

14

Solutions

CHAPTER

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A solution is a homogeneous mixture of two or more substances on molecular level. The constituent of the mixture present in a smaller amount is called the **Solute** and the one present in a larger amount is called the **Solvent**. For example, when a smaller amount of sugar (solute) is mixed with water (solvent), a homogeneous solution in water is obtained. In this solution, sugar molecules are uniformly dispersed in molecules of water. Similarly, a solution of salt ($\text{Na}^+ \text{Cl}^-$) in water consists of ions of salt (Na^+, Cl^-) dispersed in water.

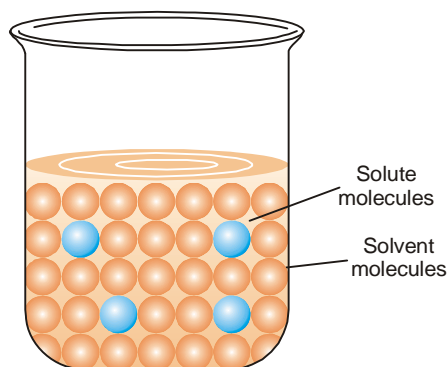
CONCENTRATION OF A SOLUTION

The concentration of a solution is defined as : **the amount of solute present in a given amount of solution.**

Concentration is generally expressed as the quantity of solute in a unit volume of solution.

$$\text{Concentration} = \frac{\text{Quantity of solute}}{\text{Volume of solution}}$$

A solution containing a relatively low concentration of solute is called **Dilute solution**. A solution of high concentration is called **Concentrated solution**.



■ **Figure 14.1**
Molecular model of a solution.

TYPES OF SOLUTIONS

The common solutions that we come across are those where the solute is a solid and the solvent is a liquid. In fact, substance in any three states of matter (solid, liquid, gas) can act as solute or solvent. Thus there are **seven types of solutions** whose examples are listed in Table 14.1.

TABLE 14.1. TYPES AND EXAMPLES OF SOLUTIONS		
State of Solute	State of Solvent	Example
1. Gas	Gas	Air
2. Gas	Liquid (Carbonated drinks)	Oxygen in water, CO ₂ in water
3. Gas	Solid	Adsorption of H ₂ by palladium
4. Liquid	Liquid	Alcohol in water
5. Liquid	Solid	Mercury in silver
6. Solid	Liquid	Sugar, Salt
7. Solid	Solid (Steel)	Metal alloys : Carbon in iron

Of the seven types of solutions mentioned in Table 14.1, we will discuss only the important ones in detail.

WAYS OF EXPRESSING CONCENTRATION

There are several ways of expressing concentration of a solution :

- Per cent by weight
- Mole fraction
- Molarity
- Molality
- Normality

Per cent by Weight

It is the **weight of the solute as a per cent of the total weight of the solution**. That is,

$$\% \text{ by weight of solute} = \frac{\text{Wt. of solute}}{\text{Wt. of solution}} \times 100$$

For example, if a solution of HCl contains 36 per cent HCl by weight, it has 36 g of HCl for 100 g of solution.

SOLVED PROBLEM. What is the per cent by weight of NaCl if 1.75 g of NaCl is dissolved in 5.85 g of water.

SOLUTION

$$\text{Wt. of solute (NaCl)} = 1.75 \text{ g}$$

$$\text{Wt. of solvent (H}_2\text{O)} = 5.85 \text{ g}$$

$$\therefore \text{Wt. of solution} = 1.75 + 5.85 = 7.60 \text{ g}$$

Hence concentration of NaCl % by weight

$$\begin{aligned} &= \frac{1.75}{7.60} \times 100 \\ &= \mathbf{23.0} \end{aligned}$$

MOLE FRACTION

A simple solution is made of two substances : one is the solute and the other solvent. Mole fraction, X , of solute is defined as **the ratio of the number of moles of solute and the total number of moles of solute and solvent**. Thus,

$$X_{\text{solute}} = \frac{\text{Moles of solute}}{\text{Moles of solute} + \text{Moles of solvent}}$$

If n represents moles of solute and N number of moles of solvent,

$$X_{\text{solute}} = \frac{n}{n + N}$$

Notice that mole fraction of solvent would be

$$X_{\text{solvent}} = \frac{N}{n + N}$$

Mole fraction is unitless and

$$X_{\text{solute}} + X_{\text{solvent}} = 1$$

SOLVED PROBLEM. Calculate the mole fraction of HCl in a solution of hydrochloric acid in water, containing 36 per cent HCl by weight

SOLUTION

The solution contains 36 g of HCl and 64 g of H₂O

$$\begin{aligned} \text{Number of Moles of HCl} &= (36 \text{ g HCl}) \left(\frac{1 \text{ mol HCl}}{36.5 \text{ g HCl}} \right) \\ &= 0.99 \end{aligned}$$

$$\begin{aligned} \text{Number of Moles of H}_2\text{O} &= (64 \text{ g H}_2\text{O}) \left(\frac{1 \text{ mol H}_2\text{O}}{18 \text{ g H}_2\text{O}} \right) \\ &= 3.55 \end{aligned}$$

$$\begin{aligned} X_{\text{HCl}} &= \frac{\text{moles of HCl}}{\text{moles of HCl} + \text{moles of H}_2\text{O}} \\ &= \frac{0.99}{3.55 + 0.99} = \mathbf{0.218} \end{aligned}$$

MOLARITY

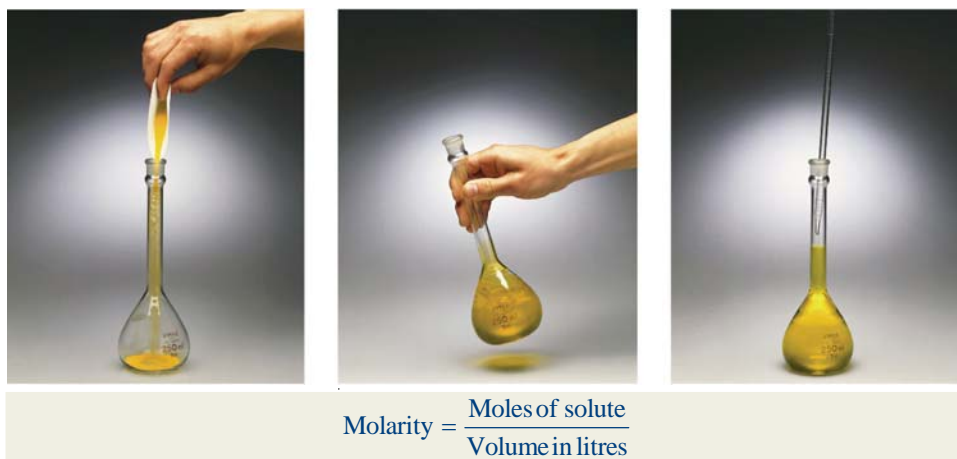
In current practice, concentration is most often expressed as molarity. Molarity (symbol M) is defined as **the number of moles of solute per litre of solution**. If n is the number of moles of solute

and V litres the volume of solution,

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume in litres}}$$

or
$$M = \frac{n}{V \text{ (in litres)}} \quad \dots(1)$$

For one mole of solute dissolved in one litre of solution $M = 1$ *i.e.*, molarity is one. Such a solution is called $1M$ (read “1 molar”). A solution containing two moles of solute in one litre is $2M$ (“two molar”); and so on. As evident from expression (1), **unit of molarity is mol litre⁻¹**.



Calculation of Molarity

Molarity of a solution can be calculated with the help of the expression (1) if moles of solute (n) and volume V (in litres) are known. When the amount of solute is given in grams and its molecular weight is MW , it can be converted to moles :

$$n = x \text{ g} \times \frac{1 \text{ mol}}{MW \text{ g}} \text{ mol}$$

Substituting in expression (1)

$$M = x \text{ g} \times \frac{1 \text{ mol}}{MW \text{ g}} \times \frac{1}{V} \quad \dots(2)$$

From expression (1) can also be found the amount of solute in grams if molarity is given.

SOLVED PROBLEM 1. What is the molarity of a solution prepared by dissolving 75.5 g of pure KOH in 540 ml of solution.

SOLUTION

$$\begin{aligned} \text{Molecular mass of KOH} &= 39.1 + 16.0 + 1.0 \\ &= 56.1 \end{aligned}$$

Calculation of moles of KOH:

$$75.5 \text{ g KOH} \times \frac{1 \text{ mol}}{56.1 \text{ g}} = 1.35 \text{ mol}$$

Calculation of volume in litres :

$$540 \text{ ml} \times \frac{1 \text{ litre}}{1000 \text{ ml}} = 0.540 \text{ litres}$$

Calculation of Molarity :

$$M = \frac{n}{V}$$

$$= \frac{1.35 \text{ mol}}{0.540 \text{ litre}} = 2.50 \text{ M}$$

Thus the solution is **2.50 M**.

SOLVED PROBLEM 2. What weight of HCl is present in 155 ml of a 0.540 M solution ?

SOLUTION

$$M = 0.540$$

$$V \text{ in litres} = \frac{155}{1000} = 0.155 \text{ litre}$$

$$n = M \times V$$

$$= 0.540 \text{ mol/litre} \times 0.155 \text{ litre}$$

$$= 0.0837 \text{ mol of HCl}$$

$$0.0837 \text{ mol of HCl} \times \frac{36.5 \text{ g}}{\text{mol HCl}} = 3.06 \text{ g HCl}$$

Thus **3.06 g of HCl** is present in 155 ml of the given solution.

MOLALITY

Molality of a solution (symbol m) is defined as **the number of moles of solute per kilogram of solvent** :

$$\text{Molality } (m) = \frac{\text{Moles of solute}}{\text{Mass of solvent in kilograms}}$$

A solution obtained by dissolving one mole of the solute in 1000 g of solvent is called **one molal** or **1m solution**.

Notice the difference between molality and molarity. **Molality is defined in terms of mass of solvent while molarity is defined in terms of volume of solution.**

SOLVED PROBLEM. What is the molality of a solution prepared by dissolving 5.0 g of toluene (C_7H_8) in 225 g of benzene (C_6H_6) ?

SOLUTION

Calculation of number of moles of solute :

$$\text{Molecular mass of toluene} = 12 \times 7 + 1 \times 8 = 92$$

$$\text{No. of moles 5 g of toluene} = \frac{5}{92} = 0.0543$$

$$\text{Mass of solvent in kg} = \frac{225 \text{ g}}{1000} = 0.225 \text{ kg}$$

$$\text{Molality} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}} = \frac{0.0543}{0.225}$$

$$= 0.24 \text{ m}$$

NORMALITY

Normality of a solution (symbol N) is defined as *number of equivalents of solute per litre of the solution* :

$$\text{Normality (N)} = \frac{\text{Equivalents of solute}}{\text{Volume of solution in litres}}$$

Thus, if 40 g of NaOH (eq. wt. = 40) be dissolved in one litre of solution, normality of the solution is one and the solution is called $1N$ (one-normal). A solution containing 4.0 g of NaOH is $1/10 N$ or $0.1 N$ or decinormal.

SOLVED PROBLEM. 5 g of NaCl is dissolved in 1000 g of water. If the density of the resulting solution is 0.997 g per ml, calculate the molality, molarity, normality and mole fraction of the solute, assuming volume of the solution is equal to that of solvent.

SOLUTION

$$\begin{aligned} \text{Number of moles of NaCl} &= \frac{\text{Mass of NaCl}}{\text{Molecular mass NaCl}} \\ &= \frac{5}{58.5} = 0.0854 \end{aligned}$$

By definition,

$$\begin{aligned} \text{Molality} &= \frac{\text{No. of moles of solute} \times 1000}{\text{Mass of solvent in grams}} \\ &= \frac{0.0854}{1000} \times 1000 = \mathbf{0.0854 m} \end{aligned}$$

$$\begin{aligned} \text{Volume of the solution} &= \frac{\text{Mass of solution in grams}}{\text{Density in gm per ml}} \\ &= \frac{1000 + 5}{0.997} = 1008 \text{ ml} \\ &= \mathbf{1.008 \text{ litre}} \end{aligned}$$

Now

$$\begin{aligned} \text{Molarity} &= \frac{\text{Number of moles of solute}}{\text{Volume of solution in litres}} \\ &= \frac{0.0854}{1.008} = \mathbf{0.0847 M} \end{aligned}$$

and

$$\begin{aligned} \text{Normality} &= \frac{\text{Number of gram equivalents of solute}}{\text{volume of solution in litres}} \\ &= \frac{0.0854}{1.008} \quad [\because \text{Mol mass of NaCl} = \text{Eq. wt. of NaCl}] \\ &= \mathbf{0.0847 N} \end{aligned}$$

To Calculate Mole Fraction of the Solute

$$\text{No. of moles of water in 1000 ml} = \frac{1000}{18} = 55.5$$

[\because 1 ml of Water = 1 g of water]

$$\begin{aligned} \text{Total number of moles} &= \text{No. of moles of solute} + \text{No. of moles of solvent} \\ &= 0.0854 + 55.5 \\ &= 55.5854 \end{aligned}$$

$$\begin{aligned}\text{Mole fraction of NaCl} &= \frac{\text{No. of moles of NaCl}}{\text{Total moles}} \\ &= \frac{0.0854}{55.5854} \\ &= 1.536 \times 10^{-3}\end{aligned}$$

SOLUTIONS OF GASES IN GASES

When a gas is mixed with another gas a completely homogeneous solution results provided of course they do not react chemically. It is obvious that such gaseous solutions will have the following characteristic properties :

(1) **Complete miscibility.** According to the *Kinetic Theory*, a gas consists of tiny molecules moving about in vacant space and thus when one gas is dissolved in another gas they form a homogeneous solution quite readily. In such a gaseous mixture, the components can be present to an unlimited extent.

(2) **Dalton's law of Partial pressures.** Since in a gaseous mixture the constituent molecules exist separately, it is obvious that the properties of the mixture will be the sum of properties of the components. Thus Dalton (1842) was the first to show that **the total pressure exerted by a gaseous mixture is the sum of the individual or partial pressures of the component gases.** If p_1, p_2, p_3, \dots be the partial pressures of the constituents, the total pressure P of the mixture is given the expression

$$P = p_1 + p_2 + p_3 + \dots$$

Like other gas laws, Dalton's law holds strictly only when the partial pressures are not too high. This law can be experimentally tested by comparing the total pressure of a gaseous mixture with the sum of the individual pressure of each gas before mixing.

SOLVED PROBLEM. At constant temperature, 250 ml of nitrogen under 720 mm pressure and 380 ml oxygen under 650 mm pressure were put into a one-litre flask. What will be the final pressure of the mixture ?

SOLUTION

Since $PV = P'V'$ at constant temperature (*Boyle's Law*)

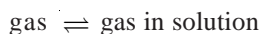
$$P_{N_2} \times 1000 = 720 \times 250 \quad \text{or} \quad P_{N_2} = 180 \text{ mm Hg}$$

$$P_{O_2} \times 1000 = 380 \times 650 \quad \text{or} \quad P_{O_2} = 247 \text{ mm Hg}$$

$$\begin{aligned}\text{Total pressure } P &= P_{N_2} + P_{O_2} \quad (\text{Dalton's Law}) \\ &= 180 + 247 = 427 \text{ mm Hg}\end{aligned}$$

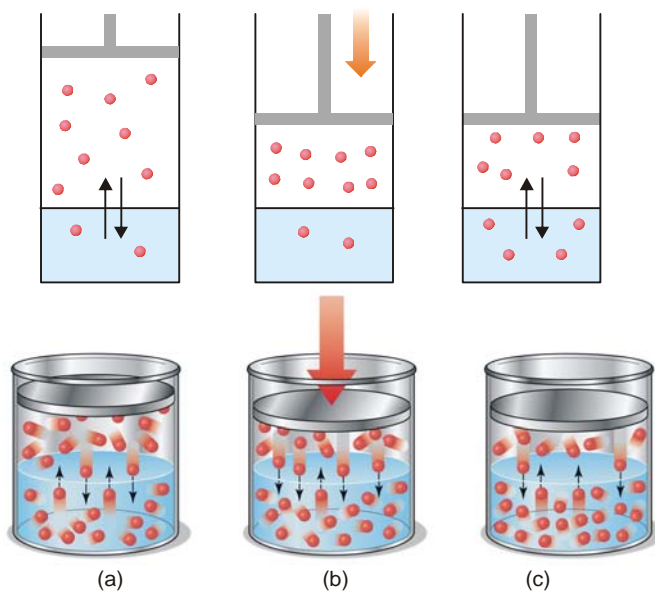
HENRY'S LAW

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.



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

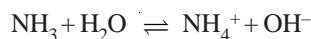
$$C = k P$$

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.



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

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

SOLUTION

Calculation of k :

$$C = k P$$

or

$$k = \frac{C}{P}$$

Substituting values for pure oxygen,

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

Calculation of Concentration of O₂ at given pressure

$$C = k P$$

$$\begin{aligned} \text{Concentration of O}_2 &= 1.38 \times 10^{-3} \frac{\text{mol/litre}}{\text{atm}} \times 0.21 \text{ atm} \\ &= \mathbf{2.9 \times 10^{-4} \text{ mole/litre}} \end{aligned}$$

SOLVED PROBLEM 2. At 20° C the solubility of nitrogen gas in water is 0.0150 g/litre when the partial pressure of N₂ is 580 torr. Find the solubility of N₂ in H₂O at 20° C when its partial pressure is 800 torr.

SOLUTION

We know that Henry's law for a gas at two different concentration and pressures can be written as

$$\frac{C_1}{P_1} = k \qquad \frac{C_2}{P_2} = k$$

Since k has the same value in two cases,

$$\frac{C_1}{P_1} = \frac{C_2}{P_2} \qquad \dots(1)$$

In this example,

$$\begin{aligned} C_1 &= 0.0150 \text{ g/litre} & C_2 &= ? \\ P_1 &= 580 \text{ torr} & P_2 &= 800 \text{ torr} \end{aligned}$$

Substituting values in equation (1), we have

$$\frac{0.0150 \text{ g/litre}}{580 \text{ torr}} = \frac{C_2}{800 \text{ torr}}$$

Thus

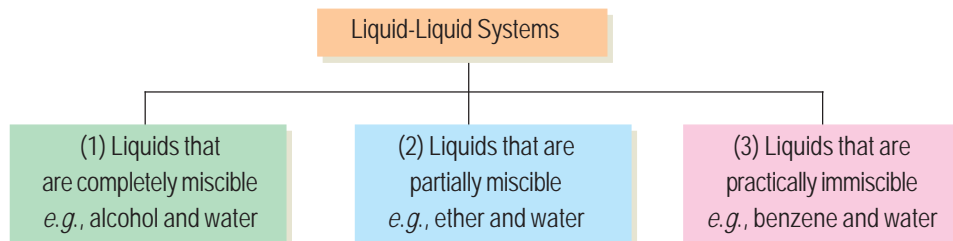
$$\begin{aligned} C_2 &= \frac{(800 \text{ torr})(0.0150 \text{ g/litre})}{(580 \text{ torr})} \\ &= \mathbf{0.0207 \text{ g/litre}} \end{aligned}$$

Thus solubility of N₂ in H₂O at 20° C at pressure of 800 torr is **0.0207 g / litre**.

Note. The above solution eliminates the calculation of k as was done in example 1.

SOLUTIONS OF LIQUIDS IN LIQUIDS

The solutions of liquids in liquids may be divided into three classes as follows :



We will now proceed to consider the more important properties of these three classes of solutions.

SOLUBILITY OF COMPLETELY MISCIBLE LIQUIDS

Liquids like alcohol and ether mix in all proportions and in this respect they could be compared to gases. The properties of such solutions, however, are not strictly additive, and

therefore their study has not proved of much interest. Generally the volume decreases on mixing but in some cases it increases. Sometimes heat is evolved when they are mixed while in others it is absorbed. The separation of this type of solutions can be effected by fractional distillation.

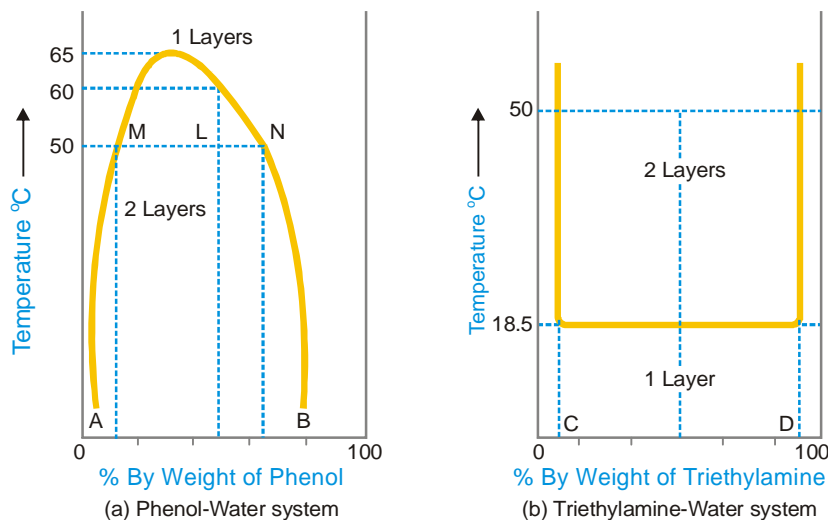
SOLUBILITY OF PARTIALLY MISCIBLE LIQUIDS

A large number of liquids are known which dissolve in one another only to a limited extent *e.g.*, ether and water. Ether dissolves about 1.2% water; and water also dissolves about 6.5% ether. Since their mutual solubilities are limited, they are only partially miscible. When equal volumes of ether and water are shaken together, two layers are formed, one of a saturated solution of ether in water and the other of a saturated solution of water in ether. These two solutions are referred to as **conjugate** solutions. The effect of temperature on the mutual solubility of these mixtures of conjugate solutions is of special interest. We will study the effect of temperature on the composition of such mixtures with reference to three typical systems :

- (1) Phenol-Water system
- (2) Triethylamine-Water system
- (3) Nicotine-Water system

PHENOL-WATER SYSTEM

The curve in Fig. 14.3 (a) represents the miscibility of phenol and water. The left hand side of the parabolic curve represents one of the two conjugate solutions which depicts the percentage of phenol dissolved in water at various temperatures. The solubility of phenol increases with temperature. The right hand side of the curve represents the other conjugate solution layer that gives the percentage of water in phenol. The solubility of water in phenol also increase with increase of temperature. The two solution curves meet at the maxima on the temperature-composition curve of the system. This point here corresponds to temperature 66°C and composition of phenol as 33%. Thus at a certain maximum temperature the two conjugate solutions merge, become identical and only one layer results. The temperature at which the two conjugate solutions (or layers) merge into one another to form one layer, is called the **Critical Solution Temperature (CST)** or Upper Consolute Temperature. This is characteristic of a particular system and is influenced very much by the presence of impurities. The determination of critical solution temperature may, therefore, be used for testing the purity of phenol and other such substances.



■ **Figure 14.3**
Temperature-composition curves.

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.

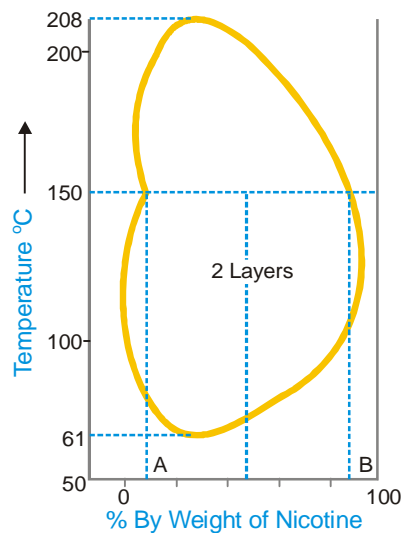


Figure 14.4 Miscibility of nicotine and water.

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**.

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

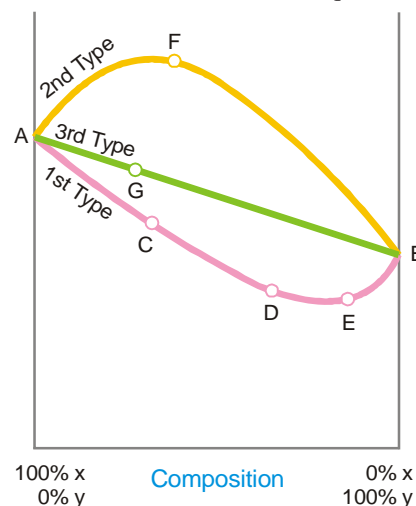


Figure 14.5
Vapour pressure of liquids.

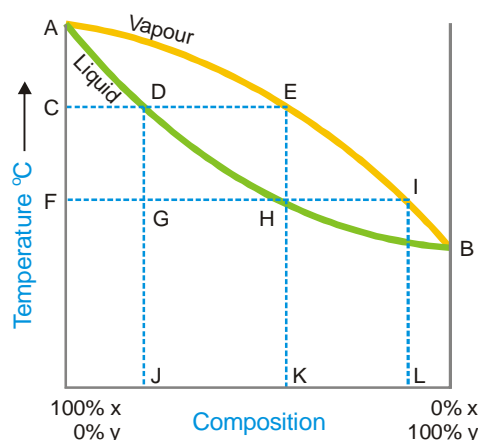
reach the 100 per cent Y -axis, when all the X will have passed over. By repeating the process of distillation with the fresh distillate which is now richer in X , we can get almost pure component X . Only in this type of solutions we can completely separate the components by fractional distillation. 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

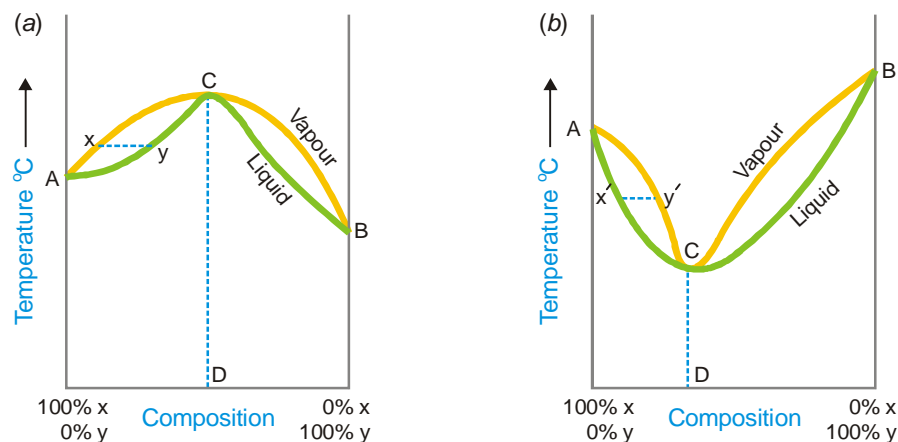
We have discussed above the vapour-pressure composition curves for the three types of solutions from a study of which we conclude that it is only in the case of the third type that a complete separation by distillation is possible. However to understand the process of fractional distillation we must 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.

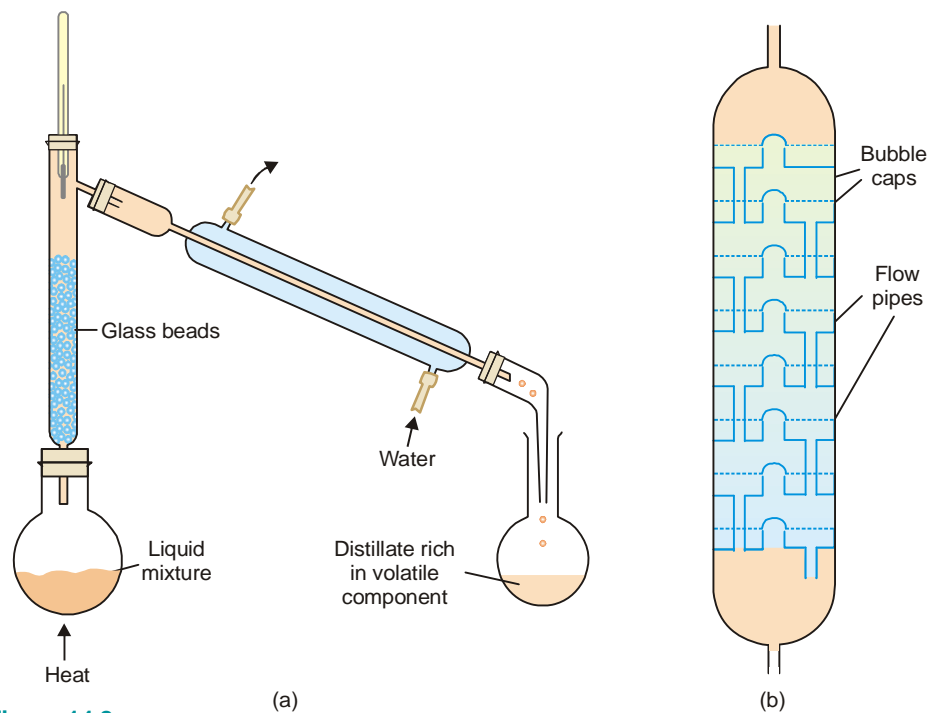
The curves AEB and ADB are the temperature composition curves for the vapour and liquid respectively. At any boiling temperature C the composition of liquid mixture is represented by J and that of the vapour in equilibrium by K . Obviously, the more volatile component Y is present in greater proportion 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**.



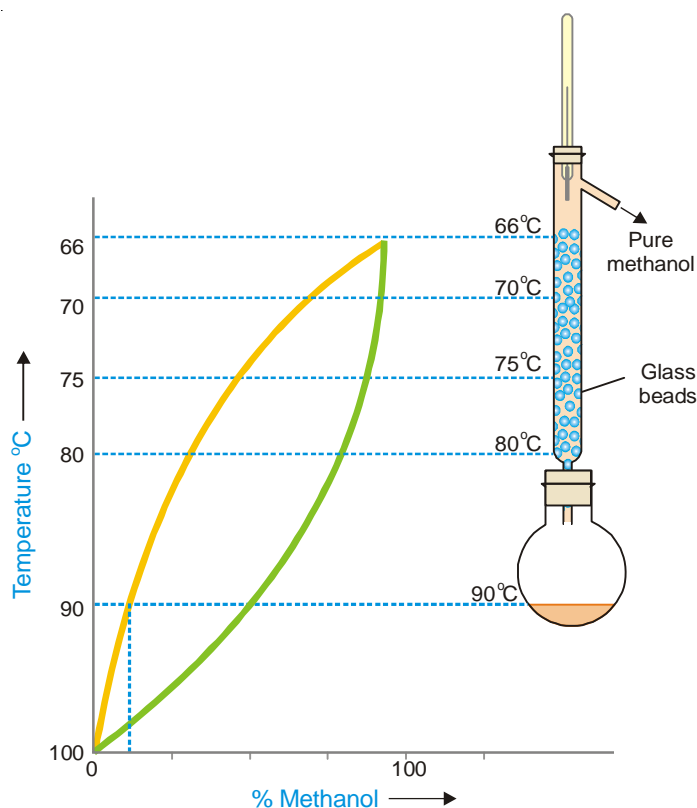
■ **Figure 14.7**
(a) Boiling point curves for 1st type of solutions;
(b) Boiling point curves for 2nd type of solutions.

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.



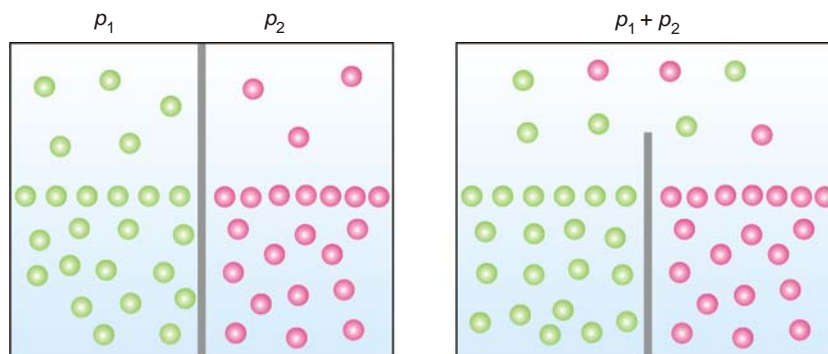
■ **Figure 14.9**
Distillation curves of mixture of methanol and water using a fractionating column.

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

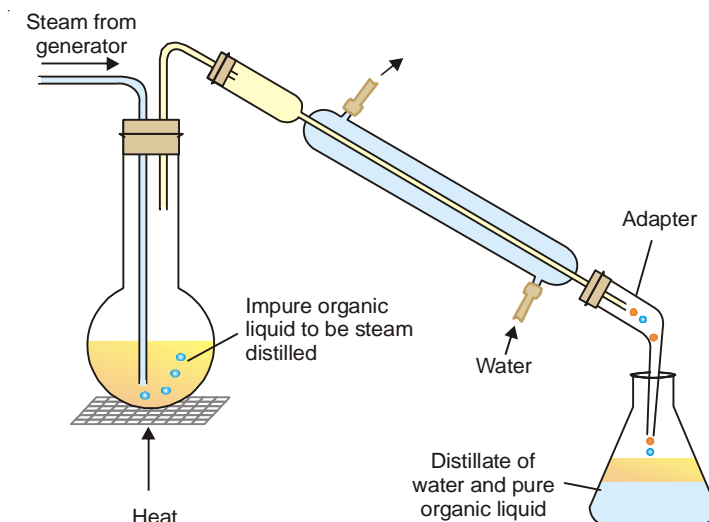
Distillation carried in a current of steam is called steam distillation. This technique is widely used for purification of organic liquids which are steam volatile and immiscible with water (*e.g.*, aniline). The impure organic liquid admixed with water containing nonvolatile impurities is heated and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

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

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 ($C_6H_5NO_2$) and water boils at $99^\circ C$. 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 $C_6H_5NO_2$.

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 $C_6H_5NO_2 = 760 - 733$
 $= 27 \text{ mm}$

p_2 , vapour pressure of water = 733 mm

M_1 , molecular mass of nitrobenzene, $C_6H_5NO_2$
 $= 12 \times 6 + 5 \times 1 + 14 \times 1 + 16 \times 2 = 123$

Substituting the values in (1)

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

\therefore Proportion of water to $C_6H_5NO_2$ in the distillate is approximately 4 : 1

SOLVED PROBLEM 2. A mixture of water and bromobenzene (C_6H_5Br) distills at $95^\circ C$, and the distillate contains 1.6 times as much C_6H_5Br as water by mass. At $95^\circ C$ the vapour pressure of water and C_6H_5Br 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 mm Hg

p_2 , vapour pressure of water = 640 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

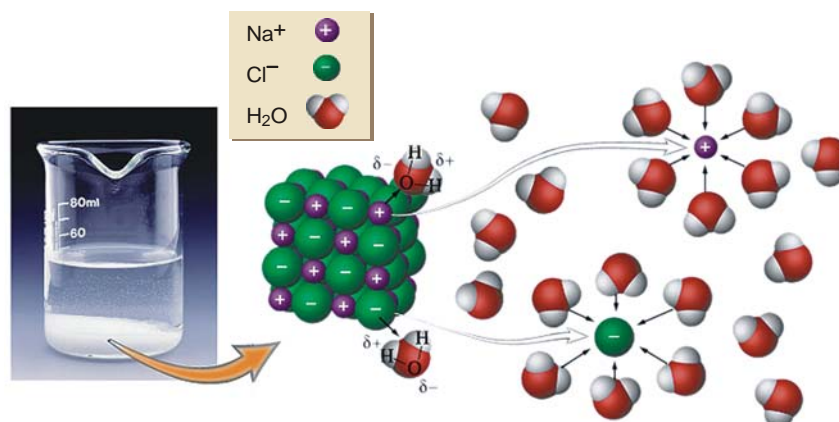
Solutions of this type are most commonly met with. The process of solution of a solid substance in a solvent is explained by the electrical forces operating between the molecules or ions of the solute and the molecules of the solvent. It is a common observation that polar solutes dissolve easily in polar 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

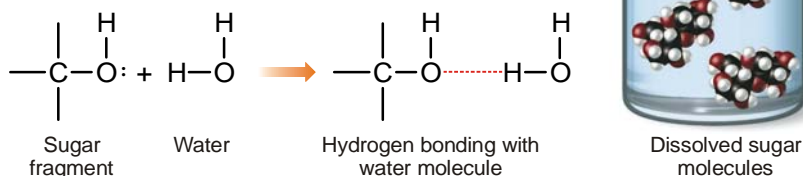


■ **Figure 14.12**
How sodium chloride dissolves in water.

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.



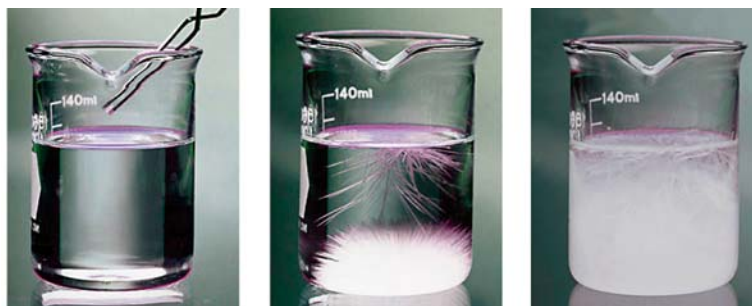
The water molecules are thus able to pull away the molecules of sugar from the crystal, which dissolve. In fact, every sugar molecule is surrounded by a number of water molecules, and these aggregates are free to migrate throughout the solution.

SOLUBILITY—ITS EQUILIBRIUM CONCEPT

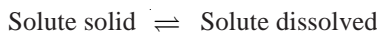
When a solid is placed in a solvent, molecules or ions, as the case may be, break away from the surface and pass into the solvent. The particles of the solid thus detached are free to diffuse throughout the solvent to give a uniform solution. The solute and the solvent molecules are constantly moving 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 :

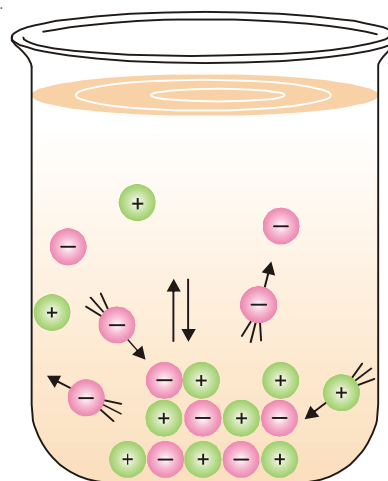
- Dissolution** – the particles of the solute leaving the solid and passing into solution.
- Recrystallisation** – the particles of the solute returning from the solution and depositing (or precipitating) on the solid.



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



■ **Figure 14.13**
Dissolution and recrystallisation.

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

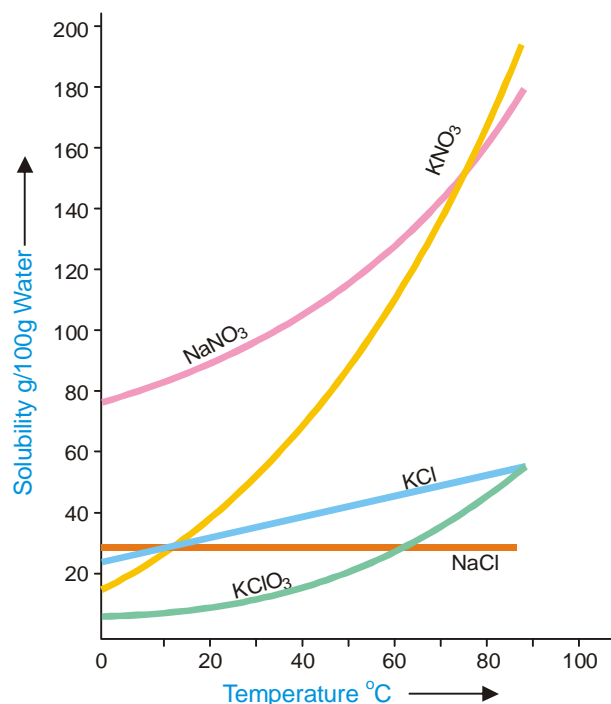
The solubility of a substance is determined by preparing its saturated solution and then finding the concentration by evaporation or a suitable chemical method.

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 spurling. 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



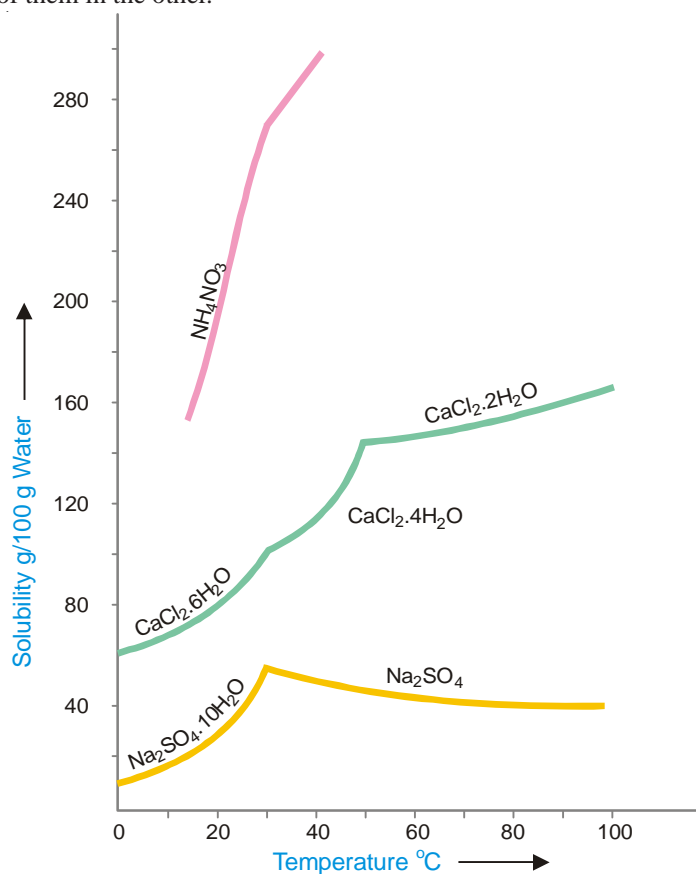
■ **Figure 14.14**
Continuous solubility curves.

Solubility curves of calcium salts of fatty acids, potassium chlorate, lead nitrate and sodium chloride are **Continuous solubility curves** as they show no sharp breaks anywhere. In case of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, no doubt the curve first shows, a rise and then a fall but it remains continuous at the maximum point. Sometimes the solubility curves exhibit sudden changes of direction and these curves are, therefore, called **Discontinuous solubility curves**. The popular examples of substances which show discontinuous solubility curves are sodium sulphate, calcium chloride, ammonium nitrate etc. In fact, at the break a new solid phase appears and another solubility curve of that new phase begins. The break in a solubility curve thus shows a point where the two different curves meet each other. The solubility curves of sodium sulphate and ferric chloride will be discussed in detail in the chapter on 'Phase Rule'.

SOLUBILITY OF SOLIDS IN SOLIDS

Solution of a solid in another solid can be prepared by melting them together and subsequent cooling of the mixture. For example, gold and silver when mixed together, melted and cooled, yield solid solutions which are perfectly homogeneous. Sometimes solid solutions may be obtained by simply pressing together the two metals and thus establishing better contact when one metal would diffuse into the other. Solutions of gold and lead have been obtained by this method. The study of solutions of solids in solids is of great practical importance in metallurgy.

The formation of solid solutions is not limited to metals only. Organic substances like naphthalene and β -naphthol when melted together form the so-called mixed crystals on cooling which are a solid solution of one of them in the other.



■ **Figure 14.15**
Discontinuous solubility curves.

EXAMINATION QUESTIONS

- Define or explain the following terms :

(a) Mole fraction	(b) Molarity
(c) Molality	(d) Normality
(e) Formality	(f) Henry's law
- Write notes on the following
 - Freezing mixtures
 - Azeotropic distillation
 - Theory of fractional distillation
- Write briefly on Raoult's law and azeotropes.
- State and explain Henry's Law. Show that the volume of a gas dissolved in a given volume of a solvent is independent of the pressure of the gas.
 - Explain the following :
 - on opening a carbonated cold drink bottle, bubbles of gas come out.
 - on adding common salt to a bottle of carbonated cold drink froth comes out.
- Define and explain the term "Solution". What are the different ways of expressing the concentration of a solution?
 - Determine the molality of a solution containing 86.53 g of sodium carbonate (mol mass = 105.99) per litre in water at 20°C. The density of the solution at this temperature is 1.0816 g ml⁻¹
Answer. (b) 0.7547
- Define the terms : (i) Molarity and (ii) Molality.
 A solution contains 25% water, 25% ethanol and 50% ethanoic acid. Calculate the mole fraction of each component.
Answer. Water = 0.503; Ethanol = 0.196; Ethanoic acid = 0.300
- What is molarity and molality of a 13% solution (by weight) of H₂SO₄? Its density is 1.09 g/ml.
 - Discuss vapour pressure-composition curves of a system containing binary mixtures of liquids which are miscible in all proportions.
Answer. (a) 1.44 M; 1.52 m
- Calculate the molality of a solution of sodium hydroxide which contains 0.2 g of sodium hydroxide in 50 g of the solvent.
Answer. 0.1 m
- Calculate the normality of a solution containing 6.3 g of oxalic acid crystals (Mol. wt. 126) dissolved in 500 ml of solution.
Answer. 0.2 N
- Mixture of alcohol and water cannot be separated by fractional distillation. Explain.
- 49 g of H₂SO₄ are dissolved in 250 ml of solution. Calculate the molarity of the solution.
 - 45 g of glucose, C₆H₁₂O₆, are dissolved in 500 g of water.
 Calculate molality of the solution.
Answer. (a) 2 M; (b) 0.5 m
- Nitrobenzene is completely immiscible with water. A mixture of the two liquids boils at 99°C and 753 torr pressure. The vapour pressure of water is 733 torr at this temperature. Find out the weight composition of liquid mixture.
Answer. 5.3:1
- Explain giving reasons :
 - Solubility of a gas in a given liquid decreases with rise in temperature.

- (b) A salt solution fails to quench thirst.
14. Which out of two, a molal solution or a molar solution, is more concentrated and why? Give reasons.
(Nehru BSc, 2000)
15. Define an ideal solution. (Kerala BSc, 2000)
16. When two components 'A' and 'B' are mixed and the resulting solution formed is almost an ideal solution. Derive an expression for free energy change of mixing. (Madurai BSc, 2000)
17. Draw only, well labelled vapour pressure-composition diagram of binary miscible real solutions at constant temperature. (Panjab BSc, 2000)
18. (a) Define the following terms :
(i) Mole fraction (ii) Molal solution
(b) Obtain a relationship for molal elevation constant from thermodynamic considerations.
(Purvanchal BSc, 2000)
19. Define the following terms :
(i) Molality (ii) Molarity
(iii) Mole fraction (Kathmandu BSc, 2001)
20. Write short notes on :
(i) Steam distillation (ii) Azeotropic mixture (Lucknow BSc, 2001)
21. (a) Explain the process of fractional distillation.
(b) Give a short note on 'azeotropes'. (MD Rohtak BSc, 2002)
22. Write how molarity, molality and mole fraction are used to express the concentration of a solution.
(Guru Nanak Dev BSc, 2003)
23. (a) Calculate the mass percent concentration of a solution containing 40 g of glucose in 280 g of water.
(b) Giving suitable sketches, distinguish between a maximum and minimum boiling azeotrope.
(Guru Nanak Dev BSc, 2004)
24. (a) Give brief accounts of
(i) Raoult's law (ii) Henry's law
(b) Discuss the principle of fractional distillation of miscible liquid pairs and describe the use of fractionating column in this connection. (Guru Nanak Dev BSc, 2004)
25. (a) Give illustration of maximum and minimum azeotropic mixtures.
(b) A sample of spirit contains 92% of ethanol by weight, the rest being water. What is the mole fraction of its constituents?
Answer. (b) 0.182; 0.818 (Assam BSc, 2004)
26. Calculate the ionic strength of a solution containing 0.2 M NaCl and 0.1 M Na₂SO₄
Answer. Na⁺ = 9.2 g l⁻¹; Cl⁻ = 7.1 g l⁻¹; SO₄²⁻ = 9.6 g l⁻¹ (Madras BSc, 2004)
27. 5 g of NaCl is dissolved in 1 kg of water. If the density of the solution is 0.997 g ml⁻¹, calculate the molarity, molality and mole fraction of the solute.
Answer. 0.085 M, 0.0847 m, 0.00153 (Sambalpur BSc, 2005)
28. Calculate the amount of Na⁺ and Cl⁻ ions in grams present in 500 ml of 1.5 M NaCl solution.
Answer. 17.3 g Na⁺ and 26.6 g Cl (Arunachal BSc, 2005)
29. Calculate the molarity and normality of a solution containing 5.3 g of Na₂CO₃ dissolved in 1000 ml solution.
Answer. 0.05 M ; 0.10 N (Gulbarga BSc, 2005)
30. Calculate the molarity of a solution containing 331g of HCl dissolved in sufficient water to makes 2 dm³ of solution.

- Answer.** 4.534 M (Vidyasagar BSc, 2005)
31. What is molarity of Fe^{2+} ions in a solution containing 200 g of FeCl_3 per litre of solution ?
Answer. 1.574 M (Mizoram BSc, 2006)
32. Calculate the number of molecules of sugar present in 1 ml of 10% sugar solution having density = 1.20 g ml^{-1} .
Answer. 2.1×10^{20} (Kalyani BSc, 2006)
33. What is the normality of a solution containing 28.0 g of KOH dissolved in sufficient water to make 400 ml of solution ?
Answer. 1.25 N (Delhi BSc, 2006)
34. A 6.90 M solution of KOH in water contains 30% by weight of KOH. Calculate the density of the solution.
Answer. 1.288 g ml^{-1} (Madras BSc, 2006)

MULTIPLE CHOICE QUESTIONS

1. The concentration of a solution is defined as
 (a) the amount of solvent present in a given amount of solution
 (b) the amount of solute present in a given amount of solution
 (c) the amount of solute present in a given amount of solvent
 (d) the amount of solvent present in a given amount of solute
Answer. (b)
2. If n represents the number of moles of a solute and N represents the number of moles of a solvent, the mole fraction of the solvent is given by
 (a) $\frac{n}{n+N}$ (b) $\frac{N}{n+N}$
 (c) $\frac{n+N}{n}$ (d) $\frac{n+N}{N}$
Answer. (b)
3. The molarity is defined as the number of moles of solute present in
 (a) one litre of the solvent (b) one litre of the solution
 (c) one kilogram of the solvent (d) one kilogram of the solution
Answer. (b)
4. The molality of a solution is defined as the number of moles of solute present in
 (a) one litre of the solvent (b) one litre of the solution
 (c) one kilogram of the solvent (d) one kilogram of the solution
Answer. (c)
5. Normality of a solution is the number of _____ of solute per litre of the solution.
 (a) moles (b) equivalents
 (c) formula weight (d) mole fraction
Answer. (b)
6. For a gas in contact with a solvent at a constant temperature, the concentration of the gas that dissolves in the solvent is directly proportional to the pressure of the gas. This law is
 (a) Henry's law (b) Raoult's law
 (c) Dalton's law (d) van't Hoff's law

Answer. (a)

7. The weight percent of a solute in a solution is given by

(a) $\frac{\text{wt of the solvent}}{\text{wt of the solute}} \times 100$

(b) $\frac{\text{wt of the solute}}{\text{wt of the solvent}} \times 100$

(c) $\frac{\text{wt of the solute}}{\text{wt of the solution}} \times 100$

(d) $\frac{\text{wt of the solution}}{\text{wt of the solute}} \times 100$

Answer. (c)

8. The Henry's law is applicable if

- (a) the temperature and pressure are moderate
 (b) the solubility of the gas in the solvent is low
 (c) the gas does not react with the solvent to form a new species
 (d) all of the above

Answer. (d)

9. The temperature at which two conjugate solutions (or layers) merge into one another to form one layer is called the

- (a) critical temperature
 (b) critical solution temperature
 (c) distillation temperature
 (d) Dalton's temperature

Answer. (b)

10. A saturated solution is defined as one which is _____ with the excess of solid at a particular temperature

- (a) in contact
 (b) in equilibrium
 (c) contains impurities
 (d) none of these

Answer. (b)

11. In a super saturated solution, the amount of solute is _____ in comparison to saturated solution.

- (a) more
 (b) less
 (c) equal to
 (d) none of these

Answer. (a)

12. The solubility generally rises with

- (a) increase in temperature
 (b) decrease in temperature
 (c) increases in volume of the solvent
 (d) none of these

Answer. (a)

13. A saturated solution of KCl on heating becomes

- (a) unsaturated
 (b) supersaturated
 (c) hydrated
 (d) none of these

Answer. (b)

14. Mathematically, Henry's law can be expressed as (C is the concentration of the gas in solution and P is the pressure of the gas)

- (a) $C \propto P$
 (b) $C = k P$
 (c) $k = C/P$
 (d) all of these

Answer. (d)

15. The Henry's law gives the relationship between

- (a) the pressure and solubility of a gas in a particular solvent
 (b) the temperature and solubility of a gas in a particular solvent
 (c) the composition of the mixture and solubility of a gas in a particular solvent
 (d) none of these

Answer. (a)

16. When two non-reacting gases are mixed, a _____ is obtained
(a) homogeneous mixture (b) heterogeneous mixture
(c) equilibrium mixture (d) none of these

Answer. (a)

17. The completely miscible solution can be separated by
(a) a separating funnel (b) evaporation
(c) fractional distillation (d) none of these

Answer. (c)

18. The liquid mixtures which distill with a change in composition are called
(a) azeotropic mixtures (b) equilibrium mixtures
(c) zeotropic mixtures (d) nonequilibrium mixtures

Answer. (c)

19. The organic liquids which are steam volatile and immiscible with water can be separated by
(a) distillation (b) fractional distillation
(c) steam distillation (d) evaporation

Answer. (c)

20. Sugar dissolves in water due to the formation of
(a) covalent bonds (b) ionic bonds
(c) co-ordinate bonds (d) hydrogen bonding

Answer. (d)

21. The rate of crystallisation is the rate at which the
(a) solid molecules go into the solvent
(b) solute molecules return to the crystal surface and are deposited on it
(c) solute molecules leave the surface of the solution
(d) solute molecules condense on the surface of the solution

Answer. (b)

22. When a saturated solution prepared at a higher temperature is cooled, we get
(a) super cooled solution (b) super saturated solution
(c) an equilibrium mixture (d) one molar solution

Answer. (b)

23. An alloy is a homogeneous mixture of
(a) two solids (b) two liquids
(c) two metals (d) two non-metals

Answer. (c)

24. The organic liquids which decompose at the boiling point are purified / separated by
(a) distillation (b) steam distillation
(c) fractional distillation (d) none of these

Answer. (b)

25. In a saturated solution there exists an equilibrium between
(a) solvent and excess of solid (b) solution and excess of solid
(c) solid and excess of solvent (d) solid and excess of solution

Answer. (b)

26. In one molal solution that contains 0.5 mole of a solute there is
(a) 1000 g of solvent (b) 1000 ml of solvent
(c) 500 ml of solvent (d) 500 g of solvent

Answer. (d)

27. Which of the following does not depend upon the temperature?

- (a) molarity (b) molality
(c) formality (d) normality

Answer. (b)

28. 36 g of glucose (molecular mass 180) is present in 500 g of water, the molality of the solution is

- (a) 0.2 (b) 0.4
(c) 0.8 (d) 1.0

Answer. (b)

29. The number of moles of a solute per kilogram of the solvent is called

- (a) formality (b) normality
(c) molarity (d) molality

Answer. (d)

30. The mole fraction of ethyl alcohol in a solution containing 36 g of H_2O and 46 g of ethyl alcohol is

- (a) $1/3$ (b) $1/2$
(c) $2/3$ (d) $3/4$

Answer. (a)

31. The molarities of 0.1 N solution of HCl and 0.1 N solution of H_2SO_4 are respectively

- (a) 0.1 M and 0.1 M (b) 0.1 M and 0.05 M
(c) 0.05 M and 0.1 M (d) 0.1 M and 0.2 M

Answer. (b)

32. For the preparation of 100 ml of 0.1 N solution of sulphuric acid, the amount of H_2SO_4 needed is

- (a) 4.9 g (b) 9.8 g
(c) 14.7 g (d) 19.6 g

Answer. (a)

33. The normalities of 1 M solution of HCl, 1 M H_2SO_4 and 1 M H_3PO_4 are respectively

- (a) 1 N, 2 N and 3 N (b) 2 N, 3 N and 1 N
(c) 0.1 N, 0.2 N and 0.3 N (d) 3 N, 2 N and 1 N

Answer. (a)

34. How many grams of glucose are present in 100 ml of 0.1 M solution

- (a) 180 g (b) 18.0 g
(c) 1.8 g (d) 3.6 g

Answer. (c)

35. In 1.0 M solution of sulphuric acid, the moles of hydrogen ions present will be

- (a) 1.0 M (b) 2.0 M
(c) 3.0 M (d) 4.0 M

Answer. (b)

36. The normality of a solution of sulphuric acid is $\frac{N}{10}$. Its molarity will be

- (a) $\frac{M}{5}$ (b) $\frac{M}{10}$
(c) $\frac{M}{20}$ (d) $\frac{M}{40}$

Answer. (c)

37. A solution of KCl contains 74.5 g of it in 90 g of water. The mole fraction of KCl will be

- (a) $1/6$ (b) $1/5$
(c) $1/4$ (d) $\frac{74.5}{90}$

Answer. (a)

38. 49 g of H_2SO_4 are dissolved in 250 ml of the solution. Its molarity will be

- (a) 0.5 M (b) 1.0 M
(c) 1.5 M (d) 2.0 M

Answer. (d)

39. The amount of Na^+ in 0.1 M Na_2SO_4 is

- (a) 2.3 g (b) 4.6 g
(c) 23 g (d) 46 g

Answer. (b)

40. 45 g of glucose is dissolved in 500 g of water. The molality of the solution is

- (a) 0.25 (b) 0.5
(c) 0.75 (d) 1.0

Answer. (b)

41. How many grams of water are present in 100 ml of 0.1 m solution of sulphuric acid?

- (a) 10 g (b) 20 g
(c) 50 g (d) 100 g

Answer. (d)

42. The total weight of 100 ml of 2 M solution of HCl will be

- (a) 1073 g (b) 107.3 g
(c) 10.73 g (d) 1.073 g

Answer. (b)

43. 1 kg of a solution of CaCO_3 contains 1 g of calcium carbonate. Concentration of the solution will be

- (a) 1 ppm (b) 10 ppm
(c) 100 ppm (d) 1000 ppm

Answer. (d)

44. A solution contains 180 g of glucose in 180 g of water. The total number of moles of both solute and solvent in the solution will be

- (a) 1 (b) 10
(c) 11 (d) 21

Answer. (c)

45. A sample of H_2O_2 used for bleaching of hair contains 5.1 g of H_2O_2 in 90 g of water. The mole fraction of H_2O_2 is

- (a) $\frac{0.15}{5}$ (b) $\frac{0.15}{5.15}$
(c) $\frac{5}{5.15}$ (d) $\frac{5}{0.15}$

Answer. (b)

46. Which one of the following has molality equal to one?

- (a) 36.5 g of HCl in 500 ml of water (b) 36.5 g of HCl in 1000 ml of water
(c) 36.5 g of HCl in 1000 g of water (d) 36.5 g of HCl in 500 g of water

Answer. (c)

47. Which weighs the most?

- (a) 1 M solution of HCl (b) 25 g of H_2SO_4
(c) 2 moles of water (d) 1 kg of CaCO_3

Answer. (a)

48. The weight of urea required to prepare 200 ml of 2 M solution will be

(a) 12 g (b) 24 g

(c) 20 g (d) 60 g

Answer. (b)

49. What is the molality of a solution prepared by dissolving 9.2 g toluene (C_7H_8) in 500 g of benzene

(a) 1/2 (b) 1/4

(c) 1/5 (d) 1/10

Answer. (c)

50. A solution of urea is prepared by dissolving 180 g of it in one kg of water. The mole fraction of urea in the solution

(a) $\frac{1}{55.5}$ (b) $\frac{1}{56.5}$

(c) $\frac{1}{100}$ (d) 1.8

Answer. (b)

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