COLLIGATIVE PROPERTIES AND DETERMINATION OF MOLAR MASS

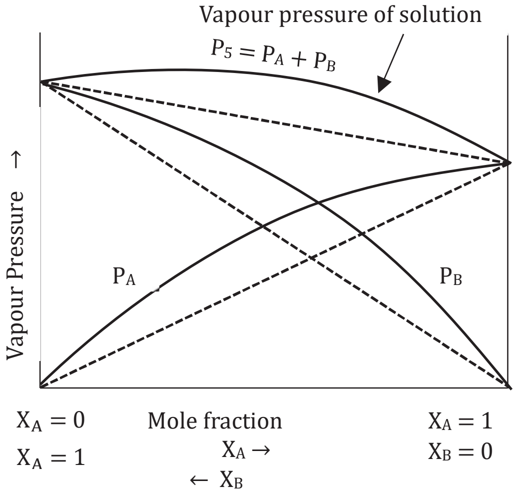
Solution with positive deviation

When the interactions between A and B in a solution are less robust than the interactions within the pure A-A and B-B liquids constituting the solution, molecules of both A and B exhibit a greater inclination to escape from the solution compared to their escape from pure liquids. Consequently, as per Raoult's law, each component of the solution demonstrates a partial vapor pressure surpassing the anticipated values. The overall vapor pressure in such a scenario exceeds the vapor pressure expected in an ideal solution with an equivalent composition. This deviation from Raoult's law is indicative of a solution displaying positive departures.

$H_{mixing > 0}$ for positive deviation.

The following are some examples of solutions with positive deviations:

- Ethyl alcohol and cyclohexane
- Acetone and carbon disulphide



Vapour pressure of diagram showing positive deviation

Solutions with negative deviation

In these solutions, the interactions between A and B are more robust than the interactions within the pure A-A and B-B liquids comprising the solution. Due to the heightened A-B interactions, molecules of both A and B exhibit a diminished inclination to escape from the solution compared to their escape from pure liquids. Consequently, following Raoult's law, each component of the solution demonstrates a partial vapor pressure that falls below the anticipated values. The overall vapor pressure in such cases is lower than the vapor pressure that would be projected in an ideal solution with an equivalent composition.

$H_{mixing} < 0$ for negative deviation

The following are some examples of solutions with positive deviations:

- chloroform and methyl acetate
- acetic acid and pyridine

Relative lowering of vapour pressure

When a non-volatile solute is dissolved in a pristine solvent, the vapor pressure of the solvent decreases, meaning that the vapor pressure of the solution is consistently lower than that of the pure solvent. This is because the escape tendency of solvent molecules diminishes, attributed to the reduced surface area available for evaporation in the solution.

If at a certain temperature P^o is the vapour pressure of pure solvent, and P_s is the vapour pressure of solution then Lowering of vapour pressure = $P^o - P_s$

Relative lowering of vapour pressure $= \frac{P^o - P_s}{P^o}$

from equation (8)

$$\frac{P^0 - P_S}{P^0} = \frac{n_A}{n_A + n_B}$$

for a more dilute solution $n_A <<< n_B$

so

$$\frac{P^0 - P_S}{P^0} = \frac{n_A}{n_B}$$

$$\frac{\Delta P}{P^0} = \frac{P^0 - P_S}{P^0} = \frac{n_A}{n_B}$$

$$\frac{\Delta P}{P^0} = \frac{n_A}{n_B} \qquad \ldots\ldots(11)$$

or

relative lowering of vapour pressure

$$= \frac{P^0 - P_S}{P^0} = \frac{n_A}{n_B} = \frac{w_A}{m_A} \times \frac{m_B}{w_B}$$

Ex. Calculate wt. of urea which must be dissolved in 400 gm of water so final solutions has V.P. 2% less than V.P. of pure water:

Sol. Let V.P be V. of water

$$P^0 - P_s = .02\text{ V}$$

$$Ps = 0.98\text{ V}$$

$$\Rightarrow \quad \frac{0.02}{0.98} = \frac{w}{60} \times \frac{18}{400} \text{ ; where w = weight of urea.}$$

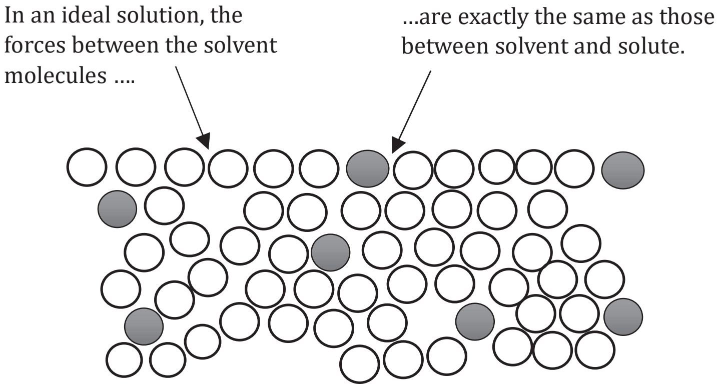
$$W = \frac{2 \times 60 \times 400}{18 \times 98}\text{ gm}$$

Limitations of Raoult's law

Raoult's Law is applicable exclusively to ideal solutions, with very dilute solutions adhering to Raoult's Law to a reasonable approximation.

Ideal Solutions

Ideal solutions are those that adhere to Raoult's law. When the forces of attraction between A-A and B-B are comparable to those between A-B, A and B will constitute an ideal solution



That means that it takes the same amount of energy for solvent molecules to break away from the surface in either case.

Properties of ideal solution

(i) Raoult's law is obeyed

(ii) $\Delta H_{mix} = 0$, i.e., there should not be enthalpy change when components of ideal solutions are mixed.

(iii) $\Delta V_{mix} = 0$, $(1L + 1L = 2L)$ i.e., there should not be change in volume on mixing.
e.g.; n-hexane and n-heptane; ethyl bromide and ethyl iodide; benzene and toluene; chlorobenzene and bromobenzene form ideal solutions.

Non-Ideal Solutions

Those solutions which do not obey Raoult's law are called non-ideal solutions. When the forces of attraction between A — A, B — B is different from A — B then 'A' and 'B' form non-ideal solutions.

For these solutions:

(i) Raoult's law is not obeyed. (ii) $\Delta H_{mix} \neq 0$. (iii) $\Delta V_{mix} \neq 0$.