CHAPTER 19

THE NERNST DISTRIBUTION LAW

Nernst Distribution law. In 1872, Berthelot and Jungfleish 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,

$$\frac{[I_2]_{CS_2}}{[I]_{H_2O}} = c_1/c_2 = K_D \quad ...(1)$$

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 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 :

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

$$K_D = s_1/s_2 \quad ...(2)$$

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.*,

$$\mu_1 = \mu_2 \quad ...(3)$$

Since $$\mu = \mu^\circ + RT \ln a, \quad ...(4)$$

therefore, $$\mu_1 = \mu_1^\circ + RT \ln a_1 \quad \text{for Phase 1} \quad ...(5)$$

and $$\mu_2 = \mu_2^\circ + RT \ln a_2 \quad \text{for Phase 2} \quad ...(6)$$

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

or $$RT \ln(a_1/a_2) = \mu_2^\circ - \mu_1^\circ \quad ...(7)$$

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

$$a_1/a_2 = \text{constant (at constant temperature)} \quad ...(8)$$

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.

$\therefore$ $$a_1/a_2 = k_1x_1/k_2x_2 = \text{constant (at constant temperature)} \quad ...(9)$$

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.

$\therefore$ $$x_1/x_2 = \text{constant (at constant temperature)} \quad ...(10)$$

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

$\therefore$ $$x_1/x_2 = c_1/c_2 = \text{constant (at constant temperature)} \quad ...(11)$$

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.

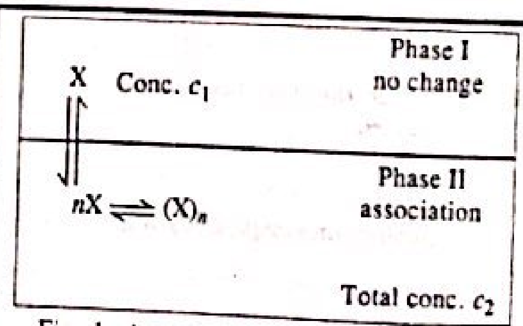

Fig. 1. Association in one of the phases.

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

$$K = [X]^n/[(X)_n] \quad ...(12)$$

or $$[X] = \sqrt[n]{K \times [(X)_n]} = \text{constant} \times \sqrt[n]{[(X)_n]} \qquad ...(13)$$

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.*,

$$[(X)_n] = c_2 \qquad ...(14)$$

From Eqs. 13 and 14, $$[X] = \text{constant} \times \sqrt[n]{c_2} \qquad ...(15)$$

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

$$c_1/[X] = \text{constant} \qquad ...(16)$$

From Eqs. 15 and 16, $$c_1/\sqrt[n]{c_2} = \text{constant} = K_D \qquad ...(17)$$

Eq. 17 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.

Example 1. Experiments in the study of the distribution of phenol between water and chloroform gave the following results :

Concentration in aqueous solutions (c_1)	**0·094**	**0·163**	**0·254**	**0·436**
Concentration in chloroform solution (c_2)	**0·254**	**0·761**	**1·850**	**5·430**

What conclusion can be drawn from these results concerning the molecular condition of phenol in chloroform solution ?

Solution : Phenol in chloroform may be present either as normal molecules or as associated molecules. In the former case, the ratio c_1/c_2 should be constant while in the latter case, the ratio $c/\sqrt[n]{c_2}$ should be constant, n giving the number of molecules of phenol which associate to give a single associated molecule.

The values of c_1/c_2 in the various cases come out to be as follows :

$$c_1/c_2 = \frac{0.094}{0.254} = 0.3701;\ \frac{0.163}{0.761} = 0.2142;\ \frac{0.254}{1.850} = 0.1373;\ \frac{0.436}{5.430} = 0.0803$$

Evidently, the ratio c/c_2 is not constant. Hence, phenol does not exist as single molecules in chloroform.

The values of $c/\sqrt{c_2}$ in the various cases come out to be as follows :

$$\frac{c_1}{\sqrt{c_2}} = \frac{0.094}{\sqrt{0.254}} = 0.1855\ ;\ \frac{0.163}{\sqrt{0.761}} = 0.1868;\ \frac{0.254}{\sqrt{1.850}} = 0.1867;\ \frac{0.436}{\sqrt{5.430}} = 0.1871$$

A fairly constant value of $c_1/\sqrt{c_2}$ shows that phenol exists as **double molecules** in chloroform.

Example 2. For the distribution of an organic solute between water (c_1) and chloroform (c_2), the following results were obtained :

c_1	**0·0160**	**0·0237**
c_2	**0·338**	**0·753**

Determine the molecular state of the solute in chloroform.

Solution : Let us assume that

$$c_2/c_1 = K_D \qquad \text{(Nernst distribution law)}$$

For the first step, $c_2/c_1 = 0{\cdot}338/0{\cdot}160 = 21{\cdot}1$ and for the second step, $c_2/c_1 = 0{\cdot}753/0{\cdot}0237 = 31{\cdot}8$. The two values are different, hence our assumption is wrong.

Let us now assume that $\sqrt{c_2}/c_1 = K_D$, *i.e.*, the solute exists as a dimer in chloroform. We find that for the first and the second steps, the values of $\sqrt{c_2}/c_1$ are 36·3 and 36·6, respectively. Since the two values are practically the same, hence $\sqrt{c_2}/c_1$ is constant. The solute thus exists as a **dimer** in chloroform.

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.

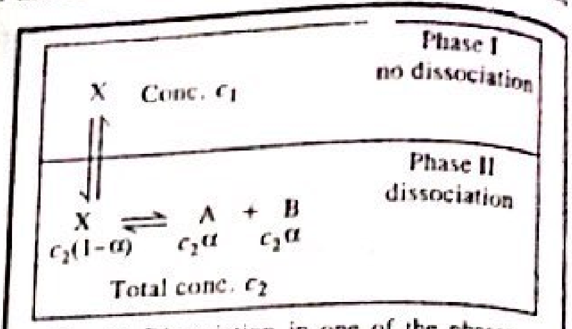

Fig. 2. Dissociation in one of the phases.

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 :

$$\underset{c_2(1-\alpha)}{X} \rightleftharpoons \underset{c_2\alpha}{A} + \underset{c_2\alpha}{B}$$

Therefore, according to the distribution law,

$$c_1/[c_2(1-\alpha)] = K_D \qquad ...(18)$$

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.

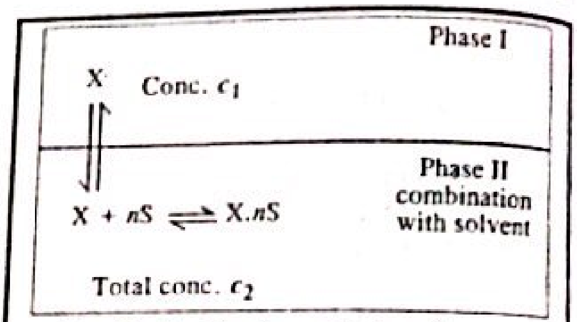

Fig. 3. Combination with the solvent.

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

$$X + nS \rightleftharpoons X.nS \qquad ...(19)$$

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. 19, we have

$$K = \frac{c_2\alpha}{c_2(1-\alpha)[\text{solvent}]^n} \qquad ...(20)$$

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

$$c_2\alpha/[c_2(1-\alpha)] = \text{constant} \qquad ...(21)$$

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

$$c_1/[c_2(1-\alpha)] = \text{constant} \qquad ...(22)$$

Dividing Eq. 22 by Eq. 21, we have

$$c_1/c_2\alpha = \text{constant} \qquad ...(23)$$

Now, α, the fraction of the solute that combines with the same solvent, is also constant at a given temperature. Eq. 23 may, therefore, be written as

$$c_1/c_2 = \text{constant} \qquad ...(24)$$

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

$$c_1/\sqrt[n]{c_2} = K_D \qquad \text{...(Eq. 17)}$$

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,

$$c_1/[c_2(1-\alpha)] = K_D \qquad \text{(Eq. 18)}$$

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. Knowing the concentrations of iodine in the two layers, the partition coefficient, K_D, 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 $= K_D(X - B) = D$ moles per litre (say)

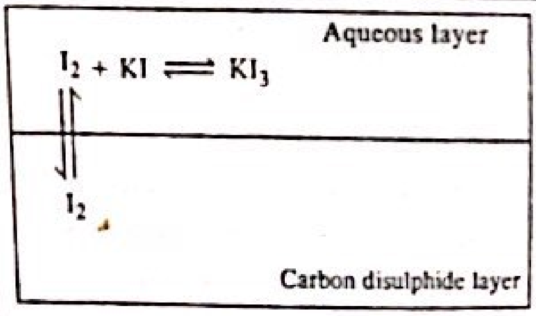

Fig. 4. Study of complex ions.

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

$$I^- + I_2 \rightleftharpoons I_3^-$$

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 the complex ion I_3^-.

Therefore, the equilibrium constant will be given by

$$K = [I_3^-]/([I_2][I^-]) \qquad \text{...(25)}$$

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

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

The results of determinations carried out at 30°C are given in Table 1.

TABLE 1

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^-.

Example 3. Calculate the dissociation constant of KI_3 from the following data : 37·8 g of iodine were shaken up with one litre of carbon disulphide and one litre of potassium iodide solution in water containing 7·92 g of KI. 35·67 g of iodine were found to be present in carbon disulphide layer. The partition coefficient K_D=410 in favour of carbon disulphide.

Solution : The dissociation of KI_3 is represented as

$$KI_3(aq) \rightleftharpoons KI(aq) + I_2$$

or

$$I_3^-(aq) \rightleftharpoons I^-(aq) + I_2$$

∴

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

According to the Nernst distribution law,

$$K_D = \frac{[I_2]_{H_2O}}{[I_2]_{CS_2}} = \frac{1}{410}$$

∴

$$[I_2]_{H_2O} = [I_2]_{CS_2} \times \frac{1}{410}$$

$$[I_2]_{CS_2} = 35{\cdot}67 \text{ g dm}^{-3}/254 \text{ g mol}^{-1} = 0{\cdot}1405 \text{ mol dm}^{-3}$$

$$[I_2]_{H_2O} = 0{\cdot}1405 \text{ mol dm}^{-3}/410 = 0{\cdot}000343 \text{ mol dm}^{-3}$$

Total free and combined iodine in aqueous layer = (37·8 - 35·67) g dm^{-3}

= 2·13 g dm^{-3} = 2·13 g dm^{-3}/254 g mol^{-1} = 0·008386 mol dm^{-3}

Free iodine in aqueous layer = 0·000343 mol dm^{-3}

Combined iodine in aqueous layer = 0·008386 - 0·000343 = 0·008043 mol dm^{-3}

Since molar concentrations of combined I_2 and I_3^- ion are the same, hence,

Concentration of KI_3 in aqueous layer = 0·008043 mol dm^{-3}

Total concentration of KI in aqueous layer = 7·92 g dm^{-3}/166 g mol^{-1} = 0·04775 mol dm^{-3}

Concentration of free KI or I^- in aqueous layer = (0·04775 - 0·00804) mol dm^{-3} = 0·03971 mol dm^{-3}

Hence,
$$K = [I^-][I_2]/[I_3^-] = \frac{(0{\cdot}03971 \text{ mol dm}^{-3})(0{\cdot}000343 \text{ mol dm}^{-3})}{0{\cdot}008043 \text{ mol dm}^{-3}} = \mathbf{0{\cdot}00169 \text{ mol dm}^{-3}}$$

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

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

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Solution : The dissociation of KI_3 is represented as

$$KI_3(aq) \rightleftharpoons KI(aq) + I_2$$

or

$$I_3^-(aq) \rightleftharpoons I^-(aq) + I_2$$

∴

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

According to the Nernst distribution law,

$$K_D = \frac{[I_2]_{H_2O}}{[I_2]_{CS_2}} = \frac{1}{410}$$

∴

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Hence,

$$K = [I^-][I_2]/[I_3^-] = \frac{(0{\cdot}03971 \text{ mol dm}^{-3})(0{\cdot}000343 \text{ mol dm}^{-3})}{0{\cdot}008043 \text{ mol dm}^{-3}} = \mathbf{0{\cdot}00169 \text{ mol dm}^{-3}}$$

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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 exracted 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

$$\frac{w_1/V}{(W - w_1)/v} = K_D \qquad ...(26)$$

or

$$w_1 = W\frac{K_D V}{K_D V + v} \qquad ...(27)$$

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

$$w_2 = w_1\frac{K_D V}{K_D V + v} = W\left(\frac{K_D V}{K_D V + v}\right)^2 \qquad ...(28)$$

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

$$w_n = W\left(\frac{K_D V}{K_D V + v}\right)^n \qquad ...(29)$$

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.

Example 4. The distribution coefficient of iodine between carbon tetrachloride and water is 85 in favour of carbon tetrachloride. Calculate the volume of carbon tetrachloride required for 95% extraction of iodine from 100 ml of aqueous solution in a single stage extraction.

Solution : $[I_2]_{CCl_4}/[I_2]_{H_2O} = 85$

Hence, $[I_2]_{H_2O}/[I_2]_{CCl_4} = 1/85 = K_D$ *(Note this step)*

After the extraction of 95% iodine, 5% still remains *unextracted*.

According to Eq. 29, $$w_n = W\left(\frac{K_D V}{K_D V + v}\right)^n \qquad ...(i)$$

In the present case, $n=1$, $w=5$, $W=100$, $V=100$ ml and $K_D=1/85$. The volume v is to be determined.

Substituting the various values in Eq. (*i*), we have

$$\frac{5}{100} = \frac{1/85 \times 100}{1/85 \times 100 + v}$$

$\therefore$ $$v = 22.35 \text{ ml}$$