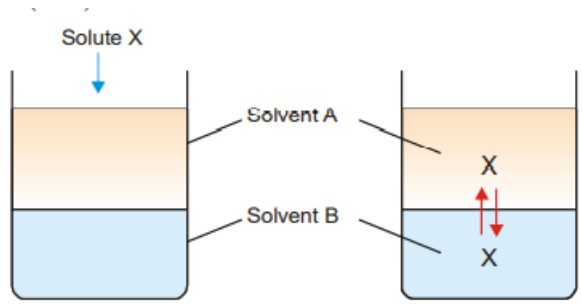
UNIT-I: Distribution Law and Phase Rule

Distribution Law – Nernst Distribution Law – Distribution Coefficient – Explanation and Limitations of Distribution Law - Modification of Distribution Law – Determination of Equilibrium Constant from Distribution Coefficient – Applications of Distribution Law.

Distribution Law/Nernst Distribution Law:

If we take two immiscible solvents A and B in a beaker, they form separate layers. When a solute X which is soluble in both solvents is added, it gets distributed or partitioned between them. Molecules of X pass from solvent A to B and from solvent B to A. Finally, an equilibrium is set up. At equilibrium, the rate, at which molecules of X pass from one solvent to the other is balanced.



Distribution of solute X between solvent A and B.

$$\frac{\text{Concentration of } X \text{ in } A}{\text{Concentration of } X \text{ in } B} = a\ constant$$

For example, the distribution of succinic acid between ether and water is constant as shown below.

Concentration of acid in ether (C_1)	Concentration of acid in water (C_2)	$\frac{C_1}{C_2}$
0.0046	0.024	0.191
0.013	0.069	0.188
0.022	0.119	0.185
0.031	0.164	0.189

This law was proposed by Nernst which states as follows:

"When a solute X distributes itself between two immiscible solvents A and B in contact with each other at constant temperature and X is in the same molecular condition in both solvents then there exists a constant ratio of distribution between the two solvents irrespective of the total amount of solute and irrespective of any other molecular species which may be present."

This is called Nernst's Distribution law (or Nernst's Partition law) or simply Distribution law or Partition law.

$$\frac{\text{Concentration of } X \text{ in } A}{\text{Concentration of } X \text{ in } B} = K_D$$

If C_1 denotes the concentration of the solute in solvent A and C_2 the concentration in solvent B, Nernst's Distribution law can be expressed as

$$\frac{C_1}{C_2} = K_D$$

The constant K_D (or simply K) is called the Distribution coefficient or Partition coefficient or Distribution ratio.

For example, when iodine is added to water and carbon disulphide, the iodine is distributed between the two solvents in such a way that at a given temperature, the ratio of its concentrations (C_1, C_2) in two layers is constant, irrespective of the amount of iodine.

$$K_d = \frac{[\text{solute}]_{\text{solvent 1}}}{[\text{solute}]_{\text{solvent 2}}} = \frac{C_1}{C_2} = \frac{[I]_{CS_2}}{[I]_{H_2O}}$$

Solubilities and Distribution Law:

When a solute is shaken with two non-miscible solvents, at equilibrium both the solvents are saturated with the solute. Since the solubility also represents concentration, we can write the distribution law as

$$\frac{C_1}{C_2} = \frac{S_1}{S_2} = K_D$$

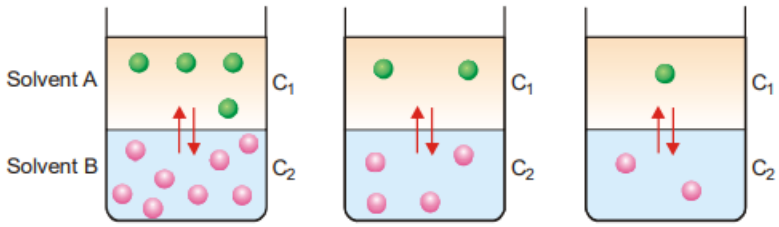
where S_1 and S_2 are the solubilities of the solute in the two solvents.

Hence knowing the value of the Distribution coefficient (K_D) and the solubility of solute in one of the solvents, the solubility of solute in the second solvent can be calculated.

Explanation of Distribution Law:

This is an equilibrium law. When the distribution of the solute X has reached equilibrium, the rate (R_1) at which molecules of X pass from solvent A to B is proportional to its concentration (C_1) in

A. The rate (R_2) at which molecules of X pass from solvent B to A is proportional to its concentration (C_2) in B. Also, at equilibrium, the rate of migration of solute from one solvent to the other is equal. Thus we have,



At equilibrium, the number of molecules of X passing from solvent A into B is proportional to its concentration in A and vice versa. Also, the rate of migration of solute molecules from A to B and B to A is equal.

$$R_1 \propto C_1$$

or $$R_1 = k_1 \times C_1 \quad \text{where } k_1 \text{ is a constant}$$

Again $$R_2 \propto C_2$$

or $$R_2 = k_2 \times C_2 \quad \text{where } k_2 \text{ is a constant}$$

Since at equilibrium $$R_1 = R_2$$

$$k_1 \times C_1 = k_2 \times C_2$$

or $$\frac{C_1}{C_2} = \frac{k_2}{k_1} = K_D$$

or $$\frac{C_1}{C_2} = K_D$$

This is the Nernst's Distribution law equation. Since k_1 and k_2 are constants at the same temperature, the distribution coefficient K_D is also constant if temperature is fixed.

Limitations of Distribution Law:

The conditions to be satisfied for the application of the Nernst's Distribution law are

- **Constant temperature:** The temperature is kept constant throughout the experiment. As temperature varies the partial coefficient value vary. Hence constant temperature is maintained for the validity of distribution law.
- **Same molecular state:** The molecular state of the solute is the same in the two solvents. The law does not hold if there is association or dissociation of the solute in one of the solvents.

- **Equilibrium concentrations:** The concentrations of the solute are noted after the equilibrium has been established.
- **Dilute solutions:** The concentration of the solute in the two solvents is low. The law does not hold when the concentrations are high.
- **Non-miscibility of solvents:** The two solvents are non-miscible or only slightly soluble in each other. The extent of mutual solubility of the solvents remains unaltered by the addition of solute to them.

Modification of Distribution Law:

It was pointed out by Nernst that C_1/C_2 is constant only if the solute exists as simple molecules in the two solvents. If the solute undergoes association or dissociation in one of the solvents, it is found that C_1/C_2 is not constant. In these cases, distribution law applies only to that part of the solute which is present as simple molecules.

1.When solute undergoes association:

Suppose the solute is present as simple molecules X in solvent A. In solvent B, n molecules of X associate to form X_n molecules. Assuming that a few single molecules X are also present in solvent B the equilibria that exist in the two solvents are shown in Figure.

Let C_1 be concentration of X in solvent A.

C_3 be concentration of X in solvent B

C_2 be concentration of X_n in solvent B.

Applying distribution law to the equilibrium

$$X \text{ in solvent } A \rightleftharpoons X \text{ in solvent } B$$

we have $\frac{C_1}{C_3} = K_D$

Applying Mass Law to the chemical equilibrium

$$nX \rightleftharpoons X_n$$

$$\frac{[X_n]}{[X]^n} = K_C \quad \text{or} \quad \frac{C_2}{C_3^n} = K_C$$

Taking nth root on both sides in equation (ii)

$$\frac{\sqrt[n]{C_2}}{C_3} = \sqrt[n]{K_C}$$

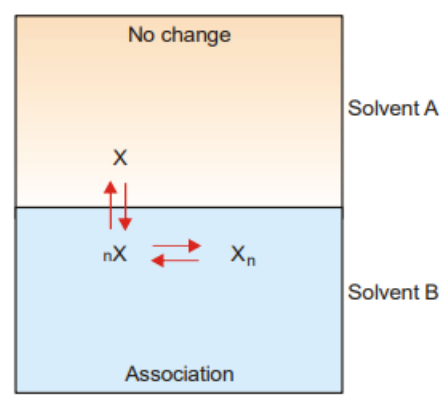
Dividing equation (i) by (iii)

$$\frac{C_1}{\sqrt[n]{C_2}} = \frac{K_D}{\sqrt[n]{K_C}} = K \text{ (a constant)}$$

Thus when association occurs in one solvent, the distribution equation is modified as

$$\frac{C_1}{\sqrt[n]{C_2}} = K_D$$

Since the solute exists largely as associated molecules, the total concentration of X determined experimentally in solvent B is taken as the concentration of the associated molecules X_n.

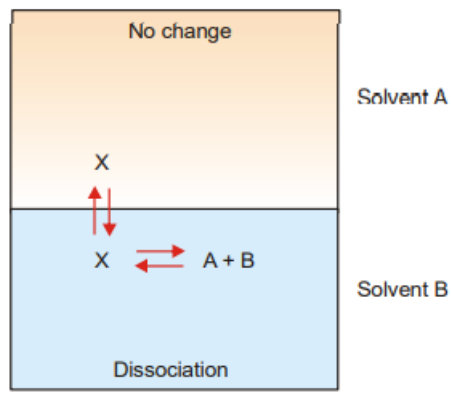


Distribution diagram when the solute is associated in one solvent.

2.When solute undergoes dissociation:

Suppose the solute is present as normal molecules X in solvent A and it dissociates into A + B in solvent B. The equilibria set up in the two solvents are shown in Figure.

Let C_1 be the concentration of X in solvent A and C_2 be the total concentration of X (dissociated and un-dissociated) in solvent B.



Distribution diagram when dissociation occurs in one solvent.

If the degree of dissociation in solvent B is x,

$$\underset{1-x}{X} \rightleftharpoons \underset{x}{A} + \underset{x}{B}$$

Hence the concentration of the un-dissociated (or normal) molecules in solvent B is C_2 (1 – x). Applying distribution law to normal molecules in the two solvents

$$\frac{C_1}{C_2(1-x)} = K_D$$

This is the modified distribution law equation when there is dissociation in one of the solvents.

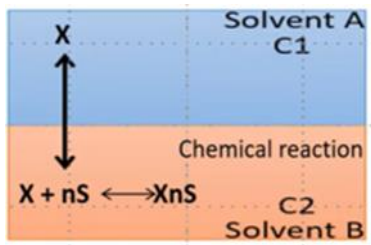
A case of this type arises in the distribution of a weak acid (e.g., succinic acid or oxalic acid) between ether and water. C_1 and C_2 can be determined by direct titration of the two layers against standard alkali solution. The value of x can be found by measuring electrical conductance of solution in solvent B.

3. When solute undergoes dissociation in both the solvents:

Let C_1 be the concentration of X in solvent A and C_2 be the total concentration of X in solvent B. If the degree of dissociation in solvent A is x, and the degree of dissociation in solvent B is x'.

By applying distribution law, $K_D = \frac{C1\,(1-x)}{C2(1-X')}$

4.Solute enters into chemical combination with one of the solvents:



When the solute X enters into chemical combination with one of the solvents, let C_1 be the concentration of solute in solvent A which exists as single molecules.

Suppose the solute X undergoes into chemical reaction with solvent (nS) molecules and forms XnS. Let C_2 be the total concentration of solute in solvent B which exists as single molecules as well as combined molecules with solvent, as represented by the equation:

$$\begin{array}{ccccc} X & + & nS & \leftrightarrow & X.nS \\ C_2(1-\alpha) & & \text{Excess} & & C_2\alpha \end{array}$$

$\propto$ is the degree of association of solute with solvent molecules

$$K_{eq} = \frac{[X.nS]}{[X][solvent]^n}$$

$$K_{eq} = \frac{[X.nS]}{[X]} = \frac{C_2\alpha}{C_2(1-\alpha)} = \text{constant} \quad \text{.....(i)}$$

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

Since the distribution law is valid for solute having similar molecular species in both the solvents, hence we have,

$$K_d = \frac{[solute]_{solvent\ 1}}{[solute]_{solvent\ 2}} = \frac{[X]_{solvent\ 1}}{[X]_{solvent\ 2}} = \frac{C_1}{C_2(1-\alpha)} \quad \text{.....(ii)}$$

From the above two equations we have,

$$\frac{K_d}{K_{eq}} = \frac{\dfrac{C_1}{C_2(1-\alpha)}}{\dfrac{C_2\alpha}{C_2(1-\alpha)}}$$

$$K = \frac{C_1}{C_2\alpha} \quad \text{or}$$

$$\frac{C_1}{C_2} = \text{constant}$$

As K_{eq}, K_d, $\propto$ are constants

Thus, the combination of the solute with one of the solvents do not change the fundamental equation of distribution law but the numerical value of partition coefficient changes.

Determination of Equilibrium constant from Distribution Coefficient:

Distribution law helps in determining the equilibrium constant of a reaction when one of the reactants is soluble in two non-miscible solvents. Let us illustrate by taking example of the reaction when potassium iodide reacts with iodine to form potassium triiodide.

$$KI + I_2 \rightleftharpoons KI_3$$

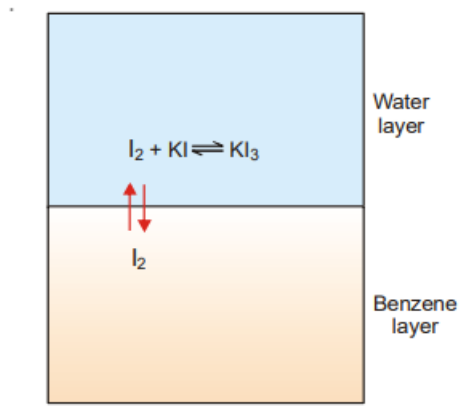
This reaction can be carried in water, while iodine is soluble in both water and benzene.

Procedure

(1) To find the distribution coefficient of I_2. Iodine is shaken with water and benzene in a bottle. The concentration of iodine in the two layers is then determined by titration against standard thiosulphate solution. Thus,

$$\frac{\text{Concentration of } I_2 \text{ in water}}{\text{Concentration of } I_2 \text{ in benzene}} = K \text{ (Distribution coefficient)}$$

(2) To find the equilibrium constant using the value of K. A solution of KI of concentration **a** is shaken with iodine in a bottle. To this some benzene is added and shaken. On standing, the mixture separates into two layers. The equilibria that are set up are shown in Figure.



Determination of equilibrium constant.

The concentration of iodine is determined in the two layers by titration against standard thiosulphate solution.

Let **b** be the concentration of I_2 in benzene layer, **c** be the concentration of I_2 in water layer which is really the total of the concentration of free I_2 and KI_3.

K is the value of distribution coefficient of iodine between water and iodine as determined earlier. Thus,

$$\frac{\text{Conc of } I_2 \text{ in water}}{\text{Conc of } I_2 \text{ in benzene}} = K$$

∴ Concentration of I_2 (free) in water layer = K × b

Hence concentration of KI_3 in water layer = c – Kb

∴ Concentration of KI in water layer = a – (c – Kb)

= a – c + Kb

We can now say that the equilibrium constant of the reaction,

$$I_2 + KI \rightleftharpoons KI_3$$

$$K_c = \frac{[KI_3]}{[KI][I_2]} = \frac{c - Kb}{(a - c + Kb)\,Kb}$$

Since all the quantities on the right-hand side are known, the equilibrium constant (K_c) can be calculated.

Applications of Distribution Law:

1. Study of association of solute: If a solute associated in one of the solvents with concentration C_2 and other solvent concentration being C_1, then according to Nernst distribution law we have

$$K_d = \frac{C_1}{\sqrt[n]{C_2}}$$

By knowing the value of partition coefficient K_d and concentrations (C_1, C_2), the value of n can be calculated which gives the extent of association of solute i.e., dimer or trimer or tetramer so on.

2. Study of dissociation of a solute: If a solute undergoes dissociation in one of the solvents with concentration C_2 and other solvent concentration being C_1, then according to Nernst distribution law we have

$$K_d = \frac{C_1}{\left[C_2(1-\alpha)\right]}$$

Thus degree of dissociation can be calculated if the value of partition coefficient K_d and concentrations (C_1, C_2) are known.

3. Confirmatory test for Bromide and Iodide:

The salt solution is treated with chlorine water. The solution is then shaken with chloroform. On standing chloroform forms the lower layer. The free bromine or iodine being more soluble in chloroform concentrates into the lower layer, making it red for bromine and violet for iodine.

4. Determination of solubility: Suppose the solubility of iodine in benzene is to be determined. Iodine is shaken with water and benzene. At equilibrium concentrations of iodine in benzene (C_b) and water (C_w) are found experimentally and the value of distribution coefficient calculated.

$$\frac{C_b}{C_w} = K_D$$

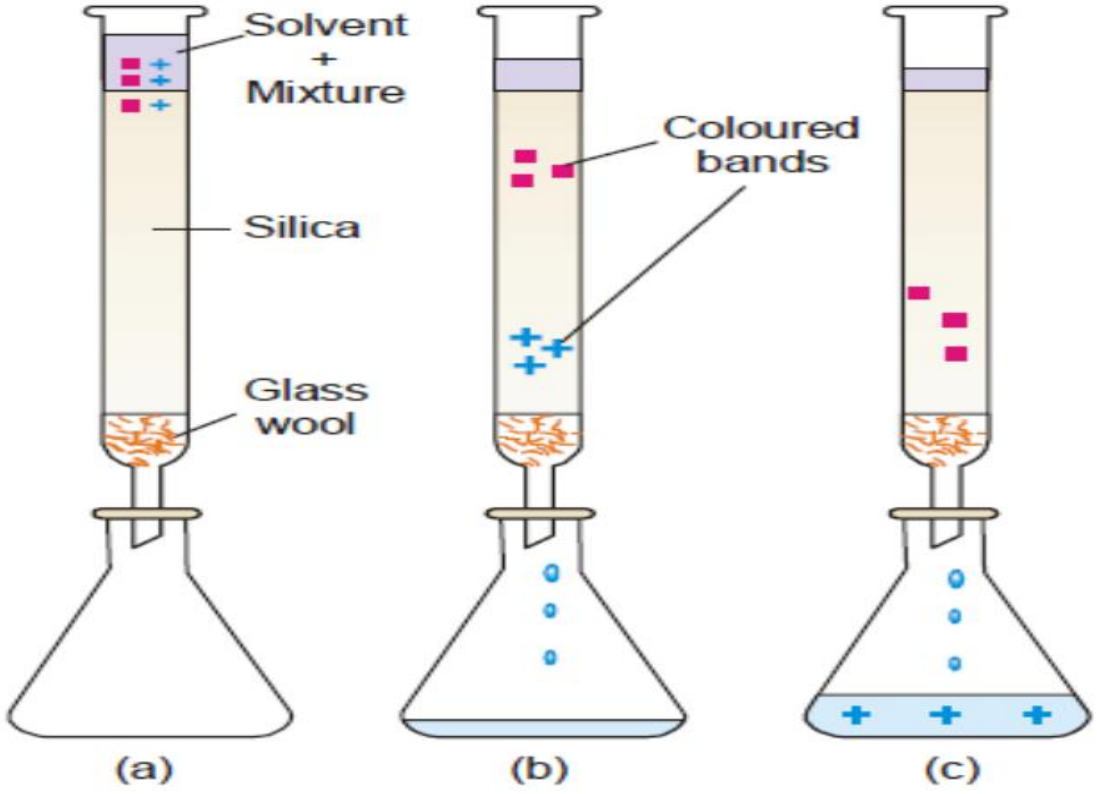
But $$\frac{S_b}{S_w} = K_D$$

where S_b = solubility in benzene; and S_w = solubility in water. If the solubility of iodine in water (S_w) is known, the solubility in benzene can be calculated.

5. Desilverization of Lead (Parke's Process): When molten zinc is added to molten lead containing silver (argentiferous lead), zinc and lead form immiscible layers and silver is distributed between them. Since the distribution ratio is about 3000 in favor of zinc at 800°C, most of silver passes into the zinc layer.

On cooling the zinc layer, an alloy of silver and zinc separates. The Ag-Zn alloy is distilled in a retort when zinc passes over leaving silver behind. The lead layer still contains any un-extracted silver, then it is treated with fresh quantities of molten zinc to recover most of the silver.

6. Partition chromatography: This is a modern technique of separating a mixture of small amounts of organic materials. A paste of the mixture is applied at the top of a column of silica soaked in water. Another immiscible solvent, say hexane, is allowed to flow down the column.

Each component of the mixture is partitioned between the stationary liquid phase (water) and the mobile liquid phase (hexane). The various components of the mixture are extracted by hexane in order of their distribution coefficients.

Thus the component with the highest distribution coefficient is first to move down in the flowing hexane which is collected separately. Similarly, a component with a lower distribution ratio comes down later and is received in another vessel.