L(x) = x/3$ so that

$$\bar{\mu}_{\text{ind}} = (\mu^2 / 3kT) E \quad \text{.....(x)}$$

Notice that $\bar{\mu}_{\text{ind}}$ decreases with increasing temperature; also, $\bar{\mu}_{\text{ind}}$ is directly proportional to E . It must, however, be pointed out that the proportionality between $\bar{\mu}_{\text{ind}}$ and E cannot be maintained if E is large since in that case saturation occurs. Thus, if all the molecules are completely oriented, further increase in E will not increase $\bar{\mu}_{\text{ind}}$.

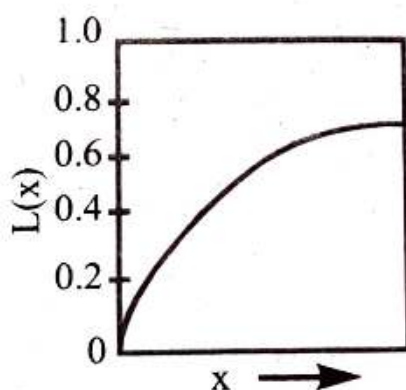


Fig. - Langevin function
 $L(x) = \coth x - (1/x)$

Defining the orientation polarizability α_μ as $\alpha_\mu = \bar{\mu}_{\text{ind}} / E$, we find from Eq. (x) that

.....(xi)

$$\alpha_{\mu} = \mu^2 / 3kT$$

We see that α_{μ} depends upon the permanent dipole moment μ and the temperature. It decreases with increasing T . At higher temperatures, thermal motion reduces the dipole orientation in the field. Thus,

$$\alpha = \alpha_d + \mu^2 / 3kT \quad \text{.....(xii)} \quad [\because \alpha = \alpha_d + \alpha_{\mu}]$$

In Clausius - Mosotti equation, the term α_{μ} had been ignored. Debye, however, took into consideration both α_d and α_{μ} when Clausius - Mosotti equation takes the form

$$P_m = \frac{\epsilon_r - 1}{\epsilon_r + 2} V_m = \frac{4}{3} \pi N_A \left(\alpha_d + \frac{\mu^2}{3kT} \right) \quad \text{.....(xiii)}$$

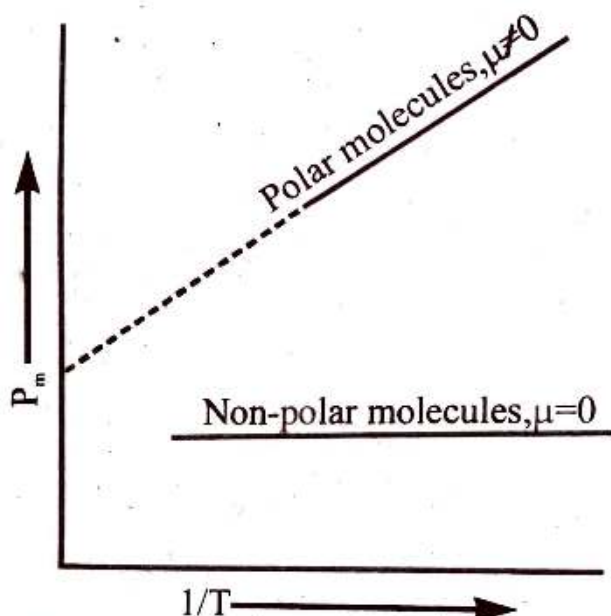


Fig. Plots of P_m versus $1/T$ for gaseous polar and non-polar molecules.

In SI units,
$$P_m = \frac{\epsilon_r - 1}{\epsilon_r + 2} V_m = \left(\frac{N_A}{3\epsilon_0} \right) \left(\alpha_d + \frac{\mu^2}{3kT} \right) \quad \text{.....(xiv)}$$

Eq. (xiii) or (xiv) is called the **Debye equation**. According to this equation, P_m varies linearly with $1/T$. The slope and the intercept of the linear Debye plot are $(4/9) \pi N_A \mu^2/k$ or $(1/9 \epsilon_0) N_A \mu^2/k$ and $(4/3) \pi N_A \alpha_d$ or $(1/3 \epsilon_0) N_A \alpha_d$, respectively. From the slope and the intercept, μ and α_d of the molecule can be determined. The Dutch physicist, Peter Debye (1884-1966) was awarded the 1936 Chemistry Nobel Prize for contributions to molecular structure through

his work on dipole moments.

Fig. shows the linear plots for a gaseous non-polar molecule (such as CH_4 with $\mu = 0$) and a gaseous polar molecule (such as HCl with $\mu \neq 0$). For a non-polar molecule, since $\mu = 0$, the plot of P_m versus $1/T$ yields a straight line parallel to the $1/T$ axis.

Remarks on units -

Since E is expressed as V m^{-1} (volt per metre) and μ_{ind} is expressed in C m , hence from dimensional analysis.

$$\alpha = \frac{\mu_{\text{ind}}}{E} = \frac{\text{Cm}}{\text{Vm}^{-1}} = \frac{\text{Cm}}{\text{JC}^{-1}\text{m}^{-1}} = \text{J}^{-1}\text{C}^2\text{m}^2$$

It is customary to define polarizability volume (α') as $(\alpha') = \alpha_d / 4\pi\epsilon_0$. Thus, α' has the units of volume :

$$\alpha' = \frac{\alpha_d}{4\pi\epsilon_0} = \frac{\text{J}^{-1}\text{C}^2\text{m}^2}{\text{J}^{-1}\text{C}^2\text{m}^{-1}} = \text{m}^3 \text{ (The units of } \epsilon_0 \text{ are } \text{J}^{-1}\text{C}^2\text{m}^{-1}\text{)}.$$

Q.6. Define specific rotation and molar rotation. (2016)

Ans. In chemistry, specific rotation ($[\alpha]$) is a property of a chiral chemical compound. It is defined as the change in orientation of monochromatic plane-polarized light, per unit distance-concentration product, as the light passes through a sample of a compound in solution. Compounds which rotate the plane of polarization of a beam of plane polarized light clockwise are said to be dextrorotary, and correspond with positive specific rotation values, while compounds which rotate the plane of polarization of plane polarized light counter-clockwise are said to be levorotary, and correspond with negative values. If a compound is able to rotate the plane of polarization of plane-polarized light, it is said to be "optically active".

Specific rotation is an intensive property, distinguishing it from the more general phenomenon of optical rotation. As such, the observed rotation (α) of a sample of a compound can be used to quantify the enantiomeric excess of that compound, provided that the specific rotation ($[\alpha]$) for the enantiopure compound is known. The variance of specific rotation with wavelength-a phenomenon known as optical rotatory dispersion-can be used to find the absolute configuration of a molecule. The concentration of bulk sugar solution is sometimes determined by comparison of the observed optical rotation with the known specific rotation.

The CRC Handbook of Chemistry and Physics defines specific rotation as:

For an optically active substance, defined by $[\alpha]_\lambda^\theta = \alpha/\gamma l$, where α is the angle through which plane polarized light is rotated by a solution of mass concentration γ and path length l . Here θ is the Celsius temperature and λ the wavelength of the light at which the measurement is carried out.

Values for specific rotation are reported in units of $\text{deg} \cdot \text{mL} \cdot \text{g}^{-1} \cdot \text{dm}^{-1}$, which are typically shortened to just degrees, wherein the other components of the unit are tacitly assumed. These values should always be accompanied by information about the temperature, solvent and wavelength of light used, as all of these variables can affect the specific rotation. As noted above, temperature and wavelength are frequently reported as a superscript and subscript, respectively, while the solvent is reported parenthetically, or omitted if it happens to be water.

Measurement: -

Optical rotation is measured with an instrument called a polarimeter. There is a linear relationship between the observed rotation and the concentration of optically active compound in the sample. There is a nonlinear relationship between the observed rotation and the wavelength of light used. Specific rotation is calculated using either of two equations, depending on whether the sample is a pure chemical to be tested or that chemical dissolved in solution.

For pure liquids

This equation is used:

$$[\alpha]_{\lambda}^T = \frac{\alpha}{\ell \times \rho}$$

In this equation, α (Greek letter "alpha") is the measured rotation in degrees, ℓ is the path length in decimeters, and ρ (Greek letter "rho") is the concentration of the liquid in g/mL , for a sample at a temperature T (given in degrees Celsius) and wavelength λ (in nanometers). If the wavelength of the light used is 589 nanometers (the sodium D line), the symbol "D" is used. The sign of the rotation (+ or -) is always given.

$$[\alpha]_{\text{D}}^{20} + 6.2^0$$

For solutions -

For solutions, a slightly different equation is used:

$$[\alpha]_{\lambda}^T = \frac{\alpha}{\ell \times c}$$

In this equation, α (Greek letter "alpha") is the measured rotation in degrees, ℓ is the path length in decimeters, c is the concentration in g/mL , T is the temperature at which the measurement was taken (in degrees Celsius), and λ is the wavelength in nanometers.

For practical and historical reasons, concentrations are often reported in units of g/100mL . In this case, a correction factor in the numerator is necessary:

$$[\alpha]_{\lambda}^T = \frac{100 \times \alpha}{\ell \times c}$$

When using this equation, the concentration and the solvent may be provided in parentheses after the rotation. The rotation is reported using degrees, and

no units of concentration are given (it is assumed to be g/100mL). The sign of the rotation (+ or -) is always given. If the wavelength of the light used is 589 nanometer (the sodium D line), the symbol "D" is used. If the temperature is omitted, it is assumed to be at standard room temperature (20 °C).

For example, the specific rotation of a compound would be reported in the scientific literature as:

$$[\alpha]_D^{20} + 6.2^0 (c 1.00, \text{EtOH})$$

Q.7. Write short note on molar volume.

(2018)

Ans. Molar Volume: -

The molar volume, symbol V_m , is the volume occupied by one mole of a substance (chemical element or chemical compound) at a given temperature and pressure. It is equal to the molar mass (M) divided by the mass density (ρ). It has the SI unit cubic metres per mole (m^3/mol), although it is more practical to use the units cubic decimetres per mole (dm^3/mol) for gases and cubic centimetres per mole (cm^3/mol) for liquids and solids.

The molar volume of a substance can be found by measuring its molar mass and density then applying the relation.

$$V_m = \frac{M}{\rho}$$

If the sample is a mixture containing N components, the molar volume is complex. It can be simply the sum of the individual components, and calculated using:

$$V_m = \frac{\sum_{i=1}^N x_i M_i}{\rho_{\text{mixture}}}$$

But this is violated by many liquid-liquid mixtures. For instance mixing pure ethanol into pure water causes a decrease in the volume calculated by this formula. This effect is called "excess volume".

Ideal gases -

For ideal gases, the molar volume is given by the ideal gas equation; this is a good approximation for many common gases at standard temperature and pressure. The ideal gas equation can be rearranged to give an expression for the molar volume of an ideal gas:

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

Hence, for a given temperature and pressure, the molar volume is the same for all ideal gases and is known to the same precision as the gas constant: $R = 0.082\,057\,338(47) \text{ L atm K}^{-1} \text{ mol}^{-1}$, that is a relative standard uncertainty of 5.7×10^{-7} , according to the 2014 CODATA recommended value. The molar vol-

ume of an ideal gas at 100 kPa (1 bar) is

0.022 710 980(38) m³/mol at 0 °C,

0.024 789 598(42) m³/mol at 25 °C.

The molar volume of an ideal gas at 1 atmosphere of pressure is

0.022 414 m³/mol at 0 °C,

0.024 465 m³/mol at 25 °C.

Crystalline solids: -

For crystalline solids, the molar volume can be measured by X-ray crystallography. The unit cell volume (V_{cell}) may be calculated from the unit cell parameters, whose determination is the first step in an X-ray crystallography experiment (the calculation is performed automatically by the structure determination software). This is related to the molar volume by

$$V_m = \frac{N_A V_{\text{Cell}}}{Z}$$

where N_A is the Avogadro constant and Z is the number of formula units in the unit cell. The result is normally reported as the "crystallographic density"

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Unit VI

Q.1. Discuss Derjaguin, Landau, Verway over beek (DLVO) Theory of the stability of colloids. What are protective colloids. (2015)

Other related questions -

Q. Describe the importance of zeta potential in stability of colloids. (2009)

Q. Write short note on zeta potential. (2016, 17)

Q. Write short note on Electrokinetic potential. (2014, 19)

Ans. DLVO Theory of the Stability of Lyophobic Colloids: -

This theory, involving the concept of zeta potential, was developed by the Russian scientists D. Derjaguin and L.D. Landua, and independently, by the Dutch scientists E. Verway and J.T.G. Overbeek. According to this theory, there is a balance between the repulsive interactions between the charges of the electrical double layers on neighbouring particles and the attractive van der Waals interactions between the molecules in the particles. The repulsive potential energy of the double layer on particles, each of radius a , is given by

$$V_{\text{rep}} = \frac{Aa^2\zeta^2}{R} e^{-s/r_D}; a \ll r_D \quad \text{.....(i)}$$

where A is a constant, ζ is the zeta potential, R is the separation of the centres, s is the separation of the surfaces of the two particles ($s = R - 2a$ for spherical particles of radius a) and r_D is the thickness of the electrical double layer, Eq.(ii) holds for a thick double layer ($a \ll r_D$). For a thin double layer ($a \gg r_D$),

$$V_{\text{rep}} = \frac{Aa\zeta^2}{2} \ln(1 + e^{-s/r_D}); a \gg r_D \quad \text{.....(ii)}$$

The potential arising from the attractive interaction is given by

$$V_{\text{att}} = -B/s \quad \text{.....(iii)}$$

where B is another constant.

Treating the electrical double layer as a simple electrical condenser, the zeta potential ζ is given by the expression,

$$\zeta = 4\pi\eta u/\epsilon_r \quad \text{.....(iv)}$$

where η are ϵ_r are the viscosity and the dielectric constant, respectively, of the dispersion medium and u is the mobility of the colloidal particles.

For water as the dispersion medium, ζ is found to lie between 0.03 and 0.06 V. The value of ζ decreases when an ion of opposite charge to that of the colloidal particle is adsorbed. This reduces the mutual repulsion between the similarly charged colloidal particles. As a result, the colloidal particles easily come closer to one another to coalesce and form bigger aggregates which lie outside the colloidal range. This phenomenon of changing colloidal state to a

suspended state is known as **coagulation, flocculation or precipitation** of colloidal solutions.

In the case of lyophobic colloids, the stability is due to the electrical charge present on the colloidal particles whereas the stability of the lyophilic colloids depends upon both the electrical charge and solvation. In order to cause precipitation of the dispersed particles, it is necessary that they coalesce into large aggregates. Since in a lyophobic sol, the charge on all the colloidal particles is of the same sign, the repulsive forces prevent the particles from approaching sufficiently close to one another and to coalesce and coagulate. The magnitude of the repulsive forces depends upon the magnitude of the surface charge and the thickness of the electrical double layer. These factors also determine the value of the zeta potential which actually governs the stability of the colloidal system. If ζ is small, the resultant potential energy is negative so that the van der Waals attraction predominates over the electrostatic repulsion and the sol coagulates rapidly.

On the other hand, in the case of lyophilic sols, solvation plays a very important role. Since the colloidal particles are enclosed in a solvent 'cage', the cage serves as a barrier preventing the particles from coalescing to form aggregates. Thus, whereas in the case of lyophobic sols, removal of electrical charge may easily bring about coagulation, in the case of lyophilic colloids, the charge removal may not necessarily result in coagulation though it may decrease the stability of the sol.

When a lyophilic colloid is added to a lyophobic colloid, the latter is rendered less sensitive to the precipitating action of an electrolyte. This is expressed by saying that the lyophilic colloid protects a lyophobic colloid from precipitation by the action of electrolytes. That is why substances such as gum acacia, gelatin, tragacanth, etc., are known as **protective colloids**. They probably function by getting adsorbed on the solid surface in the form of loops wherein water gets trapped. These loops prevent the approach of particles to cause coagulation.

Zsigmondy gave quantitative treatment of the stabilizing action of the protective colloids. He introduced a quantity called the gold number of a protective colloid. The **gold number** is defined as the largest number of milligrams of a protective colloid which, when added to 10ml of a special standard gold sol, just fails to prevent the colour change from red to blue upon the addition of one ml of 10 percent sodium chloride solution. It must be emphasized that the protective action of a lyophilic sol depends upon several factors such as sol dispersity, the molar mass of the lyophilic sol, the pH of the solution at which the experiment is carried out, and so on.

It is customary to use sols other than gold sols to determine the protective action of a high molar mass colloid. Thus, silver, sulphur, prussian blue, etc., sols have been used and the corresponding 'numbers' determined accordingly.

Protective Action of High Molar Mass Lyophilic colloids on Some Hydrophobic Sols

Protective Colloids	Numbers					
	Gold	Silver	Sulphur	Iron oxides	Rubin	Prussian blue
Gelatin	0.01	0.035	0.00012	5	2.5	0.05
Dextrin	20	100	0.125	20		250
Saponin	115	35	0.015	11.5		2.5
Potato Starch	20				20	
Hemoglobin	0.03-0.07				0.8	
Egg albumin	2.5	1.5	0.025	15	2.0	25
Gum Arabic	0.5	1.25	0.125	20		5

Note - Zeta potential is a scientific term for electrokinetic potential in colloidal dispersions.

Q.2. Write short note Donnan membrane equilibrium. (2011, 13, 14, 15)

Other Related Questions -

Q. Discuss Donnan membrane theory.

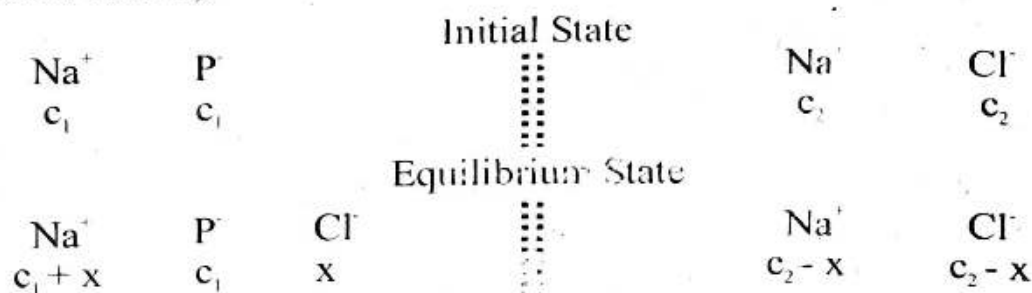
(2017)

Ans. Molar Mass of Charged Macromolecules: -

Donnan Membrane Equilibrium: -

The molar masses of charged macromolecules (e.g., proteins), determined by osmotic pressure measurements in electrolytic media were found to be considerably smaller than those determined by other methods. This was found to be due to an electrical phenomenon, known as Donnan membrane equilibrium, which occurs when a large, non-diffusible, charged ion (e.g., a protein ion), is separated by a semipermeable membrane from a diffusible salt.

Suppose a solution of a salt Na^+P^- of concentration c_1 (where P^- is a protein particle carrying a negative charge) is separated by a semipermeable membrane from a solution of sodium chloride of concentration C_2 (see the initial state shown below). During osmosis, the chloride ions tend to diffuse from a region of higher concentration c_2 on the right to a region of lower concentration c_1 on the left. However, the protein ions P^- cannot pass through the membrane. In order to maintain electrical neutrality, an equal number of Na^+ ions would pass from right to left across the membrane (see the equilibrium state shown below).



The osmotic pressure measurement would thus get complicated by the additional number of particles present on the left side, i.e., on the protein side of the membrane. Let x be the concentration change due to the diffusion of NaCl across the membrane. In both the compartments, electrical neutrality must be maintained, i.e., the total concentration of positive ions should be equal to the of the negative ions in each solution.

At equilibrium, the chemical potential of NaCl which is present on both sides of the membrane, must be the same on each side. Accordingly,

$$\mu^0 + RT \ln (a_{\text{NaCl}})_l = \mu^0 + RT \ln (a_{\text{NaCl}})_r \quad \text{.....(i)}$$

where a_{NaCl} represents the activity of sodium chloride and the subscripts l and r refer to the solutions on the left and the right of the semipermeable membrane. Thus, we have for the left compartment,

$$(a_{\text{NaCl}})_l = (a_{\text{Na}^+})_l (a_{\text{Cl}^-})_l = (\gamma_{\pm})_l^2 (\text{Na}^+)_l (\text{Cl}^-)_l \quad \text{.....(ii)}$$

and for the right compartment,

$$(a_{\text{NaCl}})_r = (a_{\text{Na}^+})_r (a_{\text{Cl}^-})_r = (\gamma_{\pm})_r^2 (\text{Na}^+)_r (\text{Cl}^-)_r \quad \text{.....(iii)}$$

Assuming that the mean ionic activity coefficients in the left and the right compartments are equal, i.e., $(\gamma_{\pm})_l = (\gamma_{\pm})_r$, which is usually the case since the ionic strengths are equal, we can express the Donnan equilibrium as

$$[\text{Na}^+]_l [\text{Cl}^-]_l = [\text{Na}^+]_r [\text{Cl}^-]_r$$

$$\text{or } (c_1 + x)x = (c_2 - x)(c_2 - x) = (c_2 - x)^2$$

$$\text{or } c_1x + x^2 = c_2^2 + x^2 - 2c_2x \text{ or } x(c_1 + 2c_2) = c_2^2$$

$$\therefore x = c_2^2 / (c_1 + 2c_2) \quad \text{.....(iv)}$$

It is evident from Eq. (iv) that the magnitude of x depends on c_2 , the concentration of salt, as well as on c_1 , the concentration of the protein. This means that the extent of diffusion of sodium chloride, viz., x , is distinctly affected by the presence of the non-diffusible protein ion P^- . If the solution behaves ideally, the osmotic pressure can be calculated with the help of the van't Hoff equation, viz., $\Pi = RTc$; the concentration term c , in the present case, being the difference in the molar concentrations on the two sides of the membrane. Thus, at equilibrium,

$$\begin{aligned} \Pi &= RT \{[(c_1 + x) + (c_1 + x)] - [(c_2 - x) + (c_2 - x)]\} \\ &= 2RT(c_1 - c_2 + 2x) \end{aligned} \quad \text{.....(v)}$$

If the concentration of the salt c_2 is small as compared to the concentration of the non-diffusible ion, c_1 , the osmotic pressure would be given by $\Pi = 2RT(c_1 + 2x)$. Since this pressure is higher than the actual pressure which should have been given by $\Pi = 2RTc_1$, the molar mass determined from osmotic pressure measurement would be smaller than the actual value.

If the concentration of the salt c_2 is large as compared to the concentration c_1 of the non-diffusible ion, then, according to Eq. (iv), $2x$ is equal to c_2 . Eq. (v), therefore, takes the form

$$\Pi = 2RTc_1 \quad \text{.....(vi)}$$

This equation does not involve the concentration of the chloride ion. In other words, the effect of Donnan equilibrium on osmotic pressure is practically eliminated by using a high concentration of salt in the solution. This is precisely the condition under which molar masses of such macromolecules should be determined from osmotic pressure measurements.

Q.3. Describe any one method for the determination the method of colloidal particles . (2016, 19)

Other related Question:-

Q. Determination of size of colloidal particles. (2014)

Q. Describe a method for determination of size of colloidal particles. (2009)

Ans. Determination of size of colloidal particles: -

There are a number of methods for the determination of size of colloidal particles. Some of these are given below.

1. By Using Ultrafilters: -

An approximate idea about the size of particles in a colloidal system can be obtained by the use of ultrafilters. These are prepared by impregnating filter papers with collodion or gelatin which are subsequently hardened by immersing in formaldehyde. The pores can be made small enough to retain particles of colloidal dimensions. The size of the pores depends upon the particular filter paper employed and the concentration of the collodion or gelatin solution used for impregnating it. It is thus possible to obtain a series of graded ultrafilters by means of which a colloidal solution may be separated into fractions containing particles of different sizes. An approximate estimate of the size of particles can be obtained from a knowledge of the dimensions of the pores of the ultrafilters. The latter parameter is determined from the pressure required to force air or water through the pores. The results obtained by this method are only approximate because pore size is by no means the only factor which determines whether a given particle will pass through an ultrafilter or not .

2. From Brownian Movement: -

Colloidal particles suspended in a liquid medium are subjected to Brownian movement. They also tend to settle down due to gravitation. Under the influence of both these effects, the particles distribute themselves in a vertical column in accordance with the equation

$$(RT/N_A) \ln (n_1/n_2) = (4/3) \pi r^3 (h_2 - h_1) (\rho - \rho')$$

Since the number of particles n_1 and n_2 at two depths h_1 and h_2 of the vertical column can be counted with the help of an ultra - microscope and densities of the particles and of the liquid medium, ρ and ρ' , can be determined by the usual methods, the radius of the particles, r , can be easily calculated. Brownian motion of colloidal system was investigated by the French physicist Jean Perrin (1870 - 1942) to determine the Avogadro's number. Perrin was awarded the 1926 Physics Nobel prize for his work on the discontinuous structure of matter and especially for his discovery of the sedimentation equilibrium.

3. From Scattering of Light: -

Zsigmondy used the ultra-microscope for determining the size of the particles of colloidal dimensions. Each spot of light viewed in ultramicroscope corresponds to a particle. The number of particles in a given volume of a solution, therefore, can be counted. The observation is repeated several times and an average is taken. The length and breadth of the field of vision are measured with the help of an eye-piece micrometer. The depth is determined by rotating the slit through 90° . From these dimensions, the exact volume of the solution containing the observed number of particles can be obtained. From this, the number of particles n , contained per unit volume of the solution can be determined.

Next, a known volume of the colloidal solution is evaporated to dryness. From the mass of the residue, the mass of colloidal particles per unit volume can easily be obtained. Let this be m . Now two assumptions are made. Firstly, the particles are spherical. Secondly, the density ρ of the colloidal particles is the same as that of the material in the bulk state. The volume of colloidal phase is m/ρ and, therefore,

$$m/\rho = (4/3) \pi r^3 \times n \text{ or } r = (3m/4 \pi \rho n)^{1/3}$$

Richard Zsigmondy (1865 - 1929), the German chemist, was the recipient of the 1925 Chemistry Nobel Prize for demonstration of the heterogeneous nature of colloidal solutions.

Q.4. Explain the stability of colloids and describe their optical and electrical properties. (2010)**Other related question -****Q. Write short note on stability of colloids. (2013)****Ans:- Stability:- Go through Q.1.****Optical Properties: -**

It was observed by Tyndall, in 1869, that when a beam of light is passed through a true solution, it cannot be seen unless the eye is placed directly in its path. However, when the same beam of light is passed through a colloidal dispersion, it becomes visible as a bright streak. This phenomenon is known as the **Tyndall effect** and the illuminated path (streak of light) is known as **Tyndall cone** (Fig.1). This phenomenon is due to the scattering of light from the surface of colloidal particles. In a true solution, there are no particles of sufficiently large diameter to scatter light and hence the beam is invisible.

The visibility of dust particles in a semi-darkened room when a sun beam enters or when light is thrown from a light projector, are familiar examples of Tyndall effect. The dust particles are large enough to scatter light and thus render the path of light visible.

The intensity of the scattered light depends on the difference between the refractive indices of the dispersed phase and the dispersion medium. In lyophobic sols, this difference is appreciable and, therefore, the Tyndall effect

is quite well-defined. In lyophilic sols, the particles are largely solvated. This lowers the difference in the refractive indices of the two phases and hence the Tyndall effect is much weaker. Thus, in the sols of freshly prepared silicic acid, blood serum, albumins, etc., there is little or no Tyndall effect.

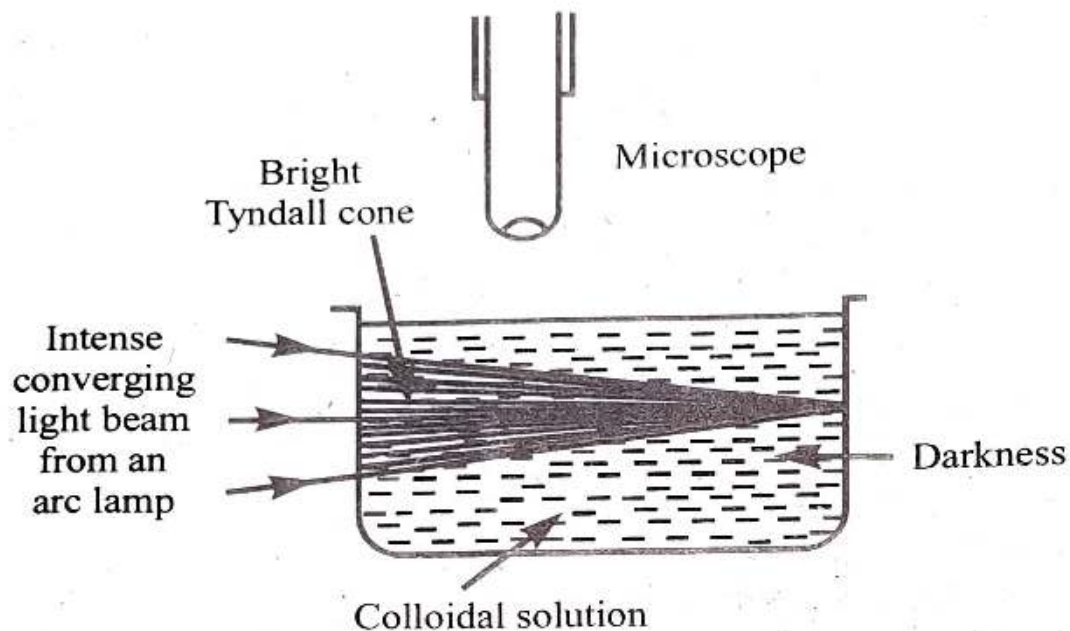


Figure 1 - Principle of ultramicroscope

The Tyndall effect has been used by Zsigmondy and Siedentopf in devising the **ultra - microscope**. A strong beam of light from an arc lamp or any other source is condensed by a system of lenses and passed through the colloidal solution. The scattered beam (Tyndall beam) is viewed through a microscope placed at right angles to the beam (Fig. 1). In this way, the colloidal particles which are too small to be seen under an ordinary microscope, can be detected as spots of light moving irregularly. It may be emphasised that we do not see the actual particles; they are too small to be visible. We see only the light scattered by them. Our eye pictures various spots of light as round or spherical particles.

Electrical Properties: -

Charge on Colloidal Particles: -

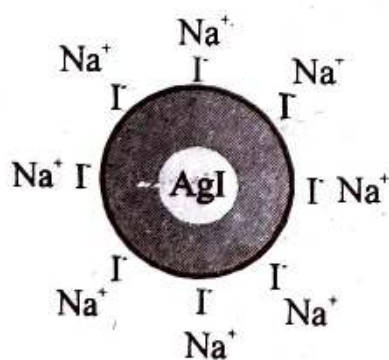
The most important property of hydrophobic colloidal dispersions is that the particles carry electric charge. All the particles in a given hydrophobic colloidal system carry the same charge and the dispersion medium has an opposite and equal charge, the system as a whole being electrically neutral. The presence of similar charges on colloidal particles is largely responsible in giving stability to colloidal systems because the mutual forces of repulsion between similarly charged particles prevent them from coalescing and coagulating or aggregating when they come closer to one another. Metallic hydroxides, some metals (such as bismuth, lead, iron), methyl violet and methylene blue, are electropositive colloids while metallic sulphides, prussian blue, many

metals (such as silver, gold, platinum), silicic acid, tannic acid and mastic are electronegative colloids.

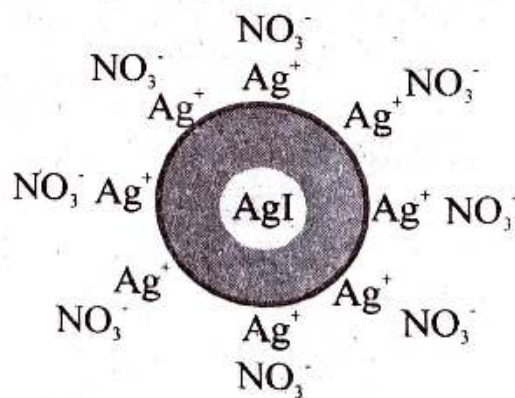
The Origin of Charge on Colloidal Particles: -

The origin of charge on colloidal particles has not been completely understood. However, it has been observed that sols are invariably associated with minute quantities of electrolytes and that if the latter are completely removed by persistent dialysis, the sols become unstable. It is believed, therefore, that the charge on the colloidal particles is due to **preferential adsorption** of either positive or negative ions on their surface. If the particles have a preference to adsorb positive ions, they acquire a positive charge and if they prefer to adsorb negative ions, they acquire a negative charge. According to this view, positive charge on ferric hydroxide sol prepared by hydrolysis of ferric chloride is largely due to preferential adsorption of Fe^{3+} ions on the surface of particles of ferric hydroxide. The ferric ions come from ionisation of ferric chloride which is always present in traces in the sol.

Similarly, the negative charge on arsenic sulphide sol is due to preferential adsorption of sulphide ions on the surface of arsenic sulphide particles. The sulphide ions are furnished by ionisation of hydrogen sulphide which is present in traces. Likewise, the negative charge on metal sols prepared by the Bredig's arc method is due to adsorption of hydroxyl ions furnished by traces of the alkali added. It should be remembered that the ion which is more nearly related chemically to the colloidal particle is preferentially absorbed by it. Thus, in ferric hydroxide sol, ferric and not chloride ion is preferred. Similarly, in arsenic sulphide sol, sulphide and not hydrogen ion is preferred.



(a) Negatively charged sol of AgI



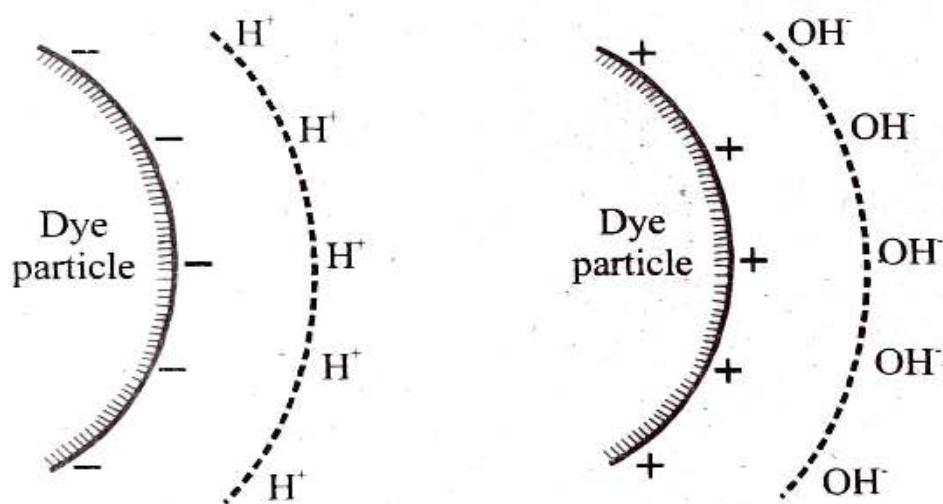
(b) Positively charged sol of AgI

Figure 2

An interesting case is furnished by stannic oxide sol. If a freshly formed precipitate of stannic oxide is peptised by a small amount of hydrochloric acid, the sol carries a positive charge but if peptised by a small amount of sodium hydroxide, the sol carries a negative charge. In the former case, a small amount of stannic chloride, SnCl_4 , is formed and the positively charged Sn^{4+} ion is preferred and the sol is positively charged. In the latter case, a small amount of sodium stannate, Na_2SnO_3 , is formed and now the negatively charged SnO_3^{2-} ion is preferred and accordingly the sol is negatively charged. The chloride

and sodium ions, known as counter ions, are directed towards the liquid phase.

Another interesting case is furnished by the formation of positively as well as negatively charged sols of silver iodide. If a dilute solution of silver nitrate is added to a slight excess of a dilute solution of sodium iodide, a negatively charged sol of silver iodide is formed. This is due to the adsorption of iodide ions. The structure of the sol particle is represented as in Fig. 2(a). But, if a dilute solution of sodium iodide is added to a slight excess of dilute solution of silver nitrate, a positively charged sol of silver iodide is formed due to the adsorption of silver ions. The structure of the sol particle is now represented as in Fig. 2(b). However, if silver nitrate and sodium iodide are mixed in equivalent amounts, there is precipitation of silver iodide and no sol is formed. It may be mentioned once again that the ions preferred by colloidal particles are those which are common to them. Thus, in the above example, in the first case, iodide prefers iodide ion and not sodium ion. In the second case, it prefers silver ion and not nitrate ion. The counter ion, in each case, is directed towards the liquid phase.



(a) An acidic dyestuff

(b) A basic dyestuff

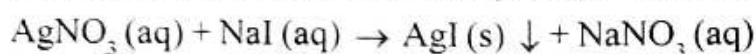
Figure 3 - Origin of charge in dyestuffs from ionisation of surface groups.

Thus, on the surface of a colloidal particle there is an electrical double layer of opposite charges.

Another possible way in which colloidal particles may acquire charge is by direct ionisation of the material constituting the particles. This phenomenon is observed mostly in the case of acidic and basic dyestuffs. An acidic dyestuff, for example, ionises yielding hydrogen ions in solution and thereby leaving an equivalent amount of negative charge on the particles. The structure of the colloidal particles of the dye may be represented as shown in Fig. 3(a). A basic dyestuff, on the other hand, ionises yielding hydroxyl ions in solution and thereby leaving an equivalent amount of positive charge on the particles. The structure of the colloidal dye particles in this case may be represented as shown in Fig.3(b).

The Electrical Double Layer:-

Central to the understanding of the electrical properties of colloids is the concept of **electrical double layer**. Consider once again the formation of silver iodide sol from the double decomposition reaction.



Let us suppose that the electrolyte used in excess is sodium iodide. This would result in preferential adsorption of I^- ions giving a negatively charged sol of silver iodide, as illustrated above (Fig.2(a)).

The ions preferentially adsorbed on the surface of a particle of a colloidal system are called potential - determining ions.

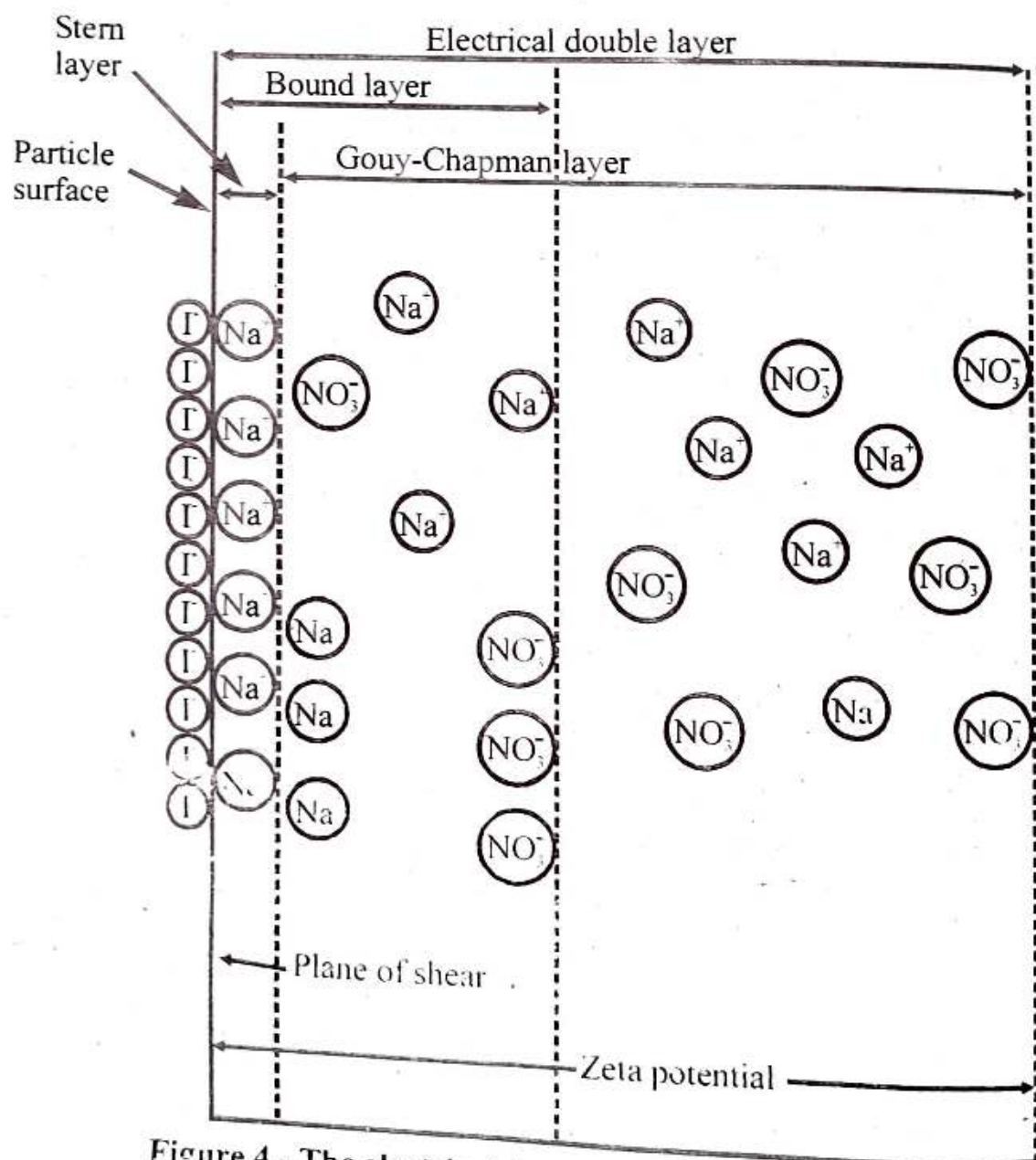


Figure 4 - The electrical double layer in colloidal systems.

The negatively charged surface of AgI particle attracts the positive ions (Na^+) and repels the negative ions (NO_3^-). As a result, the positive Na^+ ions tend to form a compact layer in the vicinity of the potential-determining I^- ion.

layer. This is called the **stern layer** (Fig.4). The ions present in the stern layer are called the counter ions.

The influence of the surface charge decreases with distance and so does the number of ions with the result that at a certain distance from the surface of the particle, the concentration of Na^+ ions equals the concentration of NO_3^- ions and a state of electroneutrality prevails (Fig.4). It must be borne in mind that the system as a whole is electrically neutral even though there exist regions of unequal distribution of anions and cations. The diffuse layer between the stern layer and the electrically neutral part of the system is referred to as the **Gouy - Chapman layer**.

The presence of charge gives rise to potential at the surface of the particle. This potential drops to zero at some distance away from the surface depending upon the concentration of the counter ions in the bulk phase. The region in which the influence of the charge is appreciable is known as the electrical double layer. The double layer consists of two parts: the Stern layer, the thickness of which is of the order of ionic dimensions and the Gouy - Chapman diffuse layer, the thickness of which is given by

$$r_D = \left(\frac{\epsilon_r RT}{2\rho F^2 I} \right)^{1/2} \quad \text{.....(i)}$$

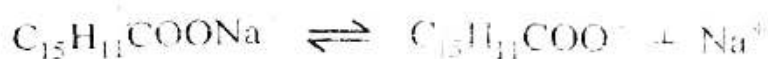
where ρ , ϵ_r and I are, respectively, the density, the dielectric constant and the ionic strength of the solution. F is the Faraday constant. The value of r_D is of the 1-100nm. It decreases as the ionic strength of the solution increases; more rapidly for counter of high valency.

A very important quantity reckoned with in the present context is the so-called **zeta potential** (ζ) defined as the difference in potential between the surface of the tightly bound layer (called the **plane of shear**) and the electroneutral region of the solution. The zeta potential is located at the shear plane. It determines the stability of colloidal systems.

Q.5. Determination of charge on colloidal particles. (2012)

Ans. The origin of the charge on the sol particles in most cases is due to the preferential adsorption of either positive or negative ions on their surface. The sol particles acquire electrical charge in any one or more of the following ways.

(1) Due to the dissociation of the surface molecules : Some colloidal particles develop electrical charge due to the dissociation / ionisation of the surface molecules. The charge on the colloidal particles is balanced by the oppositely charged ions in the sol. For example, an aqueous solution of soap (sodium palmitate) which dissociates into ions as,



The cations (Na^+) pass into the solution while the anions ($\text{C}_{15}\text{H}_{31}\text{COO}^-$) have a

tendency to form aggregates due to weak attractive forces present in the hydrocarbon chains.

(2) Due to frictional electrification:

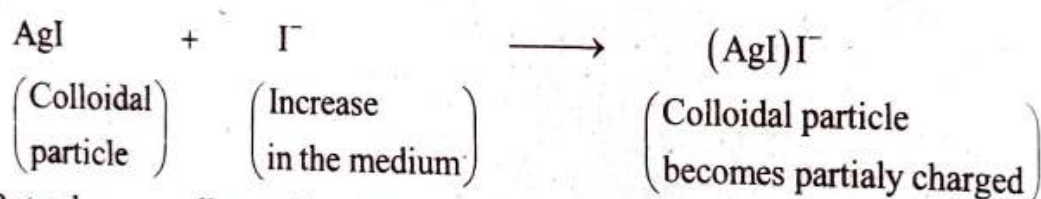
(i) It is believed that the frictional electrification due to the rubbing of the dispersed phase particles with that of dispersion medium results in some charge on the colloidal particles.

(ii) The dispersion medium must also get some charge, because of the friction. Since it does not carry any charge, the theory does not seem to be correct.

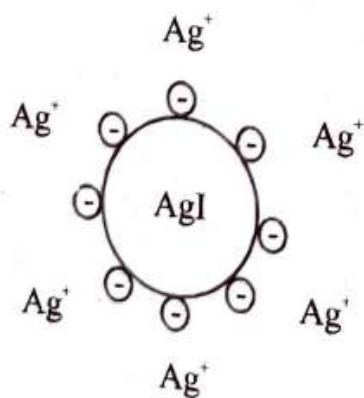
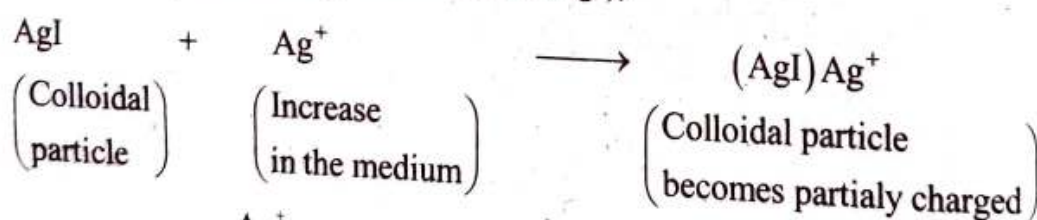
(3) Due to selective adsorption of ions:

(i) The particles constituting the dispersed phase adsorb only those ions preferentially which are common with their own lattice ions.

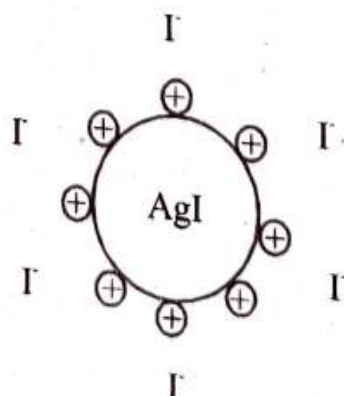
(ii) For example, when a small quantity of silver nitrate (AgNO_3) solution is added to a large quantity of potassium iodide (KI) solution, the colloidal particles of silver iodide adsorb I^- from the solution to become **negatively charged**, (at this stage KI is in excess, and I^- being common to AgI).



But, when a small quantity of potassium iodide (KI) solution is added to a large quantity of silver nitrate solution (AgNO_3); the colloidal silver iodide particles adsorb Ag^+ from the solution to become **positively charged**, (at this stage AgNO_3 is in excess and Ag^+ is common to AgI),



Ag^+ ions remain in dispersed medium (AgI, I^- sol)



I^- ions remain in dispersion medium (AgI, Ag^+ sol)

(iii) Depending upon the nature of charge on the particles of the dispersed phase, the colloidal solutions are classified into positively charged and negatively charged colloids.

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