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313en07

SOLUTIONS

You know that when sugar or salt is added to water, it dissolves. The resulting mixture is called a solution. Solutions play an important role in our life. In industry, solutions of various substances are used to carry out a large number of chemical reactions.

Study of solutions of various substances is very interesting.

In this lesson, let us learn about the various components of a solution and the ways in which concentration of solutions is expressed. We shall also learn about some properties of solutions which are dependent only on the number of solute particles. (you will learn about solute in this lesson)



OBJECTIVES

After reading this lesson, you will be able to:

- identify the components of different types of solution;
- express the concentration of solutions in different ways;
- list different types of solutions;
- state Henry's law;
- define vapour pressure;
- state and explain Raoult's law for solutions;
- define ideal solutions;
- give reasons for non-ideal behaviour of solutions;
- state reasons for positive and negative deviations from ideal behaviour;
- explain the significance of colligative properties;



Notes

- state reasons for the elevation of boiling point and depression in freezing point of solutions;
- explain the abnormal colligative properties;
- define osmosis and osmotic pressure;
- define Van't Hoff factor;
- correlate the degree of dissociation of solute and
- solve numerical problems.

7.1 COMPONENTS OF A SOLUTION

When we put sugar into water, it dissolves to form a solution. We do not see any more sugar in it. Like sugar, a large number of other substances such as common salt, urea, potassium chloride etc dissolve in water forming solution. In all such solutions, water is the solvent and substances which dissolve are the solutes.

Thus, solute and solvent are the components of a solution. Whenever a solute mixes homogeneously with a solvent, a solution is formed



A solution is a homogeneous mixture of two or more substances.

Solvent is that component of a solution that has the same physical state as the solution itself.

Solute is the substance that is dissolved in a solvent to form a solution.

7.1.1 The Concentration of a Solution

Some of the properties of solutions, e.g., the sweetness of a sugar solution or the colour of a dye solution, depend on the amount of solute compared to that of the solvent in it. This is called the solution concentration. There are several ways for describing concentration of solution. They include molarity, molality, normality, mole fraction and mass percentage.

Molarity: Molarity is defined as the number of moles of solute dissolved per litre of solution and is usually denoted by M . It is expressed as :

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

Where n is the number of moles of solute and V is the volume of the solution in litres. A 2.0 molar solution of sulphuric acid would be labelled as 2.0 M H_2SO_4 .

It is prepared by adding 2.0 mol of H_2SO_4 to water to make a litre of solution. Molarity of a solution changes with temperature because of expansion or contraction of the solution.

Molality : It is defined as the number of moles of solute dissolved per kilogram of solvent.

It is designated by the symbol m . The label 2.0 m H_2SO_4 is read “2 molal sulphuric acid” and is prepared by adding 2.0 mol of H_2SO_4 to 1 kg of solvent. Molality is expressed as:

$$m = \frac{1000 n_B}{W_A}$$

where n_B is the number of moles of the solute and W_A is the mass in grams of solvent. The molality of a solution does not change with temperature.

Example 7.1 : Find out the molarity of the solution which contains 32.0 g of methyl alcohol (CH_3OH) in 200 mL solution.

Solution : Molar mass of $\text{CH}_3\text{OH} = 12 + 1 \times 3 + 16 + 1 = 32 \text{ g mol}^{-1}$

$$\text{Number of moles of } \text{CH}_3\text{OH} = \frac{32 \text{ g}}{32 \text{ g mol}^{-1}} = 1 \text{ mol}$$

Volume of the solution = 200 mL = 0.2 litre

$$\therefore \text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of solution in litres}} = \frac{1}{0.2} = 5 \text{ M}$$

Example 7.2 : What is the molality of a sulphuric acid solution of density 1.20 g/cm^3 containing 50% sulphuric acid by mass.

Solution : Mass of 1 cm^3 of H_2SO_4 solution = 1.20 g

Mass of 1 litre (1000 cm^3) of H_2SO_4 solution = $1.20 \times 1000 = 1200 \text{ g}$

Mass of H_2SO_4 in 100 g solution of $\text{H}_2\text{SO}_4 = 50 \text{ g}$

$$\text{Mass of } \text{H}_2\text{SO}_4 \text{ in } 1200 \text{ g solution of } \text{H}_2\text{SO}_4 = \frac{50}{100} \times 1200 = 600 \text{ g}$$

\therefore Mass of water in the solution = $1200 - 600 = 600 \text{ g}$

Molar mass of $\text{H}_2\text{SO}_4 = 98 \text{ g mol}^{-1}$

$$\text{No. of moles of } \text{H}_2\text{SO}_4 = \frac{\text{Mass in grams}}{\text{Molar mass}} = \frac{600 \text{ g}}{98 \text{ g mol}^{-1}}$$



Notes



Notes

$$\begin{aligned} \therefore \text{Molarity} &= \frac{\text{No. of moles of H}_2\text{SO}_4}{\text{Mass of water in grams}} \times 1000 \\ &= \frac{600}{98} \times \frac{1}{600} \times 1000 = 6.8 \text{ m} \end{aligned}$$

Normality : Normality is another concentration unit. It is defined as the number of gram equivalent weights of solute dissolved per litre of the solution.

The number of parts by weight of a substance (element or compound) that will combine with or displace, directly or indirectly 1.008 parts by weight of hydrogen, 8 parts by weight of oxygen and 35.5 parts by weight of chlorine is known as equivalent weight. Like atomic weight and molecular weight, equivalent weight is also a number and hence no units are used to express it. However, when equivalent weight is expressed in grams, it is known as gram equivalent weight of the substance.

$$\text{Equivalent weight} = \frac{\text{Atomic or molecular weight}}{\text{Valency}}$$

$$\text{Equivalent weight of an acid} = \frac{\text{Molecular weight}}{\text{Basicity}}$$

$$\text{Equivalent weight of a base} = \frac{\text{Molecular weight}}{\text{Acidity}}$$

$$\text{Equivalent weight of a salt} = \frac{\text{Molecular weight}}{\text{Total valency of the metal atom}}$$

oxidising and reducing agents may have different equivalent weights if they react to give different products under different conditions. Thus, the equivalent weight of such substances can be calculated from the reactions in which they take part.

Normality is denoted by the symbol *N*.

$$\begin{aligned} \therefore \text{Normality (N)} &= \frac{\text{No. of gram equivalent weights of the solute}}{\text{volume of the solution in litres}} \\ &= \frac{\text{Mass of the solute in grams}}{\text{Equivalent weight of the solute}} \times \frac{1}{\text{volume of the solution in litres}} \\ &= \frac{\text{Strength of solution in grams/litre}}{\text{Equivalent weight of the solute}} \end{aligned}$$

The label 0.5 N KMnO₄ is read “0.5 normal” and represents a solution which contains 0.5 gram equivalent of KMnO₄ per litre of solution.

Mole Fraction : The mole fraction of a component in a solution is the ratio of its number of moles to the total number of moles of all the components in the solution. If a solution contains 2 mol of alcohol and 3 mol of water, the mole fraction of alcohol is $\frac{2}{5}$, and that of water $\frac{3}{5}$. The sum of mole fractions of all the components of a solution is equal to one. The mole fraction (x_A) of a component A in solution with B is :

$$x_A = \frac{n_A}{n_A + n_B}$$

Where n_A and n_B are the number of the moles of A and B respectively.

Mass Percentage : Mass percentage is the mass of solute present in 100 g of solution. Thus 5% solution of KMnO_4 in water means that 5 g of KMnO_4 is present in 100 g of the aqueous solution of KMnO_4 .

Example 7.3 : A solution contains 36.0 g water and 46.0 g ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$). Determine the mole fraction of each component in the solution.

Solution : Molar mass of water = 18 g mol^{-1}

Molar mass of $\text{C}_2\text{H}_5\text{OH}$ = 46 g mol^{-1}

No. of moles of water = $\frac{36 \text{ g}}{18 \text{ g mol}^{-1}} = 2.0 \text{ mol}$

No. of moles of $\text{C}_2\text{H}_5\text{OH}$ = $\frac{46 \text{ g}}{46 \text{ g mol}^{-1}} = 1.0 \text{ mol}$

Total number of moles in the solution = $2.0 + 1.0 = 3.0$

Mole fraction of water = $\frac{\text{No. of moles of water}}{\text{Total no. of moles in the solution}} = \frac{2.0}{3.0} = 0.67$

Mole fraction of $\text{C}_2\text{H}_5\text{OH}$ = $\frac{\text{No. of moles of } \text{C}_2\text{H}_5\text{OH}}{\text{Total no. of moles in the solution}} = \frac{1.0}{3.0} = 0.33$

Example 7.4 : Calculate the normality of a solution of NaOH if 0.4 g of NaOH is dissolved in 100 ml of the solution.

Solution : Mass of NaOH present in 100 mL of the solution = 0.4 g

\therefore Mass of NaOH present in 1000 mL of the solution = $\frac{0.4}{100} \times 1000 = 4.0 \text{ g}$

Mol. wt. of NaOH = $23 + 16 + 1 = 40 \text{ amu}$



Notes



Notes

$$\text{Eq. wt. of NaOH} = \frac{\text{Mol. Wt.}}{\text{Acidity}} = \frac{40}{1} = 40$$

$$\therefore \text{Normality} = \frac{\text{Strength in g/litre}}{\text{Eq. wt.}} = \frac{4}{40} = \frac{1}{10} \text{ N}$$

Hence, the normality of the solution = $\frac{1}{10}$ N or 0.1 N



INTEXT QUESTIONS 7.1

- List the various methods of expressing the concentration of a solution?
- Define the following
 - Molarity
 - Molality
 - Normality

7.2 TYPES OF SOLUTIONS

Solutions can be solid, liquid or gaseous. Depending upon the physical state of the solute and the solvent, there are nine possible types of solutions consisting of two components (binary solutions) Different types of solutions are given in Table 7.1.

Table 7.1 Different Types of Solutions

SOLUTE	SOLVENT	SOLUTION
Gas	Gas	Air
Gas	Liquid	Soda water
Gas	Solid	Hydrogen in palladium
Liquid	Gas	Humidity in air
Liquid	Liquid	Alcohol in water
Liquid	Solid	Mercury in gold
Solid	Gas	Camphor in air
Solid	Liquid	Sugar in water
Solid	Solid	Alloys such as brass (zinc in copper) and bronze (tin in copper)

Generally, we come across only the following three types of solutions:

- Liquids in Liquids:** In the solution of liquids in liquids such as alcohol in water, the constituent present in smaller amounts is designated as solute and the constituent present in larger amounts is called the solvent. When two liquids are mixed, three different situations may arise:

- (i) Both the liquids are completely miscible, i.e., when, two liquids are mixed, they dissolve in each other in all proportions, e.g., alcohol and water, benzene and toluene.
- (ii) The liquids are partially miscible, i.e., they dissolve in each other only to a certain extent, e.g., water and phenol.
- (iii) The liquids are immiscible, i.e., they do not dissolve in each other, e.g., water and benzene, water and toluene.

The solubility of liquids in liquids generally increases with rise in temperature.

- (b) **Gases in Liquids:** Gases are generally soluble in liquids. Oxygen is sufficiently soluble in water, which allows the survival of aquatic life in ponds, rivers and oceans. Gases like CO_2 and NH_3 are highly soluble in water. The solubility of a gas in a liquid depends on the pressure, temperature and the nature of the gas and the solvent. These factors are discussed below in detail :

- (i) **Effect of Pressure:** The variation of solubility of a gas in a liquid with pressure is governed by *Henry's law*. *Henry's law* states that

The mass or mole fraction, of a gas dissolved in a solvent is directly proportional to the partial pressure of the gas.

Henry's law is represented by

$$x = Kp$$

where K is a constant, p is the partial pressure of the gas and x is the mole fraction of the gas in the solution. Let us now see what are the conditions for the validity of Henry's law.

- (i) **Conditions for validity of Henry's law:** It is found that gases obey Henry's law under the following conditions.
 - (i) the pressure is not too high.
 - (ii) the temperature is not too low.
 - (iii) the gas does not dissociate, associate or enter into any chemical reaction with the solvent.
- (ii) **Effect of temperature:** The solubility of a gas in a liquid at constant pressure decreases with rise in temperature. For example, the solubility of CO_2 in water at 20°C is 0.88 cm^3 per cm^3 of water, where as it is 0.53 cm^3 per cm^3 of water at 40°C . This happens because on heating a solution, containing a dissolved gas, some gas is usually expelled from the solution.
- (iii) **Effect of the nature of the gas and the solvent:** Gases like CO_2 , HCl and, NH_3 are highly soluble in water where as H_2 , O_2 and N_2 , are sparingly soluble.





Notes

- (c) **Solids in liquids:** When a solid is dissolved in a liquid, the solid is referred as the solute and the liquid as the solvent. For example, in a solution of sodium chloride in water, the solute is sodium chloride and water is the solvent. Different substances dissolve to different extent in the same solvent.

7.3 VAPOUR PRESSURE

If we keep an inverted beaker over a small beaker containing a pure liquid, it is found that the molecules of the liquid start evaporating in the form of vapours and fill the empty space above the beaker containing the liquid. A time comes when the number of molecules evaporating per unit time is equal to the number of molecules condensing during that time (Fig. 7.1). An equilibrium is thus established between the vapour and the liquid phase. The pressure exerted by the vapour of the liquid in such a case is called the vapour pressure of the liquid.

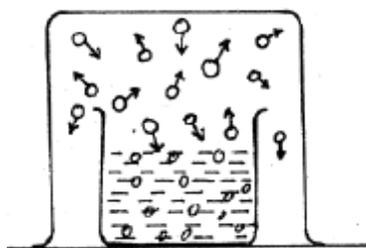


Fig.7.1 : Vapour pressure of a liquid

7.4 RAOULT'S LAW FOR SOLUTIONS

Did you ever think that if you mix two miscible volatile liquids A and B, what would be the vapour pressure of the resulting solution? The relationship between vapour pressure of a liquid and its mole fraction is given by Raoult's law.

Raoult's law states that for a solution of volatile liquids, the partial vapour pressure of each liquid in the solution is directly proportional to its mole fraction.

Raoult's law is applicable only if the liquids are miscible. The vapour phase now consists of vapours of both the liquids A and B. The partial vapour pressure of each liquid will depend upon its mole fraction in the solution. Let the mole fractions of the liquids A and B be X_A and X_B respectively. Also, if P_A and P_B are the partial vapour pressures of A and B respectively, then

$$P_A \propto X_A \text{ or } P_A = P_A^0 X_A$$

Similarly,

$$P_B = p_B^0 X_B$$

where p_A^0 and p_B^0 represent the vapour pressures of pure liquids A and B respectively.

Solutions

If the values of P_A and P_B are plotted against the values of X_A and X_B for a solution, two straight lines are obtained as shown in Fig. 7.2 the total vapour pressure P of the solution is given by the sum of partial vapour pressures P_A and P_B .

Thus,

$$P = P_A + P_B$$

or

$$P = p_A^0 X_A + p_B^0 X_B$$

The total vapour pressure (P) of a solution is represented by the line joining p_A^0 and p_B^0 . The solutions which obey Raoult's law are known as **ideal solutions**.

A solution which obeys Raoult's law over the entire range of concentration at all temperatures is called an ideal solution.

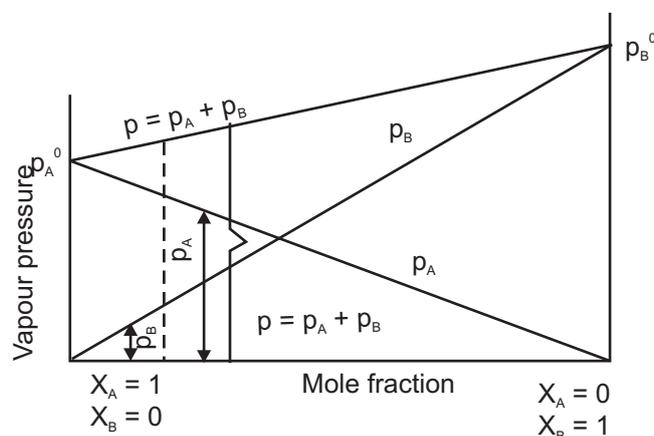


Fig. 7.2 : Relationship between vapour pressure and mole fraction in a solution



INTEXT QUESTIONS 7.2

1. State Raoult's law.
2. State Henry's law and list the conditions necessary for the validity of Henry's law

7.5 RAOULT'S LAW FOR SOLUTIONS CONTAINING NON-VOLATILE SOLUTE

If we have an aqueous solution containing a non-volatile solute, such as sugar or salt, what do you think about the vapour pressure exerted by such a solution? The vapour phase of such a solution consists of vapours of solvent (A) only because the solute is non-volatile. Since the mole fraction of the solvent in solution is less than one, therefore according to Raoult's law, the vapour pressure of the

MODULE - 3

States of matter



Notes



Notes

solution will be less than the vapour pressure of the pure solvent. If the total vapour pressure of the solution is P , then

$$P_A = p_A^0 X_A \quad \dots(7.1)$$

for a binary mixture

$$X_A + X_B = 1$$

therefore,

$$X_A = 1 - X_B$$

Substituting the value of X_A in equation (7.1) we get

$$P_A = p_A^0 (1 - X_B)$$

$$\frac{P_A}{p_A^0} = 1 - X_B$$

therefore,

$$\frac{p_A^0 - P_A}{p_A^0} = X_B$$

In the above equation, $(p_A^0 - P_A)$ represents the lowering of the vapour pressure

and $\frac{p_A^0 - P_A}{p_A^0}$ is called the relative lowering of the vapour pressure of the solution.

An alternative statement of Raoult's law for solutions of non-volatile solute is :

The relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute, when only the solvent is volatile.

7.6 IDEAL AND NON-IDEAL SOLUTIONS

Ideal solutions obey Raoult's Law and during their formation there is no change in heat and volume.

Non-ideal solutions are those solutions which do not obey Raoult's law and whose formation is accompanied by changes of heat and volume.

Most of the real solutions are non-ideal. They show considerable deviation from the ideal behaviour. Generally deviations are of two types;

(i) Positive deviation: Positive deviations are shown by liquid pairs for which the A-B molecular interactions are weaker than the A-A and or B-B molecular interactions. The total vapour pressure for such solutions is greater than predicted by Raoult's law. The total vapour pressure for such a solution will be maximum for a particular intermediate composition (Fig. 7.3)

Examples of non-ideal solutions showing positive deviation from the ideal behaviour are mixtures of liquids such as water-propanol, ethanol-chloroform, acetone- carbon disulfide, ethanol-cyclohexane etc.

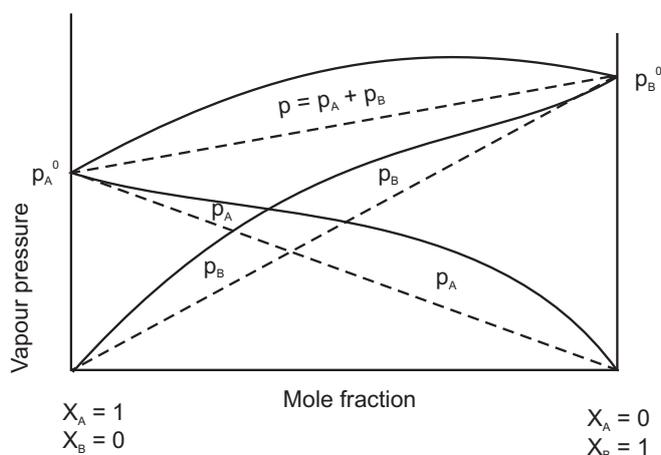


Fig. 7.3 : Positive deviation for a liquid pair

(ii) Negative Deviation: Negative deviations are shown by liquid pairs for which the A-B molecular interactions are stronger than A-A or B-B molecular interactions. The total vapour pressure for such solutions is less than that predicted by Raoult's law. For a particular intermediate composition, the total vapour pressure of such a solution will be minimum (Fig. 7.4). Examples of such liquid pairs are chloroform acetone, water-sulphuric acid, phenol-aniline, water- HCl etc.

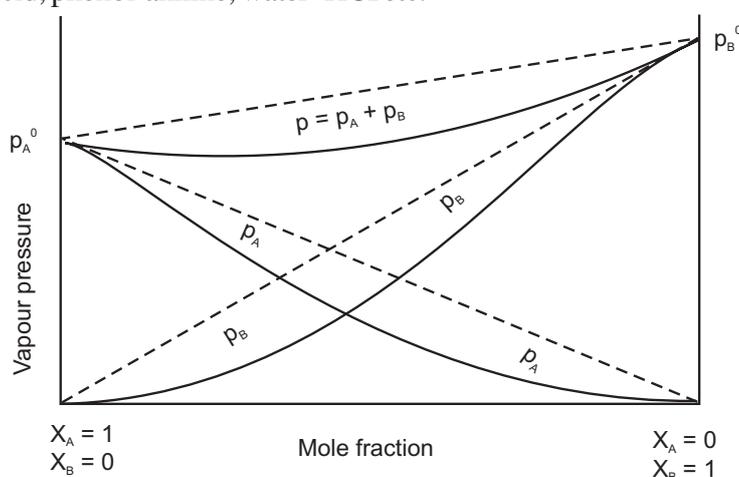


Fig. 7.4 : Negative deviation for a liquid pair

7.7 COLLIGATIVE PROPERTIES

Do you know that there are certain properties of dilute solutions which depend only on the number of particles of solute and not on the nature of the solvent and the solute? Such properties are called **colligative properties**. There are four colligative properties : relative lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure.

We shall discuss these colligative properties in detail in the following sections.



Notes



Notes

7.7.1 Relative Lowering of Vapour Pressure

According to Raoult's law for solutions containing non-volatile solute

$$\frac{P_A^0 - P_A}{P_A^0} = X_B \quad (\text{see section 7.5}) \quad \dots(i)$$

Also
$$X_B = \frac{n_B}{n_A + n_B}$$

In a dilute solution $n_B \ll n_A$. Therefore the term n_B can be neglected in the denominator.

Hence,
$$X_B = \frac{n_B}{n_A} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}} = \frac{W_B \cdot M_A}{W_A \cdot M_B}$$

Therefore equation (i) can be written as

$$\frac{P_A^0 - P_A}{P_A^0} = X_B = \frac{W_B \cdot M_A}{W_A \cdot M_B}$$

The above expression can be used to determine the molecular mass of the solute B, provided the relative lowering of vapour pressure of a solution of known concentration and molecular mass of the solvent are known. However, the determination of molecular mass by this method is often difficult because the accurate determination of lowering of vapour pressure is difficult.

Example 7.5: The relative lowering of vapour pressure produced by dissolving 7.2 g of a substance in 100g water is 0.00715. What is the molecular mass of the substance?

Solution: We know that

$$\frac{P_A^0 - P_A}{P_A^0} = \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

Substituting the values we get

$$0.00715 = \frac{7.2 \times 18}{M_B \times 100} \quad \text{or} \quad M_B = \frac{7.2 \times 18}{0.00715 \times 100}$$

\therefore Molecular mass of the substance = 181.26 amu

7.7.2 Elevation of Boiling Point

Boiling point of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.

As you know, the vapour pressure of a pure solvent is always higher than that of its solution. So, the boiling point of the solution is always higher than that of the pure solvent. If you see the vapour pressure curves for the solvent and the solution (Fig. 7.5), you will find that there is an elevation in the boiling point of the solution.

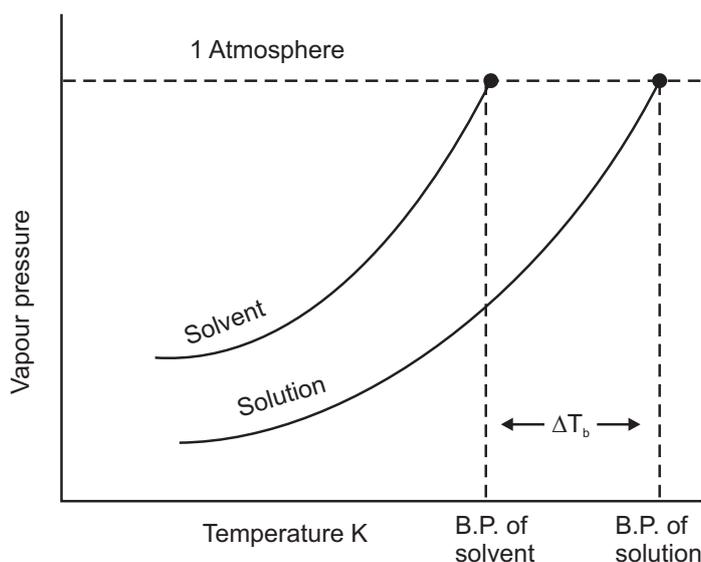


Fig. 7.5 : Vapour pressure curves for solvent and solution

Now let ΔT_b be the elevation in boiling point and Δp be the lowering in vapour pressure. Then,

$$\Delta T_b \propto \Delta p \propto X_B \text{ or } \Delta T_b = K X_B \quad (i)$$

K is the proportionality constant

As you know
$$X_B = \frac{n_B}{n_A + n_B}$$

In a dilute solution, $n_B \ll n_A$ and thus the term n_B is neglected in the denominator.

Thus,
$$X_B = \frac{n_B}{n_A} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A}} = \frac{W_B}{M_B} \times \frac{M_A}{W_A} = n_B \times \frac{M_A}{W_A}$$

Substituting the value of X_B in the equation (i) we get

$$\Delta T_b = K \times n_B \times \frac{M_A}{W_A}$$



Notes



Notes

If we take the mass of the solvent W_A in kilograms the term $\frac{n_B}{W_A}$ is molality m . Thus

$$\Delta T_b = K M_A \cdot m = K_B m$$

The constant K_b is called the **molal elevation constant** for the solvent. K_b may be defined as **the elevation in boiling point when one mole of a solute is dissolved in one kilogram of the solvent**. K_b is expressed in degree per molality.

7.7.3 Depression in Freezing Point

Freezing point is the temperature at which the solid and the liquid forms have the same vapour pressure

The freezing point of the solution is always less than that of the pure solvent. Thus, there is a depression in the freezing point of the solution This is because the vapour pressure of the solution is always less than that of the pure solvent.

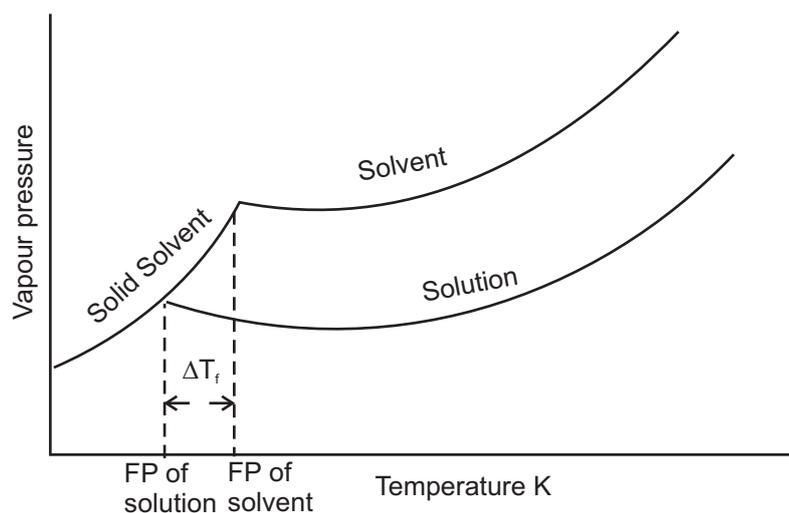


Fig. 7.6 : Vapour pressure curves for solid, solvent and solution

Let ΔT_f be the depression in freezing point. Then:

$$\Delta T_f \propto X_B$$

or

$$\Delta T_f = K X_B \quad \dots(ii)$$

Where K the proportionality constant

You know that

$$X_B = \frac{n_B}{n_A + n_B}$$

In dilute solutions $n_B \ll n_A$

Therefore, the term n_B can be neglected from the denominator. Thus,

$$X_B = \frac{n_B}{n_A} = \frac{W_B / M_B}{W_A / M_A} = \frac{W_B}{M_B} \times \frac{M_A}{W_A} = n_B \times \frac{M_A}{W_A}$$

(since $n_B = \frac{W_B}{M_B}$)

Substituting the value of X_B in equation (ii) we get

$$\Delta T_f = K \times n_B \times \frac{M_A}{W_A}$$

If the mass of the solvent W_A is taken in kg, then the term $\frac{n_B}{W_A}$ becomes molality m .

Thus,
$$\Delta T_f = K M_A \cdot m = K_f \cdot m$$

The constant (K_f) for a solution is known as **molal depression constant or molal cryoscopic constant** for the solvent. K_f may be **defined as the depression in freezing point of a solution when one mole of a solute is dissolved in 1 kilogram of the solvent.**

Example 7.6: Find the (i) boiling point and (ii) freezing point of a solution containing 0.520 g glucose ($C_6H_{12}O_6$) dissolved in 80.2g of water. ($K_f = 1.86$ K/m, $K_b = 0.52$ k/m.)

Solution: Molality of glucose =
$$\frac{\text{Wt. of glucose}}{\text{mol. Wt.}} \times \frac{1000}{\text{Wt. of solvent}}$$

$$= \frac{0.52}{180} \times \frac{1000}{80.2} = 0.036$$

$$\Delta T_b = K_b m = 0.52 \times 0.036 = 0.018 \text{ K}$$

\therefore Boiling point = $373 + 0.018 = 373.018 = 373.02 \text{ K}$

(ii) $K_f = 1.86 \text{ K/m}$

$$m = \frac{0.52}{180} \times \frac{1000}{80.2} = 0.036$$

\therefore $\Delta T_f = 1.86 \times 0.036 = 0.66 \text{ K}$

\therefore Freezing point = $273 - 0.66 = 272.34 \text{ K}$

7.7.4 Osmosis and Osmotic Pressure

You must have observed that if rasins are soaked in water for some time, they swell. this is due to the flow of water into the rasins through its skin which acts



Notes



Notes

as a semipermeable membrane (permeable only to the solvent molecules). This phenomenon is also observed when two solutions of different concentrations in the same solvent are separated by a semipermeable membrane. In this case the solvent flows from a solution of lower concentration to a solution of higher concentration. The process continues till the concentrations of the solutions on both sides of the membrane become equal.

The spontaneous flow of the solvent from a solution of lower concentration (or pure solvent) to a solution of higher concentration when the two are separated by a semipermeable membrane is known as **osmosis**.

The flow of solvent into the solution of higher concentration from a solution of lower concentration (on pure solvent) can be stopped if some extra pressure is applied to that side of the solution which has a higher concentration. The pressure that just stops the flow of the solvent is called **osmotic pressure**.

Thus, *osmotic pressure may be defined as the excess pressure that must be applied to the solution side to just prevent the passage of pure solvent into it when the two are separated by a perfect semipermeable membrane*. This is illustrated in Fig. 7.7.

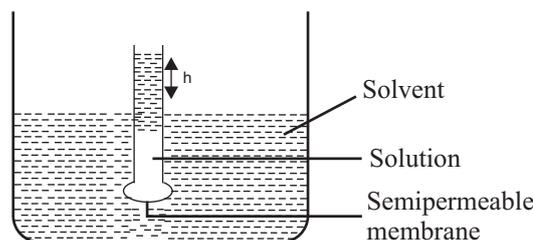


Fig. 7.7 : Osmosis

The pressure that must be applied to the solution side to prevent it from rising in the tube is the osmotic pressure. It is also equal to the hydrostatic pressure of the liquid column of height h .

If the two solutions have the same osmotic pressure, they are known as **isotonic** solutions. The osmotic pressure is a colligative property. It depends on the number of particles of solute present in the solution and not on their nature. At a given temperature T , the osmotic pressure (π) of a dilute solution is experimentally found to be proportional to the concentration of the solution in moles per litre.

Mathematically,
$$\pi = CRT$$

where π is the osmotic pressure and R is the gas constant

or
$$\pi = \frac{n_B}{V} RT$$

where n_B is the number of moles of solute present in V litres of the solution

$$\text{or} \quad \pi V = \frac{w}{M_{\text{solute}}} RT$$

where w is the mass of solute dissolved in V litres of the solution and M_{solute} is the molar mass of the solute. Thus, knowing π , V and w , the molar mass of the solute can be calculated.

Thus, the molar masses of the solutes can be determined by measuring the osmotic pressure of their solutions. This method has been widely used to determine the molar masses of macromolecules, proteins, etc., which have large molar masses and limited solubility. Therefore their solutions have very low concentrations and the magnitudes of their other colligative properties are too small to measure. yet their osmotic pressures are large enough for measurements. As the osmotic pressure measurements are done at around room temperature, this method is particularly useful for determining the molar masses of biomolecules as they are generally not stable at higher temperature.

Example 7.7 : The osmotic pressure of an aqueous solution of a protein containing 0.63 g of a protein in 100 g of water at 300 K was found to be 2.60×10^{-3} atm. Calculate the molar mass of the protein. $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$.

We know that osmotic pressure of a solution is given by the expression

$$\pi V = \frac{w}{M_{\text{solute}}} RT$$

$$\text{or} \quad M_{\text{solute}} = \frac{w}{\pi V} RT$$

Substituting the values, we get

$$\begin{aligned} M_{\text{solute}} &= \frac{(0.63\text{g}) \times (0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{(2.60 \times 10^{-3} \text{ atm}) \times (0.100 \text{ L})} \\ &= 61022 \text{ g mol}^{-1} \end{aligned}$$

Thus, molar mass of the protein is 61022 g mol^{-1} .

Reverse Osmosis and Water Purification

If a pressure higher than the osmotic pressure is applied to the solution side, the direction of flow of the solvent can be reversed. As a result, the pure solvent flows out of the solution through the semipermeable membrane. This process is called **reverse osmosis**. It is of great practical application as it is used for desalination of sea water to obtain pure water.



Notes



Notes



INTEXT QUESTIONS 7.3

1. Define colligative property. List two colligative properties.
2. What type of liquid pairs show (i) positive deviations (ii) negative deviations.
3. Why is the determination of osmotic pressure a better method as compared to other colligative properties for determining the molar masses of biomolecules.

7.8 ABNORMAL COLLIGATIVE PROPERTIES

The colligative properties of the solutions depend only upon the number of solute particles present in the solution and not on their nature. But sometimes while measuring colligative properties abnormal results are obtained due to the following reasons :

- (i) If the solution is very concentrated, the particles of the solute start interacting with each other. Therefore, the solution should not be concentrated.
- (ii) In case of **association** two or more solute molecules associate to form a bigger molecule. The number of effective molecules in the solution, therefore decreases. Consequently, the value of the colligative property (relative lowering of vapour pressure, elevation of boiling point, depression of freezing point, osmotic pressure) is observed to be less than that calculated on the basis of unassociated molecules. Since, the colligative property is inversely proportional to the molar mass, the molar mass of such solutes calculated on the basis of colligative property will be greater than the true molar mass of the solute.
- (iii) **In case of dissociation** of the solute in the solution, the number of effective solute particles increases. In such cases the value of the observed colligative property will be greater than that calculated on the basis of undissociated solute particles. The molar mass of the solute calculated from the measurement of colligative property will be lower than the true molar mass of the solute.

Van't Hoff factor

In order to account for extent of association or dissociation Van't Hoff introduced a factor 'i'.

$$i = \frac{\text{Observed colligative property}}{\text{Normal (calculated or expected) colligative property}}$$

Since the colligative property is proportional to the number of solute particles or the number of moles of solute

$$i = \frac{\text{Total number of moles of solute in the solution}}{\text{Expected (calculated) number of moles of solute}}$$

Also, since colligative properties vary inversely as the molar mass of the solute, it follows that

$$i = \frac{\text{Normal (calculated or expected) molar mass}}{\text{Observed molar mass}}$$

Here the observed molar mass is the experimentally determined molar mass whereas the normal molar mass is the molar mass calculated on the basis of chemical formula of the solute. In case of association the value of van't Hoff factor, i , is less than unity while for dissociation it is greater than unity. For example, benzoic acid associates in benzene to form a dimer. The value of i is, therefore, close to $1/2$. The value of i for aqueous NaCl is close to 2.0 because NaCl dissociates in water to form Na^+ and Cl^- ions.

The inclusion of van't Hoff factor, i , modifies the equations for the colligative properties as follows :

$$\frac{P_A^0 - P_A}{P_A^0} = i X_B$$

$$\Delta T_b = i K_b m$$

$$\Delta T_f = i K_f m$$

$$\pi V = i CRT$$

Degree of Association

Degree of association may be defined as the fraction of the total number of molecules which associate to form a bigger molecule. Let us consider the association of benzoic acid in benzene. In benzene two molecules of benzoic acid associate to form a dimer. It can be represented as



If x represents the degree of association of benzoic acid in benzene (i.e out of one molecule of benzoic acid, x molecules associate to form a dimer), then at equilibrium.

No. of moles of unassociated benzoic acid = $1 - x$

No of moles of associated benzoic acid = $\frac{x}{2}$

Total number of effective moles of benzoic acid = $1 - x + \frac{x}{2} = 1 - \frac{x}{2}$



Notes



Notes

According to definition, Van't Hoff factor is given by

$$i = \frac{\text{Total number of moles of solute in the solution}}{\text{Expected (calculated) number of moles of solute}} = \frac{1 - \frac{x}{2}}{1}$$

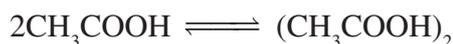
Example 7.8 : Acetic acid (CH_3COOH) associates in benzene to form double molecules. 1.60 g of acetic acid when dissolved in 100 g of benzene (C_6H_6) raised the boiling point by 273.35 K. Calculate the van't Hoff factor and the degree of association of benzoic acid. K_b for $\text{C}_6\text{H}_6 = 2.57 \text{ K kg mol}^{-1}$.

Solution :
$$\Delta T_b = i k_b m = \frac{1000 i K_b W_B}{W_A M_B}$$

Normal molar mass (M_B) of $\text{CH}_3\text{COOH} = 60 \text{ g mol}^{-1}$

$$\begin{aligned} \text{Van't Hoff factor, } i, \text{ is} &= \frac{\Delta T_b \times W_A \times M_B}{1000 \times K_b \times W_B} \\ &= \frac{0.35 \times 100 \times 60}{1000 \times 2.57 \times 1.60} \\ &= 0.51 \end{aligned}$$

Since, acetic acid associates in benzene to form double molecules, the following equilibrium exists in the solution.



If x represents the degree of association of the solute, then we would have $(1-x)$ mol of acetic acid left unassociated and $x/2$ moles of acetic acid at equilibrium.

$$\begin{aligned} \text{Therefore, total number of particles at equilibrium} &= 1 - x + x/2 \\ &= 1 - \frac{x}{2} \end{aligned}$$

The total number of particles at equilibrium equal van't Hoff factor. But van't Hoff factor (i) is equal to 0.51.

$$\therefore 1 - \frac{x}{2} = 0.51$$

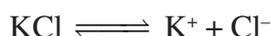
$$\text{or } \frac{x}{2} = 1 - 0.51 = 0.49$$

$$x = 0.49 \times 2 = 0.98$$

Therefore, degree of association of acetic acid in benzene is 98%,.

Degree of dissociation

Degree of dissociation may be defined as the fraction of the total number of particles that dissociate, i.e., break into simpler ions. Consider a solution of KCl in water. When KCl is dissolved in water, it dissociates into K^+ and Cl^- ions.



let x be the degree of dissociation of KCl, then at equilibrium, number of moles of undissociated $KCl = 1 - x$

According to the dissociation of KCl shown above, when x mol of KCl dissociates, x moles of K^+ ions and x mol of Cl^- ions are produced

Thus, the total number of moles in the solution after dissociation

$$= 1 - x + x + x = 1 + x$$

Hence,
$$i = \frac{\text{Total number of moles of solute in the solution}}{\text{Expected (calculated) number of moles of solute}} = \frac{1 + x}{1}$$

Example 7.9 : A 0.5 percent aqueous solution of potassium chloride was found to freeze at 272.76 K. Calculate the van't Hoff factor and the degree of dissociation of the solute at this concentration. (K_f for $H_2O = 1.86 \text{ K kg mol}^{-1}$).

Solution : Normal molecular weight of KCl = $39 + 35.5 = 74.5 \text{ g mol}^{-1}$

$$\begin{aligned} \text{Observed molecular weight, } M_B &= \frac{1000 \times W_B \times K_f}{\Delta T_f \times W_A} \\ &= \frac{1000 \times 0.5 \text{ g} \times 1.86 \text{ K kg mol}^{-1}}{(0.24 \text{ K}) \times 100 \text{ g}} \\ &= 38.75 \text{ g mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{van't Hoff factor (i)} &= \frac{\text{Normal molecular weight}}{\text{Observed molecular weight}} \\ &= \frac{74.5 \text{ g mol}^{-1}}{38.75 \text{ g mol}^{-1}} = 1.92 \end{aligned}$$

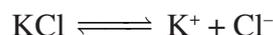


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Potassium chloride in aqueous solution dissociates as follow.



Let x be the degree of dissociation of KCl. Thus at equilibrium,

No. of moles of KCl left undissociated = $(1 - x)$ mol

No. of moles of $\text{K}^+ = x$ mol

No. of moles of $\text{Cl}^- = x$ mol

Total number of moles at equilibrium = $1 - x + x + x = 1 + x$

$$\therefore \text{Van't Hoff factor} = \frac{1+x}{1} = 1.92$$

$$\text{or } x = 1.92 - 1 = 0.92$$

$$\therefore \text{Degree of dissociation of KCl} = 92\%$$



WHAT YOU HAVE LEARNT

- Solution is a homogeneous mixture of two or more substances.
- Solvent is that component of a solution that has the same physical state as the solution itself.
- Solute is the substance that is dissolved in a solvent to form a solution.
- Molarity is expressed as the number of moles of solute per litre of solution.
- Molality is expressed as the number of moles of solute per kilogram of solvent.
- Normality is a concentration unit which tells the number of gram equivalents of solute per litre of solution.
- Mole fraction is the ratio of the number of moles of one component to the total number of moles in the solution.
- Solutions can be solid, liquid or gaseous.
- Henry's law states that mass or mole fraction of a gas dissolved in a solvent is directly proportional to the partial pressure of the gas.
- Raoult's law states that for a solution of volatile liquids, the partial pressure of each liquid in the solution is directly proportional to its mole fraction.
- A solution which obeys Raoult's law over the entire range of concentration at all temperatures is called an ideal solution.

- The relative lowering of vapour pressure for a solution is equal to the mole fraction of the solute, when only the solvent is volatile.
- Those properties of dilute solutions which depend only on the number of particles of solute and not on their nature are known as colligative properties.
- Molal elevation constant is the elevation in boiling point when one mole of solute is dissolved in one kilogram of the solvent.
- Boiling point of a liquid is the temperatures at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.
- Freezing point is the temperature at which the solid and the liquid forms of the substance have the same vapour pressure.
- Abnormal result are obtained when the solute associates or dissociates in the solution.
- Van't Hoff factor is defined as the ratio of normal molar mass to experimentally determined molar mass.



TERMINAL EXERCISE

1. What do you understand by ideal and non-ideal solutions?
2. Define freezing point and boiling point.
3. Derive the relationship $\Delta T_b = K_b m$
4. A solution containing 7 g of a non-volatile solute in 250 g of water boils at 373.26 K. Find the molecular mass of the solute.
5. 2 g of a substance dissolved in 40 g of water produced a depression of 274.5 K in the freezing point of water. Calculate the molecular mass of the substance. The molal depression constant for water is 274.85 K per molal.
6. Calculate the mole fraction of the solute in a solution obtained by dissolving 10 g of urea (mol wt 60) in 100 g of water.
7. A solution containing 8.6 g of urea (molar mass = 60 per dm^3) was found to be isotonic with a 5 per cent solution of an organic non-volatile solute. Calculate the molar mass of the non-volatile solute.
8. 2 g of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molar depression constant for benzene is 4.9 K kg mol^{-1} . What is the percentage association of $\text{C}_6\text{H}_5\text{COOH}$ if it forms double molecules in solution.



Notes



Notes



ANSWERS TO INTEXT QUESTIONS

9. The freezing point depression of 5.0×10^{-3} M solution of Na_2SO_4 in water was found to be 0.0265°C . Calculate the degree of dissociation of the salt at this concentration. (K_f for H_2O is $1.86 \text{ K kg mol}^{-1}$)

7.1

- Molarity, Molality, Normality, Mole fraction, Mass percentage.
Molarity is the number of moles of solute dissolved per litre of the solution.
- Molality is the number of moles of solute dissolved per kg of solvent.
Normality is the number of gram equivalents of solute dissolved per litre of solution.

7.2

- For a solution of volatile liquids the partial vapour pressure of each liquid is proportional to its mole fraction.
- The mass of a gas dissolved in a solvent is directly proportional to its partial pressure. Pressure should not be too high Temperature should not be too low. The gas should not associate or dissociate.

7.3

- Properties that depend upon the number of particles of solute and not on the nature of solute. e.g. Elevation of boiling point, depression of freezing point.
- For which A–B molecular interactions are:
 - weaker than A–A and B–B interactions.
 - stronger than A–A and B–B interactions.
- At low concentration the magnitude of osmotic pressure is large enough for measurement.