Teacher: DR. SUBHANKAR SARDAR

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Paper: C8T

Topic : Physical Chemistry-III

(a) Application of Thermodynamics – II

Colligative properties: Vapour pressure of solution; Ideal solutions, ideally diluted solutions and colligative properties; Raoult's law; Thermodynamic derivation using chemical potential to derive relations between the four colligative properties [(i) relative lowering of vapour pressure, (ii) elevation of boiling point, (iii) Depression of freezing point,

Reference:

Physical Chemistry by P.C. Rakshit

COLLIGATIVE PROPERTIES
(For dilute solutions)

"A colligative property of a system is one which depends only on the number of particles present and not on the nature of the particles."

Dilute solutions have many of their properties are colligative.

Addition of a solute lowers the free energy (G/A) of the solution & thus, other properties are affected;

i) Vapour-pressure is lowered,
ii) Boiling-point is raised,
iii) Freezing Point is depressed, etc.

* Extent or magnitude of these changes in solution is depends on the number of solute particles not their nature.

concentration: Amount of substance present in solution.

Molarity: gm-moles of solute / litre ⇒ (M)

$0.1\ M\ CaCl_2 \equiv 0.1$ gm-moles $CaCl_2$ / lit.

Molality: gm. moles of solute / 1000 gm. Solvent ⇒ (m)

0.1 m Urea

Mole-fraction: fraction of moles in total moles.

$A + B$ Total mole $= n_A + n_B$
(Solute) (Solvent)

Mole fraction of n_A, $x_A = \dfrac{n_A}{n_A + n_B}$

Colligative properties

A. Lowering of vapour Pressure of solutions :

Colligative properties of dilute solutions originated from the Raoults law.

Raoults law: For non volatile solutes, the vapour pressure (P_1) over a solution is equal to the vapour pressure (P_1°) of the pure solvent multiplied by the mole fraction (x_1) of the solvent in the solution. i.e.

$$\underbrace{P_1}_{\text{vapour pressure of solution}} = \underbrace{x_1}_{\text{Mole fraction}} P_1^{\circ} \longrightarrow \text{vapour pressure of pure solvent}$$

$\overset{x}{1}$ → For solvent

2 → For solute.

As $x_1 < 1, \Rightarrow P_1 < P_1^\circ$.

Clapeyron eqn : $\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$

$T \propto P$

↳ vapour pressure(P) of solute / soln always increases with increase in temperature (T).

$L \rightarrow$ Latent heat.
$V_2 \rightarrow$ vol. of vapour
$V_1 \rightarrow$ " " liquid $V_2 \gg V_1$.

From Raoult's law,

$$P_1 = (1 - x_2) P_1^\circ \text{ ——— (i)} \qquad x_1 + x_2 = 1, \quad x_1 = 1 - x_2.$$

$x_2 \rightarrow$ Mole fraction of solute,

$$\frac{P_1}{P_1^\circ} = 1 - x_2$$

$$\Rightarrow x_2 = 1 - \frac{P_1}{P_1^\circ} = \frac{P_1^\circ - P_1}{P_1^\circ}$$

$$\Rightarrow x_2 = \frac{\Delta P}{P_1^\circ} \text{ ——— (ii)}$$

As, $$\frac{P_1^\circ - P_1}{P_1^\circ} = x_2 = \frac{n_2}{n_1 + n_2}$$

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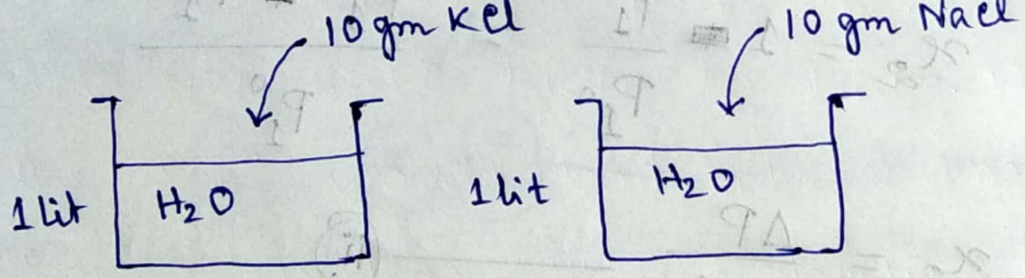
we have, $$\frac{P_1^\circ - P_1}{P_1^\circ} = x_2 = \frac{n_2}{n_1 + n_2}$$

For dilute solution, $n_1 >> n_2$.

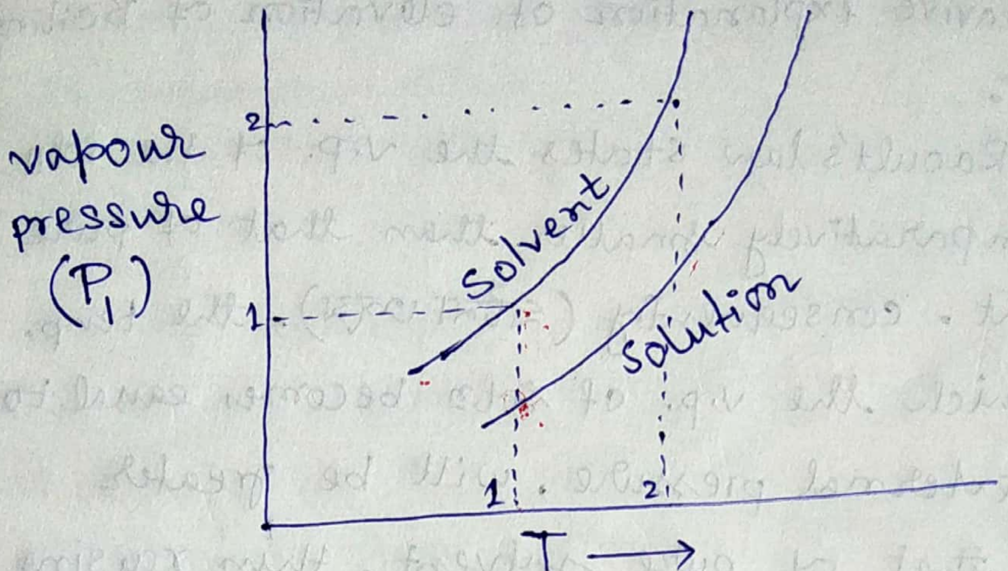
$$\frac{P_1^\circ - P_1}{P_1^\circ} \approx \frac{n_2}{n_1}$$

For definite quantity of a given solvent, n_1 and P_1° are both constants, i.e. $\boxed{\Delta P \propto n_2}$

which means that equimolecular quantities of any non volatile solute dissolved in the same quantity of the same solvent will produce same lowering of vapour pressure.



Same lowering of vapour pressure independent of Kcl or Nacl.

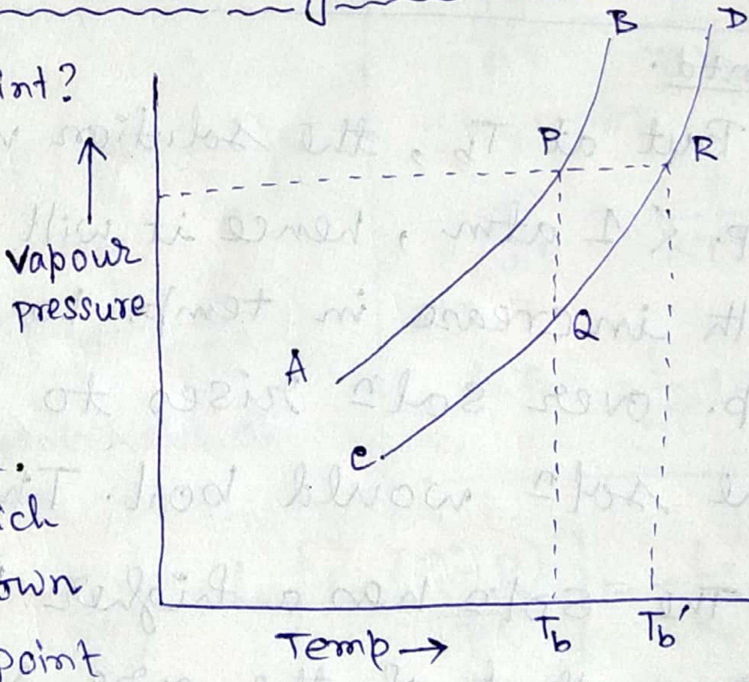


Since for a given solution, x_2 is constant, hence the relative lowering of vapour pressure ($\Delta P/p_1^0$) is independent of temperature. Note that the $\Delta P/p_1^0$ is independent, but P_1 is dependent on temperature.

B. Elevation of Boiling Point of solutions:

What is Boiling Point?

Ans: A liquid starts boiling when its vapour pressure becomes equal to the external pressure. The temp. at which it occurs is known as the boiling point of the liquid.



Let, T_b is the boiling point (temp.) of pure solvent & its v.p. = 1 atm. (at T_b)

P.T.O.

- **Qualitavive explanation of elevation of Boiling Point :**

As Raoult's law states the v.p. of the sol^{n} is comparatively smaller than that of pure solvent. consequently (ঘটনা ক্রমে), the temp. at which the v.p. of sol^{n} becomes equal to the external pressure, will be greater than that of pure solvent, thus raising its boiling point.

Since decrease in v.p. is directly proportonal to the amount of (fraction) solute in sol^{n}, therefore, the corresponding increase in b.p. also depends on the amount fraction of solute in the solution.

<u>contd.</u>

But at T_b, the solution will have a v.p. < 1 atm, hence it will not boil. with increase in temp. to T_b', the v.p. over sol^{n} rises to 1 atm. when the sol^{n} would boil. This means "The sol^{n} has a higher boiling point than that of the pure solvent."

Increase in b.pt., $PR = T_b' - T_b$

$= \Delta T$

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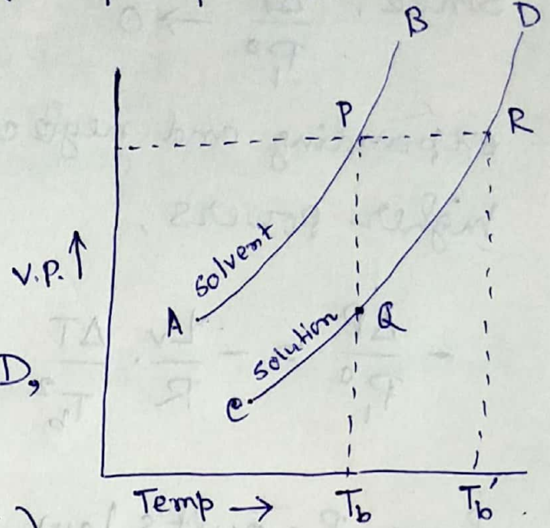
increase in pressure, $PQ = P_1^\circ - P_1 = \Delta P$.

As solution is dilute,

ΔT & ΔP are small quantities.



In the solution, vapour-pressure curve CD,

at the point Q,

pressure (P_1) & temp. (T_b).

at the point R,

pressure (P_1°) & temp. (T_b')

Applying clausius-clapeyron equation at these points,

$$\ln P_1 = -\frac{L_v}{RT_b} + Z$$

$$\ln P_1^\circ = -\frac{L_v}{RT_b'} + Z$$

i.e. $$\ln \frac{P_1}{P_1^\circ} = -\frac{L_v}{R}\left(\frac{1}{T_b} - \frac{1}{T_b'}\right)$$

$$= -\frac{L_v}{R}\left(\frac{T_b' - T_b}{T_b T_b'}\right).$$

$$\frac{dP}{dT} = \frac{L}{T(V_g - V_L)}$$

$V_g >> V_L$.

$$\frac{dP}{dT} = \frac{L}{T V_g}.$$

$\because PV_g = nRT$

$$\frac{dP}{dT} = \frac{L.P}{RT^2}$$

int^n

$$\ln P = -\frac{L}{RT} + C$$

L_v → molar latent heat of vaporisation.

$$\ln \frac{P_1}{P_1^\circ} = \ln\left(1 - 1 + \frac{P_1}{P_1^\circ}\right) = \ln\left[1 - \frac{(P_1^\circ - P_1)}{P_1^\circ}\right] = -\frac{L_v}{R}\frac{\Delta T}{T_b^2}$$

(T_b is very close to T_b', $T_b T_b' \approx T_b^2$)

$$\Rightarrow \ln\left(1 - \frac{\Delta P}{P_1^\circ}\right) = -\frac{L_v}{R}\frac{\Delta T}{T_b^2}$$

since, $\frac{\Delta P}{P_1^{\circ}} \to 0$

$$\ln(1-x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \cdots = -\sum_{n=1}^{\infty} \frac{x^n}{n}.$$

expanding and neglecting higher powers,

$$-\frac{\Delta P}{P_1^{\circ}} = -\frac{L_v}{R} \cdot \frac{\Delta T}{T_b^2}$$

from Raoult's Law, $\frac{\Delta P}{P_1^{\circ}} = x_2$ (mole-fraction of solute)

$$\Rightarrow \quad x_2 = \frac{L_v}{R} \cdot \frac{\Delta T}{T_b^2}$$

or

$$\boxed{\Delta T = \frac{R T_b^2}{L_v} \cdot x_2}$$

Relation between elevation of boiling pt. with concentration of solute in soln.

in dilute soln, $x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} = \frac{W_2/M_2}{W_1/M_1}$

Hence, $\Delta T = \frac{R T_b^2}{L_v} \cdot \frac{W_2 M_1}{W_1 M_2}$

where,
W_2 gm of solute are dissolved in W_1 gm of solvent; M_2 and M_1 are molecular wt of solute and solvent, respectively.

$$\Delta T = \frac{R T_b^2}{L_v/M_1} \cdot \frac{W_2}{W_1 M_2} = \frac{R T_b^2}{l_v} \cdot \frac{W_2}{W_1 M_2}$$

l_v → latent heat/gm.

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$$\Rightarrow \Delta T = \frac{RT_b^2}{1000 \times l_v} \underbrace{\left[\frac{W_2 \times 1000}{W_1 \times M_2} \right]}_{\text{molality (m). of the sol}^n}$$

$$\Delta T = \frac{RT_b^2}{1000 \times l_v} \cdot m$$

For a given solvent, l_v and T_b are constant.

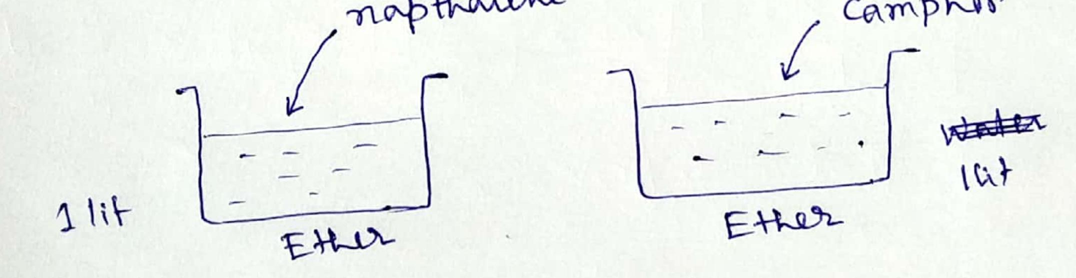
$$\Rightarrow K_b = \frac{\Delta T}{m} = \frac{RT_b^2}{1000 \times l_v}$$

→ The constant has a definite value of each solvent.

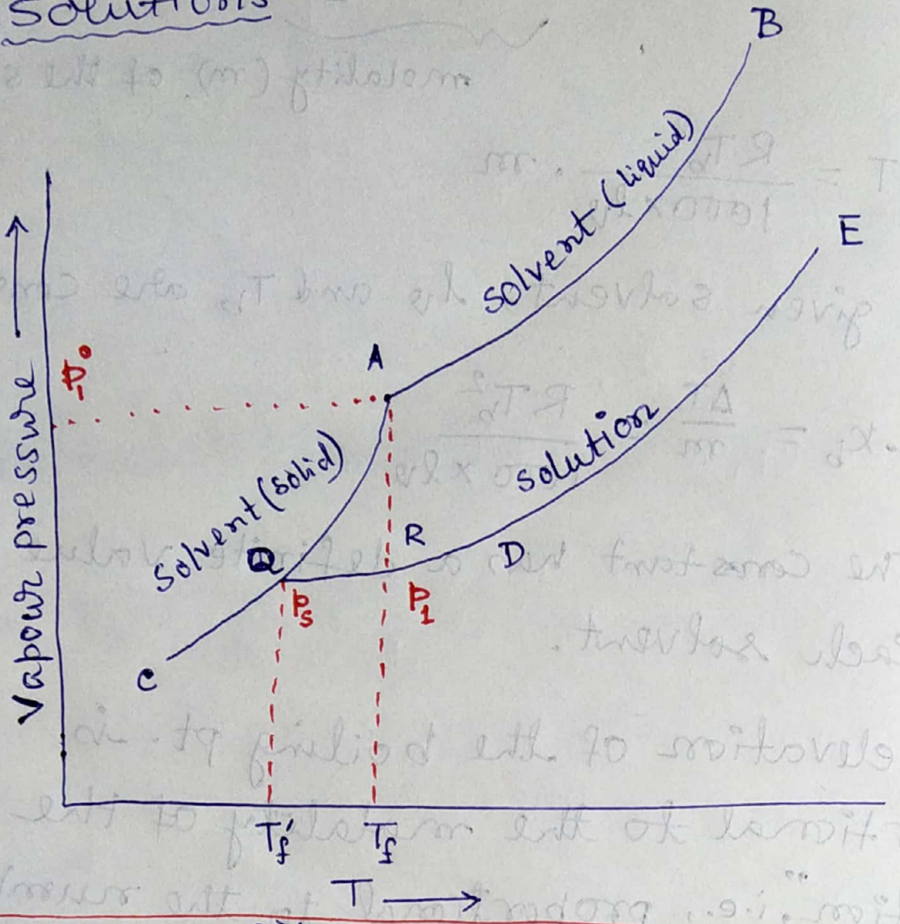
"the elevation of the boiling pt. is proportional to the molality of the solution", i.e., proportional to the number of molecules of any solute per 1000 gm of solvent.

This relation is valid for innumerable (অসংখ্য) cases of dilute sol^{n}s of non-volatile non-electrolyte solutes.

It is evident that equimolecular amounts of different substances dissolved in the same amount of a given solvent increase the boiling pt. to the same extent.



C. Depression of Freezing points of Solutions



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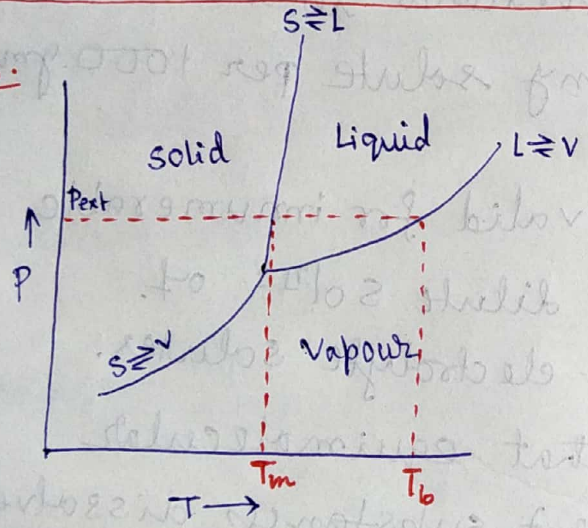

Melting pt (T_m), boiling pt (T_b). Transition pt. at given external pressure (P_{ext}) with S-L, L-V and S-S curves, respectively.

Phase diagram

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