

Solutions and Colligative Properties

Solutions

and

Colligative

Properties



SOLUTION AND COLLIGATIVE PROPERTIES

Solutions have two types of properties:-

a. **Constitutional Properties** - These depend on the nature of solute.

b. **Colligate Properties** - These depend on the number of solute particles.

These are 4 types of colligate properties.

1. Osmotic pressure

2. RLVP $\left(\frac{P^0 - P_\Delta}{P^s}\right)$

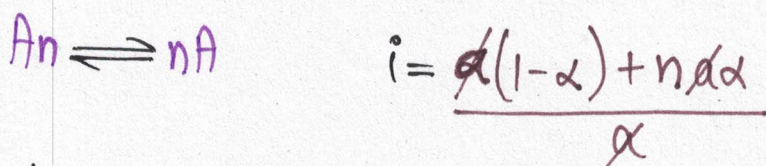
3. Elevation in BP

4. Depression in freezing point (ΔT_f)

VANT HALLF FACTOR

(2) It is observed colligative property Theoretical.

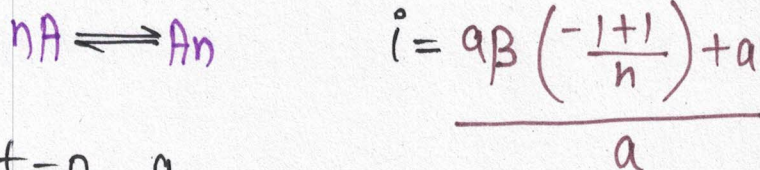
a. "i" for dissociation.



$$t = a$$

$$t = t\alpha(\alpha + 1) \quad n\alpha \quad i = 1 + (n-1)\alpha, \quad i > 1$$

b. "i" for association



$$t = 0 \quad a$$

$$t = t\alpha(1-\beta) \quad \frac{\alpha\beta}{n} \quad i = 1 + \beta\left(\frac{1}{n}-1\right), \quad i < 1$$

↪ It solute will neither associate nor $n \geq 2$ dissociate, then ($i=1$)
eg:- sucrose, urea.

OSMOSIS

When two liquids having different concⁿ are separated by semi-permeable membrane, then there will be spontaneous movement of particles from low concⁿ to high concⁿ. This process is called "osmosis".

The pressure applied that can stop osmosis is called osmotic pressure.

If osmotic pressure is " π ", then it is proportional to the concⁿ & temperature.

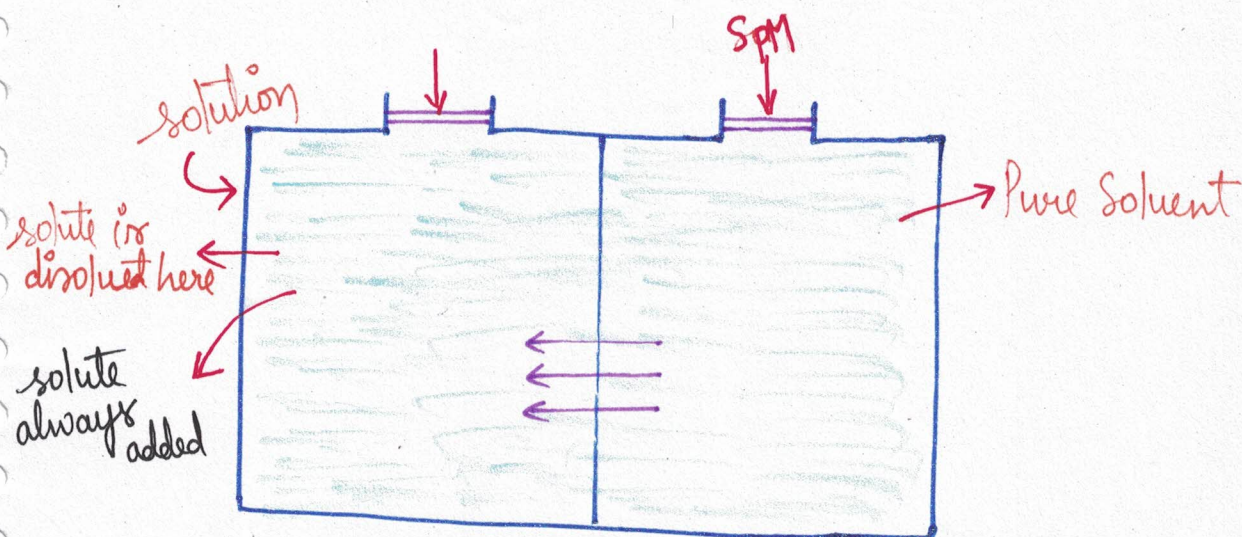
$$\pi \propto C$$

$$\pi \propto T$$

$$\pi = SCT$$

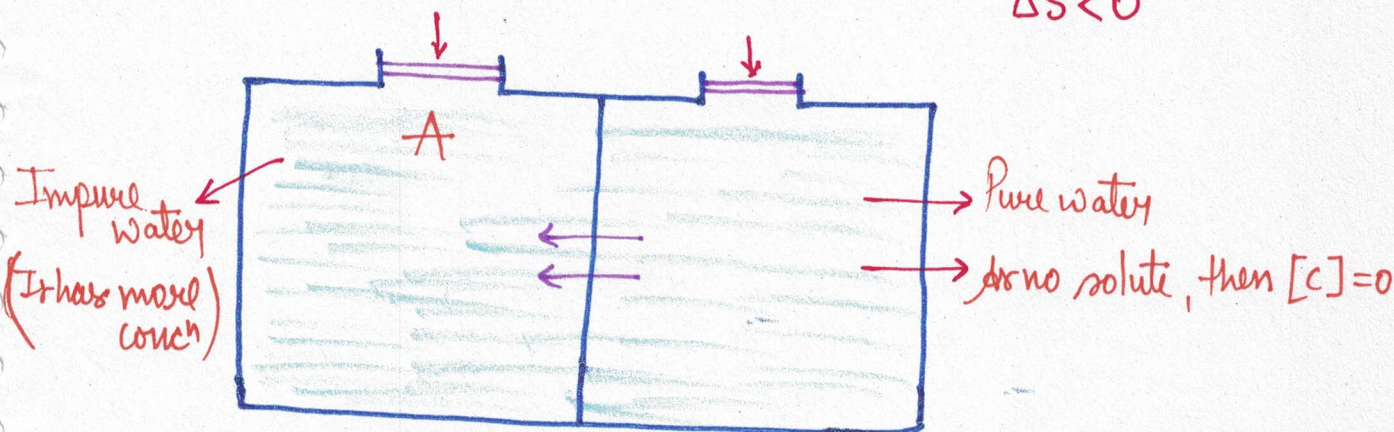
$$S = 0.0821 \text{ lt atm/mole K}$$

$$\pi = iCRT$$



some permeable membrane allows only solvent particle.

$$\Delta S < 0$$



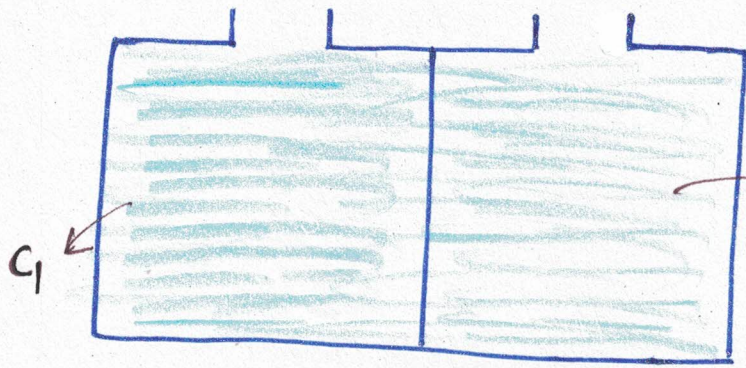
Thus the Natural process says pure water moves towards impure water. Thus, pressure has to be applied on container A.

- Natural SPM = Animal membrane
- Artificial SPM = Silicates of Fe, Co, Ni

REVERSE OSMOSIS

- When we'll apply pressure more than osmotic pressure, then

osmosis will be reversed and the process is called **reverse osmosis (RO)**.



(If solute is added in both)

$$(\pi)_{\text{Net}} = \pi_1 - \pi_2$$

$$i_1 RT = i_2 RT$$

If $\pi_1 = \pi_2 \rightarrow$ Isotonic solution

If $\pi_1 > \pi_2 \rightarrow$ solution 1 is hypertonic with soln 2.



What will be " π " of 0.1M urea solution at 27°C

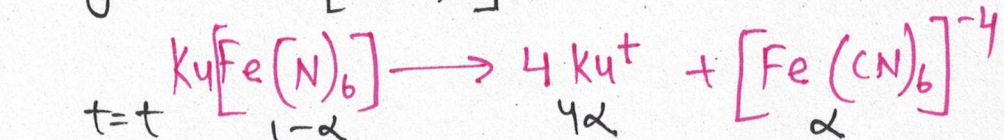
(i) $\pi = (1) \left(\frac{1}{10}\right) (0.08) (300) = \underline{2.4 \text{ atm}} = (fgh)$

As temp = K thus $P_1 V_1 = P_2 V_2$

(ii) " π " of 0.1M NaCl soln at 27°C (aq.)

$$\pi = (2) \left(\frac{1}{10}\right) \left(\frac{1}{2}\right) (300) = \underline{4.8 \text{ atm}}$$

(iii) " π " of 0.1M $K_4[Fe(CN)_6]$ $\alpha = 50\%$, $t = 27^\circ\text{C}$



$$nT = 1 + 4\alpha = 3 \quad \pi = (3)(0.1) \left(\frac{1}{10}\right) (300) = \underline{7.2 \text{ atm}}$$

(iv) " π " of soln containing 300ml 0.2M urea + 200ml 0.4M NaCl + 500ml 0.1M K_2SO_4 at 27°C

$$n_1 = 300 \times 0.2 = 60 \text{ millimoles}$$

$$n_2 = 200 \times 0.4 \times 2 = 160 \text{ millimoles}$$

$$n_3 = 500 \times 0.1 \times 3 = 150 \text{ millimoles}$$

$$[C] = \frac{60 + 160 + 150}{1000} = \left(\frac{37}{100}\right)$$

$$(\pi)_{\text{soln}} = \left(\frac{37}{100}\right) \left(\frac{1}{10}\right) (300) = \underline{\frac{37}{4} \text{ atm}}$$

$$\text{Colligative Property} \propto \frac{1}{(\text{Mass})_{\text{solute}}}$$

VAPOUR PRESSURE

It is pressure executed by vapours on its liquid when liquid is in eq^m with vapours.

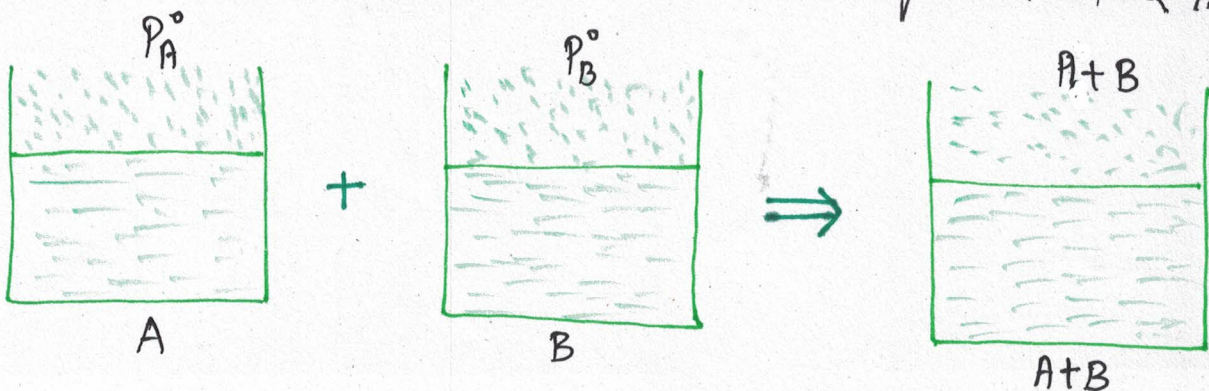
$$VP \propto T \rightarrow \text{only} \quad \log \left(\frac{P_2}{P_1} \right) = \frac{\Delta H}{(2.303)R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

If attraction force between molecules are more, then VP is Low.

VAPOUR PRESSURE OF SOLUTION

RAOULT'S LAW

V.P of any liquid will be proportional to its mole fraction in the solution.



$$P_A^\circ = \text{VP of pure A}; \quad P_B^\circ = \text{V.P of pure B}$$

$$P_A \propto x_B \longrightarrow P_A = kx_A, \quad \text{If } x_A = 1 \longrightarrow P_A = P_B^\circ$$

$$P_B \propto x_B \longrightarrow P_A = x_A P_A^\circ, \quad P_B = x_B P_B^\circ$$

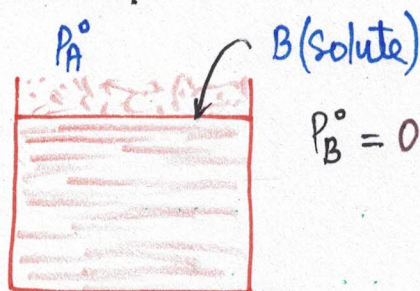
$$P_{\text{Total}} = P_A + P_B$$

$$P_{\text{solution}} = x_A P_A^\circ + x_B P_B^\circ$$

RELATIVE LOWERING IN VAPOUR PRESSURE (RLVP)

➤ When a non volatile solute is added to a volatile solvent, then Vapour Pressure will decrease. Always will multiply by

at the answer



$$P_s = x_A P_A^\circ + x_B P_B^\circ$$

When B is solute, $P_B^\circ = 0$

$$P_s = x_A P_A^\circ$$

$$P_s = (1 - x_B)(P_A^\circ) \Rightarrow$$

$$x_B = \frac{P_A^\circ - P_s}{P_A^\circ}$$

$$\frac{P_A^\circ - P_s}{P_A^\circ} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

Also,

$$-1 + \frac{P_A^\circ}{P_A^\circ - P_s} = \frac{n_{\text{solute}} + n_{\text{solvent}} + (-1)n_{\text{solute}}}{n_{\text{solute}}}$$

$$\frac{P^{\circ} - P_s}{P_s} = \frac{i \cdot n_{\text{solute}}}{n_{\text{solvent}}}$$

$P_s = \text{solution}$

$P^{\circ} = \text{Pure A}$

When the solution is very dilute $\Rightarrow n_{\text{solvent}} \gg n_{\text{solute}}$

$$\frac{P^{\circ} - P_s}{P^{\circ}} = i \frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

$P^{\circ} - P_s = \text{Lowering in V.P.}$, $\frac{P^{\circ} - P_{\Delta}}{P^{\circ}} = \text{RLVP}$

Q. - VP of ether at $20^{\circ}\text{C} = 442 \text{ mm}$. When 7.2 g of a solute is dissolved in 60 g ether, the VP is lowered by 32 units. Calculate molecular weight of solute if $M_{\text{ether}} = 74 \text{ g}$

Ans. - $(VP)_{\text{ether}} = 442 \text{ mm}$, $T = 293 \text{ K}$

$$(P^{\circ})_A = 442 \text{ mm}, \quad n_{\text{solute}} = \frac{7.2}{M}, \quad n_{\text{solvent}} = \frac{60}{74} \times 30$$

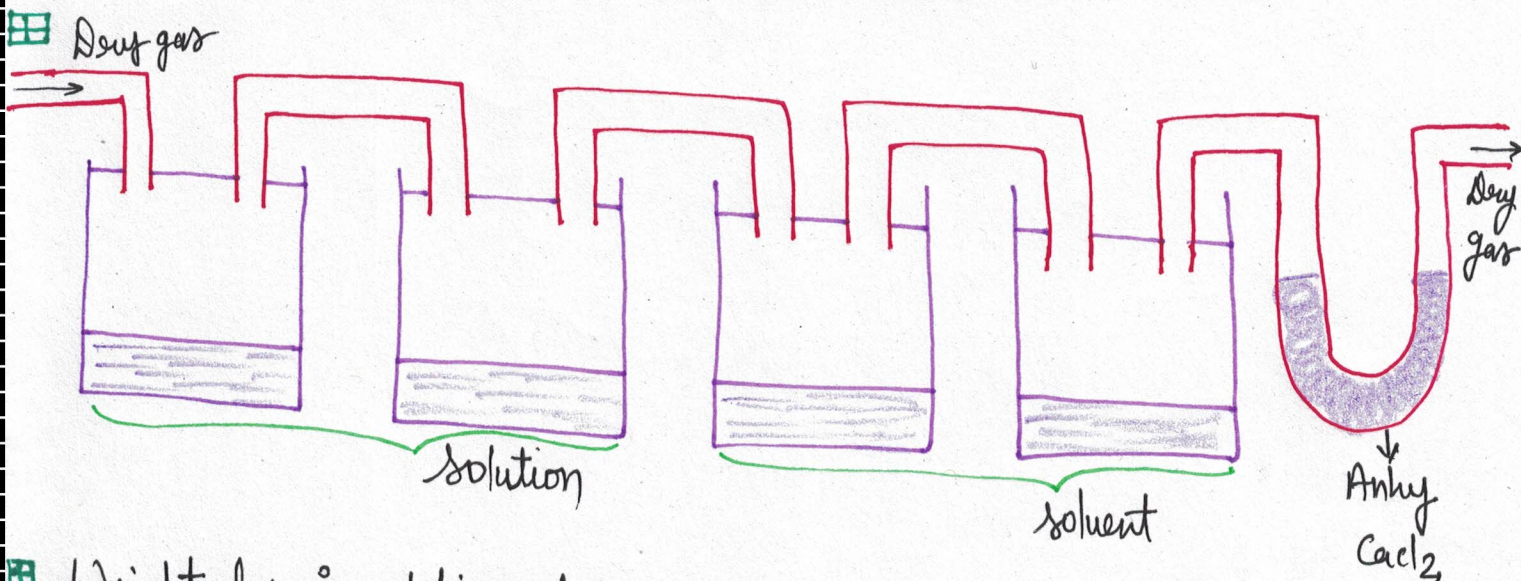
$$(P)_{\Delta} = \frac{442 - 32}{410} = 410 \text{ mm}$$

$$\therefore \frac{442 - 410}{410} = \frac{\left(\frac{7.2}{M}\right)}{\left(\frac{30}{74}\right)} = \frac{7.2 \times 37}{300M} \Rightarrow M = \frac{37 \times 37 \times 41}{8 \times 60} \text{ g}$$

$$\frac{32}{410} = \frac{7.2 \times 37}{300M}$$

$$M = 113.77 \text{ g} \quad \text{Ans.}$$

Experimental Method to determine RLVP (Ostwald Walker Method)



- Weight loss in solution container $\propto P_s$
- Weight loss in solvent container $\propto P^0 - P_s$
- Weight gain in CaCl_2 container $\propto P^0 - P_s + P_s$

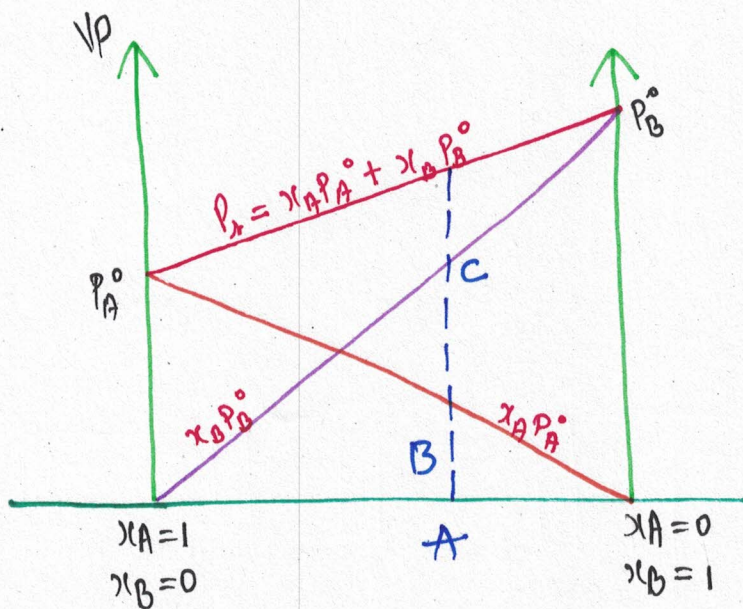
- If the solvent container would have been earlier $\propto P^0$
- Weight loss in solvent container $\propto P^0$
- Weight loss in solution container $\propto P^0 + P_s$
- Weight gain in CaCl_2 container $\propto P^0$

Ideal Solution

The solution in which $\Delta H_{\text{mixing}} = 0$ $\Delta V_{\text{mixing}} = 0$. They follow Raoult's Law.

If the forces A-A, B-B, A-B are same

$$P_s = x_A P_A^0 + x_B P_B^0$$



$$AB + AC = ?$$

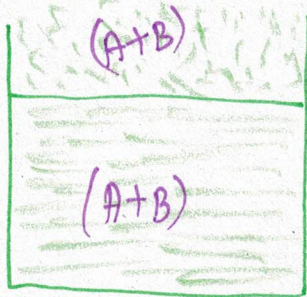
$$\downarrow \quad \quad \quad \searrow$$

$$x_A P_A^0 \quad \quad \quad x_B P_B^0$$

$$AB + AC = AD$$

VP will be between P_A^0 and P_B^0 .

More Volatile component is always costlier.



$$P_A = y_A P_2 \Rightarrow y_A = \frac{x_A P_A^0}{x_A P_A^0 + x_B P_B^0}$$

$$P_B = y_B P_2 \Rightarrow y_B = \frac{x_B P_B^0}{x_A P_A^0 + x_B P_B^0}$$

$y_A \Rightarrow$ Vapour composition of A

$y_B \Rightarrow$ Vapour composition of B

Q. V.P of pure "A" = 100 mm of Hg / Calculate :-
 V.P of pure "B" = 150 mm of Hg / Calculate :-

a. (V.P)_{Total} & Vapour composition if an liquid form 3 moles of A and 2 mole of B present.

Ans:- (a) $x_A = \frac{3}{5}, x_B = \frac{2}{5}$

$$P_2 = \left(\frac{1}{5}\right) [3 \times 100 + 2 \times 150]$$

$$P_2 = 120 \text{ mm.}$$

$$y_A = \frac{\frac{3}{5} \times 100}{120} = 0.5, y_B = 0.5$$

373

(b) If condensed, they find new mole fraction and the new (v.p)_{Total}

Ans. $(x_A = \frac{1}{2}, x_B = \frac{1}{2}) \longleftarrow (x_A)_i = \frac{3}{5}, (x_B)_i = \frac{2}{5}$

Thus, B gets enriched, it had more v.p. Thus, doing many times, we can get pure (B) \rightarrow Fractional Distillation.

$$(VP)_s = \frac{1}{2}(100) + \frac{1}{2}(150) = 125$$

(c) Now, find new vap. composⁿ of A and B.

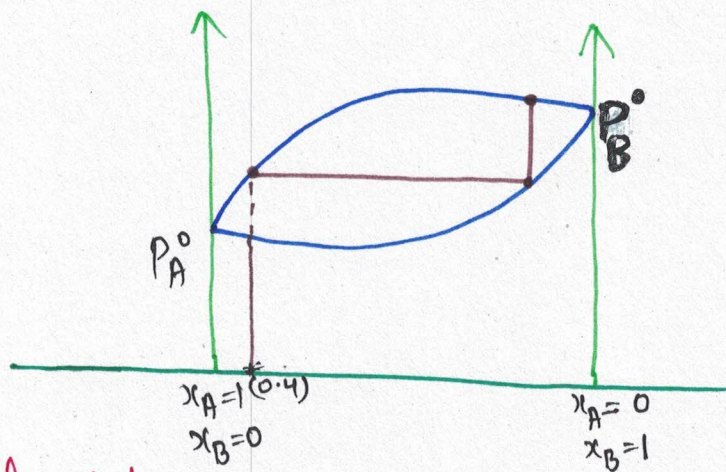
Ans. $(Y_A)_{\text{new}} = \frac{\frac{1}{2}(100)}{125} = 0.4$

$$(Y_B)_{\text{new}} = \frac{75}{125} = 0.6$$



Thus, similarly we can separate it.

The last question shows the process of distillation.



eg of Ideal solution



- a. Benzene Toluene
- b. Methyl bromide + ethyl iodide
- c. Butyl chloride + Butyl bromide
- d. $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$
- e. c1ccccc1Cl + c1ccccc1Br

NON IDEAL SOLUTION

These solution which don't follow Raoult's Law. It is of two kinds :-

(i)

Positive deviation

$$P_A > x_A P_A^\circ, \quad P_B > x_B P_B^\circ$$

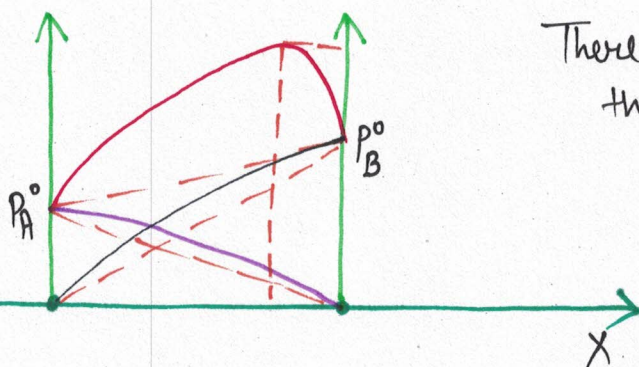
$$P_d > P_A^\circ x_A + x_B P_B^\circ$$

$$\Delta H_{mix} > 0, \quad \Delta V_{mixing} > 0.$$

Thus the mixture will be colder ($\Delta H_{mix} > 0$).

$$A-B < (A-A \text{ and } B-B)$$

The VP will be greater than P_B° at one pt.



There will be one point where the VP will be $> P_B^\circ$

l.g.:-

a. Acetone + ethanol

f. CCl4 + CH3OH

b. Acetone + CS2

g. H2O + C2H5OH

c. Acetone + Benzene

h. H2O + CH3OH

d. CCl4 + Toluene

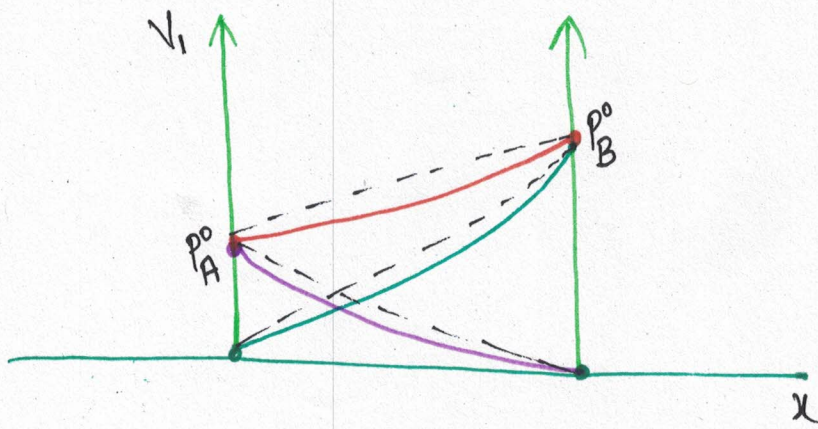
e. CCl4 + chloroform

i. C6H12 + C2H5OH

Negative deviation

$$P_A < x_A P_A^\circ, \quad P_B < x_B P_B^\circ, \quad P_d < x_A P_A^\circ + x_B P_B^\circ$$

$$\Delta H_{mix} < 0, \quad \Delta V_{mix} < 0, \quad (A-B) > (A-A, B-B)$$

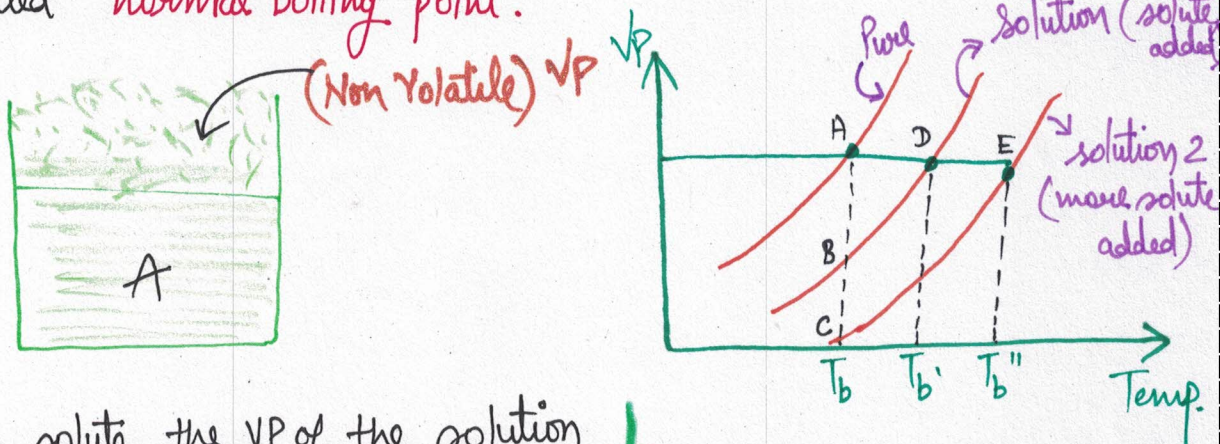


eg:-

- | | |
|---|--|
| a. Acetone + aniline | e. $\text{CH}_2\text{Cl}_2 + \text{Benzene}$ |
| b. Acetic acid + Pyridine | f. $\text{H}_2\text{O} + \text{HCl}$ |
| c. Acetic acid + CH_3OH | g. $\text{HNO}_3 + \text{H}_2\text{O}$ |
| d. $\text{CHCl}_3 + \text{lt} - \text{O} - \text{lt}$ | |

Elevation in Boiling Point

It is the temperature at which the V.P of any liquid is equal to the external atmospheric pressure. If atmospheric pressure is 1 atm, then it is called "normal boiling point".



On adding solute, the VP of the solution ↓

$$\Delta P \propto \Delta T_b$$

$$\Delta P \propto \text{molarity}$$

$$\Delta T_b = i K_b \text{ Molality}$$

units of K_b (Molal elevation constant)
 $= K \text{ kg/mol}$

$K_b \rightarrow$ ebullioscopic constant

$h \rightarrow$ latent heat of vapour

Experimentally;
$$K_b = \frac{RT_b^2}{1000h}$$

$R = 8.31 \text{ J/mole K}$ or 2 cal/mole K

$T_b =$ Normal boiling point of solvent

For Water -
$$K_b = \frac{(2)(373)^2}{(1000)(540)} = \frac{373 \times 373 \times 2}{54 \times 10^4 \times 27} = 0.515$$

$$(K_b)_{\text{water}} = 0.52 \text{ K kg/mol}$$

1. A Solution of 1g phenol in 50 ml of diethyl ether boiled at a temp. elevated by 0.632°C . The Molal elevation constant for diethyl ether is 2.12 K mol kg . Density is 0.714 g/ml . Calculate molecular formula of Phenol.

$$\Delta T_b = i K_b \quad \text{Molality} = (0.632) = (2.12)M$$

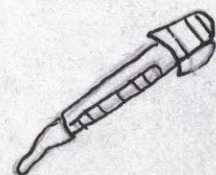
$$\text{Mass/phenol} = \frac{(0.632)}{(2.12)} \times \frac{(50)(0.714)}{(1000)} = \checkmark$$

$$\text{Mass of Solvent} = (50)(0.714)$$

2. A solution of 1.21g of a solute ($M = 152$) in 26.7g acetone boils at 329.8 K . Calculate (h_v) per mole of acetone. Pure acetone boils at 329.3 K .

$$\Delta T_b = 0.5 \text{ K} \quad K_b = \frac{(2)(329.8)^2}{(1000)(h_v)}$$

$$(0.5) = \frac{(2)(329.8)^2}{(1000)(h_v)} \cdot \frac{(1.21)}{(152)} (1000)$$



Here, "l_v" we get in (cal/gram). Then, get "l_n" in (cal/mole)

Depression in Freezing Point

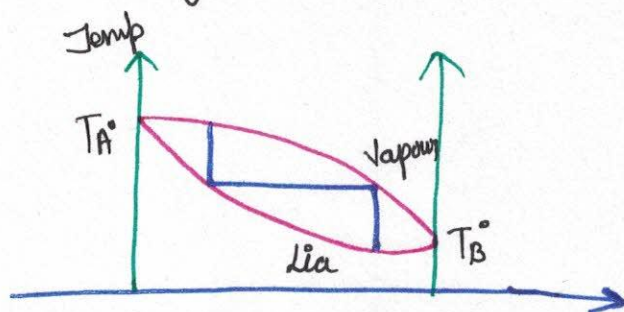
K_f = molal depression constant or cryoscopic constant. $\Delta T_f = 80 \text{ cal/gm}$

$$K_f = \frac{R(T_f)^2}{1000 l_f}, \quad K_f = 1.86 \text{ K kg/mol}$$

$$\Delta T_f = i K_f \text{ molality}$$

DISTILLATION

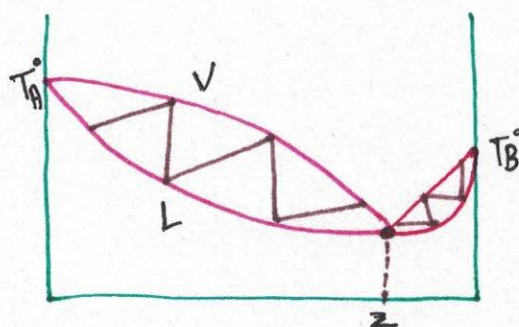
It is a process to separate two or more than two liquids having different Boiling points.



$$VP \propto \frac{1}{BP}$$

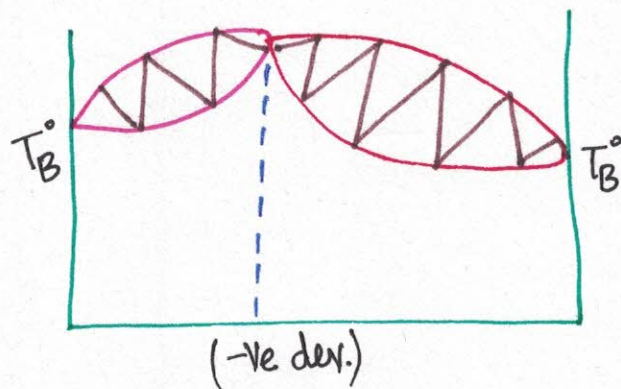
But in case of (+) deviation

Z = BP is same for both and is called azeotropic mixture.



(+) deviation

For (-)ve deviation



In a non ideal solⁿ at a certain composⁿ, both liquid will have same BP, this compⁿ is called **azeotropic mixture**.

In (+)ve deviation, In this mixture \rightarrow Minⁿ BP.

(-)ve deviation, in this mixture \rightarrow Maxⁿ BP.

Azeotropic mixture can't be distilled but it is distilled by adding a particular substance which vapourises the one of the substances.

Q. 100g of sucrose solution in water is cooled to -0.5°C . what of ice would be separated out if the solⁿ starts to freeze at -38°C
(K_F)_{H₂O} = $1.86 \text{ K mol}^{-1} \text{ kg}$.

Ans. $0 - (-0.38) = (1.86)(m_1)$
(molality)₁ = 0.204

$$\therefore [(n)_i]_{\text{solute}} = (0.204)(342) = 69.87 \text{ g}$$

Therefore, amount of water = $(100 - 69.87) \text{ g} = 30.13 \text{ g}$

$$0 - (-0.5) = (1.86)(m_2)$$

(molality)₂ = 0.268

$$\therefore [(n)_F]_{\text{solute}} = (0.268)(342) = 91.6 \text{ g}$$

Therefore, final amount of water = 8.4 g

Amount of ice separated = $(30.13 - 8.4) \text{ g}$
 $= 21.73 \text{ g}$

$P(x_1, y_1)$

$$ax + by + c = 0$$

$Q(x_2, y_2)$

P is above the line;

$$(b)(ax_1 + by_1 + c) > 0$$

Q is below the line;

$$(b)(ax_2 + by_2 + c) > 0$$