Colligative Properties

……

INTRODUCTION

A colligative property of a system is one which depends only on the number of particles present in solution and not in any way on the nature of the particles. The various colligative properties which are consider here (a) vapour pressure lowering of the solvent; (b) boiling point elevation of the solution; (c) freezing point depression of the solution and (d) osmotic pressure of the solution. Solutions may be divided into two categories, viz., (i) solutions of nonelectrolytes where the dissolved solute persists in the same form as it exists in the solid form, i.e., it does not show any tendency to undergo association or dissociation, and (ii) solutions of electrolytes which undergo either association or dissociation in solution yielding smaller or larger number of particles respectively. Consequently, the colligative properties will show an enhanced value in dissociation and a lower value in association. These properties for solutions of nonvolatile nonelectrolytic solutes will be discussed here mostly. Furthermore, it is assumed that the solutions are dilute, i.e., the interactions between the solute-solvent particles are negligibly small and the solutions behave ideally.

Colligative properties have been extensively used in the determination of molar masses of dissolved substances which are nonvolatile.

IDEAL SOLUTIONS-RAOULTS LAW

As the concept of an ideal gas has been used in the study of many thermodynamic properties, it would be helpful to find out some similar concept in case of solutions. An ideal solution is defined as the one in which there is complete uniformity in cohesive forces. The solute-solute, solvent-solvent and solute-solvent interactions are identical. Thus, if there are two components A and B forming an ideal solution, then the intermolecular forces between A-A, A-B and B-B are essentially equal.

Characteristics of an Ideal Solution: An ideal solution possesses the following characteristics:

(i) When two pure substances mix to form an ideal solution, there is no evolution or absorption of heat, i.e., the heat of mixing (ΔH_{mixing}) is zero.

(ii) The total volume of an ideal be equal to the sum of the volumes of the components mixed, i.e., the volume. of mixing (ΔV_{mixing}) is zero.

(iii) The ideal solution must obey Raoult's and Henry's law over the whole range of concentration.

Raoult's Law: An important property in the theory of solutions is the vapour pressure of a component above solution. The partial vapour pressure is a measure of the tendency of molecules of the components to escape from solution into the vapour phase. If we have an ideal solution containing volatile components 1 and 2, then the tendency of molecules 1 or 2 to escape is the same whether it is surrounded entirely by 1 molecules or by 2 molecules or partly by both 1 and 2. The vapours present above the solution (due to the escaping tendency) are in equilibrium and exert definite vapour pressures. In an ideal solution, therefore, each component exerts its equilibrium vapour pressure and the total vapour pressure is the sum of the individual vapour pressure of the components according to Dalton's law of partial pressure. If p_1 and p_2 are the partial pressures of two components 1 and 2, then the total pressure P is equal to $p_1 + p_2$ is found experimentally that the vapour pressure of the individual components of an ideal can be easily determined by Raoult's law. ***This law states that at a given temperature the vapour pressure of any volatile component of a solution is directly proportional to its mole fraction in the solution.*** If p_s is the vapour pressure of the solution and X_1 its mole fraction in the solution, then

$$p_s \infty X_1$$

$$p_s = \text{Const. } X_1$$

The value of the constant can be obtained using initial conditions. If $X_1 = 1$ (pure component), p_s = constant = p^0 = vapour pressure of the pure component. So we have

$$p_s = p^0 X_1 \qquad \text{.......... ....} \quad (1)$$

and

For a binary solution of two volatile components 1 and 2, we have

$$p_1 = p_1^0 X_1 \qquad \text{.......... ....} \quad (2a)$$

$$p_2 = p_2^0 X_2 \qquad \text{.......... ....} \quad (2b)$$

where X_1 and $X_2$are the mole fractions of 1 and 2 in the solution. An ideal solution obeys Raoult's law over the whole range of concentration. The total vapour pressure P of the solution is given by

$$\text{Since } P = p_1 + p_2 = p_1^0 X_1 + p_2^0 X_2 \qquad \text{.......... ....} \quad (3)$$

$$X_1 + X_2 = 1$$

or $$X_1 = 1 - X_2$$

Therefore, Eq. (3) can be written as $P = p_1^0 (1 - X_2) + p_2^0 X_2$

$$= p_1^0 + X_2 (p_2^0 - p_1^0) \qquad \text{.......... ....} \quad (4)$$

The relations (3 - 4) are such that if p_1 , p_2 and P are plotted against mole fraction of either of the components in the solution, say X_2 at a given temperature, straight lines will result. These plots are shown in Fig. 1.

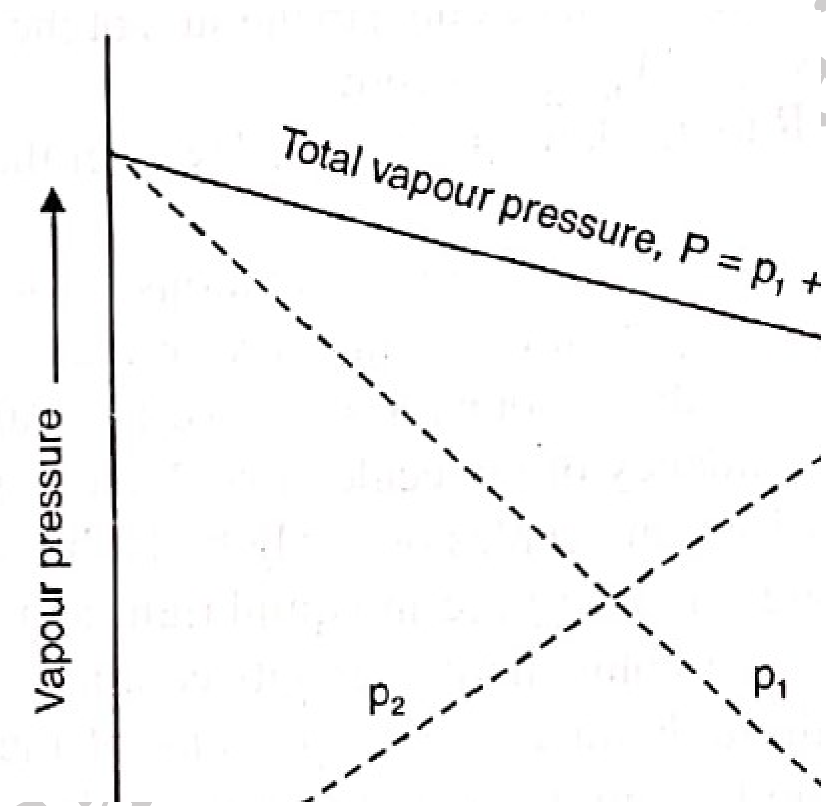

Fig. 1: Total and partial vapour pressures of ideal solutions

In Fig.1 , the dotted lines represent the plots of Eq. (2) for the partial pressures of 1 and 2. These lines pass through the origin indicating that both components are behaving ideally. When $X_2 = 1$ i.e., only pure component 2 is present, $P = p_2^0$ whereas, if $X_2 = 0$ i.e., pure component 1 is present, $P = p_1^0$. The solid line indicates the total vapour pressure of the ideal solution. At any concentration, the total pressure is the sum of the partial pressures of two components. Raoult's law may be regarded as a special case of Henry's law. From Eq. (1), we have $p_2 = K_H X_2$.

In case when Henry's law is applicable over the whole range of concentration, that is, from an infinitely dilute solution ($X_2 \rightarrow 0$, pure solvent) to the liquid solute ($X_2 \rightarrow 1$ pure solute), then p_2 would become the vapour pressure of the pure solute. Hence

$$p_2^0 = K_H$$

Substituting this value of K_H in the above equation, we get $p_2 = p_2^0 X_2$

This expression is identical with the Raoult's law Eq. (3) for a volatile solute. All systems which obey Raoult's law must satisfy Henry's law, but the reverse will only be true if Henry's law applies over the whole range of concentration.

LOWERING OF VAPOUR PRESSURE OF SOLVENT

Whenever a non volatile substance is dissolved in a solvent, the vapour pressure of the solvent is lowered. The lowering of the vapour pressure can be readily understood in terms of the Raoult's law. Consider a solution obtained from a non-volatile solute dissolved in a solvent. Let X_1 and X_2 be the mole fractions of the solvent and solute and P^o and P_s, be the vapour pressures of the pure solvent and the solution respectively. Then according to Raoult's law

$$P_s = P^o X_1 \qquad \text{.......... ....} \quad (5)$$

Since X_1, is always less than unity, hence P_s, is less then P^o, i.e., the vapour pressure of the solution is less than that of pure solvent. Thus, the addition of a non electrolytic solute to the solvent tends to lower the vapour pressure of the pure solvent. Therefore, the lowering in vapour pressure, ΔP, is given as

$$\Delta P = P^o - P_s = P^o - P^o X_1 = P^o (1 - X_1) = P^o X_2 \qquad \text{....... ....} \quad (6)$$

The above equation can be written as

$$\Delta P / P^o = (P^o - P_s) / P^o = X_2 \qquad \text{....... ....} \quad (7)$$

The quantity $(P^o - P_s) / P^o$ is known as the relative lowering of vapour pressure and is independent of the nature of the solute or solvent. However, it depends only on the mole fraction of the solute and is independent of the temperature at which it is measured. Equation (7) can now be written as

$$(P^o - P_s) / P^o = X_2 = n_2/(n_1 + n_2) \qquad \text{....... ....} \quad (8)$$

where n_1 and n_2 are the number of moles of solvent and solute respectively. For a dilute solution $n_1 >> n_2$, hence

$$(P^o - P_s) / P^o \approx n_2/n_1 \qquad \text{....... ....} \quad (9)$$

For a definite quantity of a solvent, n_1 and P^o are both constants, therefore, Equation (9) shows that the relative lowering of vapour pressure of a solvent is directly proportional to the number of moles of the solute. In other words, the relative lowering of vapour pressure of the solvent depends on the concentration of the solute only. Equation (8) can be used in determining the molar mass of the solute provided the vapour pressures of the pure solvent and the solution are known. Since

$$n_2 = W_2/M_2 \quad \text{and} \quad n_1 = W_1/M_1$$

where W_1 and W_2 are the masses of the solvent and the solute and M_1 and M_2 their molar masses respectively. Putting these values of n_1 and n_2 in Eq. (8), we get

$$\frac{P^0 - P_s}{P^0} = \frac{W_2/M_2}{W_1/M_1}$$

$$= \frac{W_2\, M_1}{W_1\, M_2}$$

or

$$M_2 = \left(\frac{P^0}{P^0 - P_s}\right)\left(\frac{W_2}{W_1}\right) M_1 \qquad \text{........ ....} \quad (10)$$

Problem 1: The vapour pressure of water at 293 K is 17.540 mm Hg and the vapour pressure of a solution of 0.10824 kg of a nonvolatile solute in 1 kg of water at the same temperature is 17.354 mm Hg. Calculate the molar mass of the solute.

Solution:

Colligative Properties

$$P^0 = 17.540 \text{ mm Hg} = \frac{1.013 \times 10^5 \times 17.54}{760} \text{ Nm}^{-2} = 2.337 \times 10^3 \text{ Nm}^{-2}$$

$$P_s = 17.354 \text{ mm} = \frac{1.013 \times 10^5 \times 17.354}{760} \text{ N m}^{-2} = 2.313 \times 10^3 \text{ N m}^{-2}$$

$W_2 = 0.10824$ kg

$M_2 = ?$

$W_1 = 1$ kg

$M_1 = 18 \times 10^{-3}$ kg mol^{-1}

We know $$\frac{P^0 - P_s}{P^0} = \frac{W_2 M_1}{M_2 W_1}$$

or $$M_2 = \frac{W_2 \times M_1 \times P^0}{W_1 \left(P^0 - P_s\right)}$$

$$= \frac{(0.10824 \text{ kg})(18 \times 10^{-3} \text{ kg mol}^{-1})(2.337 \times 10^3 \text{ N m}^{-2})}{(1 \text{ kg})(0.024 \times 10^3 \text{ N m}^{-2})}$$

$$= 0.1837 \text{ kg mol}^{-1}$$