Rank Enhancer

This column is specially designed to make your concepts crystal clear.

Colligative properties

Properties of solution which depends on number of particles but not on the nature of solute are known as colligative properties.

Types of Colligative Properties

- (I) Relative lowering of vapour pressure $\left(\dfrac{p^{\circ}_{\text{solvent}} - p_{\text{solution}}}{p^{\circ}_{\text{solvent}}}\right)$
- (II) Elevation in boiling point (ΔT_b)
- (III) Depression in freezing point (ΔT_f)
- (IV) Osmotic pressure (π)

Note : Colligative properties are properties of only dilute solutions as they only behave as ideal solutions.

I. Relative Lowering of Vapour Pressure

When a non-volatile solute is added to a volatile solvent, its vapour pressure decreases. Such decrease with respect to vapour pressure of solvent is called relative lowering of vapour pressure.

$$\frac{p^{\circ}_{\text{solvent}} - p_{\text{solution}}}{p^{\circ}_{\text{solvent}}} = X_{\text{solute}}$$

According to Raoult's law for ideal solutions

$p_{\text{solution}} = p^{\circ}_A X_A + p^{\circ}_B X_B$

$[B = \text{Solute (non-volatile)}, A = \text{Solvent (volatile)}]$

$p^{\circ}_B = 0$ as solute is non-volatile

and $X_A + X_B = 1 \Rightarrow X_A = 1 - X_B$

$P_{\text{solution}} = P^{\circ}_A(1 - X_B) + 0 \times X_B$

$p_{\text{solution}} = p^{\circ}_A - p^{\circ}_A \times X_B$

$p^{\circ}_A X_B = p^{\circ}_A - p_{\text{solution}}$

$$X_B = \frac{p^{\circ}_A - p_{\text{solution}}}{p^{\circ}_A}$$

$$\text{or} \quad \frac{p^{\circ}_{\text{solvent}} - p_{\text{solution}}}{p^{\circ}_{\text{solvent}}} = X_{\text{solute}}$$

$$\frac{p^{\circ}_{\text{solvent}} - p_{\text{solution}}}{p^{\circ}_{\text{solvent}}} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

For dilute solution, $n_{\text{solute}} <<< n_{\text{solvent}}$

$$\therefore \quad \frac{p^{\circ}_{\text{solvent}} - p_{\text{solution}}}{p^{\circ}_{\text{solvent}}} = \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$$\frac{p^{\circ}_{\text{solvent}} - p_{\text{solution}}}{p^{\circ}_{\text{solvent}}} = \frac{w_{\text{solute}} \times M_{\text{solvent}}}{w_{\text{solvent}} \times M_{\text{solute}}}$$

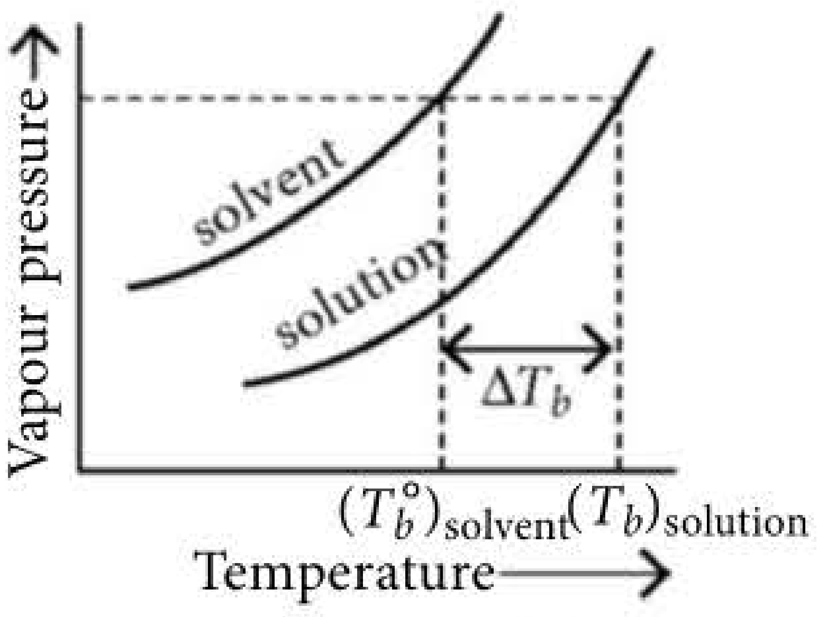
II. Elevation in Boiling Point

When a non-volatile solute is added to volatile solvent, resulting solution will have less vapour pressure. Hence, boiling point will increase. Such increase in boiling point is called elevation in boiling point. It is represented by ΔT_b.

$$\Delta T_b = (T_b)_{\text{solution}} - (T^{\circ}_b)_{\text{solvent}}$$

$$= K_b \times m = K_b \times \frac{(\text{wt.}/\text{m.wt.})_{\text{solute}}}{(\text{wt. of solvent in g})} \times 1000$$

where, K_b = Ebullioscopic constant or molal elevation constant.



Expression for molal elevation constant from enthalpy of vaporisation :

$$K_b = \frac{RT_b^{\circ 2}}{1000 \times L_v}$$

R = Universal gas constant

T°_b = Boiling point of solvent

L_v = Latent heat of vaporisation

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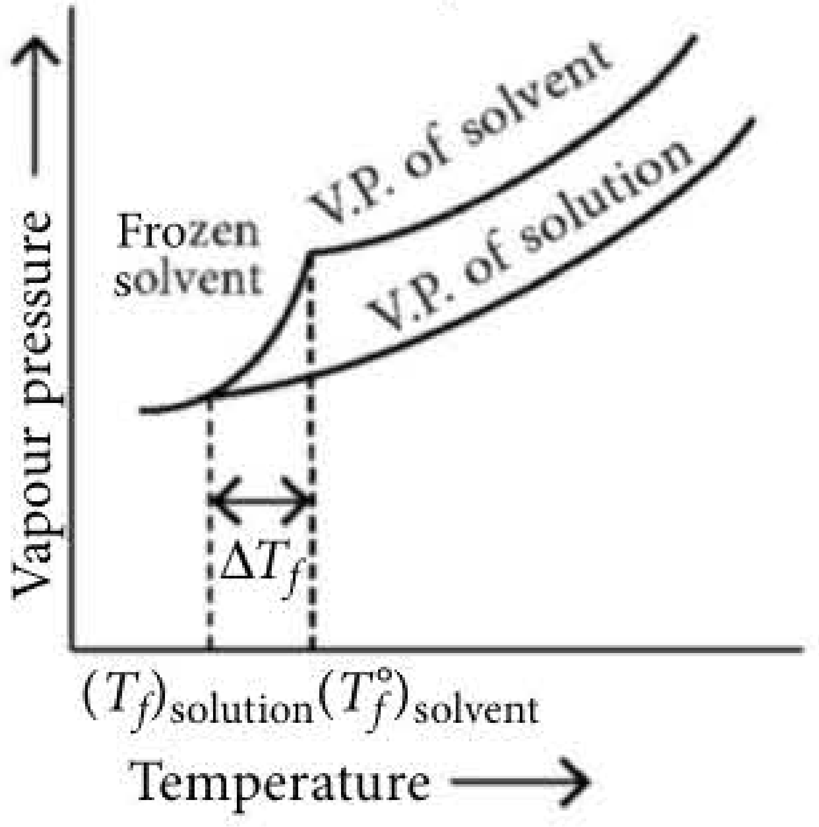
III. Depression in Freezing Point

Since vapour pressure of solution is lower than solvent, solid form separates out at a lower temperature. Such decrease in freezing point is called depression in freezing point. It is represented by ΔT_f.



$$\Delta T_f = (T_f^\circ)_{\text{solvent}} - (T_f)_{\text{solution}} = K_f \times m$$

$$= K_f \times \frac{(\text{wt.}/\text{mol. wt.})_{\text{solute}}}{(\text{wt. of solvent in g})} \times 1000$$

where, K_f = Cryoscopic constant or molal depression constant.

Expression for molal depression constant from enthalpy of fusion

$$K_f = \frac{RT_f^{\circ 2}}{1000 \times L_f}$$

where, R is universal gas constant. T_f° is freezing point of the solvent, L_f is latent heat of fusion.

IV. Osmotic Pressure

The process of flow of solvent from low concentrated solution/solvent to more concentrated solution through a semipermeable membrane is called osmosis.

The external pressure required to stop osmosis is called osmotic pressure.

Isotonic, Hypertonic and Hypotonic solutions

- If two solutions have same osmotic pressures then they are called isotonic solutions.
- If two solutions have different osmotic pressures, then the solution with higher osmotic pressure is called hypertonic and solution with lower osmotic pressure is called hypotonic solution.

Exo-osmosis and Endo-osmosis

The outward flow of solvent from cell is called exo-osmosis and the net inward flow of solvent into the cell is called endo-osmosis.

e.g., Grapes in water ⇒ Endo-osmosis
Grapes in sugar solution ⇒ Exo-osmosis
Osmotic pressure (π) = $C \times S \times T$
C = Concentration of solution
S = Universal solution constant
T = Temperature in Kelvin

Colligative Properties for Abnormal Solutions

Certain solutes show abnormal molecular masses either due to dissociation or association. Such solutions are called abnormal solutions. They are identified by van't Hoff factor(i).

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

$$= \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

$$= \frac{\text{Number of moles after dissociation/association}}{\text{Number of moles dissolved}}$$

If $i = 1$, solution is not abnormal *i.e.*, solute neither dissociates nor associates, *e.g.*, sucrose, glucose and urea.
If $i > 1$, solution is abnormal due to dissociation of solute, *e.g.*, NaCl, $CaCl_2$, $K_4[Fe(CN)_6]$, etc.
If $i < 1$, solution is abnormal due to association of solute, *e.g.*, benzoic acid in benzene.

van't Hoff factor for solute dissociating :

	A_xB_y ⇒	xA^{y+} +	yB^{x-}
Initial moles	1	0	0
After dissociation	$1 - \alpha$	$x\alpha$	$y\alpha$

$$i = \frac{1 - \alpha + x\alpha + y\alpha}{1 + 0 + 0} = 1 + (x + y - 1)\alpha$$

van't Hoff factor for solute associating :

	nA →	A_n
Intial moles	1	0
After association	$1 - \alpha$	α/n

$$i = \frac{1 - \alpha + \alpha/n}{1 + 0} = 1 - \left(1 - \frac{1}{n}\right)\alpha$$

Modified Colligative Properties for Abnormal Solutions

(1) Relative lowering of vapour pressure

$$= \frac{\overset{\circ}{p}_A - p_A}{\overset{\circ}{p}_A} = iX_B$$

(2) Elevation in boiling point (ΔT_b) = $i \times K_b \times m$
(3) Depression in freezing point (ΔT_f) = $i \times K_f \times m$
(4) Osmotic pressure (π) = $iCST$

Some facts to be remembered

(I) Methods for measuring colligative properties :

- Relative lowering of V.P.–Ostwald and Walker method
- Elevation in B.Pt.–Landsberger method
- Depression in F.Pt.–Beckmann method
- Osmotic pressure-Berkely and Hartely method

(II) Osmotic pressure is the best method for determining molecular mass of polymer as in other colligative properties, observed values are too small and accuracy lost.

(III) Ethylene glycol ($CH_2OH — CH_2OH$) is added to water before using in radiators because it is being non-volatile. It reduces freezing point thus avoid ice formation in winter. Hence called "antifreeze" and also increases boiling point thus avoids topping of radiator water in summer.

(IV) 0.9% solution of NaCl is isotonic with human RBC.

(V) Plasmolysis : Shrinking of plant cells when placed in hypertonic solutions.

PROBLEMS

1. If the observed and theoretical molecular mass of AB electrolyte is 31.80 and 58.50 respectively, then the degree of dissociation of AB is

(a) 83.96% (b) 90% (c) 8.39% (d) 100%

2. If all symbols have their usual meaning, then for non-volatile and non-electrolyte solute, the value of $\lim_{m \to 0}\left[\frac{\Delta T_b}{m}\right]$ is

(a) infinity (b) zero
(c) ΔT_b (d) K_b.

3. If two elements P and Q form compounds of molecular formulae PQ_2 and PQ_4. When 1 g of PQ_2 dissolved in 20 g of C_6H_6 then decrease in freezing point by 2.3 K. But when 1 g of PQ_4 dissolved in 20 g of C_6H_6, it decreases the freezing point by 1.3 K. Atomic masses of P and Q are (K_f of benzene is 5.1 K m^{-1}).

(a) 25.58 and 42.64 (b) 22.64 and 55.58
(c) 42.64 and 25.58 (d) 45.64 and 22.58.

4. If K_b/K_f of electrolyte AB is 0.3 and its aq. solution is 100% ionised and have boiling point 101.08 °C. If the freezing point of same solution is –1.80 °C then AB is

(a) 100% ionised at freezing point also
(b) no ionisation at freezing point
(c) 50% ionised at freezing point
(d) dimerisation takes place at freezing point.

5. If pK_a of monobasic acid HA is 4 then its van't Hoff factor of 0.01 M solution is

(a) 1.10 (b) 1.01 (c) 1.20 (d) 1.02

6. If osmotic pressure of solution of insulin at 298 K is found to be 7.2×10^{-3} atm then height of water column due to this osmotic pressure is (Density of Hg = 13.6 g/cm^3)

(a) 760 mm (b) 70.28 mm
(c) 74.42 mm (d) 0.76 mm.