

At any temperature above the critical solution temperature, phenol and water are miscible in all proportions. Outside the curve there is complete homogeneity of the system, *i.e.*, one layer only exists; and under the curve there may be complete miscibility but it depends upon the composition of the mixture. It is clear from Fig. 14.3 (a) that at a temperature below 50°C a mixture of 90% phenol and 10% water or 5% phenol and 95% water, will be completely miscible since the corresponding points do not lie under the curve. Two layers will always separate out below the curve and the curve gives compositions of the conjugate solutions constituting the two layers. At 50°C a mixture of equal proportion of phenol and water (50% each) will form two layers whose compositions are given by A and B. The line joining the points (M and N) corresponding to the compositions A and B is called the **tie line**. This line helps in calculating the relative amounts of the two layers, which is here given by the ratio MN/ML .

Some other liquid pairs behaving like phenol-water system are given below with their CST values and the percentage of the first component being given in bracket.

- (a) Methanol-Cyclohexane (49°C ; 29)
- (b) Hexane-Aniline (59.6°C ; 52)
- (c) Carbon disulphide-Methanol (49.5°C, 80)

TRIETHYLAMINE-WATER SYSTEM

The temperature-composition curve of mutual solubilities of triethylamine and water is given in Fig. 14.3 (b). The left hand side of the curve indicates the solubility curve of triethylamine in water and the right hand side of that of water in triethylamine. Unlike phenol-water system, the solubilities decrease with the increase in temperature in this system. The two conjugate solutions mix up completely at or below 18.5°C. This temperature is also called the critical solution temperature or the lower consolute temperature. As in the above case, any point above the horizontal line corresponds to heterogeneity of the system (two layers) while below it is complete homogeneity (one layer). Thus an equi-component mixture (50–50) will be completely miscible at 10°C but at 50°C there will be separating out two layers having compositions corresponding to the points C and D.

Common examples of this system with their lower critical solution temperatures and percentage of the first component are given below.

- (a) Diethylamine-Water (43°C ; 13)
- (b) 1-Methylpiperidine-Water (48°C ; 5)

NICOTINE-WATER SYSTEM

The behaviour of this type of system is as if it were a combination of the first two types. At ordinary temperature nicotine and water are completely miscible but at a higher temperature the mutual solubility decreases and as the temperature is raised further the two liquids again become miscible. In other words, the mutual solubility increases both on lowering as well as raising the temperature in certain ranges. Thus we have a closed solubility curve and the system has two critical-solution-temperatures, the upper 208°C and the lower 61°C. The effect of pressure on this system is that the lower critical temperature is raised while the upper critical temperature is lowered gradually until finally they become one. At this point the liquids are miscible at all the temperatures (Fig. 14.4).

Glycerine – *m*-Toluidine ; and Water – β -Picoline are other examples of this type.

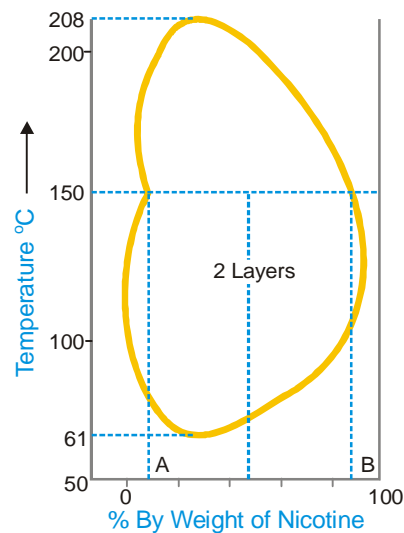


Figure 14.4
Miscibility of nicotine and water.

VAPOUR PRESSURES OF LIQUID-LIQUID SOLUTIONS

The study of the vapour pressures of mixtures of completely miscible liquids has proved of great help in the separation of the liquids by fractional distillation. The vapour pressures of two liquids with varying composition have been determined at constant temperature. By plotting the vapour pressure against composition it has been revealed that, in general, mixtures of the miscible liquids are of three types.

First Type of Mixtures of Miscible Liquids

For this type of solutions the vapour pressure curve exhibits a minimum. If we take a mixture which has an excess of X (more volatile component), we are somewhere at C on the curve. When this is distilled the vapour will contain excess of X and thus the remaining mixture will get richer in Y . Finally we reach the point D where vapour pressure is minimum and thus boiling point is maximum. Here the mixture will distil unchanged in composition. Exactly similarly if we take a mixture having a greater proportion of Y (point E), on distillation Y will pass over leaving the residue richer in X till in this way the minimum point D is again reached when the mixture will distil unchanged. It is obvious that **complete separation of this type of solutions into components is impossible**.

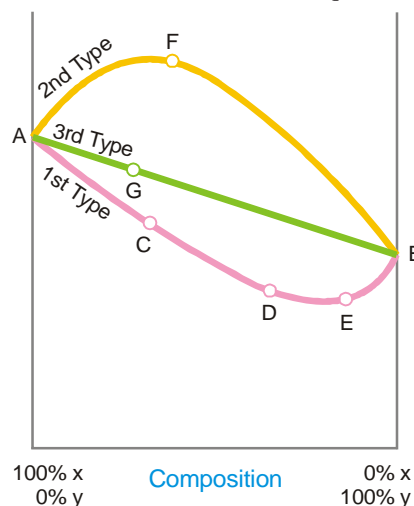


Figure 14.5
Vapour pressure of liquids.

At best it can be resolved into one pure component and the constant boiling mixture. Solutions of this type which distil unchanged at a constant temperature and show a maximum boiling point are called **maximum boiling point azeotropic solutions**. The best known example of this type is presented by hydrochloric acid which forms a constant boiling mixture at 110°C and containing 20.24% of the acid. If a mixture of any composition is distilled, either hydrochloric acid or water will pass over, the composition will move to the point of minimum vapour pressure when it distills without any change in composition.

Second Type of Mixtures of Miscible Liquids (Minimum boiling point azeotropic solutions)

Here the vapour pressure curve records a maximum at F . At this point the mixture has the highest vapour pressure and, therefore, the lowest boiling point. Thus in this type of solutions the first fraction will consist of a constant boiling mixture with a fixed composition corresponding to the maximum point until whole of one component has been exhausted. After this the temperature will rise and the other component will pass over. **In this kind of solutions also it is not possible to effect a complete separation by fractional distillation.** At best we can resolve it into a constant-boiling mixture and one component in the pure state. Ethanol and water mixtures offer a good example of this type. Ethanol-water mixture containing 95.6 per cent ethanol boils at the minimum temperature 78.13° . Thus it is very difficult to obtain pure absolute alcohol by distillation. This difficulty has, however, been overcome by adding benzene which form a low boiling mixture with water and on distillation it comes over leaving pure ethanol behind.

Third Type of Mixtures of Miscible Liquids

In this case the vapour pressures of mixtures always lie between the vapour pressures of pure components and thus the vapour-pressure composition curve is a straight line. Suppose we have a mixture containing excess of Y which is represented by point G on the curve. On distillation X component being more volatile will be obtained in greater proportion in the distillate and we gradually travel along the curve AB . The latter fractions will, of course, be poorer in X and richer in Y till we

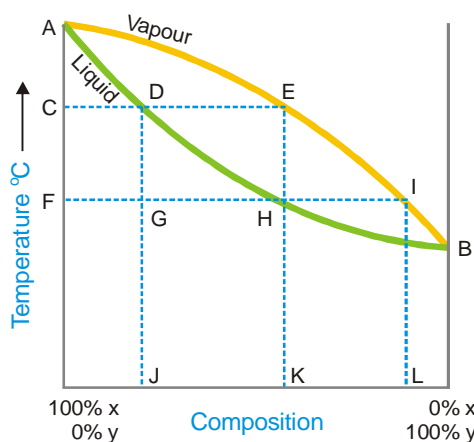
reach the 100 per cent Y -axis, when all the X will have passed over. By repeating the process of distillation with the fresh distillate which is now richer in X , we can get almost pure component X . Only in this type of solutions we can completely separate the components by fractional distillation. Thus methyl alcohol-water mixtures can be resolved into pure components by distillation. Liquid mixtures which distil with a change in composition are called **zeotropic mixtures**.

Azeotropes are Mixtures and not Pure Compounds

Although the azeotropes boil at a constant temperature and distil over without change in composition at any given pressure like a pure chemical compound, these cannot be regarded as chemical compounds. The reason is that when the total pressure is changed, both the boiling point and the composition of the azeotrope change whereas for a chemical compound the composition must remain constant over a range of temperature and pressures.

THEORY OF FRACTIONAL DISTILLATION

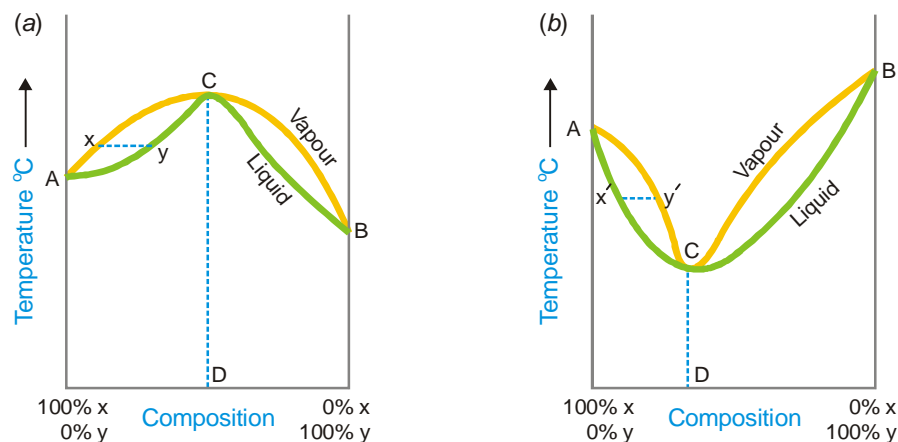
We have discussed above the vapour-pressure composition curves for the three types of solutions from a study of which we conclude that it is only in the case of the third type that a complete separation by distillation is possible. However to understand the process of fractional distillation we must have an idea of the composition of the vapour phase and that of the liquid mixtures at different boiling temperatures. Thus for this purpose it is not the vapour-pressure composition curve but rather the temperature-composition curve that is important. If we plot the boiling point of liquid mixture against its composition and the composition of the vapour in contact with it, we get two separate curves for each type of solutions. The curves obtained for the third type are shown diagrammatically in Fig. 14.6.



■ **Figure 14.6**
Curves showing the composition of vapour and liquid at various boiling temperatures.

The curves AEB and ADB are the temperature composition curves for the vapour and liquid respectively. At any boiling temperature C the composition of liquid mixture is represented by J and that of the vapour in equilibrium by K . Obviously, the more volatile component Y is present in greater proportion in the vapour than the liquid mixture. Thus the condensed vapour or the distillate will be richer in X . If the distillate so obtained be now subjected to distillation, it will boil at F and the fresh distillate will have the composition L corresponding to I . Thus the proportion of Y in the second distillate is greater than in the first one. In this way by repeating the process of fractional distillation it is obvious that we can get almost pure Y .

In first type of solutions (Fig. 14.7 *a*) if we have a boiling mixture represented by Y its vapour will be poor in Y than the liquid mixture and the boiling point would gradually rise till we reach the maximum point C where the composition of liquid and vapour is the same. Here the distillation proceeds without change of composition. Similarly in the second type (Fig. 14.7 *b*), if we have a boiling mixture represented by the point X' , the amount of Y in vapour is higher and gradually the boiling point falls to the minimum C' where the vapour and the liquid mixtures have the same composition. At this temperature the mixture boils without any change in composition. Thus it is proved that **the second and first type of solutions are not capable of being separated by fractional distillation.**

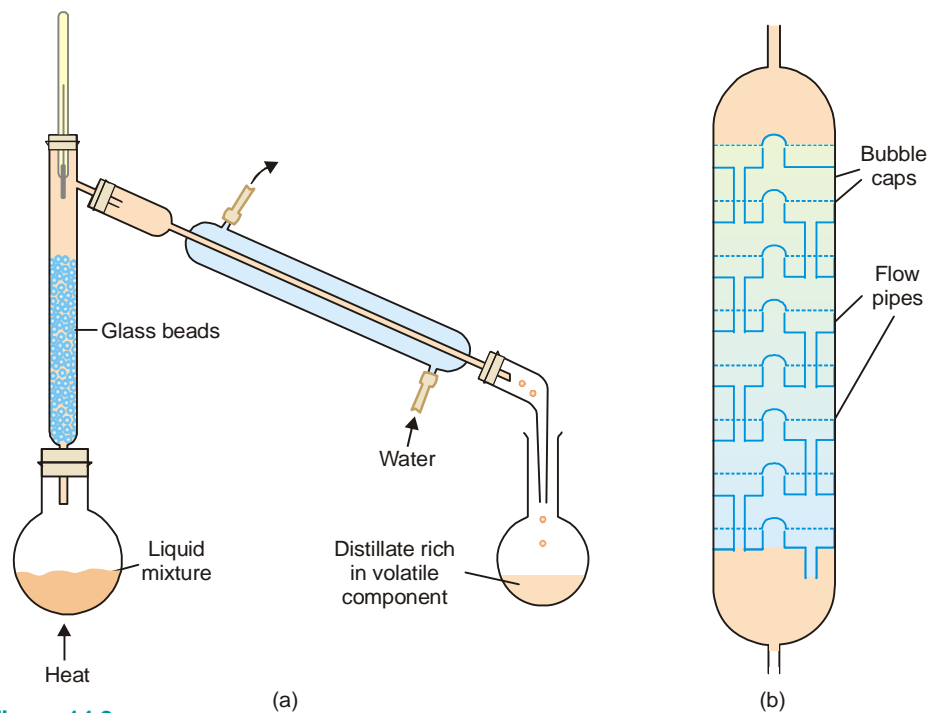


■ **Figure 14.7**

(a) Boiling point curves for 1st type of solutions;

(b) Boiling point curves for 2nd type of solutions.

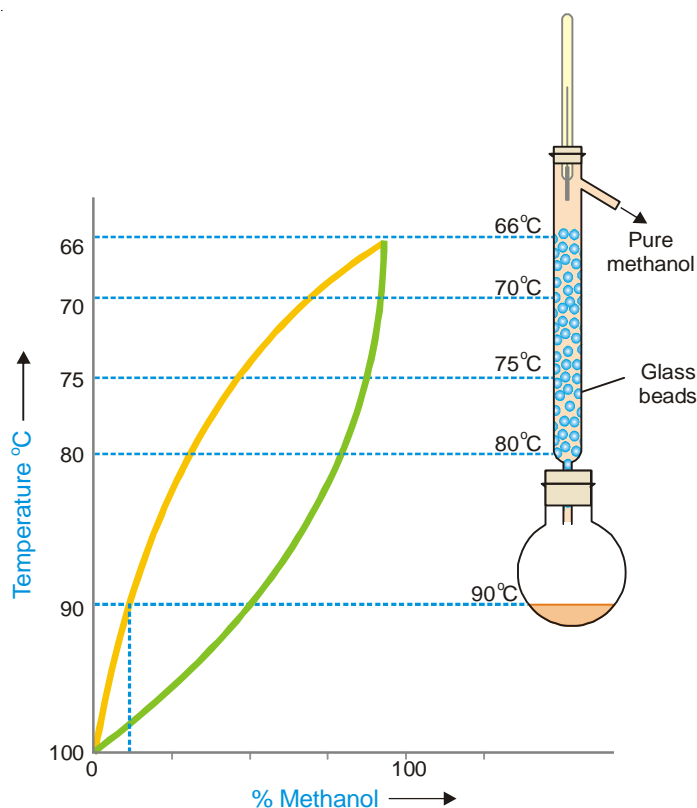
The efficiency of the process of fractional distillation is considerably enhanced by the use of the so-called **Fractionating columns**. These are of different designs. An effective and simple fractionating column usually employed for laboratory use consists of a long glass tube packed with glass beads (Fig. 14.8 a) or specially made porcelain rings. The glass tube blown into bulbs at intervals may also constitute a fractionating column. For industrial purposes a fractionating tower (Fig. 14.8 b) is employed. A fractionating tower is divided into several compartments by means of tray that are set one above the other. There is a hole in the centre of every tray which is covered by **bubble cap**. Each tray has an overflow pipe that joins it with the tray below by allowing the condensed liquid to flow down.



■ **Figure 14.8**

(a) Fractional distillation with a fractionating column; (b) Fractionating tower employed for distillations on a commercial scale.

The fractionating column or tower is fitted in the neck of the distillation flask or the still so that the vapours of the liquid being heated pass up through it. The temperature falls in the column as vapours pass from bottom to the top. The hot vapours that enter the column get condensed first in the lowest part of it. As heating is continued more vapours ascend the column and boil the liquid already condensed, giving a vapour which condenses higher up in the column. This liquid is heated in turn by more vapours ascending the column. Thus the liquid condensed in the lowest part is distilled on to the upper part. In this manner a sort of distillation and condensation goes on along the height of the column which results in the increase of the proportion of the volatile component in the outgoing vapours. At every point in the column there exists an equilibrium between liquid and vapour. This is established quickly by an upward flow of vapours and the downward flow of liquid, a large surface area and a slow rate of distillation. A simple distillation of a mixture of methanol and water and the liquid vapour equilibrium states are depicted in Fig. 14.9.



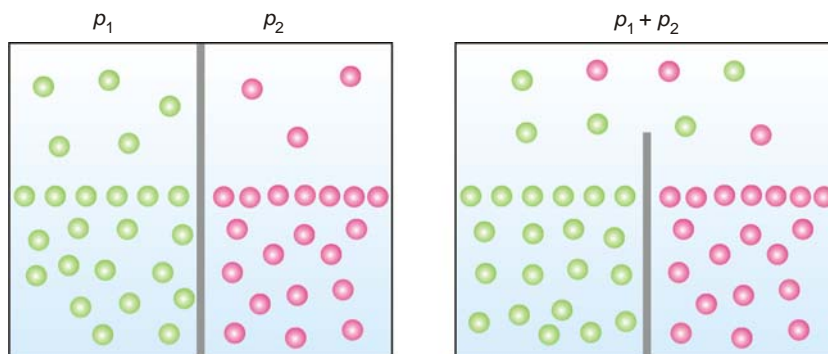
■ **Figure 14.9**
Distillation curves of mixture of methanol and water using a fractionating column.

It is clear that the liquid-vapour equilibria change regularly in moving up the column. We may withdraw mixtures of varied compositions from different points on the column. This is done in the fractional distillation of crude oil in a refinery where different products of industrial use are conveniently separated.

VAPOUR PRESSURE OF MIXTURES OF NON-MISCIBLE LIQUIDS

In a mixture of non-miscible liquids each component exerts its own vapour pressure independent of others and the total vapour pressure is thus equal to the sum of individual vapour pressures of all the liquids.

Consider two liquids in separate compartments. Each one of them would have a certain vapour pressure, say, p_1 and p_2 . When present in a vessel with a common top, they exert their own vapour pressure independently. According to Dalton's law of partial pressures, the total vapour pressure will be equal to the sum of their individual pressures. This generalisation which is the basic principle



■ **Figure 14.10**
Vapour pressure of mixtures of non-miscible liquids (illustration).

of steam distillation, has been tested experimentally in several cases. Some of the results obtained by Regnault are given below:

Temperature	Vapour Pressure of Water	Vapour Pressure of Carbon disulphide	Sum	Vapour Pressure of Mixture (Observed)
12.07°	10.5 mm	216.7 mm	272.2 mm	225.9 mm
26.87°	26.2 mm	388.7 mm	415.0 mm	412.3 mm

The observed vapour pressure of the mixture is a little less than the sum of the individual vapour pressures of water and carbon disulphide and that is to be expected since each liquid is slightly soluble in the other.

STEAM DISTILLATION

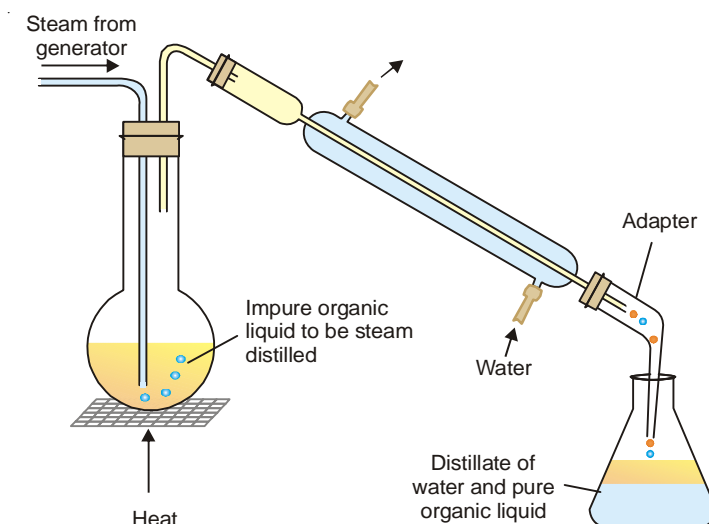
Distillation carried in a current of steam is called steam distillation. This technique is widely used for purification of organic liquids which are steam volatile and immiscible with water (*e.g.*, aniline). The impure organic liquid admixed with water containing nonvolatile impurities is heated and 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 exerts 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.

Relative Amounts of Organic Liquid and Water Distilling Over

The number of molecules of each component in the vapour will be proportional to its vapour pressure *i.e.*, to the vapour pressure of the pure liquid at that temperature.

$$\text{Hence,} \quad \frac{n_1}{n_2} = \frac{p_1}{p_2} \quad \dots(1)$$

where n_1 and n_2 are the number of moles of the two components in the vapour.

Now, from (1), we have

$$\frac{w_1/M_1}{w_2/M_2} = \frac{p_1}{p_2} \quad \dots(2)$$

where w_1 and w_2 are the masses of the two liquids distilling over, and M_1 and M_2 their molecular weights.

Since one of the two components is water (m.wt. = 18), we can write from (2)

$$\frac{\text{mass of organic liquid}}{\text{mass of water}} = \frac{p_1 \times M_1}{p_2 \times 18}$$

Thus, the ratio of masses of the organic liquid and water can be calculated from the given values of p_1 , p_2 (aqueous tension) and M_1 , the molecular weight of the organic liquid.

SOLVED PROBLEM 1. At a pressure of 760 mm, a mixture of nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$) and water boils at 99°C . The vapour pressure of water at this temperature is 733 mm. Find the proportion of water and nitrobenzene in the distillate obtained by steam distillation of impure $\text{C}_6\text{H}_5\text{NO}_2$.

SOLUTION

We apply the relation

$$\frac{w_1}{w_2} = \frac{p_1 \times M_1}{p_2 \times 18} \quad \dots(1)$$

Here, p_1 , vapour pressure of $\text{C}_6\text{H}_5\text{NO}_2 = 760 - 733$
 $= 27 \text{ mm}$

p_2 , vapour pressure of water $= 733 \text{ mm}$

M_1 , molecular mass of nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$
 $= 12 \times 6 + 5 \times 1 + 14 \times 1 + 16 \times 2 = 123$

Substituting the values in (1)

$$\frac{27 \times 123}{733 \times 18} = \frac{1}{3.97}$$

\therefore Proportion of water to $\text{C}_6\text{H}_5\text{NO}_2$ in the distillate is approximately 4 : 1

SOLVED PROBLEM 2. A mixture of water and bromobenzene ($\text{C}_6\text{H}_5\text{Br}$) distills at 95°C , and the distillate contains 1.6 times as much $\text{C}_6\text{H}_5\text{Br}$ as water by mass. At 95°C the vapour pressure of water and $\text{C}_6\text{H}_5\text{Br}$ are 640 mm Hg and 120 mm Hg respectively. Calculate the molecular weight of bromobenzene.

SOLUTION

We use the relation

$$\frac{w_1}{w_2} = \frac{p_1 \times M_1}{p_2 \times 18} \quad \dots(1)$$

Here, $w_1/w_2 = 1.6$

p_1 , vapour pressure of bromobenzene $= 120 \text{ mm Hg}$

p_2 , vapour pressure of water $= 640 \text{ mm Hg}$

Substituting values in (1)

$$1.6 = \frac{120 \times M_1}{640 \times 18}$$

$$\therefore M_1 = \frac{1.6 \times 640 \times 18}{120} = 153.6$$

Thus the molecular mass of bromobenzene is **153.6**

Note : This method of determination of molecular weight of organic liquids is not accurate and gives only approximate value.

SOLUTIONS OF SOLIDS IN LIQUIDS

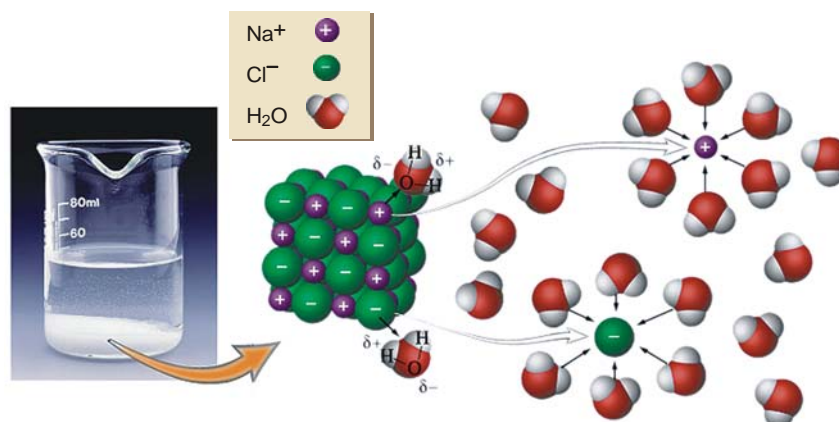
Solutions of this type are most commonly met with. The process of solution of a solid substance in a solvent is explained by the electrical forces operating between the molecules or ions of the solute and the molecules of the solvent. It is a common observation that polar solutes dissolve easily in polar solvents while they remain insoluble in non-polar solvents. For example, sodium chloride (an electrolyte) is fairly soluble in water which is highly polar solvent, while it is insoluble in a non-polar

solvent like chloroform. On the other hand, a non-polar solute does not dissolve in a polar solvent *e.g.*, benzene which is non-polar is insoluble in water. The electrical attraction between the oppositely charged ends of the solute and the solvent molecules results to form a solution.

Water being highly polar is one of the best solvents for ionised solutes. An ionic substance, when placed in water furnishes cations (+) and anions (-). These ions are surrounded by solvent molecules with their oppositely charged ends directed towards the ion. The ion enveloped by a layer of the solvent molecules in this manner, is called a **Solvated ion** or **Hydrated ion** in case water is the solvent. Thus sodium chloride dissolves in water to give Na^+ and Cl^- ions. The Na^+ ion is hydrated to have around a layer of water molecules so that their negative ends are directed towards it. The Cl^- ion, on the other hand, attracts positive ends of water molecules which envelop it (Fig. 14.12).

It is customary to represent the hydrated sodium and chloride ions as $\text{Na}^+(aq)$ and $\text{Cl}^-(aq)$. This representation indicates that the ions are in the aqueous phase.

The mechanism of solution of sodium crystal in water could be explained as follows. The polar water molecules try to pull out the Na^+ and Cl^- ions from the crystal by hydration. This becomes possible since the forces operating between the ion (Na^+ or Cl^-) and water molecules are strong enough to overcome the force binding the ion in the crystal. The ions detached from the crystal are

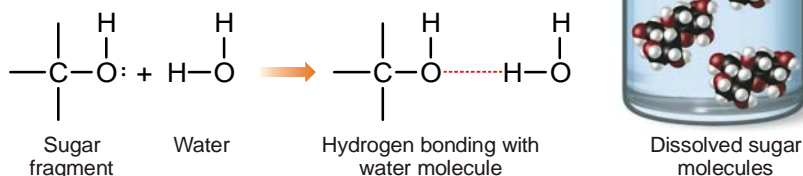


■ **Figure 14.12**
How sodium chloride dissolves in water.

now surrounded by cluster of water molecules. The layer of water molecules enveloping the ions effectively shields them and prevents them from coming in contact with each other. Thus they hardly aggregate into a crystal and remain in solution.

Dissolution Due to Hydrogen Bonding

Many non-ionic substance such as sugar also dissolve in water. Here the dissolution is due to hydrogen bonding that occurs between water and sugar molecules. The hydrogen bonding takes place through the hydroxyl group of the sugar molecules.



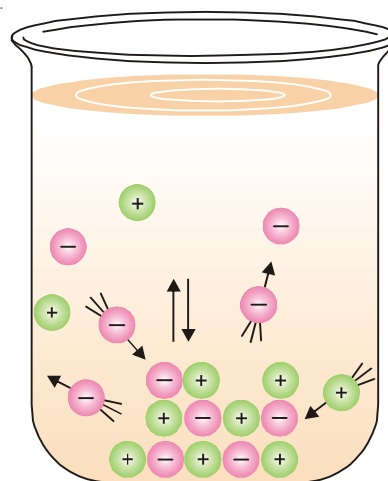
The water molecules are thus able to pull away the molecules of sugar from the crystal, which dissolve. In fact, every sugar molecule is surrounded by a number of water molecules, and these aggregates are free to migrate throughout the solution.

SOLUBILITY-ITS EQUILIBRIUM CONCEPT

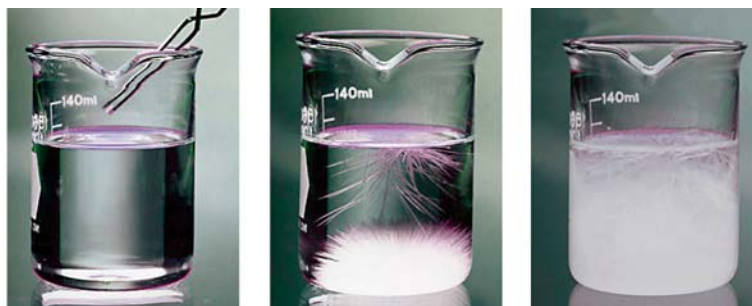
When a solid is placed in a solvent, molecules or ions, as the case may be, break away from the surface and pass into the solvent. The particles of the solid thus detached are free to diffuse throughout the solvent to give a uniform solution. The solute and the solvent molecules are constantly moving about in the solution phase because of kinetic energy possessed by them. Some of the particles are deflected back towards the solid on account of collisions with other molecules. These then strike the solid surface and may get entangled in its crystal lattice and thus get deposited on it. This process by which the solute particles from solution are 'redeposited' or 'recrystallised' is often spoken of as **recrystallisation** or **precipitation**.

In a solution in contact with solid solute, therefore, two opposing processes are operating simultaneously :

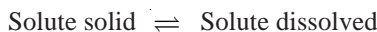
- (a) **Dissolution** – the particles of the solute leaving the solid and passing into solution.
- (b) **Recrystallisation** – the particles of the solute returning from the solution and depositing (or precipitating) on the solid.



■ **Figure 14.13**
Dissolution and recrystallisation.



To start with the rate at which the particles leave the solid is much greater than the rate at which they return to it. As the number of particles of the solute in solution increases, the rate at which they are returned to the solid also increases. Eventually, if there is excess of solid present the rate of dissolution and the rate of recrystallisation become equal. At this stage, a state of equilibrium between the molecules of the solute in solution and the solid solute is said to have been reached. Thus,



Henceforth neither the amount of the solute in solution nor the solid phase present in contact with it, will change with lapse of time. This equilibrium state will remain so, provided the 'kinetic energy' of the molecules is not changed by a change in temperature. The situation is illustrated Fig. 14.13. The competition between the two processes and the eventual equality of the rates of the two processes, points to an important phenomenon in chemistry called the **dynamic equilibrium**. The term dynamic refers to the fact that both the processes are occurring continuously but due to the

equality of the two rates (equilibrium) no net change in the amount of the solute in solution phase occurs with the passage of time.

The dynamic nature of solubility equilibrium can be demonstrated by putting a crystal of sugar having a hole in the surface, in a solution of sugar which has already attained the state of equilibrium. It will be seen that after some time the hole is filled with solid sugar and the concentration of the solution remains unchanged. This is explained by saying that the molecules from the solution get settled in the hole (process of crystallisation) while some molecules from other parts of the crystal go into the solution (process of dissolution), thereby changing the shape of the crystal.

In general, when a solid solute is in dynamic equilibrium with its solution, the rate of dissolution (R_d) evidently depends upon the number of molecules leaving the crystal surface. The larger the area of liquid-crystal surface the greater will be the rate of dissolution. That is,

$$R_d \propto A \quad \text{or} \quad R_d = k_d \times A \quad \dots(1)$$

where k_d may be called the dissolution constant. Its value is characteristic of a particular system and its value depends on temperature.

The rate of recrystallisation (R_r) is the rate at which the solute molecules return to the crystal surface from solution and are deposited on it. This is determined by two factors : (a) the surface (A) or the crystal; the larger the area, the greater the number of molecules settling on it; (b) the concentration C of the solute molecules in solution; the higher the number of solute molecules in solution, the greater their number settling down. Thus,

$$R_r \propto A \times C \quad \text{or} \quad R_r = k_r \times A \times C \quad \dots(2)$$

where k_r may be called the recrystallisation constant. Its value is also characteristic of a system and depends upon temperature.

At equilibrium the rate of dissolution and the rate of recrystallisation are equal.

$$R_d = R_r$$

$$\text{or, from (1) and (2)} \quad k_d \times A = k_r \times A \times C$$

$$\begin{aligned} \text{or} \quad C &= \frac{k_d}{k_r} = \text{constant} \\ &= K \text{ (say)} \end{aligned}$$

Hence the concentration of solute at equilibrium state in the solution is constant for a particular solvent and at a fixed temperature. The solution thus obtained is called a 'Saturated solution' of the solid substance and the concentration of this solution is termed its 'Solubility'.

Thus a saturated solution is defined as one which is in equilibrium with the excess of solid at a particular temperature.

The solubility is defined as the concentration of the solute in solution when it is in equilibrium with the solid substance at a particular temperature.

Each substance has a characteristic solubility in a given solvent. The solubility of a substance is often expressed in terms of number of grams of it that can be dissolved in 100 grams of the solvent. For example, a saturated solution of sodium chloride in water at 0°C contains 35.7 g of NaCl in 100 g of H₂O. That is, the solubility of NaCl in water at 0°C is 35.7 g/100 g.

An increase in the temperature generally causes a rise in the solubility. Thus the solubility of copper sulphate in water at 0°C is 14.3 g/100g, while at 100°C it is 75.4 g/100 g.

When a saturated solution prepared at a higher temperature is cooled, it gives a solution which would contain more solute than the saturated solution at that temperature. Such a solution is called a **supersaturated solution**. Supersaturated solutions are quite unstable and change to the saturated solution when excess of solute precipitates out. This fact is utilized in the purification of chemical substances.

DETERMINATION OF SOLUBILITY

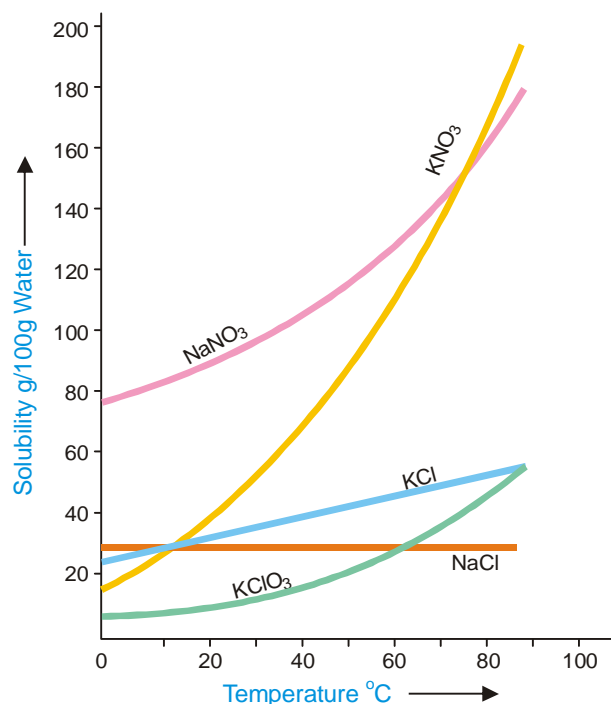
The solubility of a substance is determined by preparing its saturated solution and then finding the concentration by evaporation or a suitable chemical method.

Saturated solution of a solid substance may be prepared by shaking excess of it with the solvent in a vessel placed in a constant temperature bath and filtering the clear solution. A known volume of this saturated solution is evaporated in a china dish and from the weight of the residue the solubility can easily be calculated. This method though simple, does not yield accurate results. During filtration, cooling would take place and thus some solid may be deposited on the filter paper or in the stem of the funnel. However, this method is quite good for the determination of solubility at room temperature. The evaporation of a liquid is a highly undesirable operation as it is not possible to avoid loss of the liquid caused by spurting. This difficulty can, however, be overcome whenever a chemical method of analysis is available. Another defect in this method is that it takes a long time to establish the equilibrium between the solid and the solution so that the preparation of saturated solution by simple agitation with the solvent is delayed. This difficulty may be overcome by first preparing the saturated solution at a higher temperature and then to cool it to the desired temperature at which solubility is to be determined.

SOLUBILITY CURVES

A curve drawn between solubility and temperature is termed **Solubility Curve**. It shows the effect of temperature on the solubility of a substance. The solubility curves of substances like calcium acetate and calcium chromate show decrease in solubility with increase of temperature while there are others like those of sodium nitrate and lead nitrate which show a considerable increase of solubility with temperature. The solubility curve of sodium chloride shows very little rise with increase of temperature. In general, the solubility curves are of two types :

- (1) Continuous solubility curves
- (2) Discontinuous solubility curves



■ **Figure 14.14**
Continuous solubility curves.