

4) a) State Raoult's law of relative lowering of vapour pressure, and mention the conditions of its validity.

If we add a small portion of non volatile and non electrolyte compound to a pure solvent, then lowering of vapour pressure of that solvent is observed. This is basically coming due to decrease of chemical potential when solvent freely mixed with solute compound. From that decrease of chemical potential view point, we can theoretically explained the lowering of vapour pressure of solvent in solution.

$$\Delta G_r = V \cdot \Delta P - S \cdot \Delta T$$

At constant temp. $\Delta G_r = N \cdot \Delta P \quad \therefore \Delta P = \frac{\Delta G_r}{N}$

so, ΔP is negative as ΔG_r is negative

Now, vapour pressure of a solvent or a solution depends upon the molar concentration of the medium, i.e.,

$P_1 \propto n_1$ where P_1 be the vapour pressure of a solution, n_1 be the mole fraction of the solvent.

$$P_1 = K \cdot n_1$$

Under pure state, i.e. only the case of solvent, then $n_1 = 1$ and P_1 can be taken as P_1^0 .

$$\therefore P_1^0 = K$$

Therefore, $P_1 = P_1^0 \cdot n_1$ → This is Raoult's law,

Vapour pressure of the solution = vap. press. of pure solvent x mole fraction of solvent

Here before addition of non volatile and non electrolyte compound to the pure solvent, vapour pressure is taken as P_1^0 . Now after addition of non volatile and non electrolyte solute to the solvent, vapour pressure is taken as P_1 and where $P_1 < P_1^0$. So lowering of vapour pressure.

$$\Delta P = P_1^0 - P_1 = P_1^0 - P_1^0 n_1 = P_1^0 (1 - n_1) = P_1^0 n_2$$

$\frac{\Delta P}{P_1^0} = n_2$ → This is also Raoult's law. Here n_2 be the mole fraction of the solute.

So, relative lowering of vap. pressure is equal to the mole fraction of solute.

d) Given the density of water to be 1 gm/ml (at a given temperature), which of the following two solutions will have lower vapour pressure?

i) 1.0 molal aqueous solution of cane sugar.

ii) A cane sugar solution in which the mole fraction of cane sugar is 0.1.

i) 1 molal aqueous solution of cane sugar.

$$\text{we know, } \chi_2 = \frac{m_2}{m_1} = \frac{g/m_2}{w/m_1}$$

$$\begin{aligned} \text{Hence mole fraction of cane sugar} &= \left(\frac{g \times 1000}{w \times m_2} \right) \times \frac{m_1}{1000} \\ \text{is } \chi_2 &= 0.018. \end{aligned}$$
$$= 1 \times \frac{18}{1000} = 0.018$$

ii) mole fraction of cane sugar soln $\chi_2' = 0.1$

$$\therefore \Delta P = P^0 \times \chi_2$$

so vapour pressure will be lower when mole fraction is higher.

Hence, lowering of vapour pressure is more for ~~(i)~~ second solution [(ii)] of mole fraction $\chi_2 = 0.1$

6) a) why is the vapour pressure of a solvent lowered when a non-volatile, non-electrolytic solute is dissolved in it? why is it necessary that the solute should be non-volatile?

Discuss briefly any method for the measurement of the relative lowering of vapour pressure.

When a solute is dissolved in a pure solvent then a new solute-solvent molecular force of attraction is started. Mainly due to this escaping tendency of solvent molecules from liquid surface is decreased. So, therefore, no. of molecules in the vapour phase is less. That is why vapour pressure of the solvent in solution is lowered.

$$\Delta G_r = V \Delta P - S \Delta T$$

$$\Delta G_r T = V \cdot \Delta P$$

$$\Delta G_r < 0$$

$$\Delta P < 0$$

$$\Delta G_r = \mu - \mu^0 = RT \ln a$$

$$a < 1, \Delta G_r < 0$$

If volatile solute is used, then the magnitude of the colligative properties do not follow the Raoult's law even increasing of vapour pressure, or depression of boiling point may happen.

Thus ~~the~~ it is necessary that the solute should be non-volatile.

4) a) What are colligative properties? Why are they so called? Is it an intensive property?

• Colligative properties: - Every pure solvent, must have their fixed physical properties, i.e., under pure state boiling point should be fixed, refractive index, dipole moment, surface tension, viscosity, freezing point - etc, should have fixed value. When we add ~~some~~ a very small amount of non-volatile and non-electrolyte substance into the pure substance, then some properties of that solvent would be modified. These are,

- i) lowering of vapour pressure,
- ii) elevation of boiling ~~of~~ temperature.
- iii) depression of freezing temperature.
- iv) osmosis and osmotic pressure.

Those modified or change of physical properties of that solvent are called colligative properties.

These are called colligative properties, because the magnitude of these depends upon the number of solute particles or number of solute molecules, i.e., these are number dependent.

Colligative property is an intensive property.

A property is extensive when parts are added to give the whole, when parts do not add to give the whole, the property is intensive. This is so about colligative properties.

b) When non-volatile non-electrolyte solute is dissolved in a solvent, boiling point of the solution increases. Explain.

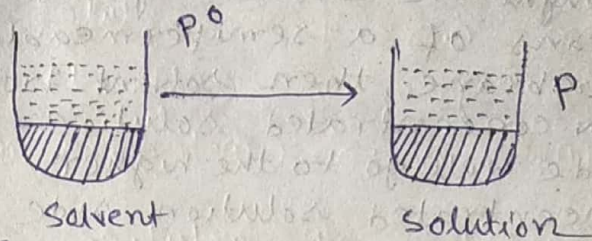
When non-volatile, non-electrolyte solute is dissolved in a solvent, then as it is a spontaneous process, free energy change is $\Delta G_{mix} < 0$. For ideal solⁿ, $\Delta H_{mix} = 0$, $\Delta S_{mix} > 0$. Therefore entropy always increases.

At the boiling point pressures of the vapour and liquid phase become equal. Now we make a solution from its pure solvent, the extra randomness in liquid phase leads to increase the entropy. The increases of entropy again decrease the vapour pressure of the liquid phase. To equalise the vapour pressure of solvent and vapour pressure of the solution, the temp. of the solution will be increased.

Thus boiling point of the solution increases. or boiling point will be elevated.

1) a) Derive thermodynamically Raoult's law of vapour pressure lowering of a solvent by a non-volatile solute.

Let us take an equilibrium between liquid state and vapour state of a pure solvent under pressure P^0 . At equilibrium, there would not have any change of free energy, i.e., $\Delta G = 0$.



Liquid \rightleftharpoons vapour, for solvent

If μ_l and μ_v be the chemical potential of liquid and vapour respectively, then,

$$\mu_l = \mu_v$$

$$\mu_l^0 + RT \ln a_l = \mu_v^0 + RT \ln a_v$$

For pure solvent, $a_l = 1$, $a_v = P^0$

$$\text{So, } \mu_l^0 = \mu_v^0 + RT \ln P^0 \quad \text{--- (1)}$$

Now, if we add non-volatile and non-electrolyte compound in the solvent, then chemical potential of liquid and vapour state both would be changed and again new equilibrium between liquid state and vapour state of the solution will be established.

Let, μ_l' and μ_v' are the chemical potential of liquid and vapour state of the solvent in solution.

At new equilibrium, $\mu_l' = \mu_v'$

$$\therefore \mu_l^0 + RT \ln a_l = \mu_v^0 + RT \ln a_v$$

$$\mu_l^0 + RT \ln \chi_1 = \mu_v^0 + RT \ln P$$

$$\mu_l^0 - \mu_v^0 = RT \ln P - RT \ln \chi_1 = RT \ln \left(\frac{P}{\chi_1} \right) \quad \text{--- (2)}$$

From equation (1), using equation (2) we get,

$$RT \ln P^0 = RT \ln \left(\frac{P}{\chi_1} \right)$$

$$\therefore P^0 = \left(\frac{P}{\chi_1} \right)$$

$$\text{or, } P = P^0 \cdot \chi_1$$

$$\therefore \Delta P = P^0 - P = P^0 - P^0 \chi_1 = P^0 (1 - \chi_1) = \chi_2 \cdot P^0$$

$$\therefore \Delta P = P^0 \cdot \chi_2$$

$$\boxed{\frac{\Delta P}{P^0} = \chi_2}$$

This is the equation of Raoult's law.