18

Distribution Law

I f 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 a dynamic equilibrium is set up. At equilibrium, the rate, at which molecules of *X* pass from one solvent to the other is balanced (18.1).
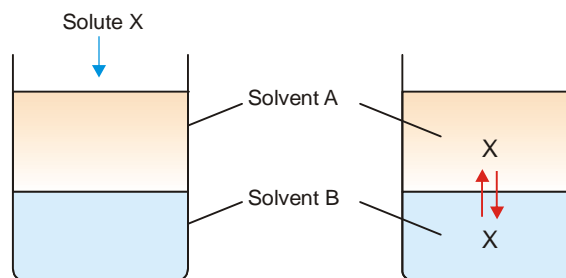
■ **Figure 18.1**
Distribution of solute X between solvent A and B.

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

For example, the following results from the distribution of

succinic acid between ether and water illustrate the constancy of the ratio of the concentrations in each layer.

TABLE 18.1. ILLUSTRATION OF CONSTANCY OF CONCENTRATION RATIO OF A SOLUTE BETWEEN LAYERS OF TWO IMMISCIBLE SOLVENTS		
Concentration of acid in ether (C_1)	Concentration of acid in water (C_2)	$\dfrac{C_1}{C_2}$
0.0046	0.024	0.191
0.013	0.069	0.188
0.022	0.119	0.185
0.031	0.164	0.189

STATEMENT OF NERNST'S DISTRIBUTION LAW

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.*

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,

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

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.**

SOLVED PROBLEM 1. A solid X is added to a mixture of benzene and water. After shaking well and allowing to stand, 10 ml of the benzene layer was found to contain 0.13 g of X and 100 ml of water layer contained 0.22 g of X. Calculate the value of distribution coefficient.

SOLUTION

$$\text{Concentration of } X \text{ in benzene } (C_b) = \frac{0.13}{10} = 0.013 \, \text{g ml}^{-1}$$

$$\text{Concentration of } X \text{ in water } (C_w) = \frac{0.22}{100} = 0.002 \, \text{g ml}^{-1}$$

According to Distribution law :

$$\frac{C_b}{C_w} = \frac{0.013}{0.0022} = \mathbf{5.9}$$

SOLVED PROBLEM 2. In the distribution of succinic acid between ether and water at 15ºC, 20 ml of the ethereal layer contains 0.092 g of the acid. Find out the weight of the acid present in 50 ml of the aqueous solution in equilibrium with it if the distribution coefficient for succinic acid between water and ether is 5.2.

SOLUTION

Let the weight of succinic acid in aqueous layer be x g

$$\text{Concentration in aqueous layer} = \frac{x}{50} \, \text{g ml}^{-1}$$

$$\text{Concentration in ethereal layer} = \frac{0.092}{20} \text{ g ml}^{-1}$$

$$\frac{C_{water}}{C_{ether}} = \frac{x/50}{0.092/20} \quad \text{or} \quad \frac{20x}{50 \times 0.092} = 5.2$$

or

$$x = \frac{5.2 \times 50 \times 0.092}{20}$$

Hence

$$x = \textbf{1.196 } \textbf{\textit{g}}$$

SOLVED PROBLEM 3. An aqueous solution of succinic acid at 15°C, containing 0.07 g in 10 ml is in equilibrium with an ethereal solution which has 0.013 g in 10 ml. The acid has its normal molecular weight in both the solvents. What is the concentration of the ethereal solution which is in equilibrium with an aqueous solution containing 0.024 g in 10 ml?

SOLUTION

Concentration in aqueous solution $C_W = \dfrac{0.07}{10}$ g ml^{-1}

Concentration in ethereal solution $C_E = \dfrac{0.013}{10}$ g ml^{-1}

Partition coefficient $\dfrac{C_W}{C_E} = \dfrac{0.07}{0.013} = \textbf{5.38}$

Concentration in aqueous solution in the second case

$$= \frac{0.024}{10} \text{ g ml}^{-1}$$

Let concentration in ethereal solution in the second case be $= x$ g ml^{-1}

$$\frac{0.024}{10x} = \frac{C_W}{C_E} = \frac{0.07}{0.013}$$

or

$$0.024 \times 0.013 = 0.7\,x$$

Hence

$$x = \textbf{0.00044 g ml}^{-1}$$

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.

SOLVED PROBLEM. At 25° C an aqueous solution of iodine containing 0.0516 g litre^{-1} is in equilibrium with a carbon tetrachloride (CCl$_4$) solution containing 4.412 g litre^{-1}. The solubility of iodine in water at 25°C is 0.34 g litre^{-1}. Find the solubility of iodine in carbon tetrachloride.

SOLUTION

(a) **To find the value of K_D**

Concentration of I_2 in water $(C_{H_2O}) = 0.0516$ g litre^{-1}

Concentration of I_2 in CCl$_4$ $(C_{CCl4}) = 4.412$ g litre^{-1}

∴ The value of distribution coefficient is

$$\frac{C_{CCl_4}}{C_{H_2O}} = \frac{4.412}{0.0516} = 85.5$$

(b) **Calculation of solubility**

Applying Distribution law,

$$\frac{\text{Solubility of iodine in CCl}_4}{\text{Solubility of iodine in water}} = 85.5$$

∴ $$\frac{\text{Solubility of iodine in CCl}_4}{0.34} = 85.5$$

or Solubility of iodine in CCl$_4$ = 85.5×0.34

= **29.07 g litre^{-1}**

EXPLANATION OF DISTRIBUTION LAW

This is an equilibrium law. When the distribution of the solute X has reached dynamic 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,
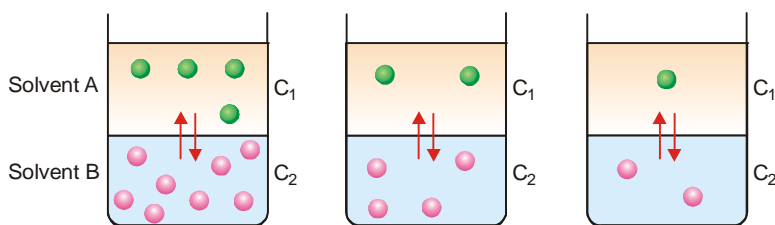
■ Figure 18.2
At equilibrium, the number of molecules of X passing from solvent A into B is proportional to its concentration in A and vice versa. Also, the rate of migration of solute molecules from A to B and B to A is equal (Illustration).

$$R_1 \propto C_1$$
or $$R_1 = k_1 \times C_1$$ where k_1 is a constant
Again $$R_2 \propto C_2$$
or $$R_2 = k_2 \times C_2$$ where k_2 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 :

1. **Constant temperature.** The temperature is kept constant throughout the experiment.
2. **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.
3. **Equilibrium concentrations.** The concentrations of the solute are noted after the equilibrium has been established.
4. **Dilute solutions.** The concentration of the solute in the two solvents is low. The law does not hold when the concentrations are high.
5. **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.

HOW IS DISTRIBUTION LAW MODIFIED BY CHANGE IN MOLECULAR STATE

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.

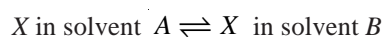### (1) When Solute undergoes Association

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 Fig. 18.3.

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 in solvent $A \rightleftharpoons X$ in solvent B

we have

■ Figure 18.3
Distribution diagram when the solute is associated in one solvent.

$$\frac{C_1}{C_3} = K_D \qquad \qquad ...(i)$$

Applying Mass Law to the chemical equilibrium

$$nX \rightleftharpoons X_n$$
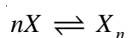
$$\frac{[X]^n}{[X_n]} = K_C \quad \text{or} \quad \frac{C_3^n}{C_2} = K_C \qquad \qquad ...(ii)$$

Taking nth root on both sides in equation (*ii*)

$$\frac{C_3}{\sqrt[n]{C_2}} = \sqrt[n]{K_C} \qquad \qquad ...(iii)$$

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.

SOLVED PROBLEM. When benzoic acid was shaken with mixtures of benzene and water at constant temperature, the following results were obtained :

Concentration of acid in benzene (C_1)	0.24	0.55	0.93
Concentration of acid in water (C_2)	0.015	0.022	0.029

Comment on the results.

SOLUTION. Calculating the ratio C_1/C_2 for each case;

$$\frac{0.24}{0.015} = 16 \qquad \frac{0.55}{0.022} = 25 \qquad \frac{0.93}{0.029} = 32$$

Thus the distribution coefficient is not constant. Therefore, benzoic acid does not exist as single molecules in both solvents.

On calculating $\sqrt{C_1/C_2}$, we have

$$\sqrt{\frac{0.24}{0.015}} = 4 \qquad \sqrt{\frac{0.55}{0.022}} = 5 \qquad \sqrt{\frac{0.93}{0.029}} = \mathbf{5.66}$$

The constant value of partition coefficient now arrived at, suggests that benzoic acid is associated into double molecules in the benzene layer.

(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 Fig. 18.4.

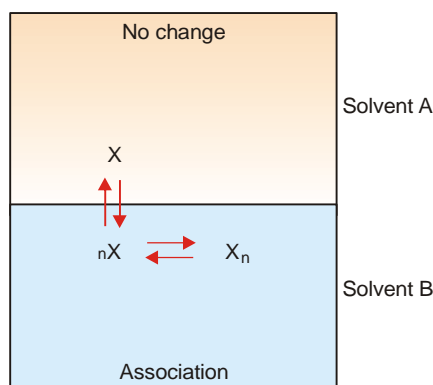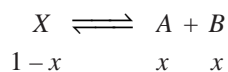Let C_1 be the concentration of X in solvent A and C_2 the total concentration of X (dissociated and undissociated) in solvent B.

If the degree of dissociation in solvent B is x,

$$X \rightleftharpoons A + B$$
$$1 - x \qquad x \qquad x$$

Hence the concentration of the *undissociated* (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.
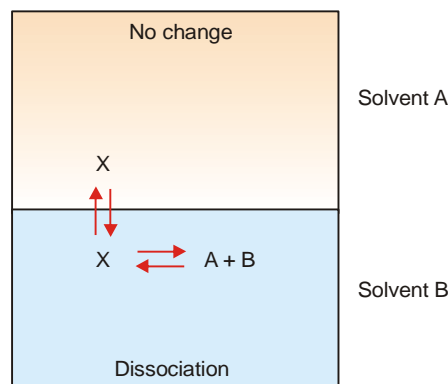
Figure 18.4
Distribution diagram when dissociation occurs in one solvent.

HENRY'S LAW – A FORM OF DISTRIBUTION LAW

Henry's law states : **at a constant temperature the solubility of a gas in a liquid is proportional to the pressure of the gas above it.** Henry's law may be mathematically expressed as

$$C = kP$$

where C is the solubility (or concentration), k is a constant, and P is the pressure of the gas, k is called **Henry's constant.**

Explanation

Henry's law is, in fact, a form of Distribution law. If a vessel containing a liquid and a gas is shaken, at equilibrium the gas can be regarded as distributed between the liquid (Phase A) and the space above (Phase B).

The influence of partial pressure on solubility is utilized in making carbonated beverages like beer, champagne, and many soft drinks. So called 'soda water' is bottled under a carbon dioxide pressure of about 4 atm. When the bottle is opened to the air, the partial pressure of CO_2 above the solution is decreased (about 0.001 atm), and CO_2 bubbles out.
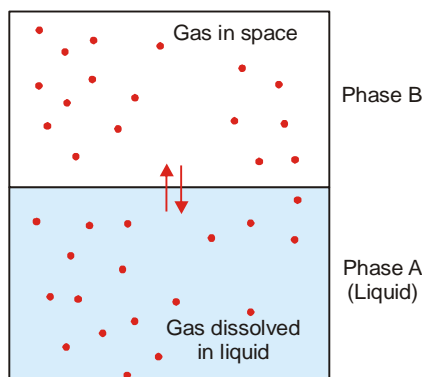
■ **Figure 18.5**
Distribution diagram illustrating Henry's law.
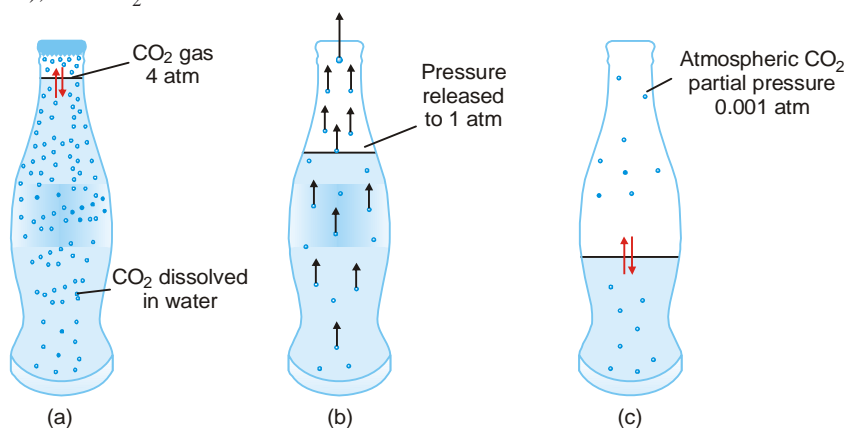
■ **Figure 18.6**
(a) CO_2 gas at 4 atm in equilibrium with dissolved CO_2 resulting in high solubility of CO_2; (b) In opened bottle pressure is released to 1 atm and hence equilibrium shifted upward, gas bubbles evolved causing brisk effervescence; (c) Partial pressure of CO_2 in air being 0.001 atm, practically the whole of CO_2 is removed from solution, leaving the soft drink flat as the equilibrium is established.

Let C_1 be the concentration of the gas in phase B

        C be the concentration of the gas in phase A

Applying the Distribution law

$$\frac{C}{C_1} = K_D \quad \text{(a constant)}$$

We know that molar concentration of gas is proportional to its pressure, P.

Hence $\dfrac{C}{P} = k$ (a constant)

or $C = k \times P$

This is **Henry's Law equation.**

Like distribution law, Henry's law holds good for dilute solutions of gases which do not react with the solvent.

If a mixture of gases is in contact with a liquid, the partial pressure of an individual gas, not their total pressure, determines the mass of each gas dissolving. In such a case, **the solubility of each gas is proportional to its partial pressure.**

SOLVED PROBLEM 1. The solubility of pure oxygen in water at 20° C and 1.00 atm pressure is 1.38×10^{-3} mole/litre. Calculate the concentration of O_2 (mole/litre) at 20°C and a partial pressure of 0.21 atm.

SOLUTION

Calculation of Henry's Constant

$$k = \frac{\text{conc } O_2}{\text{pressure } O_2}$$

$$= \frac{1.38 \times 10^{-3} \text{mole/litre}}{1.00 \text{ atm}}$$

$$= 1.38 \times 10^{-3} \frac{\text{mole/litre}}{\text{atm}}$$

Calculation of concentration of O_2

$$C = k \times P \qquad\qquad \text{(Henry's law)}$$

$$\text{Conc. of } O_2 = 1.38 \times 10^{-3} \frac{\text{mole/litre}}{\text{atm}} \times 0.21 \text{ atm}$$

$$= \mathbf{2.9 \times 10^{-4} \text{ mole/litre}}$$

SOLVED PROBLEM 2. A soda-water bottle was opened and the soft drink allowed to come to equilibrium at 25°C with air containing carbon dioxide at a pressure of 4.0×10^{-4} atm. Find the concentration of CO_2 in the soda after it had stood open and come to equilibrium. The Henry's constant for aqueous solution of CO_2 at 25° is

$$k = 3.2 \times 10^{-2} \frac{\text{mole/litre}}{\text{atm}}$$

SOLUTION

$$C = kP \qquad\qquad \text{(Henry's law)}$$

Substituting into Henry's law equation, we get for the opened soft drink at equilibrium with atmospheric CO_2,

$$C = \left(\frac{3.2 \times 10^{-2} \text{ mole/litre}}{\text{atm}} \right) \left(4.0 \times 10^{-4} \text{ atm} \right)$$

$$= \mathbf{1.28 \times 10^{-5} \text{ mole/litre}}$$

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.

$$KI + I_2 \rightleftharpoons KI_3$$
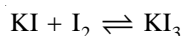
This reaction can be carried in water, while iodine is soluble in both water and benzene.

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 is added some benzene and shaken. On standing, the mixture separates into two layers. The equilibria that are set up are shown in Fig. 18.7.

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,

Water layer

$I_2 + KI \rightleftharpoons KI_3$

I_2

Benzene layer

■ **Figure 18.7**
Determination of equilibrium constant.

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

$\therefore$ Conc of I_2 (free) in water layer $= K \times b$

Hence conc of KI_3 in water layer $= c - Kb$

$\therefore$ Conc of KI in water layer $= a - (c - Kb)$

$$= a - c + Kb$$

We can now say that the equilibrium constant of the reaction

$$I_2 + KI \rightleftharpoons KI_3$$

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

The square brackets denote concentrations in water layer.

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

STUDY OF COMPLEX IONS

If the value of K_c comes out to be constant by taking different concentrations of KI and I_2 to start with, it proves the existence of KI_3 or the complex ion I_3^-.

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

The distribution law is, therefore, helpful in the study of complex ions.

Other examples of complex formation are :

$$CuSO_4 + 4NH_3 \rightleftharpoons CuSO_4 . 4NH_3 \text{ or } [Cu(NH_3)_4]^{2+} SO_4^{2-}$$

$$\underset{\text{Aniline}}{C_6H_5NH_2} + HCl \rightleftharpoons \underset{\text{Anilinium chloride}}{C_6H_5NH_3^+Cl^-}$$

Figure 18.8
Extraction in a separatory funnel.

EXTRACTION WITH A SOLVENT

The extraction (removal by a solvent) of an organic substance from an aqueous solution is probably the most important application of Distribution law. The process is carried by shaking the aqueous solution with a immiscible organic solvent, say ether (ethoxyethane), in a separatory funnel. The distribution ratio being in favour of ether, most of the organic substance passes into ether layer. On standing, the aqueous and ether layers separate in the funnel. The lower aqueous layer is run out, leaving the ether layer behind. This is then transferred to a distillation flask. Ether is distilled over while the organic substance is left as residue in the flask.

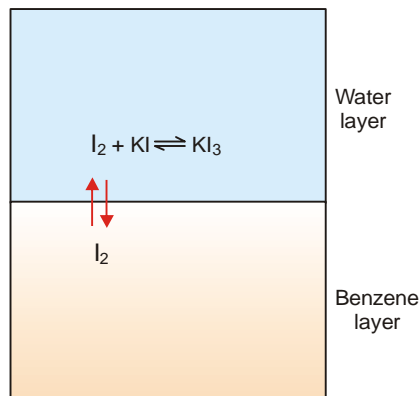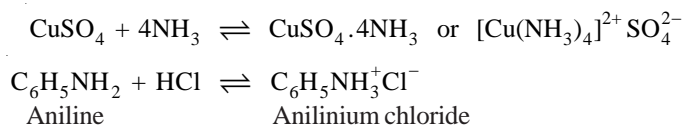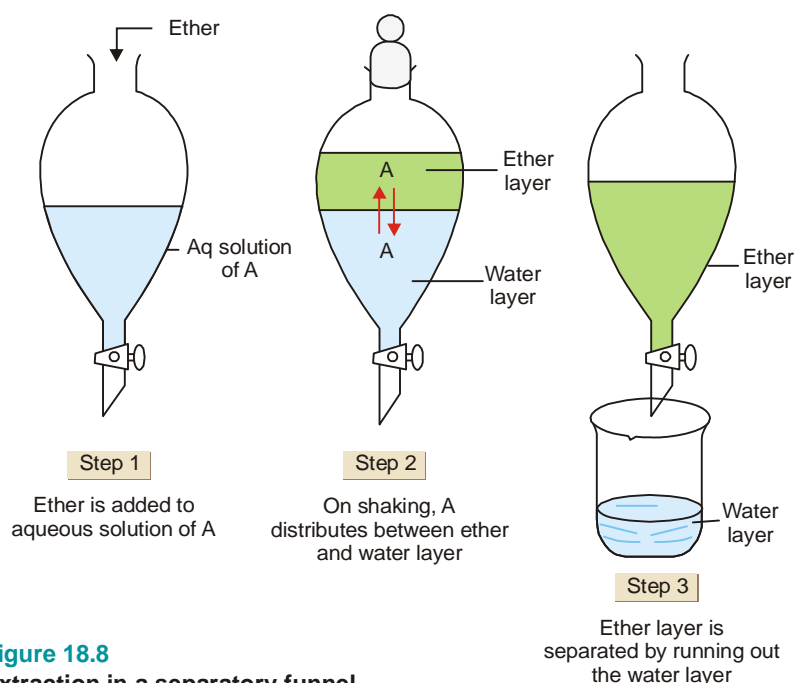If desired, the process may be repeated with aqueous layer left after the first extraction with a fresh quantity of the solvent.

The other common solvents used for extraction are hexane, benzene, chloroform, acetone, carbon disulphide, etc.

The greater the distribution ratio is in favour of the organic solvent, the greater will be the amount extracted in any one operation.

MULTIPLE EXTRACTION

The process of extraction when carried with the total amount of the given solvent in a single operation, is referred to as **simple extraction. To recover the maximum amount of the substance from aqueous solution, the extraction is made in two or more successive operations using small portions of the solvent provided.** This is called **multiple extraction** or **multi-step extraction.**

In such a process the aqueous solution is first extracted with a portion of the solvent in a separatory funnel. The aqueous layer from which some substance has been removed is then transferred to another funnel. This is shaken with a second portion of the solvent. Similarly, the aqueous layer from the second extraction is treated with a third portion of solvent, and so on.
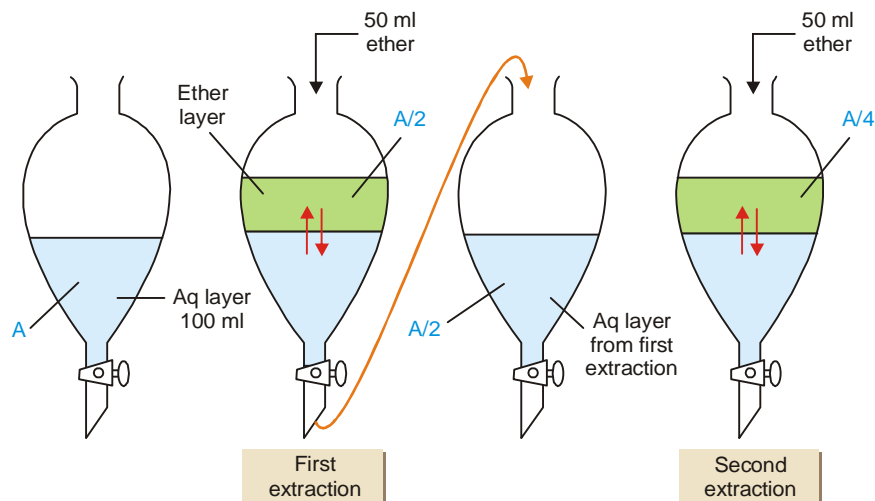
■ Figure 18.9

Illustration of Multiple extraction. The given solvent (ether) is used in two successive portions of 50 ml each.

WHY MULTIPLE EXTRACTION IS MORE EFFICIENT?

The fact that it is more efficient to use a specified volume of solvent in small portions rather than in one whole, may be illustrated in a simple way.

Suppose we have 100 ml of an aqueous solution containing A grams of an organic substance. We can extracts the substance with ether (ethoxyethane), its distribution ratio being twice in favour of ether. We are provided with 100 ml of ether which may be used in one lot or in two portions of 50 ml each.

(1) **Using all the ether in one lot.** Let x grams be the weight of the substance extracted in the solvent layer. Then the amount of substance left in the water layer $= A - x$ grams. Therefore,

Concentration in ether layer $= x/100$

Concentration in water layer $= (A - x)/100$

$$\frac{C_{ether}}{C_{water}} = K \qquad \text{(Distribution law)}$$

$$\therefore \qquad \frac{x/100}{(A - x)/100} = 2$$

Hence $\qquad\qquad x = 2/3\,A$

Thus 66% of substance is extracted.

(2) **Using two 50 ml portions of ether.** Let x_1 grams of substance be extracted in the first operation with 50 ml ether. Thus,

Concentration in ether layer $= x_1/50$

Concentration in water layer $= (A - x_1)/100$

$$\frac{C_{ether}}{C_{water}} = 2$$

or $\qquad\qquad \dfrac{x_1/50}{(A - x_1)/100} = 2$

Hence $\qquad\qquad x = 1/2\,A$

$\therefore$ 50% of substance is extracted.

The substance left in water layer is $\frac{1}{2}$ A. Let x_2 grams be the substance removed from the water layer when it is extracted with another 50 ml portion of ether. Hence,

Concentration in ether layer $= x_2/50$

Concentration in water layer $= 1/2\,A - x_2$

$$\frac{x_2/50}{(1/2A - x_2)/100} = 2$$

Hence $\qquad\qquad x_2 = 1/4\,A$

∴ 25% of substance is extracted.

Thus 75 per cent of substance is extracted by using two 50 ml portions of the solvent as against 66 per cent when 100 ml solvent is used in one lot.

Similarly, it can be shown that by using four 250 ml portions of ether it is possible to extract 80.2% of substance. Five 200 ml portions of ether would likewise remove 83.8%.

It is clear from above that it is more advantageous to use a given quantity of the solvent in as many portions as conveniently possible. It must be understood, however, that **it is not possible to remove the whole of the dissolved substance, however large the number of extractions may be.** Every time, the substance distributes itself between the two solvents and a quantity, howsoever small, must always be left behind.

SOLVED PROBLEM 1. The distribution coefficient of X for benzene and water is 10. Find the amount of X extracted if 1 g of it dissolved in 100 ml of water is equilibrated in a separatory funnel with 100 ml of benzene.

SOLUTION

Let amount of X extracted with 100 ml of benzene $= x$ g

The amount of X left in 100 ml water $= 1 - xg$

$$\frac{C_{benzene}}{C_{water}} = 10$$

∴ $\qquad\qquad \frac{x/100}{(1-x)/100} = 10$

or $\qquad\qquad x = 10\,(1-x)$

$\qquad\qquad 11x = 10$

$\qquad\qquad x = \frac{10}{11} = 0.909$

Hence the amount of X extracted with 100 ml benzene is **0.909 grams**.

SOLVED PROBLEM 2. An aqueous solution contains $10g$ of solute per litre. When 1 litre of the solution is treated with 100 ml of ether, $6g$ of the solute are extracted. How much more of the solute would be extracted from the aqueous solution by a further 100 ml ether? Assume that the molecular state of the solute is the same in ether and water.

SOLUTION

(a) **To find distribution coefficient**

In the first extraction :

Concentration in ether $(C_{ether}) = \frac{6}{100}$

Concentration in water $(C_{water}) = \frac{10-6}{1000} = \frac{4}{1000}$

Applying distribution law, $\dfrac{C_{ether}}{C_{water}} = \dfrac{6}{100} \times \dfrac{1000}{4} = 15$

(b) **Substance recovered in second extraction**

Let x be the substance extracted with a further 100 ml of ether.

The concentration in ether $(C_{ether}) = \dfrac{x}{100}$

The concentration in water $(C_{water}) = \dfrac{4-x}{1000}$

Applying distribution law, $\dfrac{C_{ether}}{C_{water}} = \dfrac{x/100}{4-x/1000} = 15$

$$10x = 15(4-x)$$
$$= 60 - 15x$$
$$25x = 60$$
$$\therefore \qquad x = \textbf{2.4}$$

Hence a further amount of **2.4 g** will be extracted.

SOLVED PROBLEM 3. The distribution coefficient of isobutyric acid between ether and water is 3 at 25°C. What will be the amount of isobutyric acid removed if 4 g of isobutyric acid in 100 ml of water is extracted with 100 ml of ethoxyethane (ether) at 25°C. What would the effect have been if two successive 50 ml portions of ether had been used to extract the aqueous layer ?

SOLUTION

(a) **Extraction with 100 ml ether**

$$\dfrac{C_{ether}}{C_{water}} = 3 \,(\text{at } 25°C)$$

Let x g be the amount of the acid extracted with 100 ml of ether.

$$\therefore \qquad \dfrac{x/100}{(4-x)/100} = 3$$

Hence $x = 3\ g$

Thus we can separate $3g$ (75%) of isobutyric acid from the aqueous layer with 100 ml ether.

(b) **Two extractions with 50 ml ether each :**

Let x_1 be the acid removed in the first extraction,

$$\dfrac{x_1/50}{(4-x_1)/100} = 3$$

Whence $x_1 = 2.4\ g$

The acid left in water layer is $(4-2.4) = 1.6\ g$

The 1.6 g of the acid is then extracted with a second 50 ml portion of ether. If x_2 is the amount removed by ether

$$\dfrac{x_2/50}{(1.6-x_2)/100} = 3$$

Hence $x_2 = 0.96\ g$

That is, two successive extractions with 50 ml portion of ether each would remove $(2.4\ g + 0.96g) = \textbf{3.36 g (84\%)}$ of isobutyric acid from aqueous layer.

SOLVED PROBLEM 4. A solution of 6 g of substance X in 50 ml of aqueous solution is in equilibrium, at room temperature, with a solution of X in diethyl ether (ethoxyethane) containing 108 g of X in 100 ml. Calculate the mass of X extracted by shaking 100 ml of an aqueous solution containing 10 g of X with (a) 100 ml of ether; (b) 50 ml of ether twice at room temperature.

SOLUTION

(a) **Calculation of Distribution coefficient**

$$\frac{C_{\text{ether}}}{C_{\text{water}}} = \frac{108/100}{6/50}$$

$$= \frac{108}{100} \times \frac{50}{6} = \frac{9}{1}$$

(b) **Mass extracted with 100 ml of ether**

Let x g of X be extracted from aqueous solution. Then

$$\frac{x/100}{(10-x)/100} = 9$$

$$\frac{9(10-x)}{100} = \frac{x}{100}$$

$$10x = 90$$

$$x = 9$$

$i.e.$, 9 g of X pass into ether.

(c) **Two extractions with 50 ml each time**

Let x_1 g of substance be extracted with 50 ml ether.
Then,

$$\frac{x_1/50}{(10-x_1)/100} = \frac{9}{1}$$

$$\frac{9(10-x_1)}{100} = \frac{x_1}{50}$$

$$11x_1 = 90$$

$$x_1 = 8.2 \text{ g (approx)}$$

The amount of X left in aqueous solution after extraction with 50 ml ether is

$$10 - 8.2 = 1.8 \text{ g}$$

When shaken with fresh 50 ml ether, let the amount extracted be x_2. Thus,

$$\frac{x_2/50}{(1.8-x_2)/100} = 9$$

$$11 x_2 = 16.2$$

$$x_2 = 1.47$$

Hence the total X extracted by two 50 ml portions is

$$(8.2 + 1.47) \text{ g} = \textbf{9.67 g}$$

General Formula for Substance Left Unextracted

Suppose V ml of an aqueous solution contain A grams of an organic substance. This solution is extracted with v ml of the given organic solvent at a time

(1) **First extraction.** Let x_1 be the substance left unextracted in aqueous solution in the first operation. Now,

$$\text{Concentration in aqueous layer} = \frac{x_1}{V}$$

$$\text{Concentration in solvent} = \frac{A - x_1}{v}$$

$$\frac{C_{water}}{C_{solvent}} = K \qquad\qquad \text{(Distribution law)}$$

Thus,

$$\frac{x_1/V}{(A - x_1)/v} = K$$

Hence
$$x_1 = A\,\frac{KV}{KV + v} \qquad\qquad\qquad ...(1)$$

(2) **Second extraction.** Let x_2 be the substance left unextracted in the aqueous layer in the second extraction made with fresh v ml solvent. Now,

$$\text{Concentration in aqueous layer} = \frac{x_2}{V}$$

$$\text{Concentration in solvent} = \frac{x_1 - x_2}{v}$$

Substituting the values of concentration in the Distribution law equation

$$\frac{x_2/V}{(x_1 - x_2)/v} = K$$

Hence
$$x_2 = x_1\,\frac{KV}{KV + v}$$

Substituting the value of x_1 from equation (1)

$$x_2 = A\,\frac{KV}{KV + v} \times \frac{KV}{KV + v}$$

$$= A\left(\frac{KV}{KV + v}\right)^2 \qquad\qquad\qquad ...(2)$$

(3) **n-th extraction.** Following the above procedure for first and second extraction, the amount of substance left unextracted (x_n) in the n-th extraction would be

$$x_n = A\left(\frac{KV}{KV + v}\right)^n \qquad\qquad\qquad ...(3)$$

This general formula enables the calculation of the amount of substance left unextracted after a specified number of extractions with v ml portion of the solvent each time.

(4) **Extraction with whole lot of solvent.** If the entire quantity of the given solvent is used for a single extraction, the amount of substance unextracted (x') would be

$$x' = A\left(\frac{KV}{KV + nv}\right) \qquad\qquad\qquad ...(4)$$

Since the quantity within the bracket is less than unity, x_n is smaller than x'. Also, x_n will be smaller the greater the value of n. Hence it is more economical to use the solvent in small portions in a number of extractions.

SOLVED PROBLEM 5. The distribution coefficient of an alkaloid between chloroform and water is 20 in favour of chloroform. Compare the weights of the alkaloid remaining in aqueous solution when 100 ml containing 1-gram has been shaken with : (*a*) 100 ml chloroform; and (*b*) two successive 50 ml portions.

SOLUTION

$$K = \frac{C_{\text{water}}}{C_{\text{chlorofom}}} = \frac{1}{20}$$

(1) When 100 ml is used in one lot, the amount unextracted is

$$x' = 1 \times \left(\frac{KV}{KV + v} \right)$$

$$= 1 \times \left(\frac{(1/20) \times 100}{(1/20) \times 100 + 100} \right) = \frac{5}{105} = \textbf{0.0476 g}$$

(2) When 50 ml chloroform is used in each of two stages, the amount unextracted is

$$x_2 = 1 \times \left(\frac{KV}{KV + v} \right)^2$$

$$= 1 \times \left(\frac{(1/20) \times 100}{(1/20) \times 100 + 50} \right)^2 = \left(\frac{5}{55} \right)^2 = \textbf{0.0083 g}$$

LIQUID–LIQUID CHROMATOGRAPHY (Partition Chromatography)

This is a versatile and wide-spread technique for separation of a mixture of small amounts of organic substances. The operation is carried in a glass tube packed with an inert solid material (silica) soaked in a solvent 1 (water). The mixture paste is applied to the column top. Then a layer of another immiscible solvent 2 (*hexane*) is allowed to flow down the column (Fig. 18.10). A film of solvent 1 held by the silica forms the **stationary liquid phase,** while the running solvent 2 the **mobile liquid phase.** Each component of the mixture distributes itself between the stationary liquid phase and the mobile liquid phase. Thus,

$$\frac{C_s}{C_m} = K_D$$

where C_s = concentration in stationary liquid phase and C_m = concentration in the mobile liquid phase.

Different components in the mixture have different distribution coefficient. They pass into the mobile phase in order of their distribution coefficients. **The component (say S_2) with higher distribution coefficient is extracted (eluted) first and is the first to move down the column. The location of the components is easy if these are coloured.** Otherwise they are visualised with the help of a locating agent. The portion of the solvent (or band) containing each component is received in a separate vessel and the solute recovered from it by distillation.

APPLICATIONS OF DISTRIBUTION LAW

There are numerous applications of distribution law in the laboratory as well as in industry. Here we will discuss some more important ones by way of recapitulation.

(1) Solvent Extraction

This is the process used for the separation of organic substances from aqueous solutions. The aqueous solution is shaken with an immiscible organic solvent such as ether (or benzene) in a separatory funnel. The distribution ratio being in favour of ether, most of the organic substance passes into the ethereal layer. The ethereal layer is separated and ether distilled off. Organic substance is left behind.
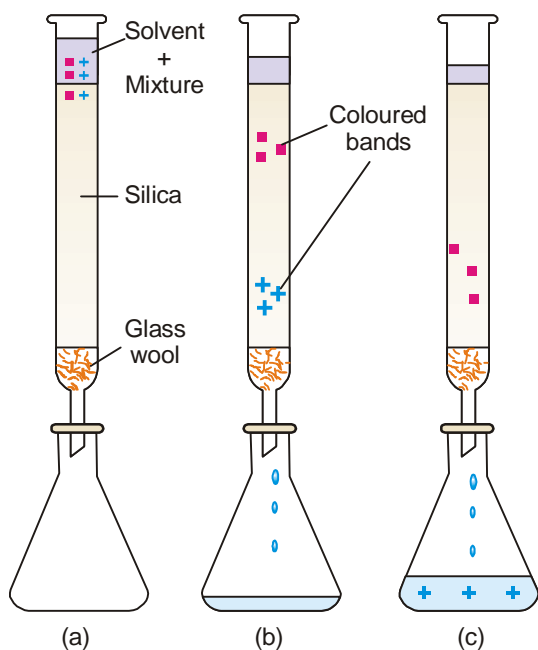
■ Figure 18.10
Details of a chromatography column.
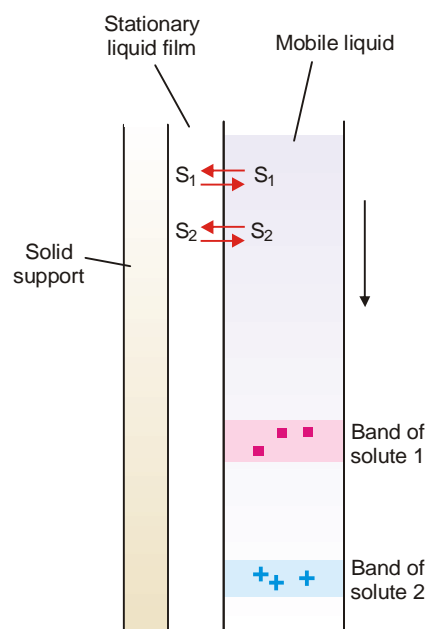
■ Figure 18.11
In partition chromatography, the liquid film on the solid support is the stationary phase. The second phase is an immiscible solvent flowing down. Each solute (S_1 and S_2) is distributed between the stationary liquid film and the mobile liquid phase. The solute (say S_2) with higher distribution ratio comes down first.

The process of extraction is more efficient if the solvent is used in a number of small portions than in one whole lot. Thus multiple extraction is preferred to simple extraction.

The multiple extraction is also the basis of the industrial **counterflow solvent extraction.** A dilute solution of the substance enters at the top of a column or tower. At the same time the extracting solvent enters at the bottom. As the aqueous solution and the solvent pass each other, the solute distributes itself in favour of the solvent. Since the process of extraction is repeated many times at different levels in the tower, maximum quantity of substance is removed in the solvent.

(2) 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.

(3) 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 300

in favour 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 unextracted silver. This is treated with fresh quantities of molten zinc to recover most of the silver.

(4) Confirmatory Test for Bromide and Iodide

The salt solution is treated with chlorine water. Small quantity of bromine or iodine is thus liberated. The solution is then shaken with trichloromethane (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.

(5) Determination of Association

When a substance is associated (or polymerized) in solvent A and exists as simple molecules in solvent B, the Distribution law is modified as

$$\sqrt[n]{\frac{C_A}{C_B}} = K \qquad \qquad ...(1)$$

when n is the number of molecules which combine to form an associated molecule.

Suppose benzoic acid is associated to bimolecules, $(C_6H_5COOH)_2$, in benzene and is present as simple molecules in aqueous layer. Then equation (1) can be written as follows where $n = 2$.

$$\frac{-\sqrt[2]{C_{benzene}}}{C_{aqueous}} = K \qquad \qquad ...(2)$$

The concentrations in benzene and aqueous layer are determined experimentally. If the under root of the concentration in benzene divided by the concentration in aqueous layer gives a constant value benzoic acid exists as bimolecules (*dimer*) in benzene.

(6) Determination of Dissociation

Suppose a substance X is dissociated in aqueous layer and exists as single molecules in ether. If x is the degree of dissociation (or ionisation), the distribution law is modified as

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

where
$$C_1 = \text{concentration of } X \text{ in benzene}$$
$$C_2 = \text{concentration of } X \text{ in aqueous layer}$$

The value of x can be determined from conductivity measurements, while C_1 and C_2 are found experimentally. Thus the value of K can be calculated. Using this value of K, the value of x for any other concentrations of X can be determined.

(7) 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.

(8) Deducing the Formula of a Complex Ion (I_3^-)

Some iodine is added to a solution of KI and the reaction mixture shaken with benzene.

(a) The [I_2] in water layer can be found knowing the value of K_D (determined separately) and concentration of iodine in benzene (determined by titration against thiosulphate).

(b) The total concentration of iodine, [I_2] + [I_3^-] in water layer is found by titration against thiosulphate. Knowing [I_2] from (a), [I_3^-] can be calculated.
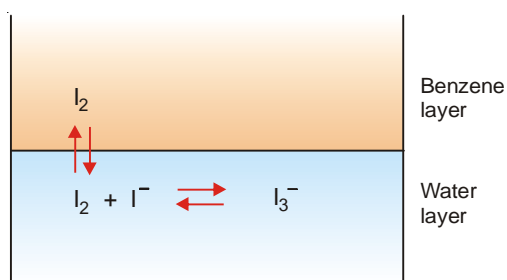
(c) The initial concentration of KI taken is represented by the equilibrium concentrations [I^-] + [I_3^-]. Knowing [I_3^-] from (b), [I^-] can be found.

Substituting the above values of concentrations in the law of Mass Action equation of the reaction in water layer,

$$\frac{[I_3^-]}{[I_2][I^-]} = K$$

the value of equilibrium constant K can be calculated. If it comes out to be constant for different concentrations of iodine, it stands confirmed that the formula of the complex I_3^-, which we assumed is correct.

(9) Distribution Indicators

In iodine titrations, the end point is indicated by adding starch suspension which turns blue. A greater sensitivity can be obtained by using what we may call 'Distribution Indicator'. A few drops of an immiscible organic solvent such as chloroform (or carbons tetrachloride) is added to the solution. The bulk of any iodine present passes into the organic layer and imparts intense violet colour to it.

EXAMINATION QUESTIONS

1. Define or explain the following terms :
   (a) Nernst's distribution law (b) Henry's law
2. State Nernst distribution law. What are its important applications?
3. State and explain Nernst Distribution law. The solubility of a substance is twice as greater in ether as in water. Compare the quantities extracted from 100 ml of aqueous solution by
   (a) 100 ml of ether in a single operation
   (b) two successive operations of 50 ml ether in each.
4. Give thermodynamic basis for the Nernst Distribution law. Indicate its applications.

5. Deduce an expression for the Nernst Distribution law. State conditions under which the law is strictly valid.

6. Deduce the formulae for distribution law in the case of :
   (*a*) Association of solute in one of the phases
   (*b*) Dissociation of solute in one of the phases

7. The solubility of a substance is twice as great in ether as in water. Compare the quantities extracted from 100 cc of aqueous solution by:
   (*a*) 100 cc ether in a single operation
   (*b*) 50 cc ether in two successive operations

8. (*a*) Apply Distribution law to the case when the solute forms a dimer in one of the solvents.
   (*b*) Show that the process of extraction by a given volume of the solvent is more efficient if it is carried out in parts.

9. (*a*) What is Nernst Distribution law?
   (*b*) Nernst reported the following results for the distribution of acetic acid between water and CCl_4 :

Conc of acetic acid in CCl_4 (moles/1)	0.292	0.725	1.41
Conc of acetic acid in H_2O (moles/1)	4.87	7.98	10.70

   Assuming that acetic acid has its normal molecular weight in water, calculate its molecular weight in CCl_4.

   Answer. 120

10. At 25°C the iodine solution in water which contains 0.0516 g lit^{-1} is in equilibrium with CCl_4 solution containing 4.1280 g lit^{-1} of iodine. If at 25°C iodine solution contains 0.410 g lit^{-1} of iodine, find out the solubility of iodine in CCl_4 solution.

    Answer. 32.8 g litre^{-1}

11. If Henry's law constant for oxygen at 25°C is 3.30×10^{-7} mm Hg, find the solubility of oxygen in 1000 g of water at 25°C and a partial pressure of 190 mm Hg.

    Answer. 0.825×10^{-7} g litre^{-1}

12. Succinic acid was shaken with a mixture of water and ether. After distribution, upon analysis the concentrations of the acid in two layers are found as follows :

In aqueous layer (mole lit^{-1})	0.0252	0.071	0.121
In ethereal layer (mole lit^{-1})	0.0046	0.013	0.022

    If succinic acid has similar molecular weights in ether and water, determine its partition coefficient.

    Answer. 5.4798

13. The following data have been obtained on the distribution of phenol between water and chloroform

C_1	0.094	0.163	0.254	0.436
C_2	0.254	0.761	1.850	5.430

    where C_1 is the concentration in the aqueous layer and C_2 is the concentration in the chloroform layer. What conclusions do you draw from these results regarding the molecular condition of phenol in the chloroform solution?

    Answer. Phenol exists as dimer

14. (*a*) State Distribution law and give the conditions under which the law is applicable.
    (*b*) Succinic acid was shaken with a mixture of water and ether. The concentrations of acid in two layers per 100 cc of the solution are as follows:

Concentration in water layer (C_W)	25.4	33.2	42.6
Concentration in ether layer (C_E)	4.2	5.5	7.1

    Find out the partition coefficient. If succinic acid has normal molecular weight of 118 in water, find its molecular weight in ether.

    Answer. (*b*) 6.02; 118

15. The distribution coefficient of iodine between water and carbon disulphide is 0.0017. One litre of aqueous solution containing one gram of iodine is shaken with 100 ml of carbon disulphide till the

equilibrium is reached. Find the amount of iodine extracted by carbon disulphide.

Answer. 0.983 g

16. At 298 K, an aqueous solution of iodine containing 0.0387×10^{-3} kg per dm^3 of solution is in equilibrium with 3.31×10^{-3} kg/dm^3 of iodine in carbon tetrachloride. If solubility of iodine in CCl_4 is 0.0291 kg/dm^3, what is the solubility of iodine in water?

Answer. 0.00034 kg/dm^3

17. An organic acid was dissolved in two immiscible solvents (A) and (B). At equilibrium the concentration of the acid in (A) and (B) was found to be 0.40 and 0.64 mole/litre respectively. Calculate the distribution coefficient of the organic acid, if it forms dimers in the solvent (B).

Answer. 0.5

18. (*a*) How is distribution law modified when the solute undergoes dissociation in one of the solvents? What would happen if the solute is completely dissociated in one of the solvents?

(*b*) An organic acid is distributed between 500ml each of a solvent A and water. In water it is dissociated. The amount of the acid in aqueous layer was 6 gram and in solvent A, it was 0.72 gram. If the distribution coefficient of the acid between the solvent A and water is 0.16, calculate the degree of dissociation, assuming that the acid has normal molecular weight in A.

Answer. (*b*) 0.25

19. (*a*) Explain how is distribution law modified when there is a change in molecular state.

(*b*) State Nernst's Distribution law explaining the significance of the term distribution coefficient.

(*c*) A solid X is added to a mixture of benzene and water. After shaking well and allowing it to stand. 10 ml of benzene layer was found to contain 0.13 gm of X, and 100 ml of water layer contained 0.22 gm of X. Calculate the value of distribution coefficient.

Answer. (*b*) 5.9090 (*Bundelkhand BSc, 2000*)

20. If the distribution coefficient of benzoic acid between water and benzene is 3.304 at 20°C, calculate the number of molecules of benzoic acid which may be extracted from 100 ml of 0.2 molar aqueous solution by 10 ml of benzene.

Answer. 0.046 mole (*Agra BSc, 2001*)

21. (*a*) Define a solution and discuss factors affecting solubility. Explain solution of solids and liquids with examples.

(*b*) When a substance is distributed between two immiscible liquids and its molecule associates in one of them, the distribution constant is given by

(*i*) $\dfrac{C_1}{C_2}$ (*ii*) $\dfrac{C_1}{\sqrt[n]{C_2}}$ (*iii*) $\sqrt{\dfrac{C_1}{C_2}}$ (*Jiwaji BSc, 2002*)

22. (*a*) Explain Nernst distribution law. How is it modified when a solute undergoes (*i*) association in a solvent and (*ii*) dissociation in the solvent?

(*b*) Briefly describe the various applications of distribution law. (*MD Rohtak BSc, 2002*)

23. What are the conditions of validity for Nernst distribution law? (*Arunachal BSc, 2002*)

24. How is Nernst distribution law used in the study of complex ions? (*MD Rohtak BSc, 2002*)

25. Discuss the applications of Nernst distribution law in studying the molecular state of benzoic acid in benzene. (*Panjab MSc, 2003*)

26. Describe Nernst distribution law from thermodynamic considerations (*Arunachal BSc, 2003*)

27. In the distribution of benzoic acid between water and benzene, the following results were obtained :

C_1 (in water)	1.50	1.95	2.97
C_2 (in benzene)	24.20	41.20	97.00

Assuming that benzoic acid exists as single molecules in water, show that it exists as dimers in benzene.

(*Delhi BSc, 2003*)

28. (*a*) State Nernst distribution law. How is it used in the process of extraction of solutes?

(*b*) 12 g of an organic substance A is present in 100 g of its aqueous solution. How much of it would

be left behind after extracting the solution with two successive applications of 50 ml each of ether? The distribution coefficient of A between water and ether is 2 in favour of ether.

Answer. (*b*) 3.0 g   (*Bangalore BSc, 2004*)

29. (*a*) Derive distribution law from thermodynamic consideration. How is it modified when the solute undergoes association in one of the solvent?

   (*b*) An organic compound is twice more soluble in ether than in water. Calculate the amount of the compound extracted when 100 ml of aqueous solution containing 1 g of compound is shaken with

   (*i*) 100 ml of ether at one time   (*ii*) two successive quantities of 50 ml each

   Answer. *(b)* (*i*) 0.67 g; (*ii*) 1.0 g   (*Baroda BSc, 2004*)

30. Calculate how much succinic acid would be extracted from 100 ml of water containing 5 gm of acid if extracted with 50 ml of ether. Partition coefficient of succinic acid between water and ether is 5.5.

   Answer. 4.545 g   (*Jiwaji BSc, 2004*)

31. The partition coefficient of a substance between benzene and water is 10.1. How much substance will be extracted from its 250 ml aqueous solution containing 2.5 g of it by using 200 ml benzene in

   (*i*) two equal portions and (*ii*) a single lot?   (*Madurai BSc, 2004*)

   Answer. (*i*) 2.0 g; (*ii*) 2.4 g

32. The distribution coefficient of an organic acid between benzene and water is 80. An aqueous solution of the acid containing 2.25 g in 100 cm^3 was extracted with (i) 10 cm^3 of benzene in one lot and (ii) twice with 5cm^3 benzene each time. Calculate the amount of acid extracted in each experiment.

   Answer. (i) 2 g (ii) 2.16 g   (*Madras BSc, 2005*)

33. In an experiment on distribution of succinic acid between water and ether at 20°C, 10 ml of ethereal layer contains 0.046 g of acid. Calculate the amount of succinic acid present in 25 ml of the aqueous solution in equilibrium with it if the distribution coefficient of succinic acid between water and ether is 5.2.

   Answer. 0.598 g   (*Allahabad BSc, 2005*)

34. The solubility of iodine in water is 0.35 g lit^{-1}. Calculate its solubility in carbon tetrachloride, if the distribution constant of iodine in CCl_4 and water is 88.

   Answer. 30.8 g lit^{-1} (*Bhopal BSc, 2005*)

35. 100 g of an acid was dissolved in 1 litre of water. The distribution coefficient of acid between ether and water is 3. One litre of ether in one lot was used to extract acid. Calculate the amount of acid extracted.

   Answer. 37.5   (*Jiwaji BSc, 2006*)

36. A solid *Y* was added to mixture of benzene and water. After shaking well and allowing it to stand, 20 cm^3 of the benzene was found to contain 0.26 g of *Y* and 200 cm^3 of water layer contained 0.44 g of *Y*. Calculate the value of distribution constant.

   Answer. 5.9   (*Banaras BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. The expression $K_D = \dfrac{C_1}{C_2}$ where C_1 and C_2 denote the concentration of a solute in two solvents A & B, and K_D is the constant, is called
   (*a*) equilibrium law   (*b*) rate law
   (*c*) Nernst distribution law   (*d*) none of these
   Answer. (*c*)

2. For the study of distribution law the two solvents should be
   (*a*) miscible   (*b*) non-miscible
   (*c*) volatile   (*d*) reacting with each other
   Answer. (*b*)

3. While studying the distribution law
   (a) the temperature should be constant throughout
   (b) there should be no association or dissociation of the solute
   (c) the concentration of the solute in solvents
   (d) all of the above
   Answer. (d)

4. When a solute undergoes association in one of the solvent, the following expression of distribution law is applicable

   (a) $\dfrac{C_1}{C_2} = K_D$ (b) $\dfrac{C_1}{C_2^2} = K_D$

   (c) $\dfrac{C_1}{\sqrt[n]{C_2}} = K_D$ (d) $\dfrac{C_1}{\sqrt{C_2}} = K_D$

   Answer. (c)

5. The modified distribution law for the solute undergoing dissociation in one of the solvents is

   (a) $K_D = \dfrac{C_1}{\sqrt{C_2}}$ (b) $K_D = \dfrac{C_1}{C_2(1-\alpha)}$

   (c) $K_D = \dfrac{C_1}{C_2(\alpha-1)}$ (d) $K_D = \dfrac{C_1}{C_2^2}$

   Answer. (b)

6. At a constant temperature, the solubility of a gas in a liquid is proportional to the pressure of the gas above it. This law is
   (a) Nernst's distribution law   (b) Henry's law
   (c) Le Chatelier's principle   (d) Raoult's law
   Answer. (b)

7. If a mixture of gases is in contact with a liquid, the partial pressure of the individual gas determines the mass of each gas dissolving *i.e.,* the solubility of each gas is proportional to its _____
   (a) total pressure   (b) concentration of the liquid
   (c) partial pressure   (d) temperature
   Answer. (c)

8. The Henry's law equation is
   (a) $C = k \times P$ (b) $k = C \times P$
   (c) $P = C \times k$ (d) $C = k \times \sqrt{P}$
   Answer. (a)

9. The Nernst distribution law equation $C_1/C_2 = K_D$ applies when
   (a) the molecular state of the solute is the same in both the solvents
   (b) the molecular state of the solute is different in both the solute
   (c) the molecular state of the solute may be the same or different in both the solute
   (d) none of the above
   Answer. (a)

10. Benzoic acid when shaken with mixtures of benzene and water undergoes dimerisation in benzene. The distribution law applicable here is

    (a) $\dfrac{C_1}{C_2} = K_D$ (b) $\dfrac{C_1}{\sqrt[3]{C_2}} = K_D$

(c) $\dfrac{C_1}{\sqrt[2]{C_2}} = K_D$ (d) none of these

Answer. (c)

11. The greater the distribution ratio in favour of the organic solvent, the _____ will be the amount extracted in any one operation

(a) greater   (b) lesser

(c) equal   (d) none of these

Answer. (a)

12. Multiple extraction is _____ efficient as compared to single extraction

(a) more   (b) less

(c) the same   (d) none of these

Answer. (a)

13. With the help of distribution law we can

(a) determine the association or dissociation of the solute in one of the solvents

(b) determine the solubility of solute in various solvents

(c) reduce the formula of complex ions

(d) all of the above

Answer. (d)

14. The _____ extraction is more efficient

(a) single   (b) double

(c) multiple   (d) none of these

Answer. (c)

15. The distribution law is applied in the

(a) Haber's process for the manufacture of NH_3

(b) Parke's process for the extraction of Ag

(c) Contact process for the manufacture of H_2SO_4

(d) none of the above

Answer. (b)

16. In the first extraction, the amount of the substance left unextracted is given by the formula (K is distribution coefficient, V ml of the aqueous solution contain A gram of an organic substance)

(a) $x_1 = A\dfrac{KV}{KV + v}$ (b) $x_1 = A\dfrac{KV}{KV + v^2}$

(c) $x_1 = A^2\dfrac{KV}{KV + v}$ (d) $x_1 = A\dfrac{K^2V}{KV + v}$

Answer. (a)

17. The Nernst distribution law $K_D = C_1/C_2$ is not applicable if the solute undergoes

(a) association in one of the solvents

(b) dissociation is one of the solvents

(c) association or dissociation in one of the solvents

(d) none of the above

Answer. (c)

18. When succinic acid or oxalic acid is shaken with ether and water it _____ in water.

(a) associates to form dimer   (b) dissociates into ions

(c) remains the same   (d) none of these

Answer. (b)

19. When a bottle of soda-water is opened, the partial pressure of CO_2 _____.
    (*a*) decreases
        (*b*) increases
    (*c*) remains the same
        (*d*) none of these
    Answer. (*a*)

20. Is it possible to extract the whole of the dissolved substance by using large number of extractions?
    (*a*) yes
        (*b*) no
    (*c*) sometimes
        (*d*) none of these
    Answer. (*b*)

21. In liquid-liquid chromatography technique, the component with _____ distribution coefficient is extracted first
    (*a*) lower
        (*b*) higher
    (*c*) intermediate
        (*d*) none of these
    Answer. (*b*)

22. The Nernst's distribution law does not hold good if
    (*a*) the temperature throughout the experiment is not constant
    (*b*) concentration of the solute in two solvents are high
    (*c*) there is association or dissociation of the solute in one of the solvents
    (*d*) all of the above
    Answer. (*d*)

23. The Nernst's distribution law is also known as
    (*a*) partition law
        (*b*) Henry's law
    (*c*) Raoult's law
        (*d*) equilibrium law
    Answer. (*a*)

24. In the process of extraction of a substance from aqueous solution, the use of a _____ is made
    (*a*) conical flask
        (*b*) measuring flask
    (*c*) burette
        (*d*) separating funnel
    Answer. (*d*)

25. When the solute undergoes association in one of the solvent, the Nernst distribution law as modified as
    (*a*) $C_1 = \sqrt{C_2} \times K_D$
        (*b*) $\sqrt{C_2} \times C_1 = K_D$
    (*c*) $C_1 = K_D \times C_2^2$
        (*d*) $C_1 = K_D \times C_2^3$
    Answer. (*a*).

Top