COLLIGATIVE PROPERTIES: STUDY MATERIAL AND NUMERICAL PROBLEMS

1. VAPOUR PRESSURE OF SOLUTIONS

Vapour Pressure: The pressure exerted by the vapour of a liquid in thermodynamic equilibrium with its liquid phase at a given temperature in a closed system.

When a non-volatile solute is dissolved in a solvent, the vapour pressure of the solvent above the solution decreases. This is because the solute particles occupy some of the surface area, reducing the rate of evaporation, and also interact with solvent molecules, reducing their tendency to escape into the vapour phase. This phenomenon is known as **Vapour Pressure Lowering**.

2. IDEAL SOLUTIONS, IDEALLY DILUTE SOLUTIONS, AND COLLIGATIVE PROPERTIES

Ideal Solution: A solution that obeys Raoult's Law at all concentrations and temperatures. In an ideal solution, the intermolecular forces between solute-solute, solvent-solvent, and solute-solvent particles are approximately equal. No heat is absorbed or evolved during mixing, and the volume of the solution is the sum of the volumes of the components.

Non-Ideal Solution: A solution that deviates from Raoult's Law. Intermolecular forces are not equal, and there may be heat changes or volume changes upon mixing.

Ideally Dilute Solution: A solution in which the concentration of the solute is very low. In such solutions, the solute particles are far apart, and their interactions with each other are negligible. The solvent properties dominate, and the solute particles behave almost independently. For ideally dilute solutions, colligative properties become significant.

Colligative Properties: These are properties of solutions that depend solely on the number of solute particles in a given amount of solvent, irrespective of the chemical nature (identity, size, or charge) of the solute particles. These properties are directly proportional to the concentration of solute particles.

The four main colligative properties are:

- Vapour Pressure Lowering
- Boiling Point Elevation
- Freezing Point Depression
- Osmotic Pressure

3. RAOULT'S LAW

Statement: For a solution of volatile components, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction in the solution. For a solution containing a non-volatile solute, the vapour pressure of the solvent is directly proportional to its mole fraction in the solution.

Mathematically:

For a volatile solvent (A) and volatile solute (B):

$P_A = X_A * P_A^o$

$P_B = X_B * P_B^o$

Where:

- P_A and P_B are the partial vapour pressures of components A and B, respectively.
- X_A and X_B are the mole fractions of components A and B, respectively.
- P_A^o and P_B^o are the vapour pressures of pure components A and B, respectively.

For a solution containing a non-volatile solute:

The vapour pressure of the solution ($P_{solution}$) is equal to the vapour pressure of the solvent, as the solute does not contribute to the vapour pressure.

$P_{solution} = P_A = X_A * P_A^o$

Since $X_A + X_B = 1$, we have $X_A = 1 - X_B$.

Therefore, $P_{solution} = (1 - X_B) * P_A^o$

$P_{solution} = P_A^o - X_B * P_A^o$

Rearranging, $P_A^o - P_{solution} = X_B * P_A^o$

The term $(P_A^o - P_{solution})$ is the vapour pressure lowering (ΔP). So, $\Delta P = X_B * P_A^o$.

This shows that vapour pressure lowering is directly proportional to the mole fraction of the solute.

4. THERMODYNAMIC DERIVATIONS RELATING COLLIGATIVE PROPERTIES TO SOLUTE CONCENTRATION

For ideally dilute solutions, the chemical potential (μ) of the solvent can be used to derive the relationships between colligative properties and solute concentration. The chemical potential of a component in a solution is given by:

$\mu_A = \mu_A^o + RT\ ln(a_A)$

where a_A is the activity of component A. For an ideally dilute solution, the activity of the solvent (a_A) can be approximated by its mole fraction (X_A).

(i) Elevation of Boiling Point (ΔT_b)

The boiling point of a solution is the temperature at which its vapour pressure equals the external atmospheric pressure. Dissolving a non-volatile solute lowers the vapour pressure. To reach the boiling point, the solution must be heated to a higher temperature than the pure solvent. This difference in boiling points is the boiling point elevation.

Thermodynamically, at equilibrium (boiling point), the chemical potential of the solvent in the liquid phase equals that in the vapour phase.

The derivation leads to the relationship:

$\Delta T_b = K_b * m$

Where:

- ΔT_b is the elevation in boiling point ($T_{b,\ solution} - T_{b,\ solvent}$).

- K_b is the ebullioscopic constant (or molal boiling point elevation constant) of the solvent.
- m is the molality of the solute (moles of solute / kg of solvent).

For ideally dilute solutions containing a non-volatile nonelectrolyte solute, molality (m) is often used.

(ii) Depression of Freezing Point (ΔT_f)

The freezing point of a solution is the temperature at which the solid phase of the solvent is in equilibrium with the solution. The presence of a solute disrupts the solvent's ability to form a crystalline lattice, thus lowering the freezing point. This difference is the freezing point depression.

At the freezing point, the chemical potential of the solvent in the liquid solution is equal to that in the solid solvent.

The derivation yields:

$\Delta T_f = K_f * m$

Where:

- ΔT_f is the depression in freezing point ($T_{f,\ solvent}$ - $T_{f,\ solution}$).
- K_f is the cryoscopic constant (or molal freezing point depression constant) of the solvent.
- m is the molality of the solute.

Again, for ideally dilute solutions with non-volatile nonelectrolyte solutes, molality is the preferred concentration term.

(iii) Osmotic Pressure (Π)

Osmosis is the spontaneous flow of solvent molecules from a region of higher solvent concentration (lower solute concentration) to a region of lower solvent concentration (higher solute concentration) through a semipermeable membrane. Osmotic pressure is the minimum pressure that needs to be applied to the solution to prevent the inward flow of its pure solvent across a semipermeable membrane.

For ideally dilute solutions, the osmotic pressure can be derived from the equilibrium condition of chemical potentials across the semipermeable membrane.

The derivation leads to:

$\Pi = CRT$

Where:

- Π is the osmotic pressure.
- C is the molar concentration of the solute (moles of solute / litre of solution).
- R is the ideal gas constant.
- T is the absolute temperature (in Kelvin).

This equation is analogous to the ideal gas law ($PV = nRT$, or $P = (n/V)RT = CRT$). For ideally dilute solutions, molar concentration (Molarity) is used.

Relationship between Colligative Properties and Concentration:

These properties are directly proportional to the concentration of solute particles. For ideally dilute solutions of non-volatile, non-electrolyte solutes:

- $\Delta P \propto X_{solute}$
- $\Delta T_b \propto m$
- $\Delta T_f \propto m$
- $\Pi \propto C$

Since for dilute solutions, molality (m) and molarity (C) are approximately equal (especially when the density of the solvent is close to 1 g/mL), and mole fraction is related to molality, these properties are all directly related to the amount of solute present.

5. APPLICATIONS IN CALCULATING MOLAR MASSES

Colligative properties are particularly useful for determining the molar masses of unknown solutes, especially complex organic molecules which are often non-volatile and behave as non-electrolytes in solution.

Using the relationships derived:

A. From Boiling Point Elevation (ΔT_b):

$\Delta T_b = K_b * m$

Molality m = (moles of solute / mass of solvent in kg) = (n_B / w_A)

where n_B is the moles of solute and w_A is the mass of solvent in kg. If the molar mass of solute is M_B and its mass is w_B, then $n_B = w_B / M_B$.

Substituting these into the ΔT_b equation:

$\Delta T_b = K_b * (w_B / M_B) / w_A$

Rearranging to find molar mass M_B:

$M_B = (K_b * w_B * 1000) / (\Delta T_b * w_{A \text{ (in grams)}})$

B. From Freezing Point Depression (ΔT_f):

$\Delta T_f = K_f * m$

Similar to boiling point elevation, substituting $m = (w_B / M_B) / w_A$:

$\Delta T_f = K_f * (w_B / M_B) / w_A$

Rearranging for molar mass M_B:

$M_B = (K_f * w_B * 1000) / (\Delta T_f * w_{A \text{ (in grams)}})$

C. From Osmotic Pressure (Π):

$\Pi = CRT$

Molar concentration C = (moles of solute / volume of solution in Litres) = (n_B / V)

Substituting $n_B = w_B / M_B$:

$\Pi = (w_B / M_B) * (1 / V) * RT$

Rearranging for molar mass M_B:

$M_B = (w_B * RT) / (\Pi * V_{(in\ Litres)})$

If volume is in mL, use $V_{(in\ mL)} / 1000$ and adjust R accordingly if needed.

6. ABNORMAL COLLIGATIVE PROPERTIES AND THE VAN'T HOFF FACTOR (I)

The formulas for colligative properties assume that the solute particles are discrete and do not interact or change in number in the solution. However, some solutes dissociate into ions, and others associate to form larger molecules in solution.

***Dissociation:** For electrolytes like NaCl, which dissociate into ions ($NaCl \rightarrow Na^+ + Cl^-$), the number of particles in the solution increases. This leads to a higher observed colligative property than predicted.*

***Association:** For some molecules, like acetic acid in benzene, they may associate to form dimers ($2\ CH_3COOH \rightarrow (CH_3COOH)_2$). This reduces the number of particles, leading to a lower observed colligative property than predicted.*

*To account for these deviations, the **Van't Hoff factor (i)** is introduced. It is defined as the ratio of the observed colligative property to the colligative property calculated assuming no dissociation or association.*

i = (Observed Colligative Property) / (Calculated Colligative Property based on molar concentration)

Alternatively, i is the ratio of the number of particles after dissociation/association to the number of particles before dissociation/association.

The formulas for colligative properties are modified by multiplying them by i:

- ***Vapour Pressure Lowering:*** *$\Delta P = i * X_{solute} * P_A^o$*
- ***Boiling Point Elevation:*** *$\Delta T_b = i * K_b * m$*
- ***Freezing Point Depression:*** *$\Delta T_f = i * K_f * m$*
- ***Osmotic Pressure:*** *$\Pi = i * C * R * T$*

For a solute that dissociates:

Let α be the degree of dissociation. If 1 mole of solute dissociates into n ions, then:

$i = 1 + \alpha(n - 1)$

For a solute that associates:

Let α be the degree of association. If n molecules associate to form 1 molecule, then:

$i = 1 - \alpha + \alpha/n$

The Van't Hoff factor allows us to calculate molar masses even for solutes that dissociate or associate, by using the observed colligative property and the modified formulas.

7. NUMERICAL PROBLEMS

Problem 1 (Boiling Point Elevation): *18.0 g of glucose (molar mass = 180 g/mol) is dissolved in 100 g of water. Calculate the boiling point elevation. (K_b for water = 0.52 K kg/mol). Assume glucose is a non-electrolyte.*

Solution:

Mass of solute (glucose), w_B = 18.0 g

Molar mass of solute, M_B = 180 g/mol

Mass of solvent (water), w_A = 100 g = 0.100 kg

K_b for water = 0.52 K kg/mol

Moles of solute, $n_B = w_B / M_B$ = 18.0 g / 180 g/mol = 0.1 mol

Molality, $m = n_B / w_{A\ (kg)}$ = 0.1 mol / 0.100 kg = 1.0 mol/kg

Boiling point elevation, $\Delta T_b = K_b * m$

*ΔT_b = 0.52 K kg/mol * 1.0 mol/kg = 0.52 K*

The boiling point of the solution will be 0.52 K higher than that of pure water (100 °C).

***Problem 2 (Freezing Point Depression & Molar Mass):** 7.5 g of a non-volatile compound was dissolved in 100 g of water. The freezing point of the solution was found to be -1.53 °C. Calculate the molar mass of the compound. (K_f for water = 1.86 K kg/mol).*

Solution:

Mass of solute, w_B = 7.5 g

Mass of solvent (water), w_A = 100 g = 0.100 kg

Freezing point depression, ΔT_f = 0 °C - (-1.53 °C) = 1.53 °C (or 1.53 K, as the difference is the same)

K_f for water = 1.86 K kg/mol

Using the formula $\Delta T_f = K_f * m$, we find molality:

$m = \Delta T_f / K_f = 1.53\ K / 1.86\ K\ kg/mol \approx 0.8226\ mol/kg$

Now, using $m = (w_B / M_B) / w_{A\ (kg)}$:

$0.8226\ mol/kg = (7.5\ g / M_B) / 0.100\ kg$

$M_B = (7.5\ g) / (0.8226\ mol/kg * 0.100\ kg)$

$M_B \approx 91.18\ g/mol$

The molar mass of the compound is approximately 91.18 g/mol.

Problem 3 (Osmotic Pressure & Molar Mass): *A solution containing 2.7 g of a solute in 500 mL of solution was found to have an osmotic pressure of 5 atm at 300 K. Calculate the molar mass of the solute. (R = 0.0821 L atm / mol K).*

Solution:

Mass of solute, $w_B = 2.7\ g$

Volume of solution, V = 500 mL = 0.500 L

Osmotic pressure, $\Pi = 5\ atm$

Temperature, T = 300 K

Gas constant, R = 0.0821 L atm / mol K

Using the formula $\Pi = CRT$*, we find molarity C:*

*$C = \Pi / RT = 5$ atm / (0.0821 L atm / mol K * 300 K)*

$C \approx 5 / 24.63$ mol/L ≈ 0.203 mol/L

Now, using $C = (w_B / M_B) / V_{(L)}$:

0.203 mol/L = (2.7 g / M_B) / 0.500 L

*M_B = (2.7 g) / (0.203 mol/L * 0.500 L)*

$M_B \approx 2.7 / 0.1015$ mol ≈ 26.6 g/mol

The molar mass of the solute is approximately 26.6 g/mol.

Problem 4 (Van't Hoff Factor & Dissociation): *The freezing point depression of a 0.1 molal aqueous solution of KCl was found to be -0.348 °C. Calculate the Van't Hoff factor (i) for KCl and determine the degree of dissociation (α). (K_f for water = 1.86 K kg/mol).*

Solution:

Given:

Molality of KCl solution, m = 0.1 mol/kg

Observed freezing point depression, $\Delta T_{f\ (obs)}$ = 0.348 °C (or 0.348 K)

K_f for water = 1.86 K kg/mol

First, calculate the theoretical freezing point depression assuming KCl does not dissociate (i=1):

*$\Delta T_{f\ (calc)} = K_f * m$ = 1.86 K kg/mol * 0.1 mol/kg = 0.186 K*

Now, calculate the Van't Hoff factor (i):

$i = \Delta T_{f\ (obs)} / \Delta T_{f\ (calc)} = 0.348\ K / 0.186\ K \approx 1.87$

Since KCl dissociates into K^+ and Cl^-, it produces 2 ions (n=2).

Using the formula $i = 1 + \alpha(n - 1)$:

$1.87 = 1 + \alpha(2 - 1)$

$1.87 = 1 + \alpha$

$\alpha = 1.87 - 1 = 0.87$

The degree of dissociation (α) for KCl in this solution is approximately 0.87 or 87%.

Problem 5 (Van't Hoff Factor & Association): *Benzoic acid (C_6H_5COOH) in benzene shows a freezing point depression that corresponds to only half of the expected value for a non-electrolyte. Calculate the Van't Hoff factor (i) and determine the extent of association.*

Solution:

The problem states that the observed freezing point depression is half of the expected value. This means the number of particles (due to association) is effectively halved compared to the number of molecules initially dissolved.

i = (Observed Colligative Property) / (Calculated Colligative Property)

Since freezing point depression is directly proportional to the number of particles, the observed ΔT_f is half of the calculated ΔT_f if it were a non-electrolyte.

Therefore, $i = 0.5 * (\text{Calculated } \Delta T_f) / (\text{Calculated } \Delta T_f) = 0.5$

Benzoic acid molecules associate in benzene to form dimers:

$2\ C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$

Here, 2 molecules associate to form 1 molecule, so $n = 2$ (for association, n is the number of molecules forming an associated particle).

Using the formula for association: $i = 1 - \alpha + \alpha/n$

$0.5 = 1 - \alpha + \alpha/2$

$0.5 = 1 - \alpha/2$

$\alpha/2 = 1 - 0.5$

$\alpha/2 = 0.5$

$\alpha = 1.0$

This indicates that the degree of association is 100%, meaning all benzoic acid molecules in this solution have formed dimers.