18

The Nernst Distribution Law

The 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 away 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,

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

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

$$K_D = s_1/s_2 \qquad \ldots(2)$$

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.*,

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

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

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

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

Hence,
$$\overset{\circ}{\mu_1} + RT \ln a_1 = \overset{\circ}{\mu_2} + RT \ln a_2 \quad \text{or} \quad RT \ln(a_1/a_2) = \overset{\circ}{\mu_2} - \overset{\circ}{\mu_1} \qquad ...(7)$$

Now, at constant temperature, the standard chemical potentials $\overset{\circ}{\mu_1}$ and $\overset{\circ}{\mu_2}$ are constant. Since R is also a constant (being the gas constant), it follows that

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

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.

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

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.

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

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

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

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

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

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.

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

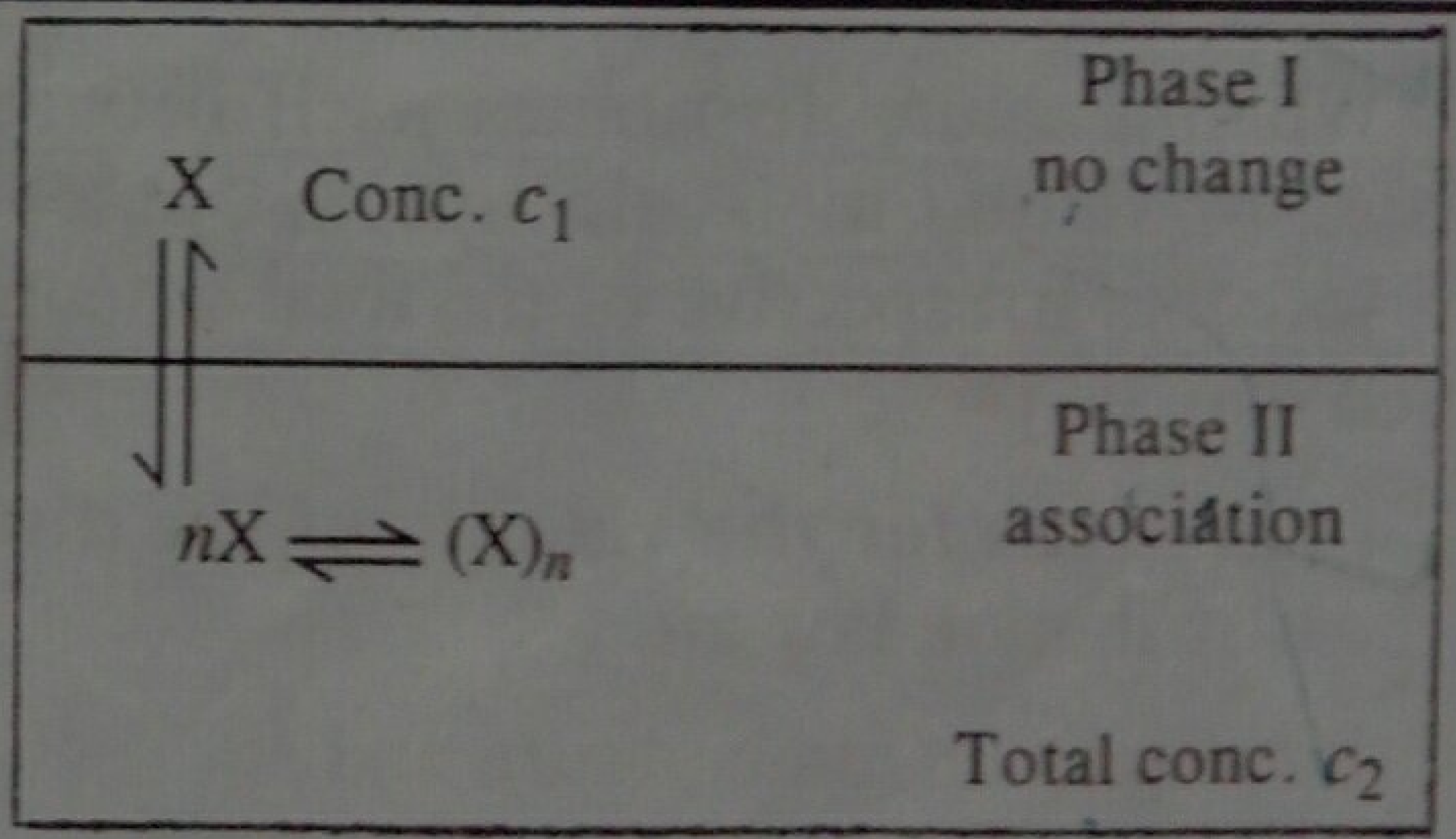

Fig. 1. Association in one of the phases.

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

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

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

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

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

second solvent with which it enters into chemical combination forming complex molecules, as rep by the equation

$$X + nS \rightleftharpoons X.nS$$

If α is the fraction of the solute that enters into chemical combination with the solvent 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

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

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

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

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

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

Dividing Eq. 22 by Eq. 21, we have

$$c_1/c_2\alpha = \text{constant}$$

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

$$c_1/c_2 = \text{constant}$$

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

Applications of the Nernst Distribution Law

1. Study of Association of a Solute. As shown above, if a solute associates in one of the 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 possible to show by studying distribution of acetic acid and benzoic acid between water and ben 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 disso one of the solvents in which its concentration is c_2 but not in the other in which its concentr 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 concentration can be obtained, since K_D is constant.

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

4. Study of Complex Ions. The Nernst distribution law has been successfully applied in de the formula of the complex ions formed between bromine and bromide ion as well as between io 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.

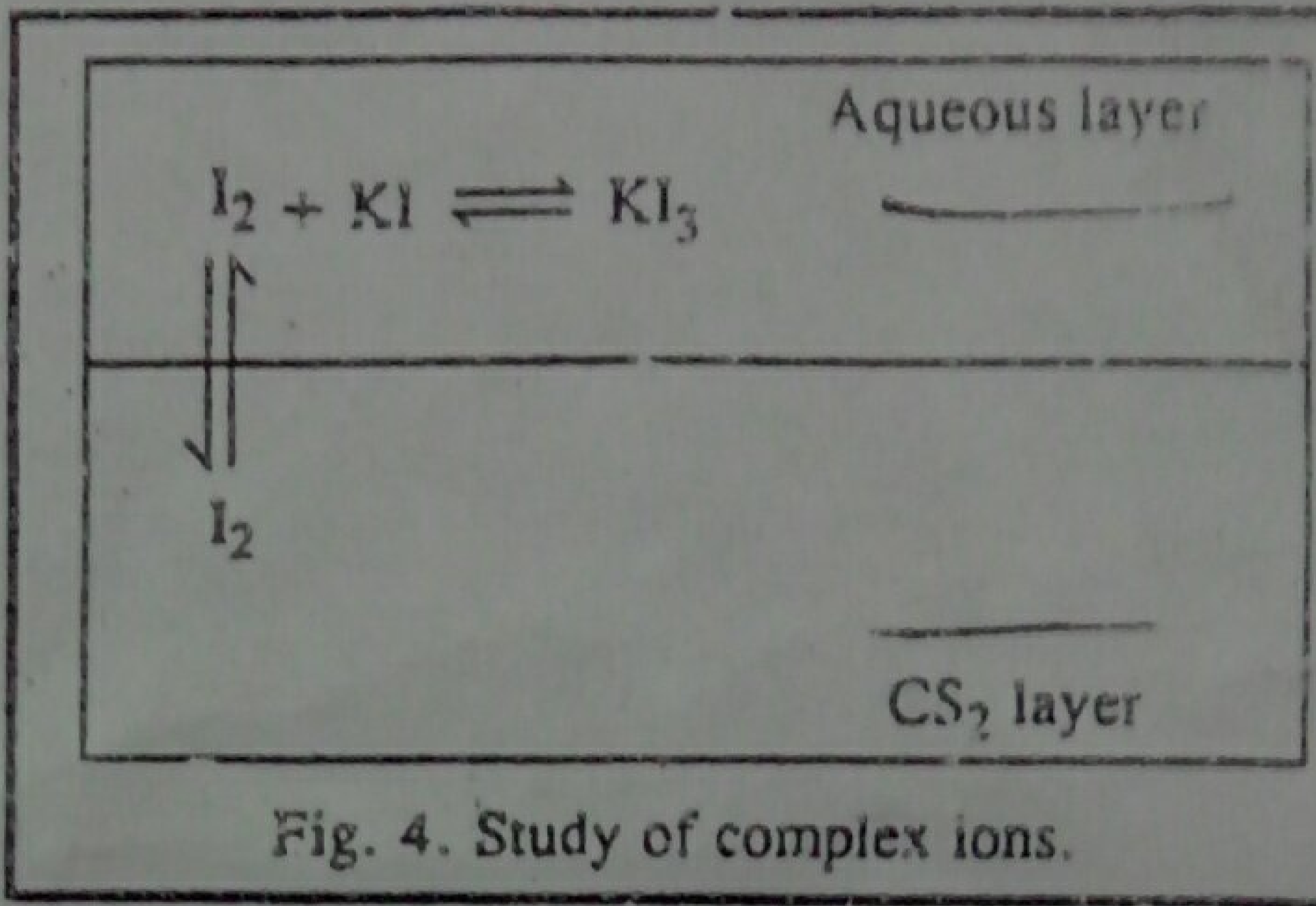

Fig. 4. Study of complex ions.

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)

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 KI_3.

Therefore, the equilibrium constant will be given by

$$K = [I_3^-]/([I_2]\,[I^-]) \qquad \ldots(25)$$

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 complex ion is I_3^-.

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, 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.

We can derive a general formula which enables the calculation of the amount that is left extracted after a given number of operation. Let V ml of a solution containing W gram of solute be repeatedly extracted with v ml of another solvent which is immisicible with the first. Let w1 be the mass of the solute that remains unextracted at the end of the first operation. The K_D will be given by

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

✓

$\frac{W}{V}$ / $W - w_1 V$

or

$$w_1 = W \frac{K_D V}{K_D V + v}$$

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

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

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

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

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

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

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

Example 2. The distribution coefficient of iodine between carbon tetrachloride and water is 85 in favour of tetrachloride. Calculate the volume of carbon tetrachloride required for 95% extraction of iodine from 100 ml of solution in a single stage extraction.

25

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

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

$$\frac{5}{100} = \frac{1/85 \times 100}{1/85 \times 100 + v} \qquad \therefore \qquad v = 22{\cdot}35 \text{ ml}$$

Example 3. For the distribution of an organic solute between water (c_1) and chloroform (c_2), the 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

$$c_2/c_1 = K_D \qquad \text{(Nernst distrib}$$

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 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 second steps, the values of $\sqrt{c_2}/c_1$ are 36·3 and 36·6, respectively. Since the two values are practically the sam $\sqrt{c_2}/c_1$ is constant. The solute thus exists as a dimer in chloroform.

ample 4. When 0·83 g of succinic acid was shaken with 100 ml each of water and ether, the water layer was to contain 0·70 g of the acid. Calculate the quantity of the acid that can be extracted from 1 litre of ether containing 1 g of the acid using 100 ml of water (*i*) in two equal instalments and (*ii*) in a single stage ction.

$$K_D = \frac{C_{\text{ether}}}{C_{\text{water}}} = \frac{0{\cdot}13}{0{\cdot}70} = 0{\cdot}19$$

ding to Eq. 35,

$$w_n = W\left(\frac{K_DV}{K_DV+v}\right)^n \qquad \ldots(i)$$

In the first case :

$$W = 1\text{ g}\,;\ V = 1000\text{ ml}\,;\ v = 100\text{ ml},\ n = 2$$

$$w_2 = 1\text{g}\left(\frac{0{\cdot}19 \times 1000\text{ml}}{0{\cdot}19 \times 1000\text{ml} + 50\text{ml}}\right)^2 = 0{\cdot}627\text{g}$$

is the amount left *unextracted*.

the amount extracted = 1·0 g − 0·627 g = 0·373 g

In the second case :

$$W = 1\text{ g}\,;\ V = 1000\text{ ml}\,;\ n = 1$$

$$w_1 = 1\text{g}\left(\frac{0{\cdot}19 \times 1000\text{ml}}{0{\cdot}19 \times 1000\text{ml} + 1 \times 100\text{ ml}}\right) = 0{\cdot}655\text{g}$$

The amount extracted = 1·0 g − 0·655 g = 0·345 g

the amount extracted is greater if the extraction is carried out in two instalments than in one instalment.

ple 5. (*c*) **Calculate the minimum volume of benzene required to extract in one step 90 per cent of H_2S one litre of 0·1 M aqueous solution.**

alculate the total volume of benzene required if the 90 per cent extraction is to be completed in three equal volumes of benzene.

How many extractions would be required for completing 90 per cent extraction if 100 ml benzene is used ep. The partition coefficient of H_2S between water (c_1) and benzene (c_2) defined as $c_1/c_2 = 0{\cdot}17$.

on : (*a*) Let *v* litres be the volume of benzene required. Then, after *one extraction*,

$$c_1 = 0{\cdot}1\text{ M}/10 = 0{\cdot}01\text{ M};\ c_2 = 0{\cdot}1 \times 0{\cdot}9 \times 1/v = (0{\cdot}09/v)\text{ M}$$

$$c_1/c_2 = \frac{0{\cdot}01\text{M}}{(0{\cdot}09/v)\text{M}} = 0{\cdot}17\ \text{(given)}$$

ce

$$v = 1{\cdot}53\text{ litres}$$

the total volume required for three equal extractions = 3*v* litres

ording to Eq. 35,

$$\frac{w_n}{W} = \left(\frac{K_DV}{K_DV+v}\right)^n \qquad \ldots(i)$$

is case, w_n=0·01 mol ; W=0·1, V=1 litre; K_D=0·17 ; v is to be determined.

tituting the various data in Eq. (*i*) and solving for *v*, we get

$$v = 0{\cdot}196\text{ litre}$$

nce,

$$3v = 0{\cdot}588\text{ litre}$$

Using the expression,

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

0·1 mol; w_n=0·01 mol ; v=0·1 litre ; V=1 litre, we find after substituting the data and taking logs of both sides that us, the number of extractions required = 5.

ample 6. Calculate the dissociation constant of KI_3 from the following data : 37·8 g of iodine were shaken up with of carbon disulphide and one litre of potassium iodide solution in water containing 7·92 g of KI. 35·67 g of iodine und to be present in carbon disulphide layer. The partition coefficient K_D=410 in favour of carbon disulphide.

olution : The dissociation of KI_3 is represented as

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

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

$$\therefore \quad K = [I^-][I_2]/[I_3^-]$$

According to the Nernst distribution law,

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

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

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

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

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

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

Free iodine in aqueous layer = $0{\cdot}000343$ mol dm^{-3}

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

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

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

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

QUESTIONS AND PROBLEMS

I. Review Questions

1. State the Distribution law. Under what conditions is it valid ? How is the law derived from thermodynamic considerations ?
2. How is the distribution law modified when *(i)* the solute undergoes association in one of the solvents? *(ii)* the solute enters into chemical combination with one of the solvents?
3. How is the Distribution law used in the process of extraction ? Derive the expression which enables calculation of the amount of a solute left unextracted after a given number of extractions.
4. Discuss the practical applications of the Distribution law.

II. Problems

1. The following data were obtained for the distribution of I_2 between CS_2 and H_2O at 25°C :

Conc. of I_2 in H_2O (g dm^{-3})	0·100	0·161	0·314	0·423
Conc. of I_2 in CS_2 (g dm^{-3})	41	66	129	174

Calculate K_D of I_2 between CS_2 and H_2O. **[Ans. Approx 410]**

2. The following data were obtained at 298 K for the distribution of I_2 between H_2O and CCl_4 :

$[I_2]_{H_2O}$ (mol dm^{-3}) $\times 10^4$ 2·35 4·69 7·03 9·30

$[I_2]_{CCl_4}$ (mol dm^{-3}) $\times 10^2$ 2·00 4·00 6·00 8·00

Verify that the data obey Nernst distribution law and calculate K_D in favour of CCl_4. **[Ans. 85·5]**

3. The following data were obtained for the distribution of benzoic acid between H_2O and C_6H_6 at 25°C :