Unit II

Ideal solutions: A solution of two components is said to be ideal if each component of the solution obeys Raoult's law at all temperatures and concentrations. That is the vapour pressure of each component in the solution at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that component in the pure state at the same temperature. Thus if two liquids *A* and *B* are mixed together, the solution formed by them will be ideal if

$$P_A = x_A \times P_A^o$$

and

$$P_B = x_B \times P_B^o$$

where p_A = vapour pressure of component *A* in the solution

x_A = mole fraction of the component *A* in the solution

p_A^o = vapour pressure of the liquid *A* in the pure state

P_B, x_B, P_B^o are the corresponding terms for the component *B*.

It is observed that *the solution formed by two liquids A and B is ideal if the interactions (i.e., the intermolecular forces of attraction) among the molecules of A and B in the solution are just the same as among the molecules of pure A or B.*

Further, it is observed that *the solution formed on mixing the two liquids is ideal if*

(*i*) *there is no volume change on mixing i.e.,* $\Delta V_{mix} = 0$

(*ii*) *there is no enthalpy change on mixing i.e.,* $\Delta H_{mix} = 0$

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For example, if 50 ml of *n*-hexane are mixed with 50 ml of *n*-heptane, the total volume of the solution is found to be 100 ml and the temperature of the solution is found to be same as that of pure *n*-hexane and *n*-heptane before mixing showing that no heat is evolved or absorbed on mixing. Such a solution is an ideal solution.

Non-ideal solution: On the other hand, a solution formed by mixing two liquids is said to be non-ideal if it does not obey Raoult's law or the interactions of *A* and *B* molecules in the solution are not similar to those of pure *A* and pure *B* or $\Delta V_{mix} \neq 0$, and $\Delta H_{mix} \neq 0$.

CONCEPT OF ACTIVITY AND ACTIVITY COEFFICIENT

From the studies of solutions, G.N. Lewis discovered that **the experimentally determined value of concentration whether of molecules or ions in solution is less than the actual concentration.**

The apparent value of concentration is termed 'activity'. It may be defined as : **the effective concentration of a molecule or ion in a solution.**

The **activity coefficient 'γ'** is defined as : **the ratio between the activity, denoted by *a*, or effective concentration and actual concentration of the molecule or ion in solution.** That is,

$$\gamma = \frac{\text{effective concentration}}{\text{actual concentration}} = \frac{a}{c}$$

or $$a = \gamma c$$

γ can be determined experimentally and is given in Tables. Thus the value of activity can be calculated by applying the above relation.

Explanation

The effective number of cations and anions in solution becomes less as these tend to form ion-pairs (Fig. 15.12) because of strong electrostatic attractions. Thus the effective concentration of the ions becomes less than the actual concentration.

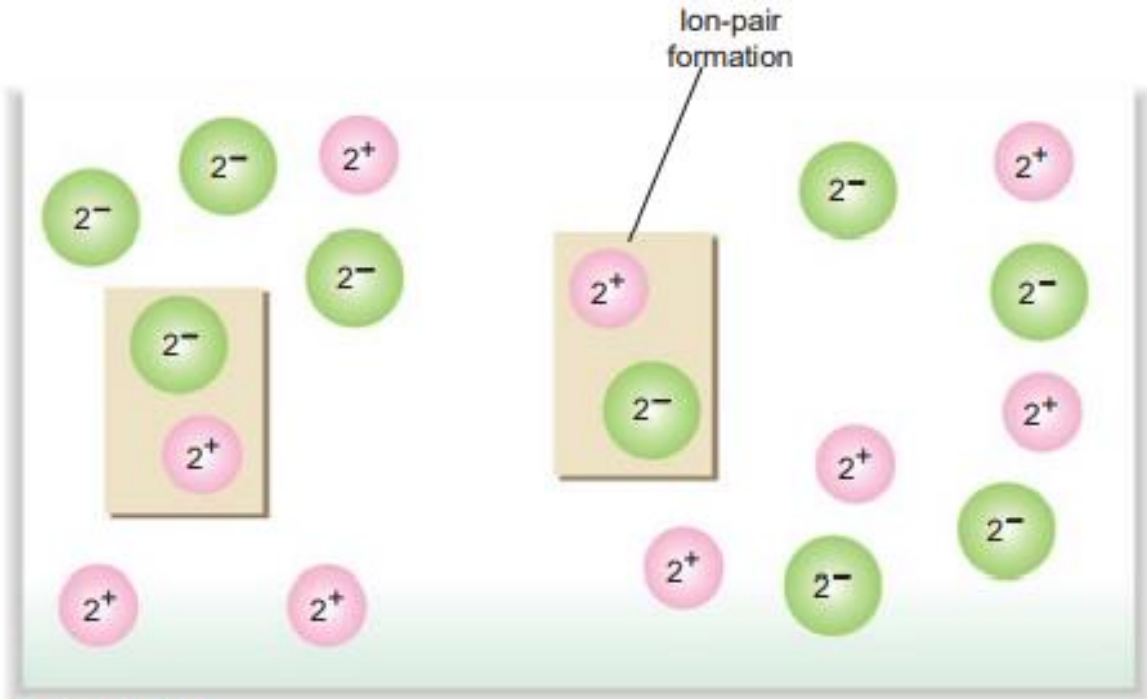


Figure 15.12
Ion-pair formation of a 2^+ cation and a 2^- anion in a solution reduces the effective concentration of ions compared to actual concentration.

SOLVED PROBLEM. Calculate the effective concentration of a 0.0992 M solution of NaCl at 25°C for which activity coefficient is 0.782.

SOLUTION

We know that : $a = \gamma c$

Substituting the values, we have

$$a = (0.782)(0.0992\ \text{M})$$
$$= 0.0776\ \text{M}$$

Raoult's Law

The vapour pressure of a pure solvent is decreased when a non-volatile solute is dissolved in it. If p is the vapour pressure of the solvent and p_s that of the solution, the lowering of vapour pressure is $(p - p_s)$. This lowering of vapour pressure relative to the vapour pressure of the pure solvent is termed the **Relative lowering of Vapour pressure.** Thus,

$$\text{Relative Lowering of Vapour Pressure} = \frac{p - p_s}{p}$$

As a result of extensive experimentation, Raoult (1886) gave an empirical relation connecting the relative lowering of vapour pressure and the concentration of the solute in solution. This is now referred to as the **Raoult's Law.** It states that : **the relative lowering of the vapour pressure of a dilute solution is equal to the mole fraction of the solute present in dilute solution.**

Raoult's Law can be expressed mathematically in the form :

$$\frac{p - p_s}{p} = \frac{n}{n + N}$$

where n = number of moles or molecules of solute

N = number of moles or molecules of solvent.

Ideal Solutions and Deviations from Raoult's Law

A solution which obeys Raoult's law strictly is called an **Ideal solution.** A solution which shows deviations from Raoult's law is called a **Nonideal** or **Real solution.**

Suppose the molecules of the solvent and solute are represented by A and B respectively. Now let γ_{AB} be the attractive force between A and B, and γ_{AA} between A and A. If

$$\gamma_{AB} = \gamma_{AA}$$

the solution will show the same vapour pressure as predicted by Raoult's law and it is an ideal

$$\gamma_{AB} > \gamma_{AA}$$

molecule A will escape less readily and the vapour pressure will be less than that predicted by Raoult's law (**Negative deviation**). On the other hand, if

$$\gamma_{AB} < \gamma_{AA}$$

A molecule will escape from the solution surface more readily and the vapour pressure of the solution will be higher than predicted by Raoult's law **(Positive deviation).**

In very dilute solutions of nonelectrolytes, the solvent and solute molecules are very much alike in both molecular size and molecular attractions. Thus such solutions tend to approach the ideal behaviour and obey Raoult's law fairly accurately.

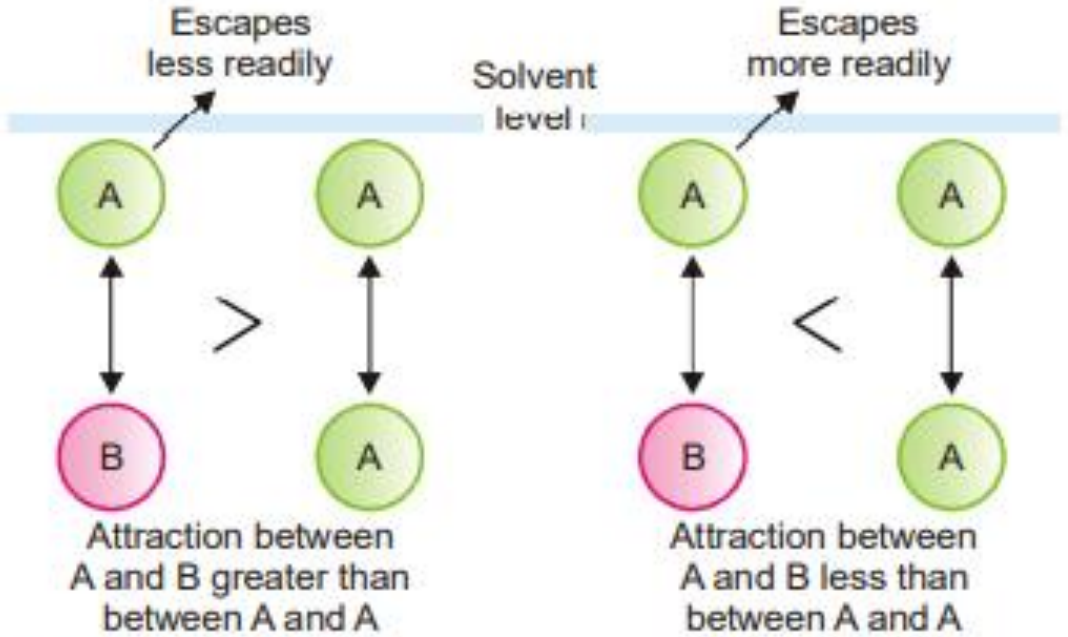


Figure 15.2
Negative deviation and Positive deviation.

HENRY'S LAW

The solubility of a gas in a solvent depends on the pressure and the temperature. When a gas is enclosed over its saturated solution, the following equilibrium exists.

$$\text{gas} \rightleftharpoons \text{gas in solution}$$

If pressure is increased on the system, the equilibrium will move in the direction which will reduce the pressure (Le Chatelier Principle). The pressure can be reduced by more gas dissolving in solvent. Thus solubility or concentration of a gas in a given solvent is increased with increase of pressure. A kinetic molecular explanation of the effect of pressure on gas-solution system is illustrated in Fig. 14.2.

The relationship between pressure and solubility of a gas in a particular solvent was investigated by William Henry (1803). He gave a generalisation which is known as **Henry's Law.** It may be stated as : **for a gas in contact with a solvent at constant temperature, concentration of the gas that dissolves in the solvent is directly proportional to the pressure of the gas.**

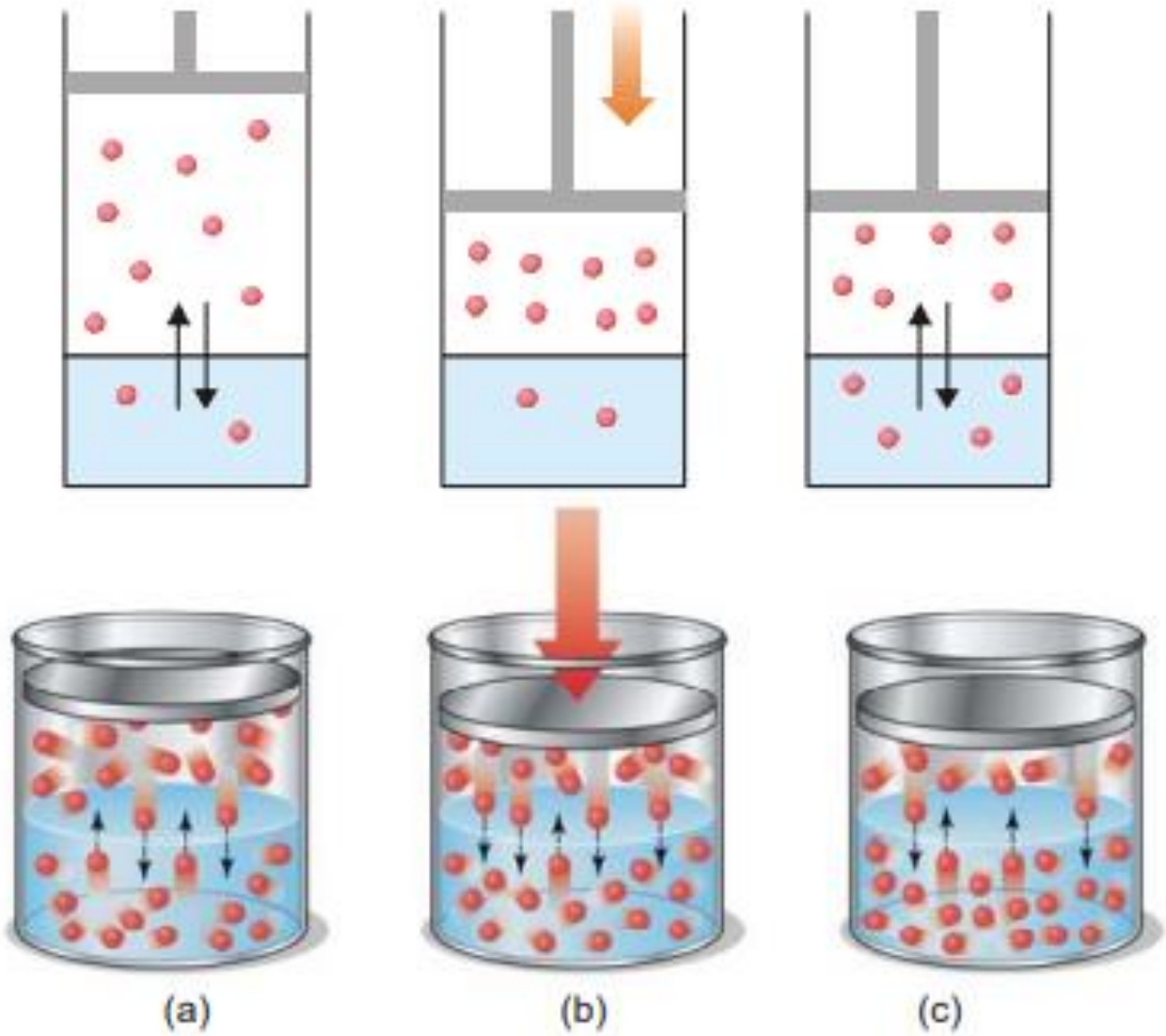


Figure 14.2

(*a*) Equilibrium exists between the gas molecules and those in solution; (*b*) When pressure is applied, gas volume decreases and concentration in gas phase increases; (*c*) More gas molecules pass into solution to reestablish equilibrium whereby the pressure above the gas is decreased.

Mathematically, Henry's Law may be expressed as

$$C \propto P$$

or

$$C = k\,P$$

where P = pressure of the gas; C = concentration of the gas in solution; and k = proportionality constant known as **Henry's Law Constant.** The value of k depends on the nature of the gas and solvent, and the units of P and C used.

Limitations of Henry's Law

It applies closely to gases with nearly ideal behaviour.

(1) at moderate temperature and pressure.

(2) if the solubility of the gas in the solvent is low.

(3) the gas does not react with the solvent to form a new species. Thus ammonia (or HCl) which react with water do not obey Henry's Law.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

(4) the gas does not associate or dissociate on dissolving in the solvent.

Ans. (*a*) **Azeotropes:** Mixtures of liquids which boil at constant temperature like a pure liquid such that the distillate has the same composition as that of the liquid mixture are called constant boiling mixtures or azeotropic mixtures or simply azeotropes. Evidently, the compo-nents of an azeotrope cannot be separated by fractional distillation. These azeotropes are of two types.

(*b*) **Minimum boiling (point) azeotropes:** These azeotropes are formed by those liquid pairs which show positive deviations from ideal behaviour. Such an azeotrope corresponds to an intermediate composition for which the total vapour pressure is the highest and hence the boiling point is the lowest. Such azeotropes have boiling points lower than either of the pure components. Ethyl alcohol-water is an example of this type of azeotrope.

(*c*) **Maximum boiling (point) azeotropes:** These azeotropes are formed by those liquid pairs which show negative deviations from ideal behaviour. Such an azeotrope corresponds to an intermediate composition for which the total vapour pressure is minimum and hence the boiling point is maximum. Such azeotropes have boiling points higher than either of the pure components. Water—HCl is an example of this type of azeotrope.

The temperature at which the two liquids, which are otherwise partially miscible at ordinary temperature, become completely miscible is called **critical solution temperature** (*CST*). There can be three types of partially miscible systems. Each type is briefly discussed below by taking one example.

Type I. System with an upper critical solution temperature (upper consolute temperature) Phenol-water system. If phenol and water are mixed in roughly equal proportions, two layers are produced, one of a solution of phenol in water and the other of a solution of water in phenol. At any given temperature, the composition of these layers is fixed and can be determined by suitable analytical methods. If the system is warmed, the amount of water in phenol layer increases as well as the amount of phenol in the water layer increases.

Ultimately, at a particular temperature, the composition of both the layers becomes the same and thus the two become completely miscible. Experiments have shown that the minimum temperature at which phenol and water become completely miscible is 66°C and the composition is 34% of phenol by weight. Thus phenol-water system has an upper critical solution temperature of 66°C. The results on being plotted give a parabolic curve as shown in Fig. 3.15.

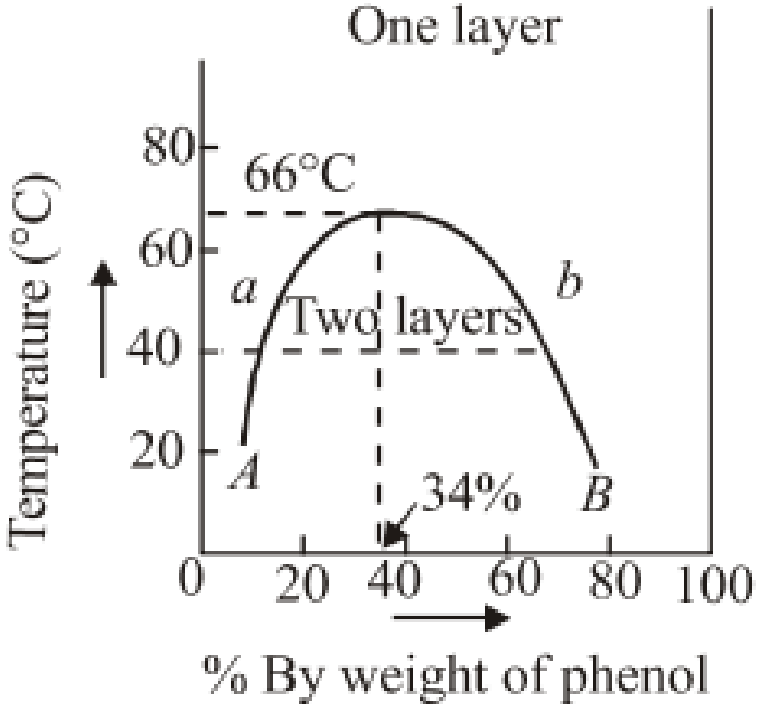


Fig. 3.15. Phenol-water system.

Alternatively, the same curve is obtained if solutions of phenol of different suitable compositions are prepared and the temperature at which the two liquids become completely miscible is determined in each case (from the disappearance of turbidity) and then plotted against the composition.

Type II. System with a lower critical solution temperature (lower consolute temperature): Triethylamine-water system. In this system, it is observed that the mutual solubility of the two liquids increases not with increase of temperature but with decrease of temperature. Thus on cooling such a system, ultimately a stage is reached when the two liquids become completely miscible. This temperature is called the *lower consolute temperature* and is 18.5°C for thriethylamine-water system. This means that below 18.5°C, triethylamine and water are completely miscible in all proportions. The curve obtained by plotting the temperatures against composition is just an inverted form of Type I and is shown in Fig. 3.16.

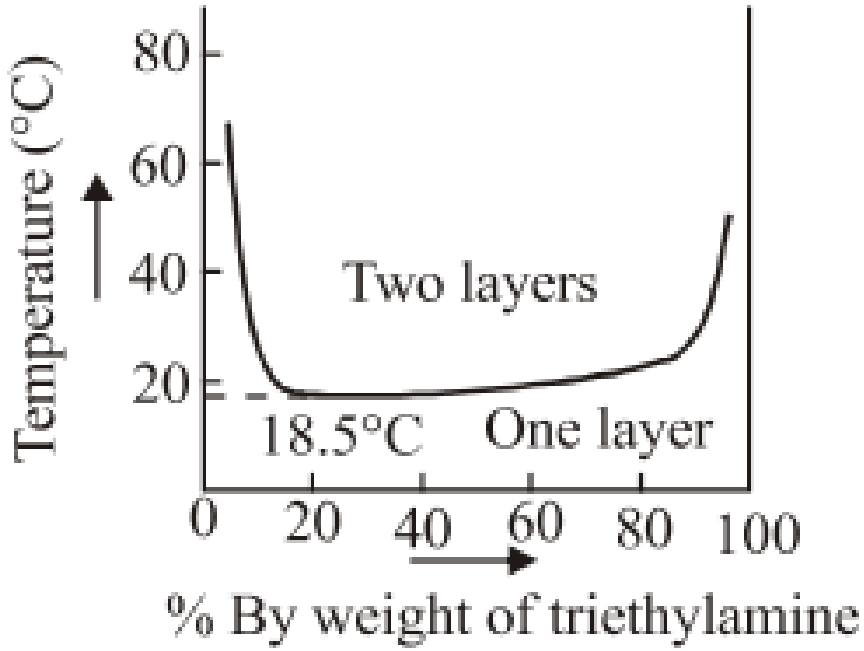


Fig. 3.16. Triethylamine-water system.

Type III. System with an upper as well as a lower critical solution temperature : Nicotine-water system.

This is the system in which the mutual solubility of the two liquids increases with increase of temperature as well as with decrease of temperature. Thus in such systems, the two liquids become completely miscible above a particular temperature as well as below a particular temperature. In other words, such systems have an upper critical solution temperature as well as a lower critical solution temperature which are 208°C and 60.8°C respectively for nicotine-water system. The plot obtained between temperature and composition in such cases is a closed curve as shown in Fig. 3.17. As before, for temperature and composition corresponding to any point within the closed curve, there are two layers while outside it, there is one layer only.

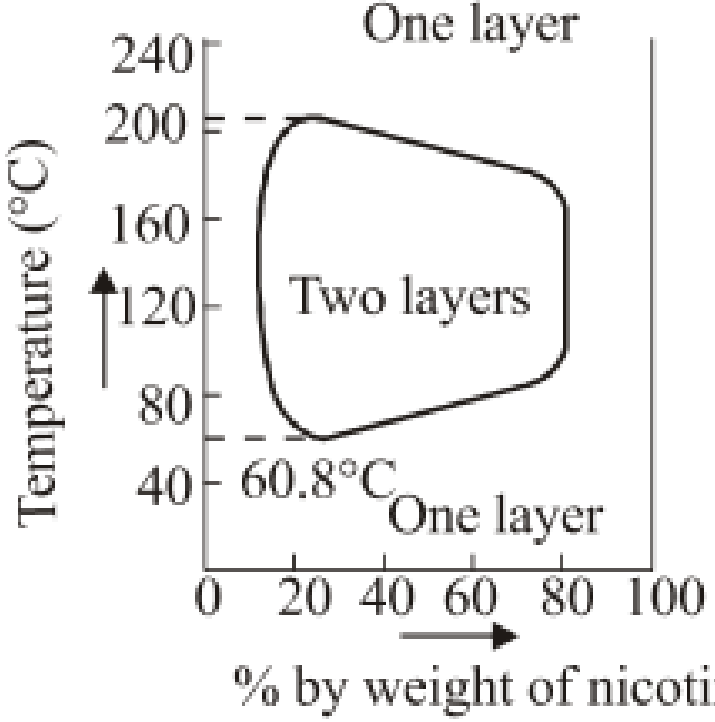


Fig. 3.17. Nicotine-water system.

STEAM DISTILLATION

Distillation carried in a current of steam is called steam distillation. This technique is widely used for purification of organic liquids which are steam volatile and immiscible with water (*e.g.*, aniline). The impure organic liquid admixed with water containing nonvolatile impurities is heated and steam passed into it (Fig. 14.11). The vapour of the organic liquid and steam rising from the boiling mixture pass into the condenser. The distillate collected in the receiver consists of two layers, one of the pure organic liquid and the other of water. The pure liquid layer is removed by means of a separatory funnel and further purified.

Theory of Steam Distillation

The vapour pressure of a liquid rises with increase of temperature. When the vapour pressure equals the atmospheric pressure, the temperature recorded is the boiling point of the given liquid. In case of a mixture of two immiscible liquids, each component exert its own vapour pressure as if it were alone. The total vapour pressure over the mixture (P) is equal to the sum of the individual vapour pressures (p_1, p_2) at that temperature.

$$P = p_1 + p_2$$

Hence the mixture will boil at a temperature when the combined vapour pressure P, equals the atmospheric pressure. Since $P > p_1$ or p_2, **the boiling point of the mixture of two liquids will be lower than either of the pure components.**

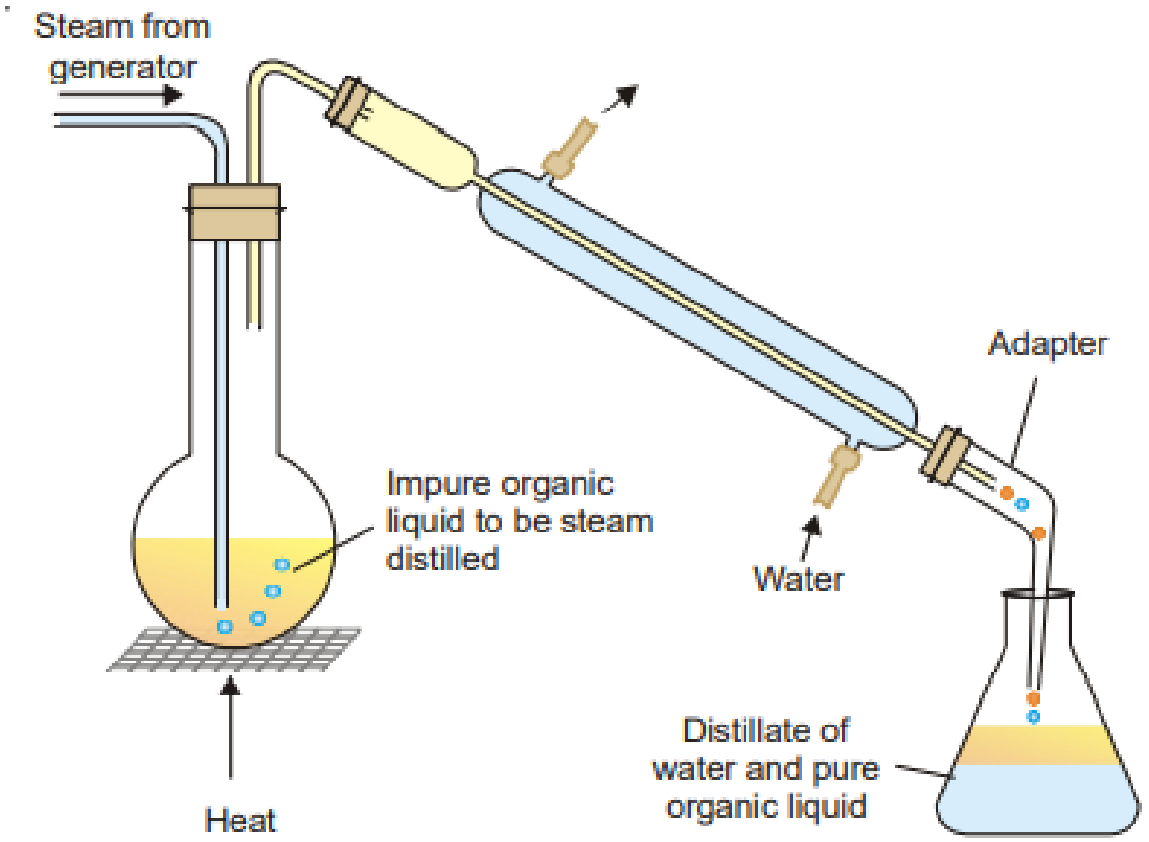


Figure 14.11
Steam Distillation.

In steam distillation the organic liquid is mixed with water (bp 100°C). Therefore the organic liquid will boil at a temperature lower than 100°C. For example, phenylamine (aniline) boils at 184°C but the steam distillation temperature of aniline is 98°C.

Steam distillation is particularly used for the purification of an organic liquid (such as phenylamine) which decomposes at the boiling point and ordinary distillation is not possible.

Nernst distribution law states as follows:

A solute distributes itself between two immiscible solvents in such a way that the ratio of the concentrations of the solute in the two solvents is constant at constant temperature, independent of any other molecular species present, provided that the solute has the same molecular state in both the solvents.

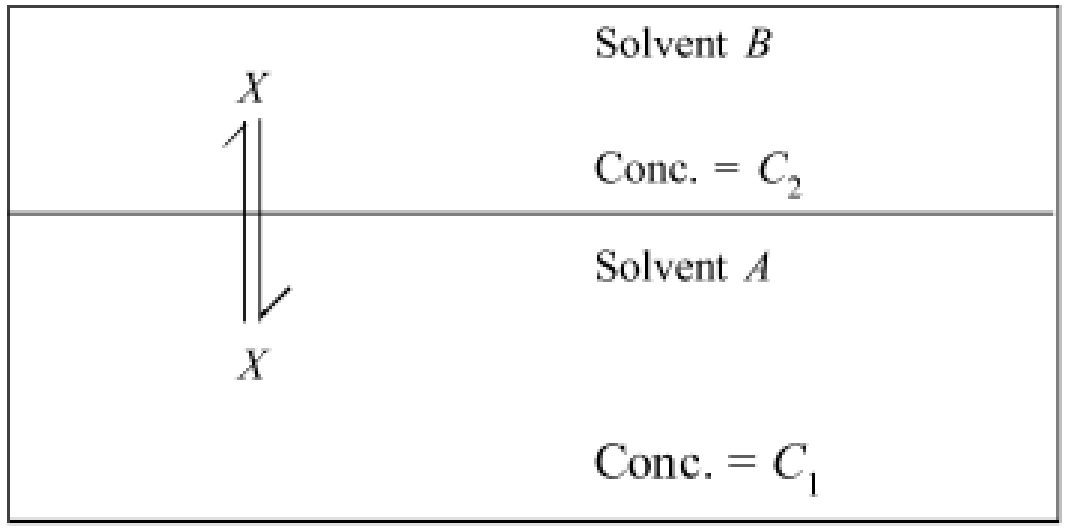


Fig. 15.1. Distribution of solute X between immiscible solvents A and B.

Thus if a solute X distributes itself between the two immiscible solvents A and B (Fig. 15.1), Then we have

$$\frac{\text{Concentration of } X \text{ in solvent } A}{\text{Concentration of } X \text{ in solvent } B} = \frac{C_1}{C_2} = K \text{ (constant)}$$

provided X remains in the same molecular species in both the solvents. The constant K is called *Distribution coefficient* or *Partition coefficient.*

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.

. Derive distribution law from thermodynamic considerations.

Ans. The thermodynamic derivation of the distribution law is based upon the principle that *if there are two phases in equilibrium (in this case two immiscible solvents containing the same solute dissolved in them), the chemical potential of a substance must be same in both the phases.*

From thermodynamics, we know that the chemical potential (μ) of a substance is a solution given by

$$\mu = \mu^\circ + RT \ln a$$

where μ° is the standard chemical potential and *'a'* is activity of the substance (solute) in the solution.

Thus for the solute in liquid *A*, we have

$$\mu_A = \mu_A^\circ + RT \ln a_A \quad \ldots (i)$$

Similarly for the solute in liquid *B* we have

$$\mu_B = \mu_B^\circ + RT \ln a_B \quad \ldots (ii)$$

Since the liquids *A* and *B* are in equilibrium,

$$\mu_A = \mu_B \quad \ldots (iii)$$

$$\therefore \quad \mu_A^\circ + RT \ln a_A = \mu_B^\circ + RT \ln a_B$$

or $$RT \ln a_A - RT \ln a_B = \mu_B^\circ - \mu_A^\circ$$

or $$\ln \frac{a_A}{a_B} = \frac{\mu_B^\circ - \mu_A^\circ}{RT} \quad \ldots (iv)$$

Further at a given temperature, μ_A° and μ_B° are constant for given substance in the particular solvents. Hence at constant temperature, we have from equation (*iv*)

$$\ln \frac{a_A}{a_B} = \text{constant} \qquad \ldots (v)$$

and therefore,

$$\frac{a_A}{a_B} = \text{constant} \qquad \ldots (vi)$$

This is the exact expression for the distribution law. However, if the solutions are dilute, the activities are equal to the concentrations so that the expression (*vi*) is modified to

$$\frac{C_A}{C_B} = \text{constant}$$

which is the original form of the distribution law.

Ans. Some applications of distribution law are given below:

(*i*) To determine the solubility of a solute in a solvent.

(*ii*) To determine the extent of association or dissociation of a solute in a solvent.

(*iii*) To study chemical equilibrium of reactions involving complex ions.

(*iv*) In the process of extraction.

(*v*) In the Parke's process of desilverisation of lead.

(*vi*) To determine hydrolysis constant and degree of hydrolysis.

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.

Reference books

Essentials of Physical Chemistry by Bahl and Arun Bahl

S. Chand success guide by R. L. Madan