

# CHEMISTRY STUDY MATERIALS FOR CLASS 12

## (NCERT BASED NOTES OF CHAPTER -02)

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### Ideal and non-ideal solutions

Liquid – liquid solutions can be classified into ideal and non-ideal solutions on the basis of Raoult's law.

#### 1. Ideal solutions:

These are solutions which obey Raoult's law over the entire range of concentration. For such solutions, the enthalpy of mixing ( $\Delta H_{\text{mix}}$ ) of the pure components is zero and also volume of mixing ( $\Delta V_{\text{mix}}$ ) is zero. i.e. for an ideal solution,

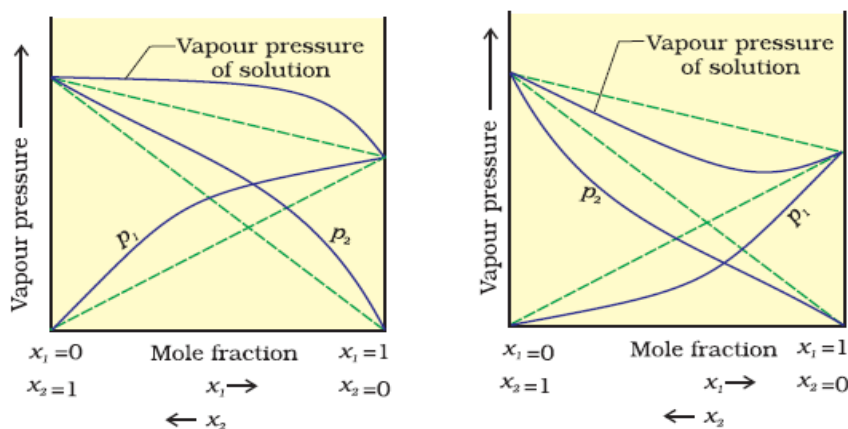
$$P_1 = P_1^0 x_1, P_2 = P_2^0 x_2, \Delta H_{\text{mix}} = 0 \text{ and } \Delta V_{\text{mix}} = 0$$

Ideal behaviour can be explained by considering two components A and B. In pure components, the inter molecular attractive interactions will be of types A-A and B-B. In solution, in addition to these two interactions, A-B type of interaction will also be present. If the A-A and B-B interactions are nearly equal to the A-B interaction, the solution behaves ideally. i.e. solute-solute interactions and solvent-solvent interactions are nearly equal to solute-solvent interaction.

A perfectly ideal solution is rare. But some solutions are nearly ideal in behaviour. E.g. solutions of n-hexane and n-heptane, bromoethane and chloroethane, benzene and toluene etc.

#### 2. Non-ideal solutions:

These are solutions which do not obey Raoult's law over the entire range of concentration. The vapour pressure of such a solution is either higher or lower than that predicted by Raoult's law. If it is higher, the solution exhibits *positive deviation* and if it is lower, it exhibits *negative deviation* from Raoult's law. The plots of vapour pressure against mole fractions for such solutions are as follows:



In the case of *positive deviation from Raoult's law*, A-B interactions are weaker than A-A and B-B interactions. i.e., in this case solute-solvent interactions are weaker than solute-solute and solvent-solvent interactions. So more molecules are escaped to vapour phase and hence the vapour pressure of the solution increases. e.g. Solutions of ethanol and acetone, acetone and  $\text{CS}_2$ , acetone and  $\text{CCl}_4$  etc.

In case of *negative deviation from Raoult's law*, the A-B interactions are stronger than A-A and B-B interactions. i.e. solute-solvent interactions are stronger than solute-solute interaction and solvent-solvent interaction. So number of molecules escaped to vapour phase decreases and hence the vapour pressure of the solution decreases.

e.g. solution of phenol and aniline, chloroform and acetone etc.

### Azeotropes

They are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature. For such solutions, it is not possible to separate the components by fractional distillation. There are two types of azeotropes: minimum boiling azeotrope and maximum boiling azeotrope.

The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a particular composition. e.g 95% ethanol solution by volume.

The solutions which show large negative deviation from Raoult's law form maximum boiling azeotrope at a particular composition. E.g. a mixture of 68% Nitric acid and 32% water by mass forms a maximum boiling azeotrope at 393.5 K.

## **COLLIGATIVE PROPERTIES AND DETERMINATION OF MOLAR MASS**

The properties which depend only on the number of solute particles and not on their nature are called Colligative properties. The important colligative properties are: Relative lowering of Vapour pressure, Elevation of Boiling point, Depression of Freezing point and Osmotic Pressure.

### **1. Relative lowering of Vapour Pressure**

When a non-volatile solute is added to a pure solvent, the vapour pressure (V.P) of the resulting solution is lower than that of the pure solvent. The difference between the vapour pressure of pure solvent and that of the solution is called lowering of vapour pressure ( $\Delta P$ ).

Consider a binary solution containing a non-volatile solute 2 dissolved in a solvent 1. Let  $P^0$  be the vapour pressure of pure solvent 1 and  $P_1$  be the vapour pressure of solution. Then according to Raoult's law,

$$P_1 = P_1^0 \cdot x_1$$

The lowering of vapour pressure of the solvent ( $\Delta P_1$ ) =  $P_1^0 - P_1$   
 $= P_1^0 - P_1^0 \cdot x_1$

$$\text{Or, } \Delta P = P_1^0(1-x_1)$$

But  $x_1 + x_2 = 1$ . Therefore  $1-x_1 = x_2$  So  $\Delta P = P_1^0 \cdot x_2$

$$\text{Or, } \frac{\Delta P}{P_1^0} = x_2, \text{ the mole fraction of the solute.}$$

Where  $\Delta P/P_1^0$  is called relative lowering of vapour pressure. It is defined as the ratio of the lowering of vapour pressure to the vapour pressure pure solvent.

$$\text{But } x_2 = \frac{n_2}{n_1 + n_2}$$

Where  $n_1$  and  $n_2$  are the number of moles of solvent and solute respectively.

For dilute solutions,  $n_2 \ll n_1$  and hence  $n_2$  in the denominator can be neglected.

$$\text{So, } x_2 = n_2/n_1$$

$$\text{Therefore, } \frac{\Delta P}{P_1^0} = \frac{n_2}{n_1}$$

$$\text{Or, } \frac{\Delta P}{P_1^0} = \frac{w_2/M_2}{w_1/M_1}$$

$$\text{Or, } \boxed{\frac{\Delta P}{P_1^0} = \frac{w_2 \times M_1}{w_1 \times M_2}}$$

Where  $w_1$  and  $w_2$  are the masses and  $M_1$  and  $M_2$  are the molar masses of solvent and solute respectively.

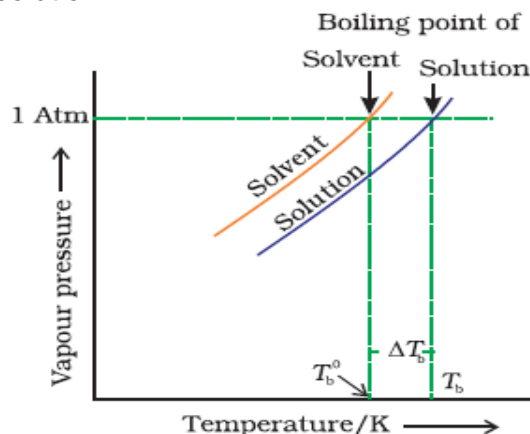
## 2. Elevation of Boiling Point ( $\Delta T_b$ )

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

When a non-volatile solute is added to a pure solvent, the boiling point of the resulting solution is always greater than that of the pure solvent. The difference between the boiling point of solution ( $\Delta T_b$ ) and that of the pure solvent ( $T_b^0$ ) is called elevation of boiling point ( $\Delta T_b$ ).

$$\text{i.e. } \Delta T_b = \text{Boiling point of solution} - \text{Boiling point of pure solvent} \quad \text{or, } \Delta T_b = T_b - T_b^0$$

If we plot a graph between the vapour pressure and temperature, we get the following graphs for the pure solvent and the solution.



For dilute solutions, the elevation of boiling point is directly proportional to molality ( $m$ ).

$$\text{i.e. } \Delta T_b \propto m$$

$$\text{or, } \Delta T_b = K_b \cdot m$$

Where  $K_b$  is a constant called *Boiling Point Elevation Constant* or *Molal Elevation Constant* or *Ebullioscopic Constant*. It is defined as the elevation of boiling point for 1 molal solution.

The unit of  $K_b$  is K kg/mol. For water,  $K_b = 0.52 \text{ K kg/mol}$ .

$$\text{But molality } m = \frac{w_2 \times 1000}{M_2 \times w_1}$$

$$\text{Therefore, } \Delta T_b = \frac{K_b \cdot w_2 \times 1000}{M_2 \cdot w_1}$$

$$\text{Or, } \boxed{\Delta T_b = \frac{1000 K_b \cdot w_2}{w_1 \cdot M_2}}$$

Where  $w_1$  = mass of solvent,  $w_2$  = mass of solute,  $M_2$  = molar mass of solute.

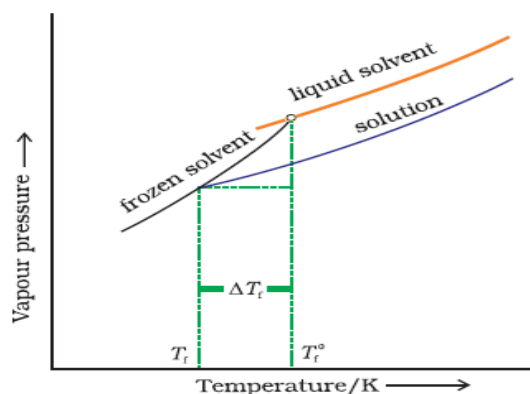
By using this equation, we can calculate the molar mass of unknown solute.

## 3. Depression of Freezing point ( $\Delta T_f$ )

Freezing point is the temperature at which the solid phase and liquid phase of a substance has the same vapour pressure.

According to Raoult's law, when a non-volatile solute is added to a pure solvent, its vapour pressure decreases. Now it would become equal to that of solid solvent at lower temperature. Thus the freezing point of the solvent decreases. The difference between the freezing point (f.p) of pure solvent ( $T_f^0$ ) and that of the solution ( $T_f$ ) is called depression of freezing point ( $\Delta T_f$ ). i.e.  $\Delta T_f = T_f^0 - T_f$

The vapour pressure–temperature graph representing the freezing point of pure solvent and solution is as follows:



For dilute solutions, it is found that the depression of freezing point ( $\Delta T_f$ ) is directly proportional to molality ( $m$ ) of the solution.

Thus  $\Delta T_f \propto m$

Or,  $\Delta T_f = K_f \cdot m$

Where  $K_f$  is a constant called Freezing Point Depression Constant or Molal Depression Constant or Cryoscopic constant. It is defined as the depression of freezing point for 1 molal solution. The unit of  $K_f$  is K kg/mol. For water,  $K_f = 1.86$  K kg/mol.

We know that molality  $m = \frac{w_2 \times 1000}{M_2 \times w_1}$

Therefore,  $\Delta T_f = \frac{K_f \cdot w_2 \times 1000}{M_2 \cdot w_1}$

Or,

$$\Delta T_f = \frac{1000 K_f \cdot w_2}{w_1 \cdot M_2}$$

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