E-Content on
TOPIC: COLLIGATIVE PROPERTIES
Sub: Physical Chemistry
BSc Part I

By

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Introduction

Raoult's law:

In 1986, a French Chemist named Francois Marte Raoult proposed a quantitative relation between partial pressure and mole fraction of volatile liquids. The law states that partial vapour pressure of a solvent in a solution is equal to the vapour pressure of the pure solvent multiplied by its mole fraction in the solution.

Mathematically, Raoult's law equation is written as;

$$\textbf{P}_{\textbf{solution}} = \textbf{X}_{\textbf{solvent}} \textbf{P}^{\textbf{0}}_{\textbf{solvent}}$$

Where,

$P_{solution}$ = vapour pressure of the solution

$X_{solvent}$ = mole fraction of the solvent

$P^{0}_{solvent}$ = vapour pressure of the pure solvent

Ideal and Non-ideal solutions

On the basis of Raoult's Law, liquid-liquid solutions are classified into two types of solutions, they are:

- *Ideal Solutions*

- *Non-ideal Solutions*

The solutions which obey Raoult's law at all compositions of solute in solvent at all temperature are called **ideal solutions**.

An ideal solution should have following characteristics

- It should obey Raoult's law

- Δ Hmixing = 0, i.e. no heat should be absorbed or evolved during mixing

- ΔVmixing = 0, i.e. no expansion or contraction on mixing

- Two liquids A and B form an ideal solution when A –A and B–B molecular attractions will be same and hence A–B molecular atrraction will be almost same as A–A and B–B molecular attraction.

$$P_A = X_A P^0_A$$
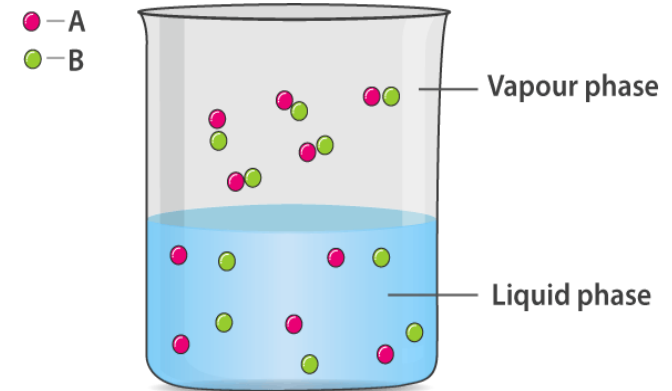
Where P_A is the partial pressure of A.

P^0_A is vapour pressure of pure A at that temperature.

X_A is mole fraction of A in the liquid phase.

Similarily, $P_B = X_B P^0_B$

Examples of Ideal solutions:
✓Ethyl chloride and ethyl bromide
✓n–hexane and n–heptane
✓CCl4 and SiCl4

- The solution which deviate from ideal behavior are called **non** *ideal solution* or *real solutions* and they do not obey Raoult's law over entire range of composition.

- It has been found that on increasing dilution, a non ideal solution tend to be ideal.

- For non ideal so

$$P_A \neq X_A P^0_A$$

- i.e, they do not obey Raoult's law

$\Delta Hmixing \neq 0$ • $\Delta Vmixing \neq 0$

- **Case: I**
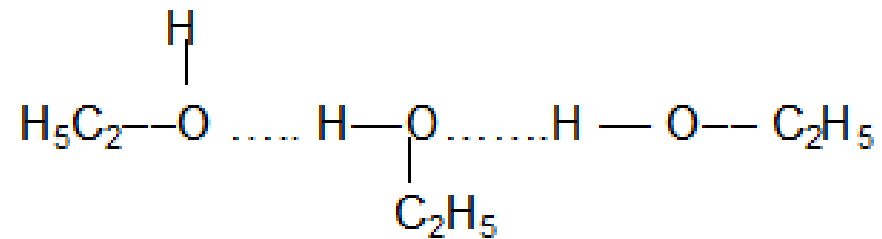
$$P_A > X_A P_A^0 \ \& \ P_B > X_B P_B^0$$

$$\Delta H_{mix} > 0$$

$$\Delta V_{mix} > 0$$

Such a solution shows *positive deviation* from Raoult's Law

e.g. cyclohexane and ethanol.

$$H_5C_2\!-\!\!O \ ..... \ H\!-\!\!\underset{\underset{C_2H_5}{|}}{\overset{\overset{H}{|}}{O}} ......H \longrightarrow O\!-\!\!C_2H_5$$

(In ethanol the molecules are held together due to hydrogen bonding, when cyclohexane is added to ethanol the molecules of cyclohexane tend to occupy the space between ethanol molecules due to which some hydrogen bonds break due to which inter molecular attraction between cyclohexane and ethanol is reduced and hence show higher vapour pressure.)

- **Case: II**

$$P_A < X_A P_A^0, \qquad P_B < X_B P_B^0$$

$$\Delta H_{mix} < 0$$

$$\Delta V_{mix} < 0$$

Solutions of above type show ***negative deviation*** from Raoult's law and their observed boiling point is found to be higher than the calculated value

eg. When acetone and chloroform are mixed together a hydrogen bond is formed between them which increases inter molecular attraction between them and hence decreases the vapour pressure.
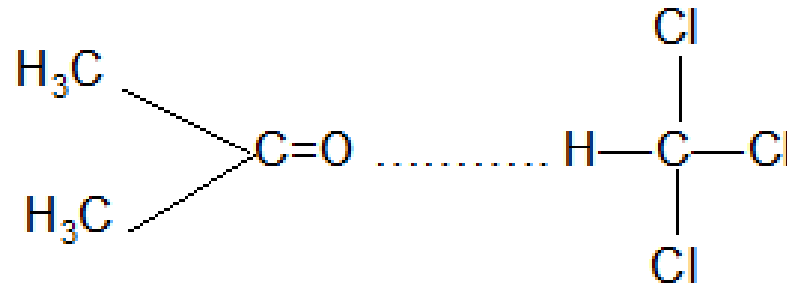
Colligative properties

The dilute solutions show more or less ideal behavior and obey Raoult's law. The properties of dilute solutions which depend only on number particles of solute present in the solution and not on their identity are called *colligative properties.*

Here the solute is assumed to be *non-volatile.*

The various colligative properties are:

- Lowering of vapour pressure

- Elevation of boiling point

- Depression of freezing point

- Osmotic pressure

Lowering of vapour pressure

- when a non-volatile solute is dissolved in a liquid, the vapour pressure of the solution becomes lower than the vapour pressure of the pure solvent.

- Let us consider n moles of a non-volatile solute is dissolved in N moles of a volatile solvent. Then mole fraction of the solvent, $X_1 = N/(n+N)$ and mole fraction of the solute, $X_2 = n/(N+n)$.

- According to Raoult's law, the vapour pressure of a solvent (P_1) in an ideal solution is given by the expression;

$$P_1 = X_1 P_1^0 \cdots\cdots\cdots (1)$$

where P_1^0 is the vapour pressure of the pure solvent. Since $X_1 + X_2 = 1$, Eq. 1 may be written as

$$P_1 = (1 - X_2)P_1^0 \qquad \ldots(2)$$

$$\text{or} \quad P_1/P_1^0 = 1 - X_2$$

$$\text{or} \quad \boxed{\frac{P_1^0 - P_1}{P_1^0} = X_2} \qquad \ldots(3)$$

Equation 3 can be stated as
"The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute present in the solution.'

- Since mole fraction of the solute, X_2 is given by $n/(N+n)$, Equation (3) may be expressed as

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{n}{N+n} \qquad \dots (4)$$

- From Equation (4) that the lowering of vapour pressure of a solution depends upon the number of moles (and hence on the number of molecules) of the solute and not upon the nature of the solute dissolved in a given amount of the solvent. Hence, *lowering of vapour pressure is a colligative property.*

Determination of Molar Masses from Lowering of Vapour Pressure

- It is possible to calculate molar masses of non-volatile non-electrolytic solutes by measuring vapour pressures of their dilute solutions.

- Suppose, a given mass, w gram, of a solute of molar mass m, dissolved in W gram of solvent of molar mass M, lowers the vapour pressure from P_1^0 to P_1. Then, by equation (4)

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{n}{N+n} = \frac{w/m}{W/M + w/m} \qquad \ldots(5)$$

Since in dilute solutions, n is very small as compared to N, Equation (5) may be put in the approximate form as

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{n}{N} = \frac{w/m}{W/M} = \frac{wM}{Wm} \qquad or, \; m = \frac{wM}{W \; (P_1^0 - P_1)/P_1^0} \qquad \ldots(6)$$

Elevation of boiling point

- The boiling point of a liquid is the temperature at which its *vapour* pressure becomes equal atmospheric pressure. Since

- Addition of a non-volatile solute lowers the vapour pressure of the solvent

- The vapour pressure of a solution is always lower than that of the pure solvent, and hence it must be heated to a higher temperature to make its vapour pressure equal to atmospheric pressure.

- Thus the solution boils at a higher temperature than the pure solvent. If T_b^0 is the boiling point of the solvent and T_b is the boiling point of the solution, the difference in boiling points (ΔT_b) is called the ***elevation of boiling point***
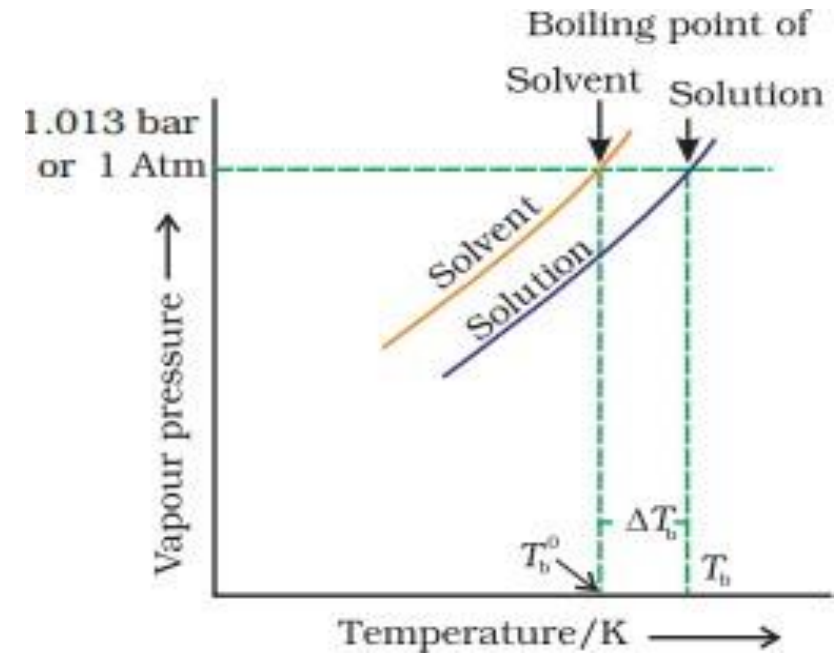
$\Delta T_b = T_b - T_b^0$

$T_b \alpha$ m

$\Delta T_b = K_b \times$ m

Kb : molal elevation constant or
      Ebullioscopic constant

m : molality of the solution

Boiling point elevation in a dilute solution is directly proportional to the number of moles of the solute dissolved in a given amount of the solvent and is quite independent of the nature of the solute. Hence, *boiling point elevation is a colligative property*

- **_Molal boiling point elevation constant or ebullioscopic constant_** of the solvent, is defined as _the elevation in boiling point which may theoretically be produced by dissolving one mole of any solute in 1000 g of the solvent._

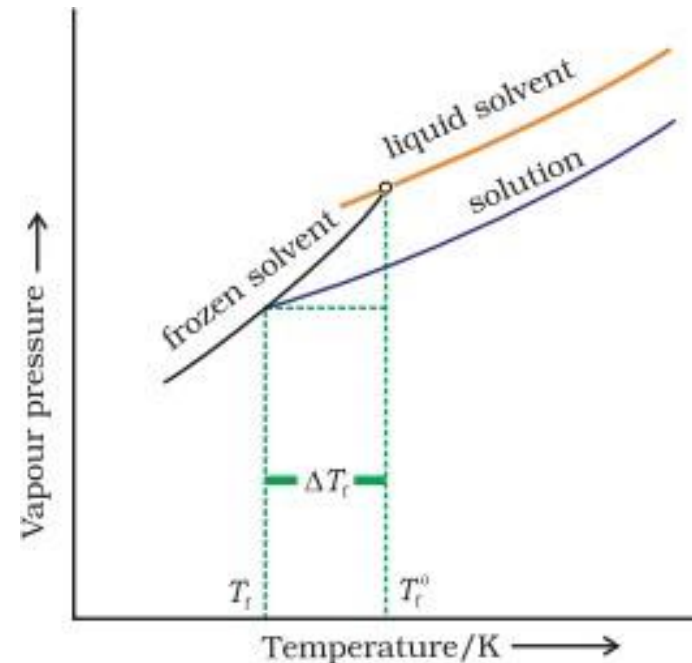$$\Delta T_b = \frac{1000 \times K_b \times w}{m_1 \times W},$$

where m1 = molecular weight of solute and w and W are weights of solute and solvent

DEPRESSION OF FREEZING POINT BY A NON-VOLATILE SOLUTE

- *Freezing point is the temperature at which solid and liquid states of a substance have the same vapour pressure.*

- It is observed that the freezing point of the solution (T_f) containing non volatile solute is always less than the freezing point of the pure solvent (T_f^0). Thus, $T_f^0 - T_f = \Delta T_f$

- It can be seen that $T_f \, \alpha \, m$ or, $\Delta T_f = K_f \times m$

K_f : molal freezing point depression constant

of the solvent or cryoscopic constant

m : molality of the solution

- Molal freezing point depression constant of the solvent or cryoscopic constant, is defined as the depression in freezing point which may theoretically be produced by dissolving 1 mole of any solute in 1000g of the solvent.

$$\Delta T_f = \frac{1000 \times K_f \times w}{m_1 \times W}$$

 where m_1 = molecular weight of solute and w and W are weights of solute and solvent

- Thus, freezing point depression of a dilute solution is directly proportional to the number of moles of the solute dissolved in a given amount of the solvent and is independent of the nature of solute.

OSMOSIS AND OSMOTIC PRESSURE

*The phenomenon of the passage of pure solvent from a region of lower concentration (of the solution) to a region of its higher concentration through a semi-permeable membrane is called **osmosis**.*

The difference in the pressure between the solution And the solvent system is called ***osmotic pressure***. It is the excess pressure which must be applied to a solution in order to prevent flow of solvent into the solutionthrough the semi-permeable membrane.

Osmosis

Concentrated solution

Water (solvent)

Osmotic pressure

Semipermeable membrane
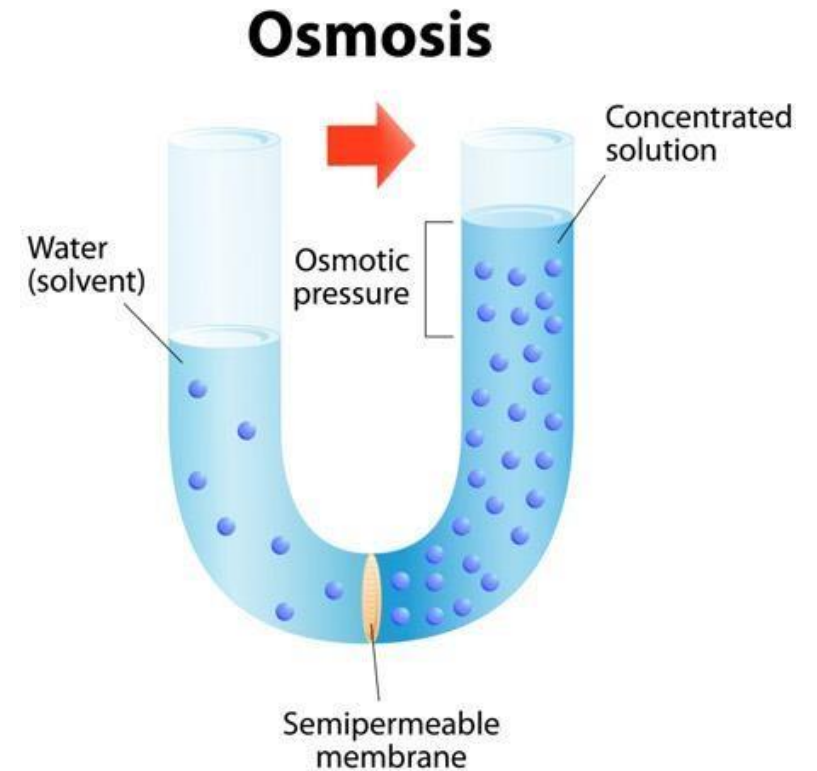
- *Van't Hoff equation* for dilute solutions is

$$\pi V = nRT$$

where π = Osmotic pressure,

      V= volume of solution,

   n= no. of moles of solute that is dissolved,

      R = Gas constant,

      T= Absolute temperature

(Isotonic Solutions: A pair of solutions having same osomotic pressure is called isotonic solutions.)

Reverse Osmosis

When a solution is separated from pure water by a semipermeable membrane, water moves towards solution on account of osmosis. This process continues till osmotic pressure becomes equal to hydrostatic pressure or osmosis can be stopped by applying external pressure equal to osmotic pressure on solution. If external pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, i.e., in reverse direction of the ordinary osmosis. This type of osmosis is termed reverse osmosis. Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.

Reverse osmosis
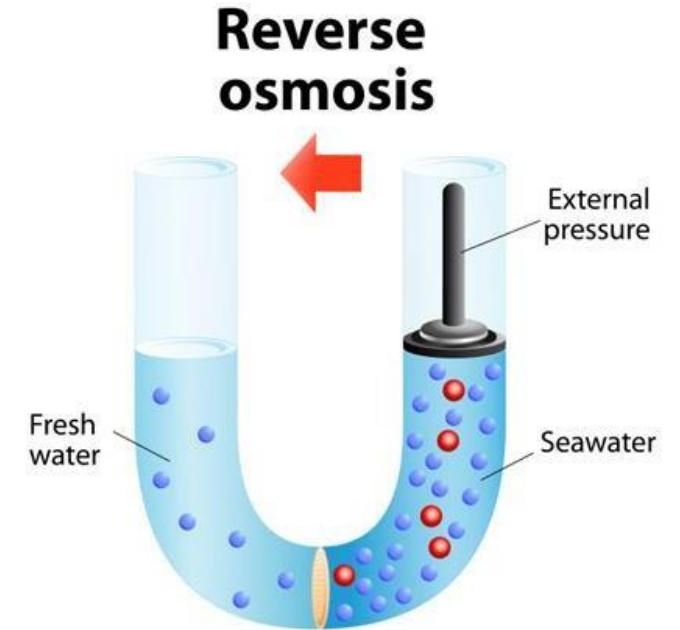
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