B.Sc. Part-II (Chemistry Honours)

Paper-III A (Physical Chemistry)

DISTRIBUTION LAW

- Nernst distribution law
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- Limitations of Nernst Distribution Law
- Nernst Distribution Law: Modification in case of association, dissociation and chemical changes
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Nernst distribution law

When two immiscible solvents A and B taken in a beaker, they form separate layers. Now 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 B to A. finally a dynamic equilibrium is set up. At equilibrium, the rate, at which molecules of X pass from one solvent to the other is balanced.

$$\frac{Concentration\ of\ X\ in\ A}{Concentration\ of\ X\ in\ B} = a\ constant \text{ ………..(1)}$$

Nernst (1891) studied the distribution of several solutes between different appropriate pairs of solvents. He gave a generalization which governs the distribution of a solute between two non-miscible solvents. This is called **Nernst's Distribution law** or Nernst's Partition law or simply Distribution law or Partition law.

It states that,

" if a solute X distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents."

$$\frac{Concentration\ of\ X\ in\ A}{Concentration\ of\ X\ in\ B} = K_D \text{ ………..(2)}$$

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

$$\frac{C_1}{C_2} = K_D \qquad \text{…………..(3)}$$

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

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, the Distribution Law is also written as,

$$\frac{C_1}{C_2} = \frac{S_1}{S_2} = K_D \qquad \text{………(4)}$$

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

Thermodynamic derivation of Nernst Distribution Law:-

Suppose a solute X is present in two immiscible solvents A and B in contact with each other. Now suppose that the chemical potential of solute in solvent A is μ_1 and in solvent B is μ_2. When two phases are in equilibrium, their chemical potentials too will be equal to one another. So that,

$$\mu_1 = \mu_2 \qquad \text{…………(1)}$$

Since $$\mu = \mu^o + RT \ln a \qquad \text{…………..(2)}$$

Where, μ^o is the chemical potential of the pure state and a is the activity.

Therefore, $\mu_1 = \mu_1^o + RT \ln a_1$ for Phase 1 ……..…..(3)

And $\mu_2 = \mu_2^o + RT \ln a_2$ for Phase 2 ………….(4)

Hence, $\mu_1^o + RT \ln a_1 = \mu_2^o + RT \ln a_2$

Or, $\mu_2^o - \mu_1^o = RT \ln \frac{a_1}{a_2}$ ………….(5)

Since R is a gas constant. At constant temperature, the standard chemical potentials μ_1^o and μ_2^o are also constant. And hence,

$$\frac{a_1}{a_2} = constant\ (at\ constant\ temperature) \qquad \text{………(6)}$$

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

$$\frac{a_1}{a_2} = \frac{k_1 \chi_1}{k_2 \chi_2} = constant\ (at\ constant\ temperature) \qquad \text{…….(7)}$$

Where χ_1 and χ_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.

$$\frac{\chi_1}{\chi_2} = constant\ (at\ constant\ temperature) \qquad \text{………(8)}$$

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

$$\frac{\chi_1}{\chi_2} = \frac{c_1}{c_2} = constant\ (at\ constant\ temperature) \quad \text{………(9)}$$

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

$$\frac{c_1}{c_2} = constant\ (at\ constant\ temperature) = K_D \text{ ……..(10)}$$

This is the Nernst Distribution Law.

Limitations of the Nernst Distribution Law:

The law is valid when the molecular state of the solute is same in both the solvents. If the solute undergoes dissociation or association in any one of the solvents, then in such cases the distribution law no longer holds good.

The distribution law can be applied in such cases with some modifications.

Modification in case of association, dissociation and chemical changes

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, 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.

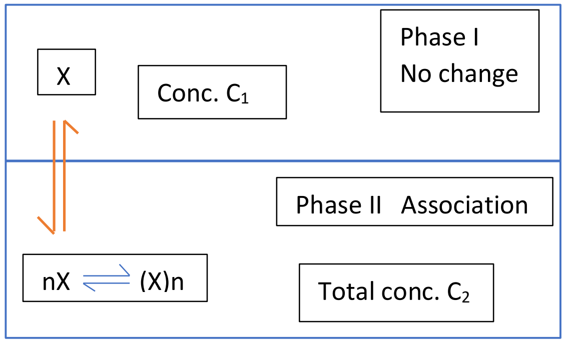

Fig. 1. Association in one of the phases.

Applying the law of chemical equilibrium to the equilibrium between the associated and single molecules, in the second phase, we have

$$(X)_n \leftrightharpoons nX$$

$$K = [X]^n/[(X)_n] \qquad \text{……….(1)}$$

$$\text{Or, } [X] = \sqrt[n]{K \times [(X)_n]} = constant \times \sqrt[n]{[(X)_n]} \text{ ……….(2)}$$

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.

$$[(X)_n] = c_2 \qquad \text{..........(3)}$$

From equation (2) and (3), $[X] = constant \times \sqrt[n]{c_2}$ ....(4)

Since the distribution law is valid only for concentration of similar molecular species in the two phases, hence, $\frac{c_1}{[X]} = constant$ ....(5)

From equation (4) and (5) we have, $\frac{c_1}{\sqrt[n]{c_2}} = constant = K_D$ ....(6)

Equation (6) has been checked by studying the distribution 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, but dissociates into A and B in the solvent marked II

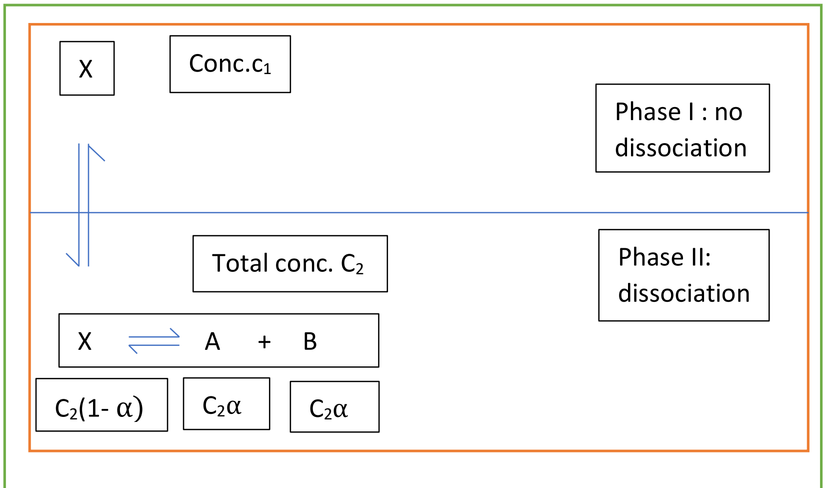

Fig. 2. Dissociation in one of the phases.

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.

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:

$$\begin{array}{ccccc} X & \leftrightharpoons & A & + & B \\ C_2(1-\alpha) & & C_2\alpha & & C_2\alpha \end{array}$$

Therefore, according to the distribution law,

$$\frac{c_1}{c_2(1-\alpha)} = K_D \qquad \text{..........(7)}$$

3. The solute enters into chemical combination with one of the solvents.

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

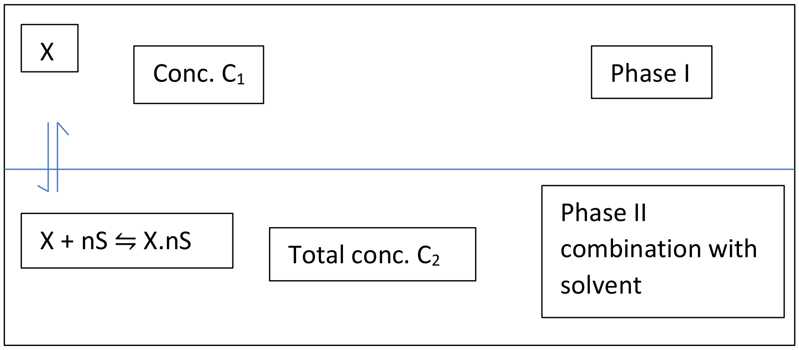

Fig.3. combination with the solvent

Let c_1 be the concentration of the solute X in one of the solvents in which it does not undergo any chemical change 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

$$X \quad + \quad nS \quad \leftrightharpoons \quad X.nS \qquad \text{.........(3)}$$

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

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 equation (3), we have

$$K = \frac{c_2\alpha}{c_2(1-\alpha)[solvent]^n} \quad \ldots\ldots\ldots\ldots(4)$$

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

$$\frac{c_2\alpha}{[c_2(1-\alpha)]} = constant \quad \ldots\ldots\ldots\ldots(5)$$

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

$$\frac{c_1}{[c_2(1-\alpha)]} = constant \quad \ldots\ldots\ldots(6)$$

Dividing equation (6) by equation (5), we have

$$\frac{c_1}{c_2\alpha} = constant \qquad \ldots\ldots\ldots(7)$$

Now, α, the fraction of the solute that combines with the same solvent, is also constant at a given temperature, equation (7) may, therefore, be written as

$$\frac{c_1}{c_2} = constant \ldots\ldots\ldots\ldots(8)$$

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.

Limitations of Distribution law

The two essential prerequisites 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:
3. The solutions are dilute.
4. The two liquids are mutually insoluble or only very sparingly soluble (e.g., benzene and water) and their mutual solubility is not altered by the presence of the solute.

Applications of the Nernst Distribution law:

1. **Study of Association of a solute**

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 n being the number of simple molecules which combine to form one associated molecule.

$$\frac{c_1}{\sqrt[n]{c_2}} = K_D \qquad \text{……..(1)}$$

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

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

$$\frac{c_1}{[c_2(1-\alpha)]} = K_D \qquad \text{…………(2)}$$

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.

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, 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.