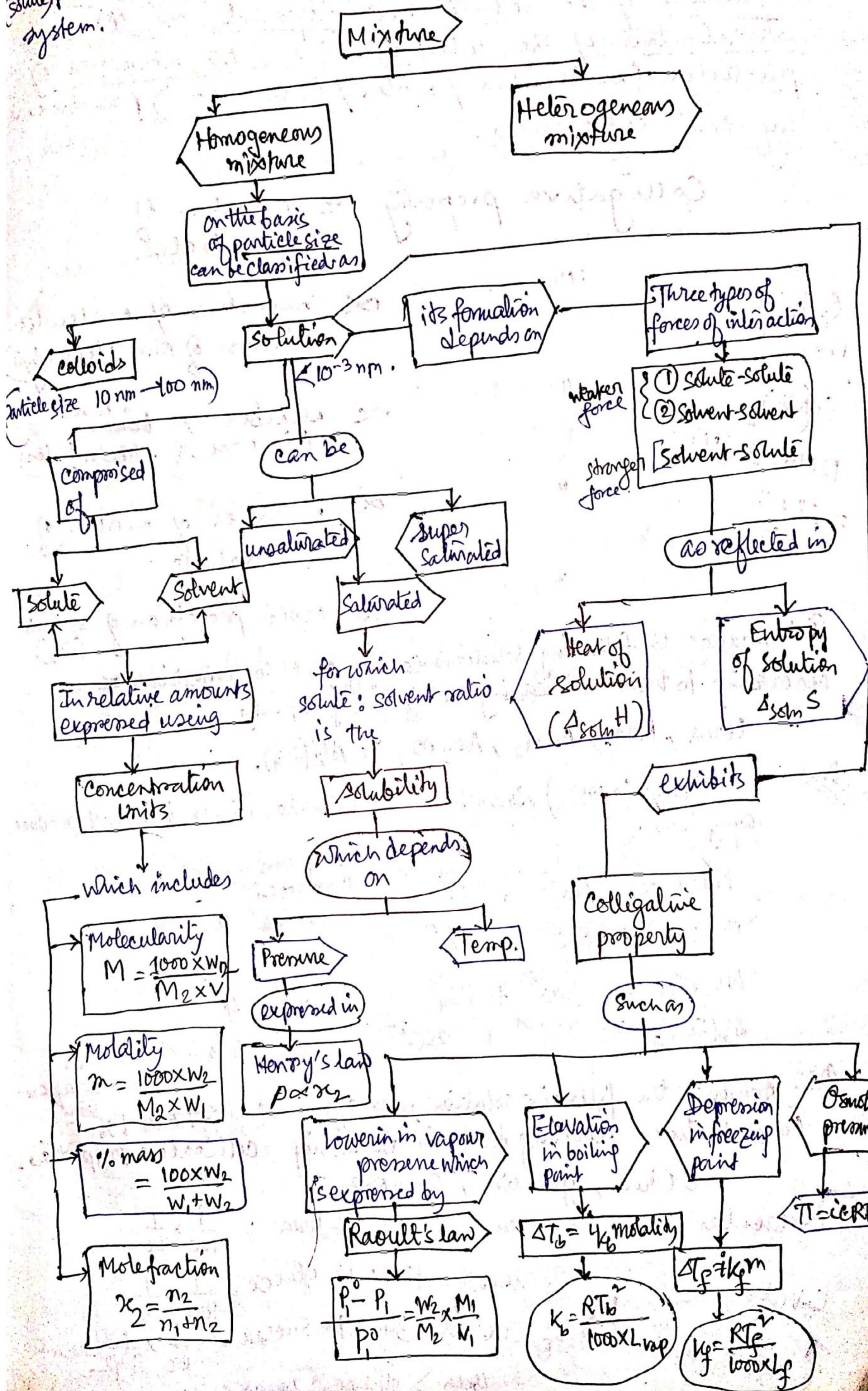


16/03/19 Class XII

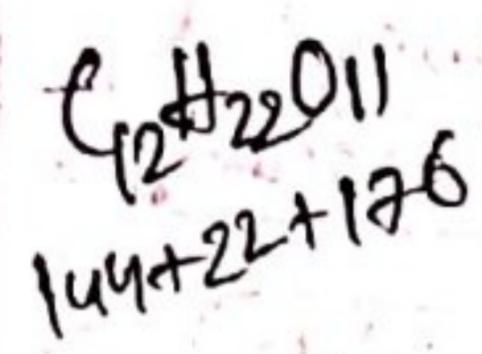
Solution

- Solution is a homogeneous mixture of two phases namely dispersed (solute) phase and dispersion medium (solvent), but solution is a single phase system.



Colligative property: Colligative properties of are such properties of dilute solutions of some non-volatile substances which do not depend upon the nature of the solute but depends on the concentration of the solution, i.e., the number of particles (molecules / moles / ions etc.) produced by that substance.

Colligative property \propto number of particles.



$$= \text{CO}(\text{NH}_2)_2$$

$$12 + 16 + 2 \times 16$$

$$= 28 + 32$$

$$= 60$$

\propto number of molecules
(in case of non-electrolytes)

\propto number of ions
(in case of electrolytes)

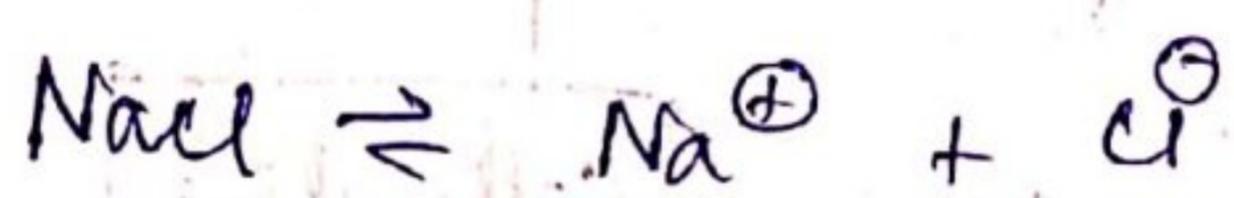
\propto number of moles of solute

\propto mole fraction of solute (x_2)

Q1. Arrange the following solutions each of 0.1 M concentrations ~~of the~~ according to their increasing colligative property.

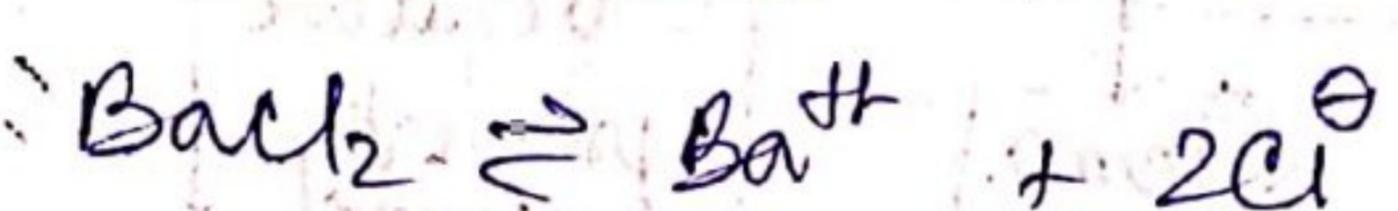
Urea, NaCl, BaCl₂, Na₃PO₄, Al₂(SO₄)₃

~~Ans~~ Urea [CO(NH₂)₂] doesn't ionise in water, since it doesn't produce any ions.

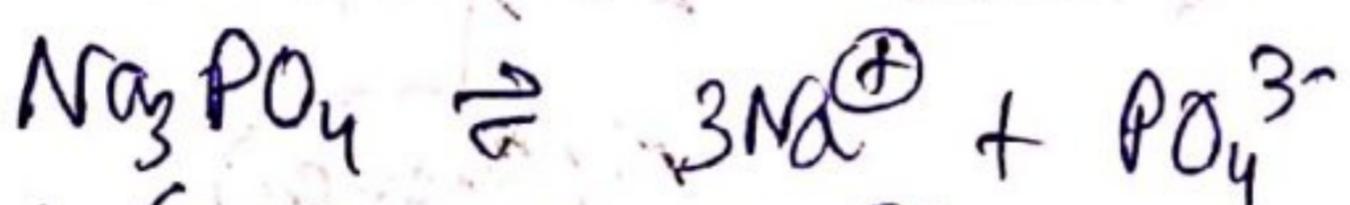


No. of ions produced

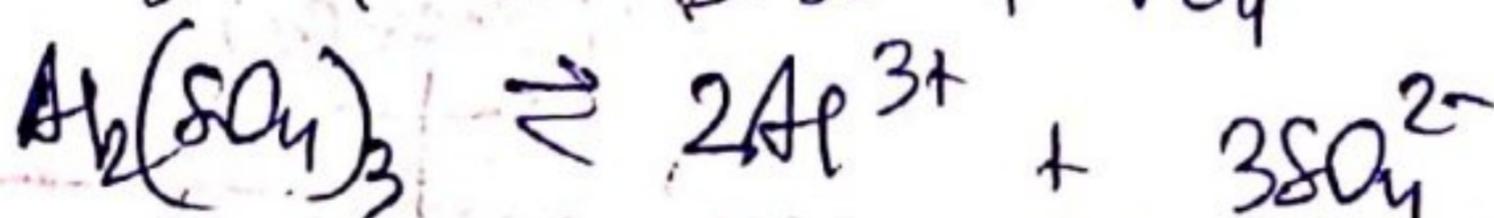
$$n = 2$$



$$n = 3$$



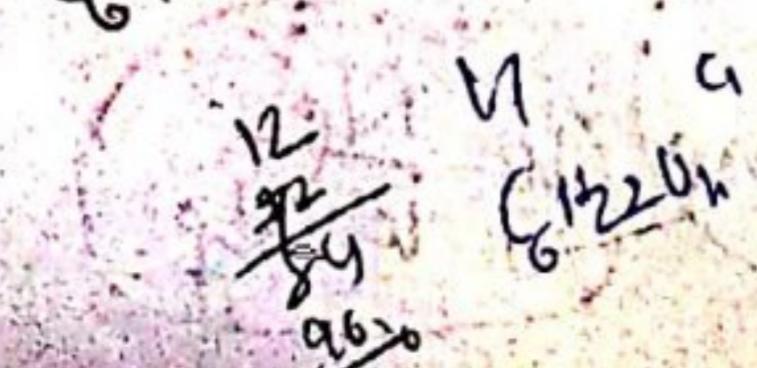
$$n = 4$$



$$n = 5 \text{ maximum no.}$$

Q2. Arrange the following solution, each of which has ~~1%~~ ^{of ions in aqueous} concentrations according to their increasing colligative properties.
Urea, glucose, sucrose.

Molecular mass of urea = 60, 1% urea = $\frac{1}{100} \times \frac{1}{60}$



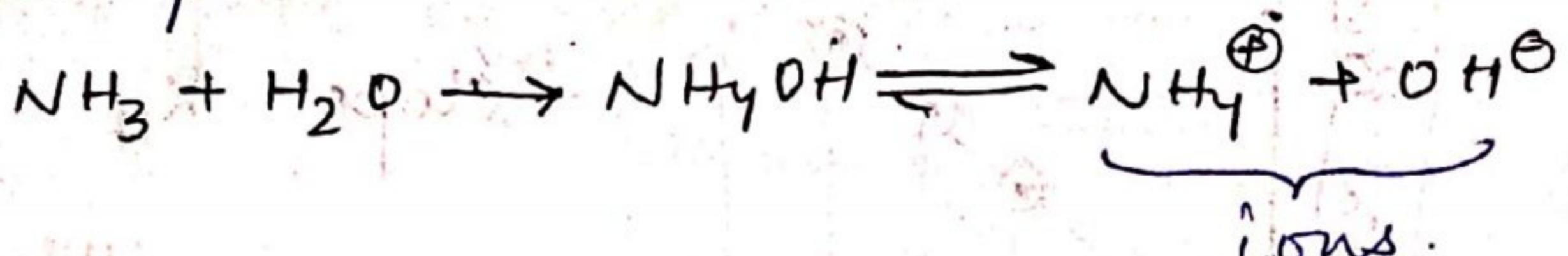
of glucose = 180, 1% glucose = $\frac{1}{100} \times \frac{1}{180}$

of sucrose = 342, 1% sucrose = $\frac{1}{100} \times \frac{1}{342}$

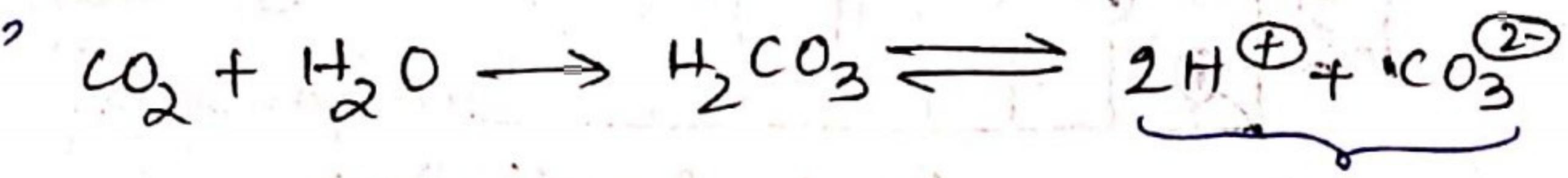
Urea $>$ glucose $>$ sucrose

Solubility of gas in liquid solvent

- Gases which form ions in that solvent such as NH_3 , CO_2 both are soluble in water because both of them can produce ions in aqueous solution.



Similarly



Hence, both of NH_3 and CO_2 do not dissolve in benzene because no one can produce ions in Benzene.

- Gases which can be liquefied easily, are more soluble in H_2O than the other gases which aren't liquefied easily.

- Solubility of gas in liquid also depends on the pressure as stated by Henry's law.

"The solubility of a gas in a liquid is directly proportional to the partial pressure of the dry gas in that solvent."

If p be the partial pressure of the gas and x_2 be the mole fraction, then by Henry's law,

$$p \propto x_2 \quad \text{or} \quad p = K_H x_2 \quad \text{where, } K_H = \text{constant}$$

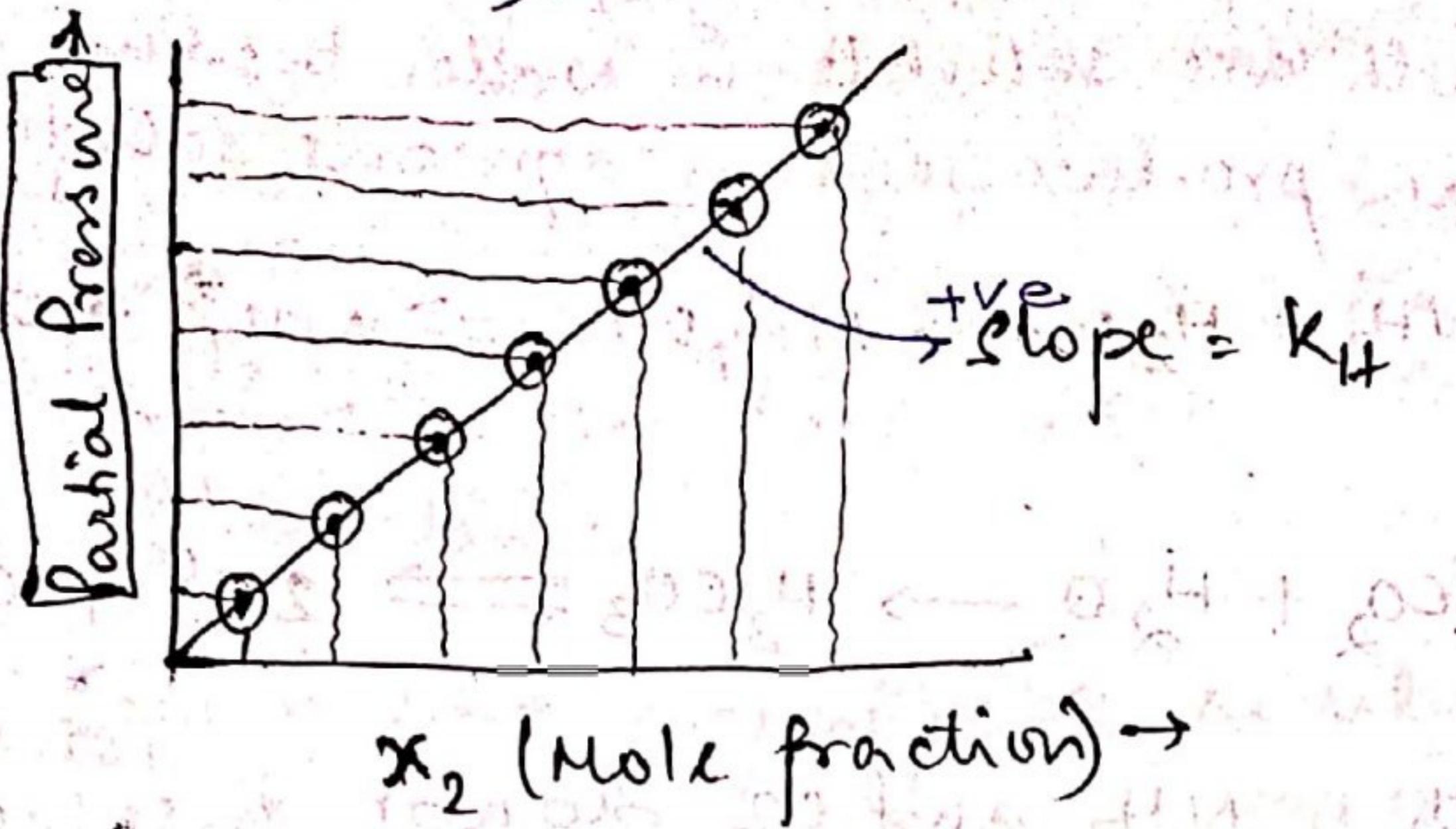
K_H being a proportionality constant whose value depends on the nature of the gas at constant temperature. [K_H is the characteristic constant of individual gas] and x_2 represents the solubility of the gas.

K_H is directly proportional to temperature,

$$K_H \propto \text{Temp.}$$

If Henry's law is true then if a graph is drawn taking different values of partial pressure with their corresponding mole fractional values then we will get a straight line passes through the origin.

with a positive slope representing Henry's law constant (K_H).



- To increase the solubility of CO_2 in soft drinks and soda-water the bottle is sealed under high pressure.
- Higher the value of K_H at given pressure, the lower is the solubility of the gas in the liquid.

from Henry's law

where m = mass of the dissolved gas
 P = partial pressure of the gas

$$P = K_H x_2$$
$$K_H = \frac{P}{x_2}$$

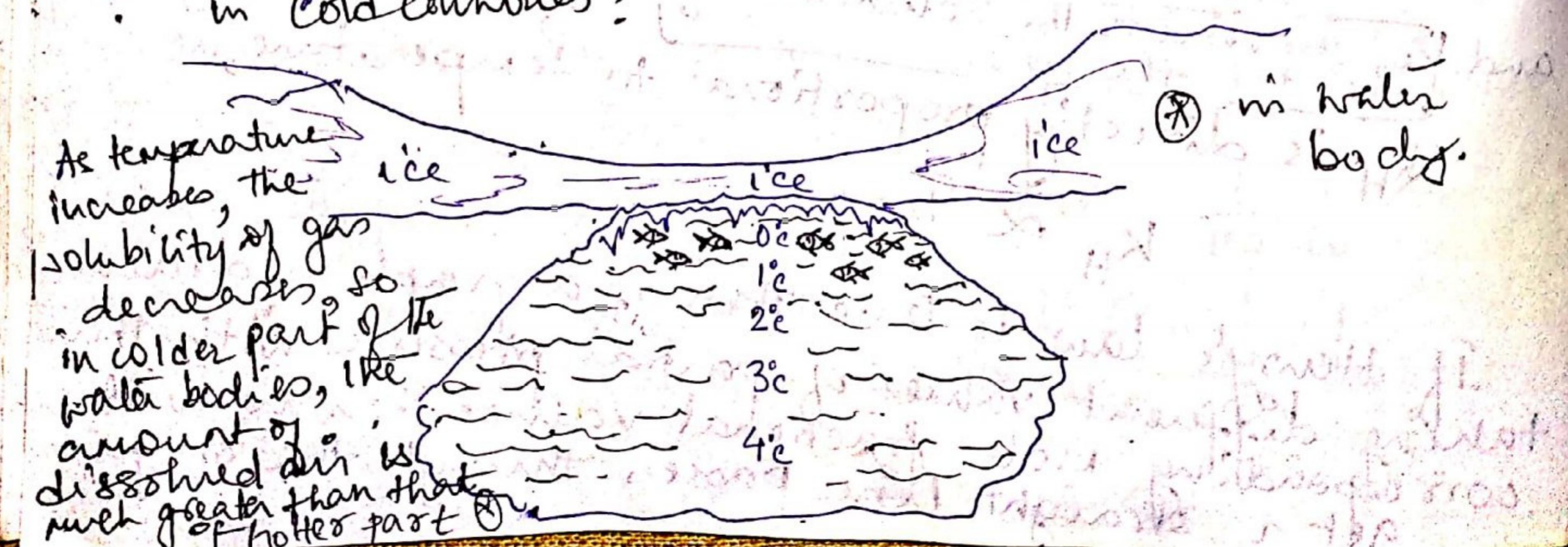
$m \propto P$ This is another form of Henry's law

$$m = K_H P$$

$\uparrow K_H \propto \frac{1}{x_2}$ where P is kept constant

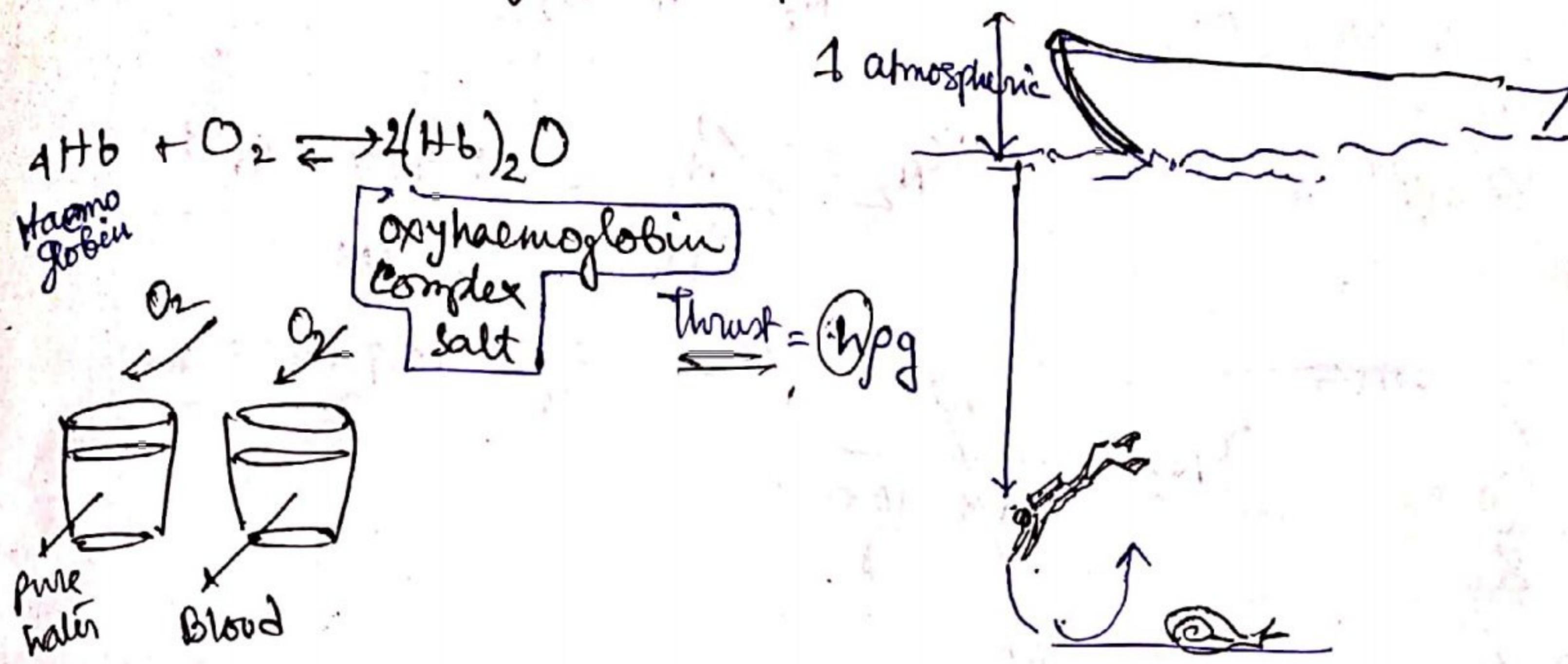
On raising temp. the value of K_H increases as a result of which x_2 as well as solubility of gas decreases.

Q Why the aquatic lives feel comfort in colder part rather than in hotter part of a water body during winter time in cold countries?



23/03/19

Q. To avoid the painful effect why does He ~~is~~ mixed with O₂ in O₂-cylinder of the deep sea divers?



To minimise the painful effects accompanying the decompression of deep-sea divers, O₂ diluted with less soluble He gas is used as breathing gas.

K_H values for both N₂ and O₂ increases with increase of temperature and thus solubility of gases decreases with increase in temperature.

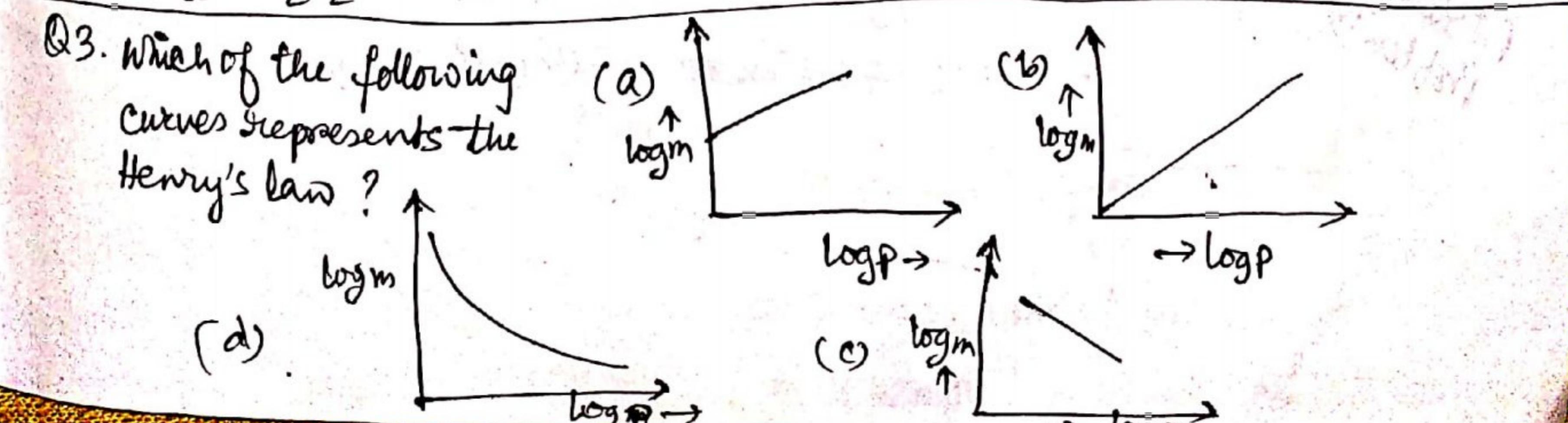
In lungs where oxygen is present in air with high partial pressure, haemoglobin combines with oxygen to form oxyhaemoglobin. In tissues when partial pressure of O₂ is too low, oxyhaemoglobin releases O₂ for utilisation in cellular activities.

Q2. Henry's law constants for aqueous solution of CO, O₂, CO₂ and C₂H₂ gases are respectively at 25°C as 58 × 10³, 43 × 10³, 1.61 × 10³, and 1.34 × 10³. The solubility of these gases decreases in the order:

(a) CO > O₂ > CO₂ > C₂H₂ (b) O₂ > CO₂ > CO > C₂H₂

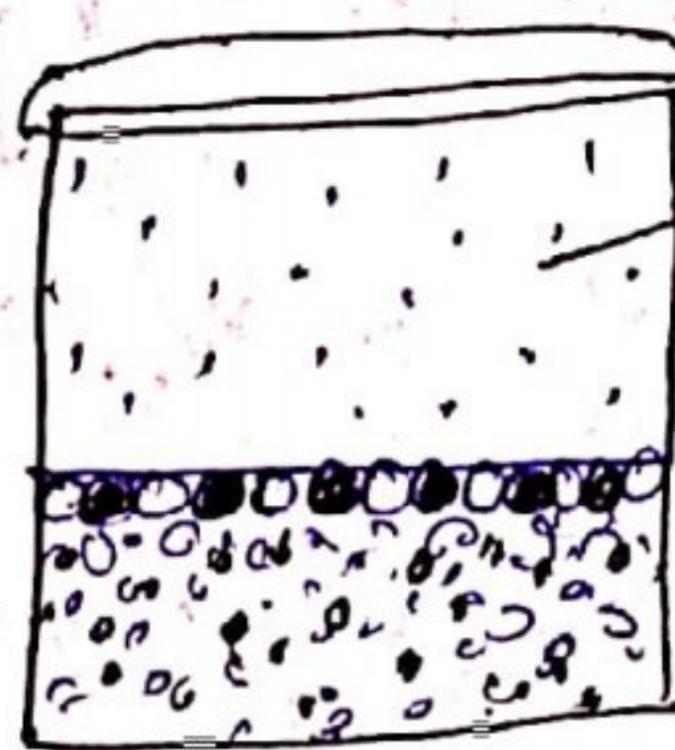
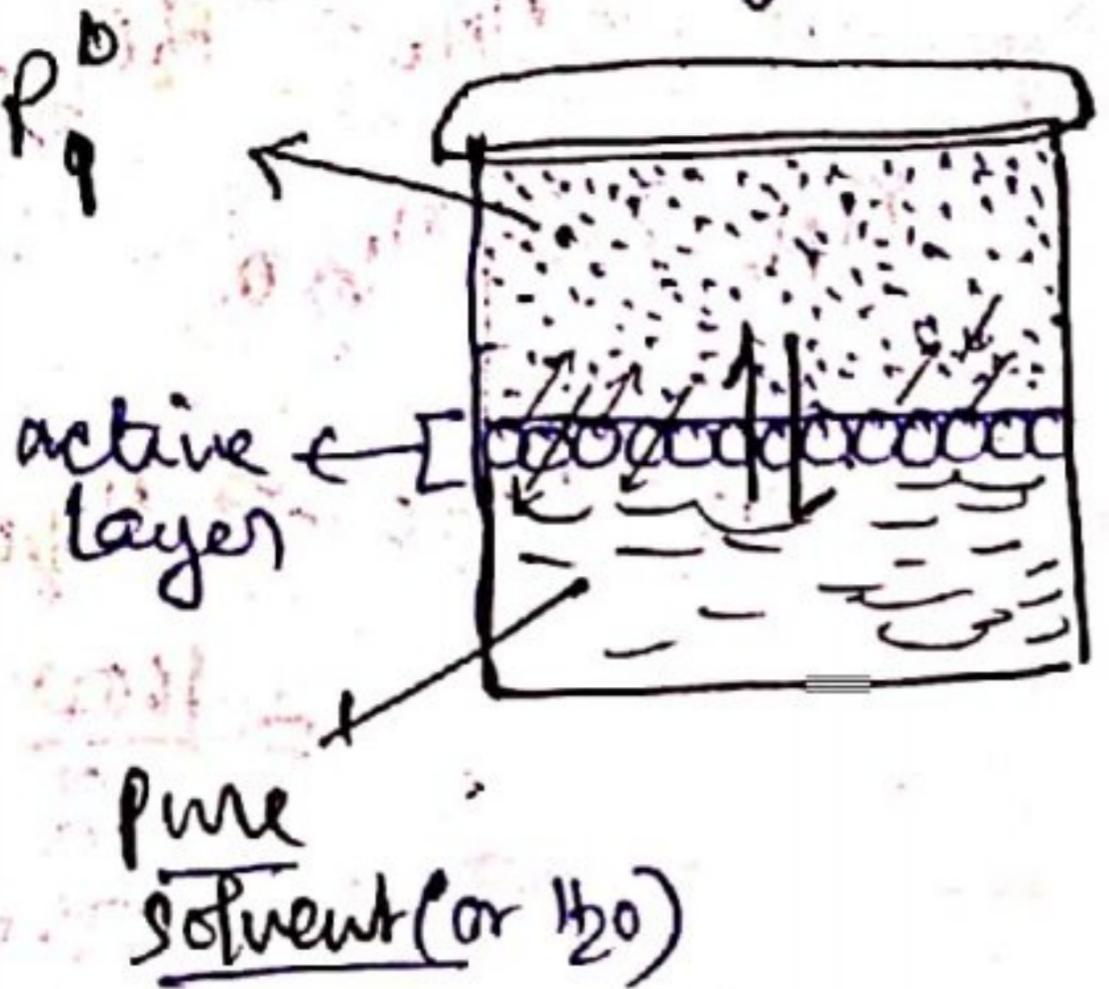
(c) C₂H₂ > CO₂ > O₂ > CO (d) O₂ > CO₂ > C₂H₂ > CO

Q3. Which of the following curves represents the Henry's law?



Lowering in vapour pressure on addition of nonvolatile solute in a volatile solvent

Whenever a nonvolatile solute is added to a liquid solvent, the vap. pressure of the solvent is lowered. This is due to the fact that,



P_1 in solution from volatile Solute molecule replace some of the solvent molecules on the surface layer.

$$P_1^{\circ} = \text{vap. pressure of pure solvent (or } H_2O\text{)}$$

$$P_1 = \text{vap. pressure of solvent when it is in solution (mixture)}$$

$$P_1^{\circ} > P_1$$

$$(P_1^{\circ} - P_1) = +ve$$

= Lowering in vap. pressure

$\left(\frac{P_1^{\circ} - P_1}{P_1^{\circ}} \right)$ Relative lowering in vap. pressure.

is a colligative property.

With the help of Raoult's law for nonvolatile solute which states that - At any given temp., the partial vapour pressure of solvent (P_1) of a solution is equal to its mole fraction (x_1) multiplied by the vap. pressure of the solvent when it is in pure state (P_1°).

$$P_1 = P_1^{\circ} x_1$$

Where x_1 & x_2 are the mole fraction

$$\text{or } P_1 = P_1^{\circ} (1 - x_2)$$

of solvent & solute respectively

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

$$x_1 + x_2 = 1$$

$$x_1 = 1 - x_2 \therefore$$

Both x_1 or x_2 are smaller than 1.

$$\left(\frac{P_1^{\circ} - P_1}{P_1^{\circ}} \right) = x_2$$

Since the relative lowering in vap. pressure is a colligative property

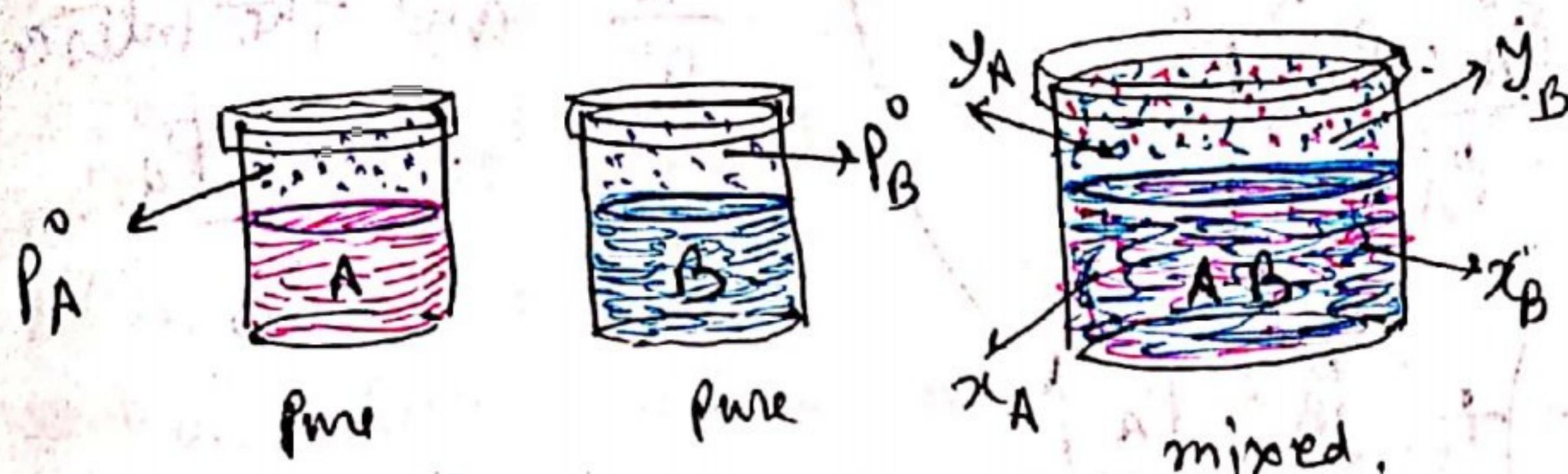
$$\text{or } \frac{P_1^{\circ} - P_1}{P_1^{\circ}} = \frac{n_2}{n_1 + n_2}$$

in dilute solution $n_2 \ll n_1$

$$\rightarrow \frac{P_1^{\circ} - P_1}{P_1^{\circ}} \approx \frac{n_2}{n_1} = \frac{W_2}{M_2} \times \frac{M_1}{W_1} \quad \therefore \text{neglecting } n_2 \text{ we get} \rightarrow$$

$$\frac{P_1 - P_1}{P_1} = \frac{W_2/M_2}{W_2 + W_1} \quad \text{or} \quad \frac{W_2}{M_2} \times \frac{M_1}{W_1}$$

Raoult's law for two volatile liquids



Let A & B are two volatile liquids have vap. pressures P_A^o and P_B^o when they are in pure state.

If A & B are mixed together then x_A & x_B are molefractions of A and B respectively in liquid phase (or in solution) while y_A and y_B are molefractions of A & B respectively in vapour phase. The total pressure on the solution (A-B) is considered as

$$P_T = P_A + P_B$$

where P_A and P_B are the partial vapour pressure of A and B respectively when they are in solution.

$$P_T = P_A^o x_A + P_B^o x_B$$

$$P_T = P_A^o x_A + P_B^o (1-x_A)$$

$$\text{or } P_T = P_A^o x_A + P_B^o - P_B^o x_A$$

$$P_T = P_B^o + (P_A^o - P_B^o) x_A$$

$$P_T = P_A^o (1-x_B) + P_B^o x_B$$

$$\text{or, } P_T = P_A^o - P_A^o x_B + P_B^o x_B$$

$$P_T = P_A^o + x_B (P_B^o - P_A^o)$$

Relationship between molefraction of the components of an ideal solution in the liquid phase and vapour phase

According to Dalton's partial pressure law

$$y_A \times P_T = P_A$$

molefraction of A component in vap. phase Total pressure on solution Partial vap. pres. of A

$$y_A = \frac{P_A}{P_T}$$

$$y_A = \frac{P_A^o x_A}{P_B^o + (P_A^o - P_B^o) x_A}$$

$$\frac{1}{y_A} = \frac{P_B^o + (P_A^o - P_B^o) x_A}{P_A^o x_A}$$

$$\Rightarrow \frac{1}{y_A} = \frac{P_B^{\circ} + (P_A^{\circ} - P_B^{\circ})x_A}{P_A^{\circ} x_A}$$

$$\therefore \frac{1}{y_A} = \frac{P_A^{\circ} - P_B^{\circ}}{P_A^{\circ}} + \left(\frac{P_B^{\circ}}{P_A^{\circ}} \right) \frac{1}{x_A}$$

$$\frac{1}{x_A} = \left(\frac{1}{y_A} - \frac{P_A^{\circ} - P_B^{\circ}}{P_A^{\circ}} \right) \frac{P_A^{\circ}}{P_B^{\circ}}$$

$$\text{a, } \frac{1}{x_A} = \frac{1}{y_A} \cdot \left(\frac{P_A^{\circ}}{P_B^{\circ}} \right) + \frac{P_B^{\circ} - P_A^{\circ}}{P_B^{\circ}}$$

$$y = m(x) + c$$

Hence a plot of $\frac{1}{x_A}$ vs. $\frac{1}{y_A}$
will be a linear curve
with a slope of $\frac{P_A^{\circ}}{P_B^{\circ}}$ and the intercept
 $c = \frac{P_B^{\circ} - P_A^{\circ}}{P_B^{\circ}}$

Q.3. Solutions of two volatile liquids A & B obey Raoult's law. At a certain temperature, it is found that when the total pressure above a given soln. is 400 mm of Hg, the mole fraction of A in a vapour phase is 0.45 and in the liquid it is 0.65. What are the vapour pressures of the two liquids in the pure states at the given temperature?

~~2 volatile liquids A & B are given, $P_T^{\text{(Total pressure on the solution)}} = 400 \text{ mm of Hg}$~~

mole fraction of A, $y_A = 0.45$
in vapour phase

mole fraction of A, $x_A = 0.65$, $P_A^{\circ} = ?$
in liquid phase

Applying Dalton's partial pressure law

$$y_A = \frac{P_A}{P_T}$$

$$P_A = (0.45 \times 400) \text{ mm}$$

$$\text{a, } P_A^{\circ} x_A = 180 \text{ mm of Hg}$$

$$P_A^{\circ} = \frac{180}{0.65} = 276.92 \approx 277 \text{ mm of Hg}$$

$$P_T - P_A = P_B$$

$$P_B = 400 - 180$$

$$P_B^o = 220 \text{ mm of Hg}$$

$$P_B^o = \frac{220}{0.35} = 628.57 \text{ mm of Hg}$$

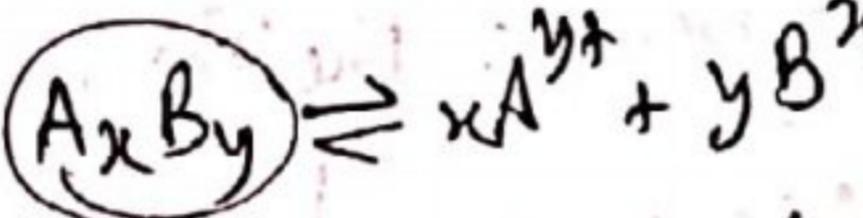
$$x_B = (1 - x_A)$$

$$= (1 - 0.65)$$

$$= 0.35$$

Limitations of Raoult's Law → This law is applicable only for

- Dilute solutions.
- The solute must be nonvolatile.
- The solute must not be either associate or dissociate into the solution.



Initial no. of moles 1 0
 If α be the degree of ionisation per mole of $A_x B_y$ then after ionisation 1 - α $x\alpha$ $y\alpha$

$$\text{Total no. of ions at equilibrium} = 1 - \alpha + x\alpha + y\alpha$$

$$= 1 + \alpha(x+y-1)$$

The cause of abnormality $i =$ Van't Hoff factor for ionisation $i > 1$

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

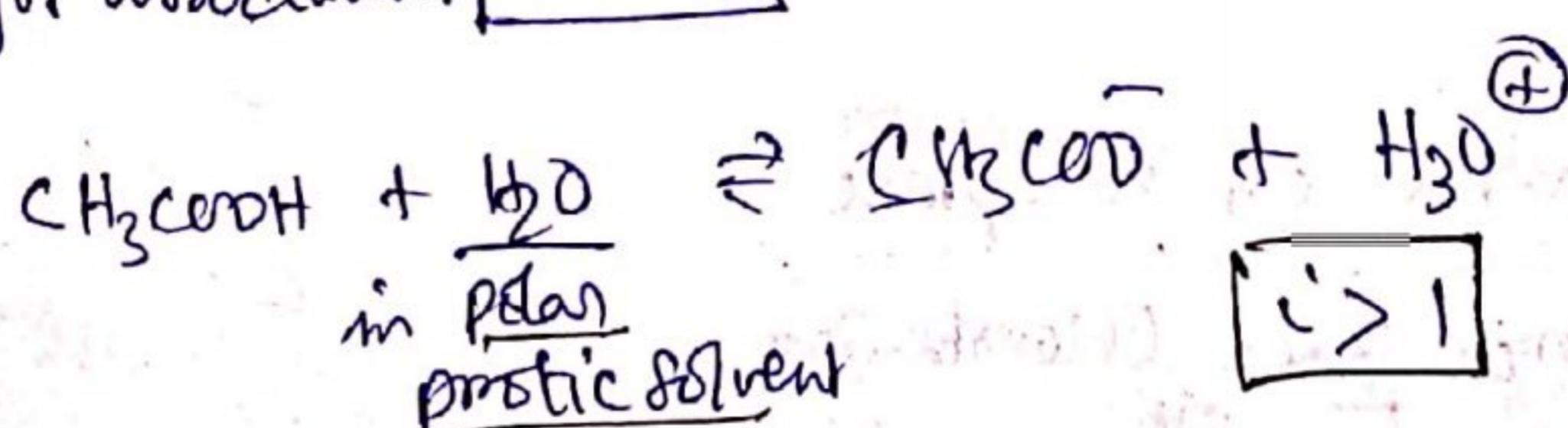


$$i = \frac{\text{Initially}}{\text{At equilibrium}} \frac{1}{1 - \alpha}$$

if α' be the degree of association

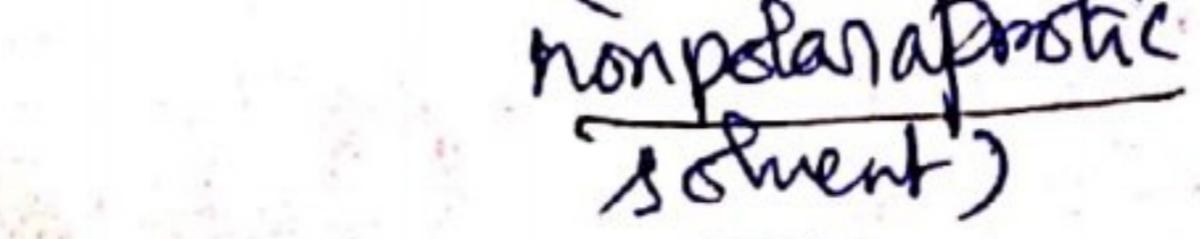
$$\text{Total no. of particles} = 1 - \alpha + \frac{\alpha'}{n} = 1 - \left(1 - \frac{1}{n}\right)\alpha$$

for association $i < 1$

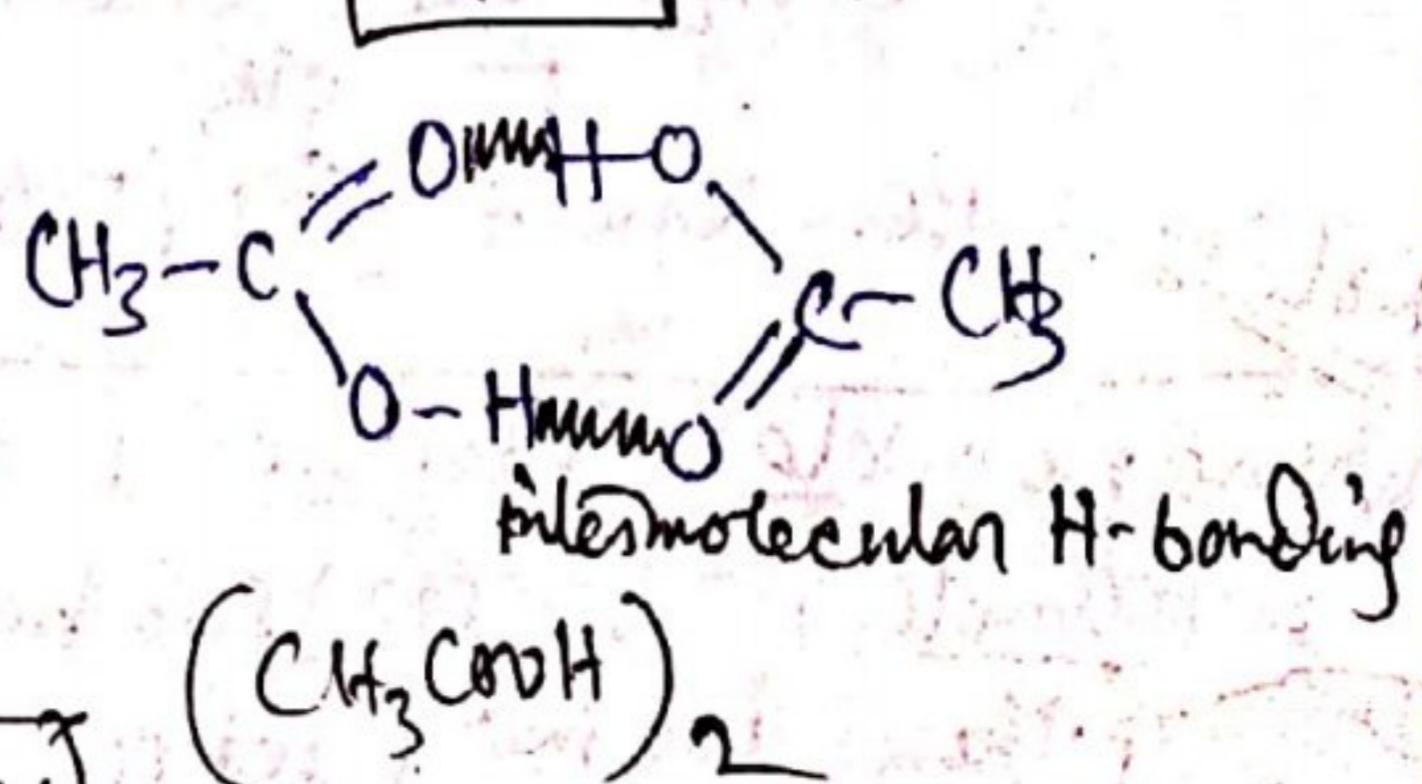


$i > 1$

Dimersiation
 (in benzene nonpolar protic solvent)



$i < 1$



29/03/19

classification of solution on the basis of the fact whether the solutions obey / disobey Raoult's law

Ideal Solution

In this case, there is no difference among the three intermolecular forces of attraction between

$$\text{Solvent...solute} = \text{Solvent...solvent} = \text{solute...solute}$$

i.e. $E_{A...B} = E_{A...A} = E_{B...B}$

as a result of which Total pressure on the soln

$$(P_T) = P_A + P_B$$

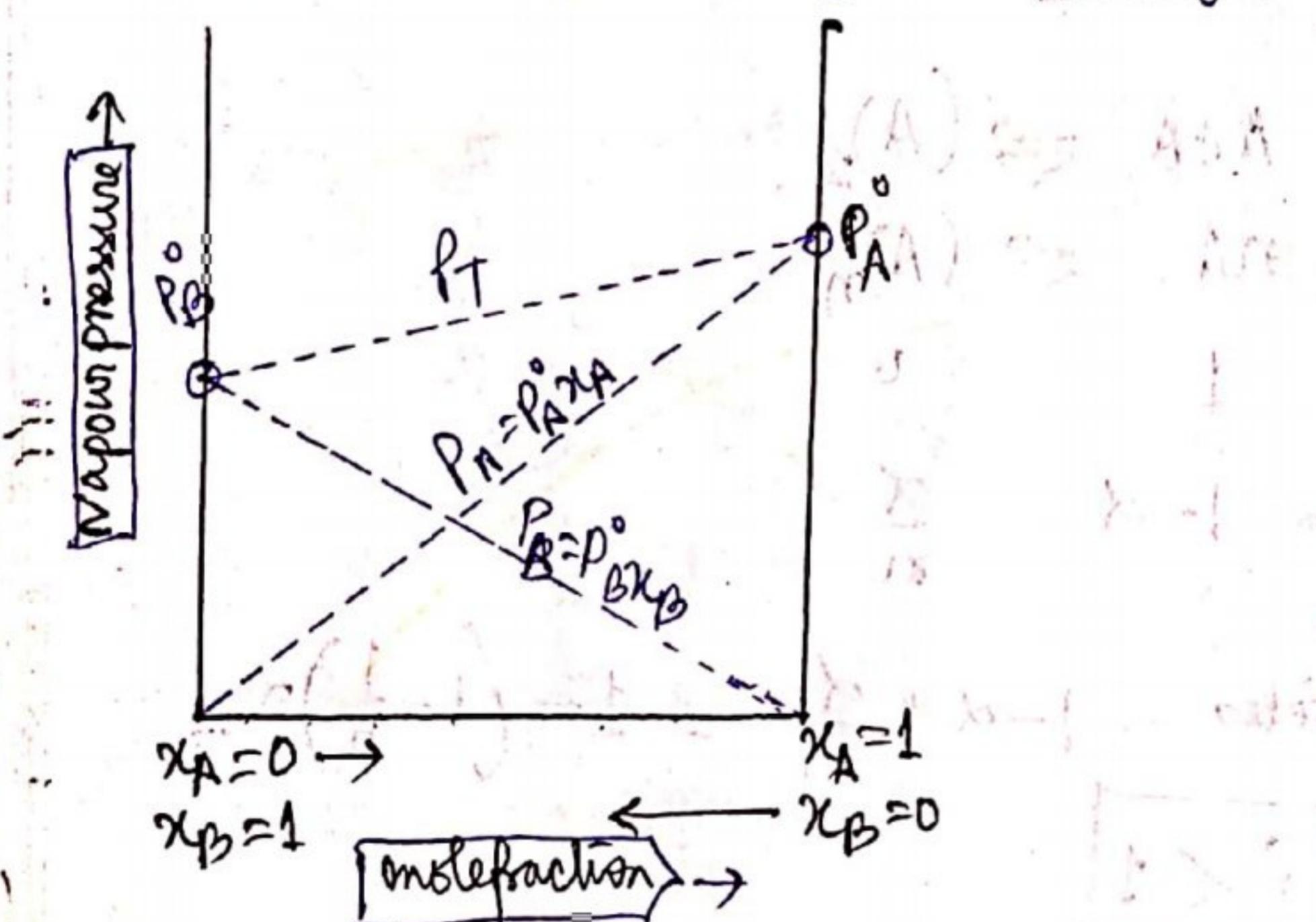
$$\begin{cases} P_A = P_A^0 x_A \\ P_B = P_B^0 x_B \end{cases}$$

$$\Delta_{\text{mix}} H = 0, \Delta_{\text{mix}} V = 0$$

Boiling point of the soln remains

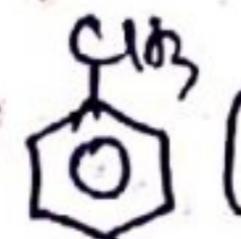
Same to the boiling point of individual components before & after the mixing.

In this case, no deviation of Raoult's law can occur



Example: n-hexane + n-heptane

Bromobenzene + Chlorobenzene

Note: Benzene +  (Toluene)

When a nonpolar substance is mixed with another nonpolar substance then we may get an ideal solution.

Nonideal solution

In this case, the three types of intermolecular forces of attraction among solvent-solute, solute-solute & solvent-solvent

must be different from each other i.e.

$$E_{A...B} \neq E_{A...A} \neq E_{B...B}$$

as a result of which $\Delta_{\text{mix}} H \neq 0, \Delta_{\text{mix}} V \neq 0$

$$P_T \neq P_A + P_B$$

$$P_A \neq P_A^0 x_A$$

$$P_B \neq P_B^0 x_B$$

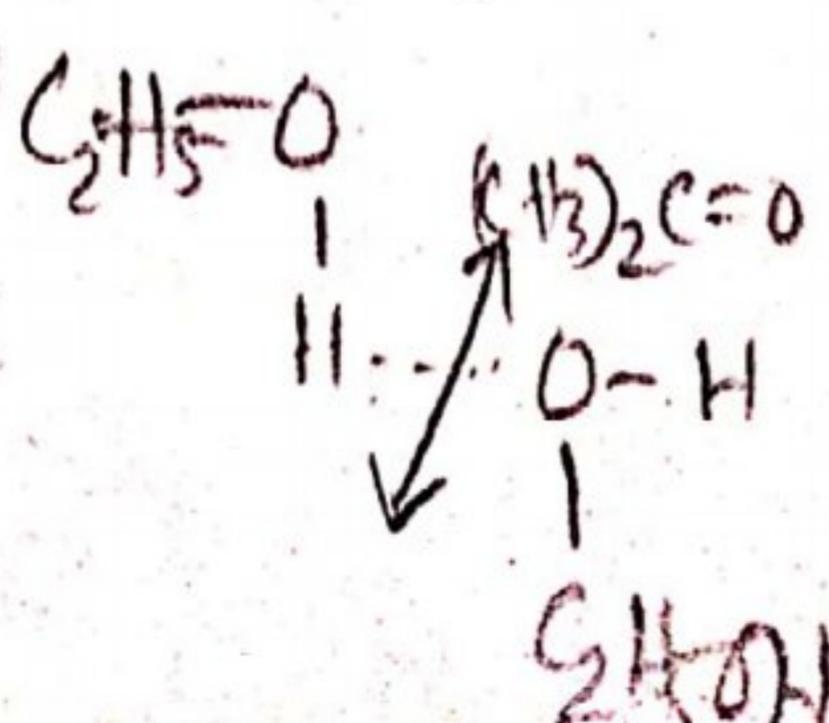
These type of solutions must be deviated from Raoult's law either

a) Negative deviation from Raoult's law

b) Positive deviation from Raoult's law

ethanol + acetone

show +ve deviation



-ve deviation from Raoult's law

When the force of attraction between solvent...solute becomes stronger than the average force of interaction among solvent...solvent & solute...solute.

$$\text{i.e. } E_{A...B} > \frac{E_{A...A} + E_{B...B}}{2}, \text{ i.e.}$$

The new interactive force becomes much stronger than $A...A$ & $B...B$.

as a result of which $\Delta_{\text{mix}} H < 0$

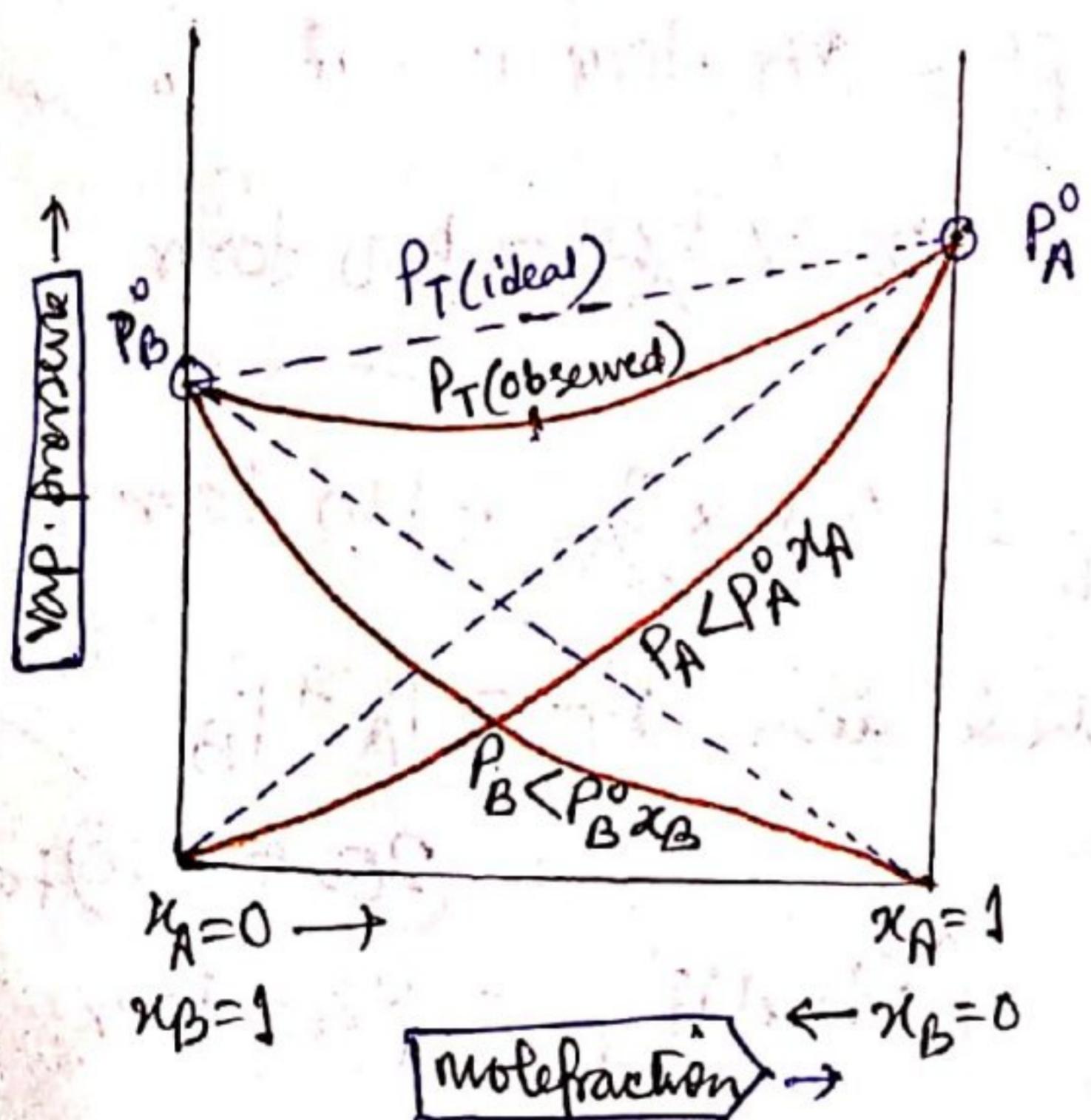
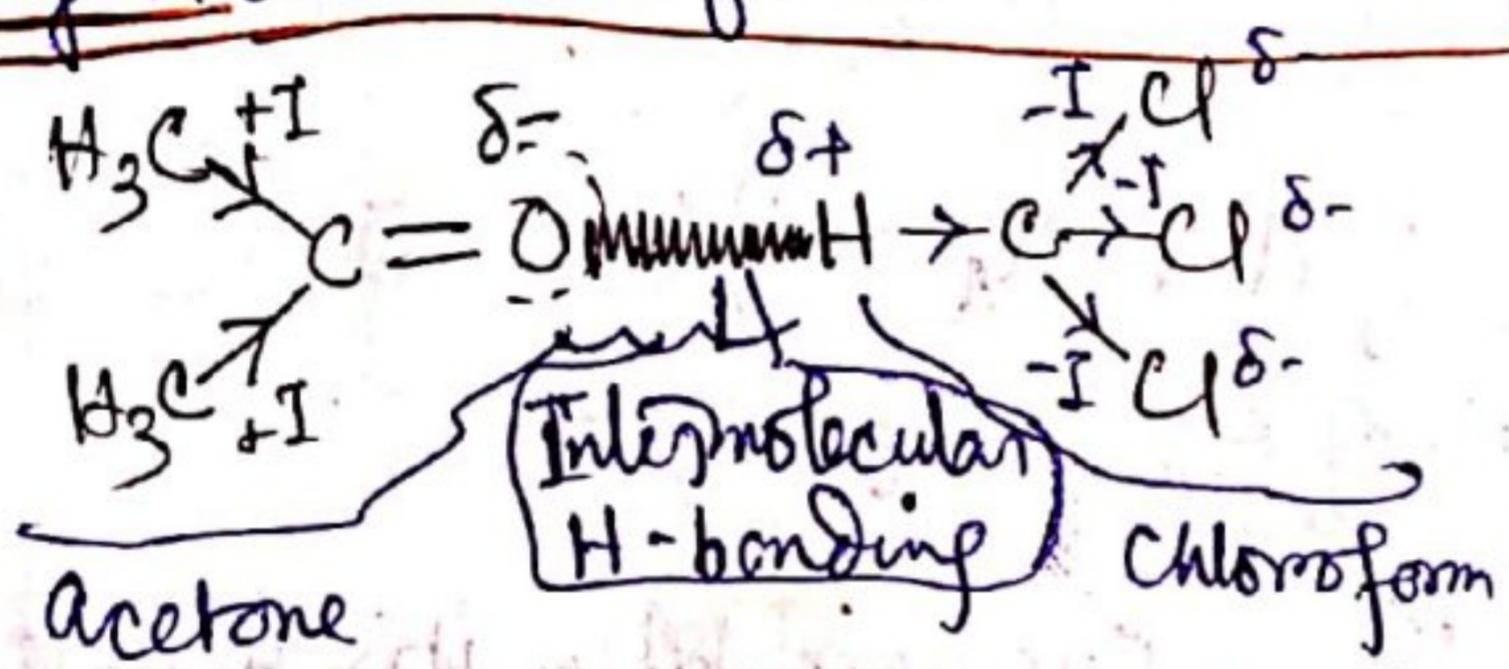
i.e. $\Delta_{\text{mix}} H = -\text{ve}$ and $\Delta_{\text{mix}} V < 0$ (exothermic)

i.e. $\Delta_{\text{mix}} V = -\text{ve}$ and

$$(\text{observed}) P_T < P_A + P_B$$

$$\text{and } P_A < P_A^0 x_A \text{ and } P_B < P_B^0 x_B$$

Boiling point of the solution becomes larger than that of the individual components



Example

- $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$;
- $\text{HCl} + \text{H}_2\text{O}$; $\text{HBr} + \text{H}_2\text{O}$
- $\text{HNO}_3 + \text{H}_2\text{O}$; $\text{CH}_3\text{OH} + \text{CH}_3\text{COOH}$;
- CH_3COOH + pyridine ; acetone + aniline;
- $\text{CHCl}_3 + \text{CH}_3\text{COOCCH}_3$

Note: When a polar substance is mixed with another polar substance then solution produced showing -ve deviation of Raoult's law.

+ve deviation from Raoult's law

when the force of attraction between solvent...solute becomes weaker than the average force of interaction among solvent...solvent and solute...solute

$$\text{i.e. } E_{A...B} < \frac{E_{A...A} + E_{B...B}}{2},$$

The new interactive force becomes much weaker than $A...A$ & $B...B$, as a result of which $\Delta_{\text{mix}} H > 0$

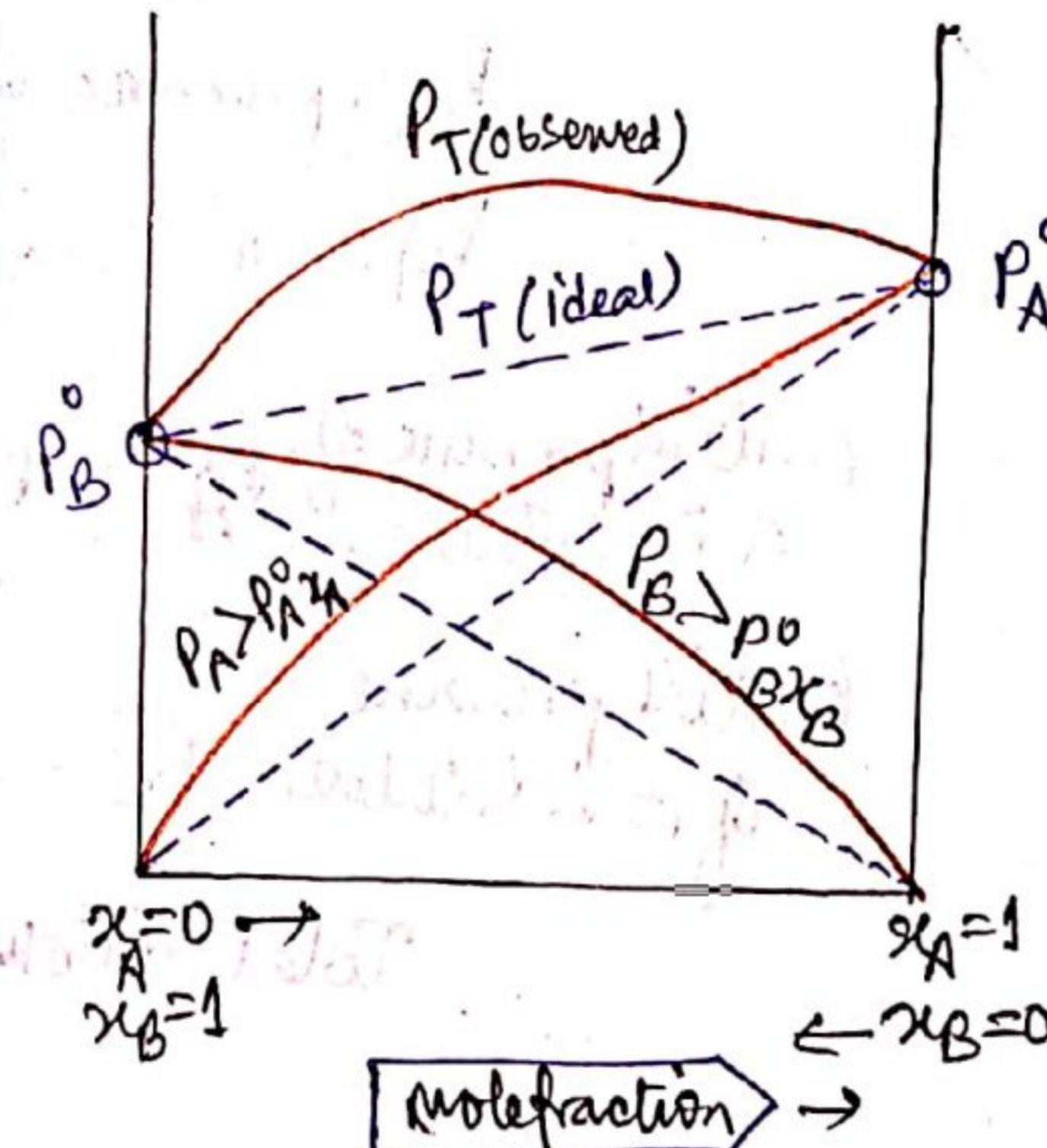
i.e. $\Delta_{\text{mix}} H = +\text{ve}$ (endothermic process) and $\Delta_{\text{mix}} V > 0$ i.e. $\Delta_{\text{mix}} V = +\text{ve}$

and

$$(\text{observed}) P_T > P_A + P_B$$

$$\text{and } \begin{cases} P_A > P_A^0 x_A \\ P_B > P_B^0 x_B \end{cases} \text{ and}$$

Boiling point of the solution becomes smaller than that of the individual components.



Example . acetone + ethanol ;

water + ethanol ;

$\text{CCl}_4 + \text{CHCl}_3$; $\text{CHCl}_3 + \text{ethanol}$;

acetone + CS_2 ; acetone + benzene ;

$\text{CH}_3\text{COOCCH}_3 + \text{H}_2\text{O}$; $(\text{CH}_3)_2\text{CO} + \text{CH}_3\text{OH}$

$\text{C}_2\text{H}_5\text{OH} + \text{CCl}_4 \rightleftharpoons \text{C}_2\text{H}_5\text{OH} + \text{C}_6\text{H}_6$

Note: When a polar substance is mixed with a non polar substance or vice versa then the solution is produced showing +ve deviation of Raoult's law.

Deviations	Pressure	ΔH_{soln}	Examples
+ve	$P_{(\text{soln})} > P_{(\text{ideal})}$	+ve i.e. Endothermic	Polar substance + nonpolar $\text{CH}_3\text{OH} + \text{C}_8\text{H}_6$ substance
Ideal	$P_{(\text{soln})} = P_{(\text{ideal})}$	almost zero	mixing of 2 nonpolar substance
-ve	$P_{(\text{soln})} < P_{(\text{ideal})}$	-ve i.e. Exothermic	When the 2 components combined are polar substance e.g. $\text{CH}_3\text{OH} + \text{H}_2\text{O}$

Q9. 2 moles of substance A mixes with 3 moles of substance B. The vap. pressure of substance A & B are 500 torr & 200 torr respectively. The vap. pressure of the solution is observed to be 294 torr. Is this an ideal solution or is there a deviation from Raoult's law? If so, is it a +ve / -ve deviation? Moreover from the result predict the nature of the components.

No. of moles of A, $n_A = 2$ moles Total no. of moles = 5

No. of moles of B, $n_B = 3$ moles

molefraction of A, $x_A = 2/5$

molefraction of B, $x_B = 3/5$

Vap. pressure of A $\nabla P_A^0 = 500$ torr when it's in pure state

Vap. " " B, $P_B^0 = 200$ torr "

Partial pressure of A in solution $P_A = P_A^0 x_A = 500 \times 2/5 = 200$ torr

Partial pressure of B in solution $P_B = P_B^0 x_B = 200 \times 3/5 = 120$ torr

Total pressure on the solution $P_T = P_A + P_B$

$= (200 + 120)$ torr

(ideal) $P_T = 320$ torr

Given the observed pressure, $P_T = 294$ torr

Observed pressure $<$ ideal pressure

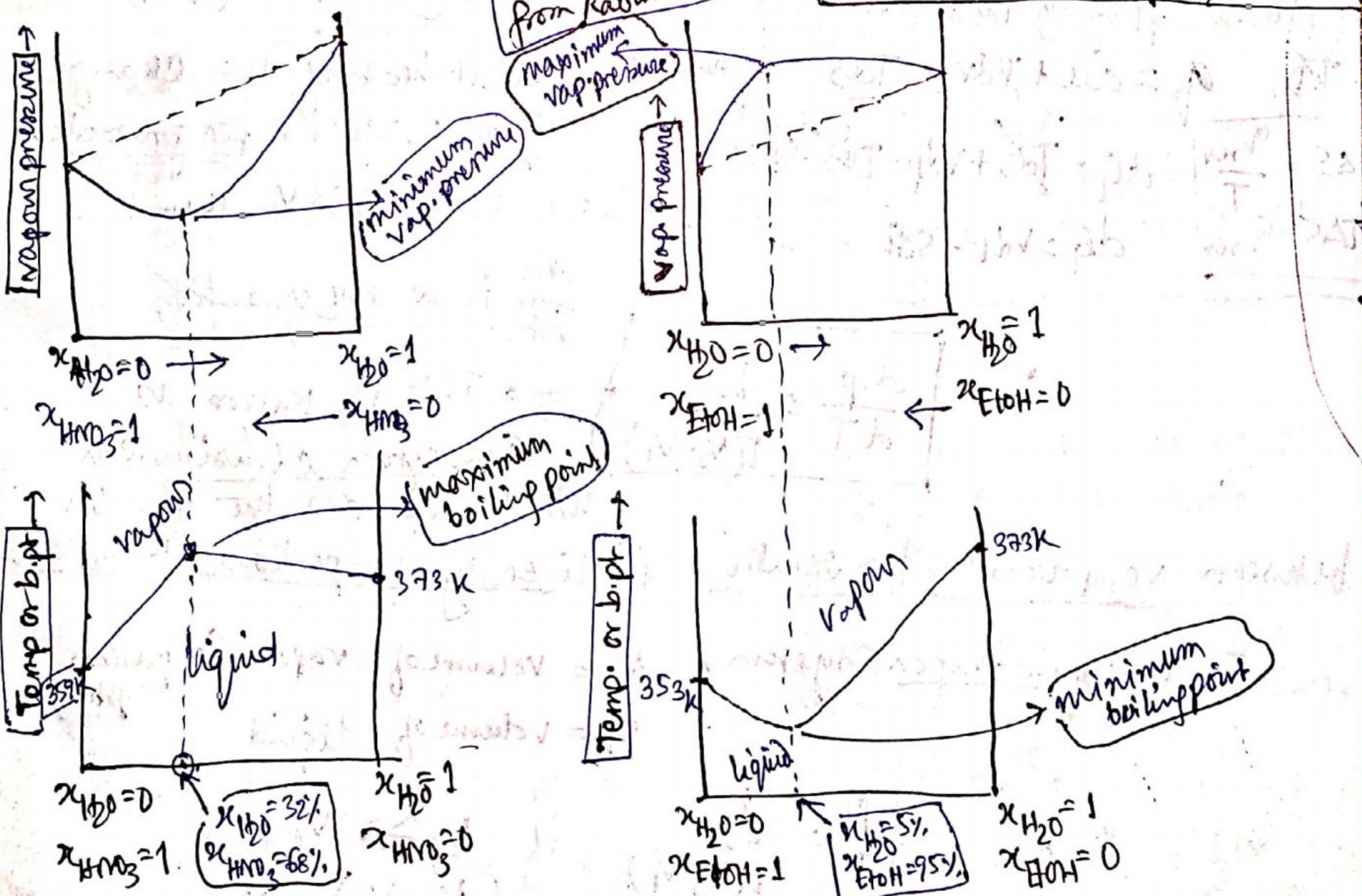
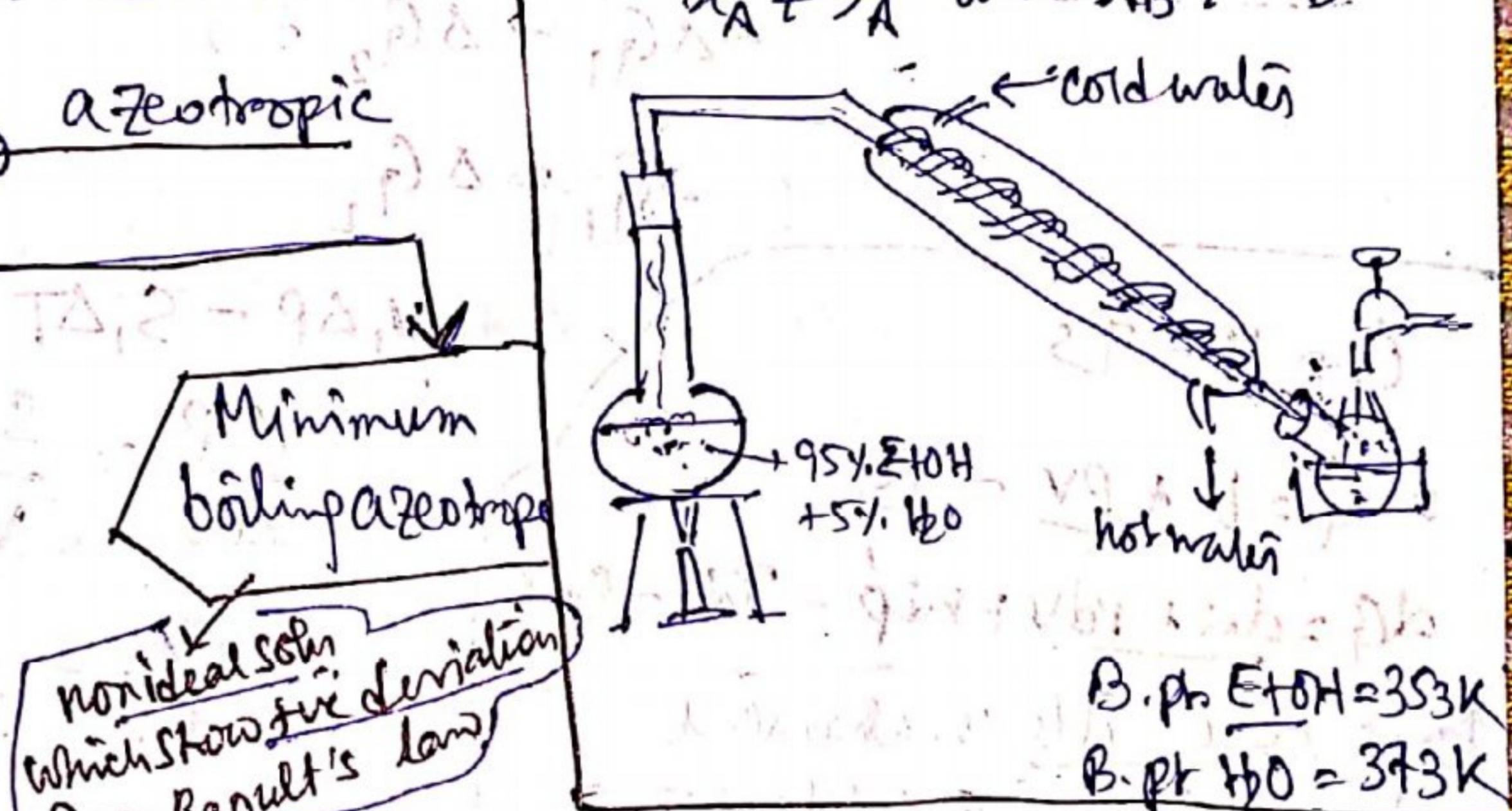
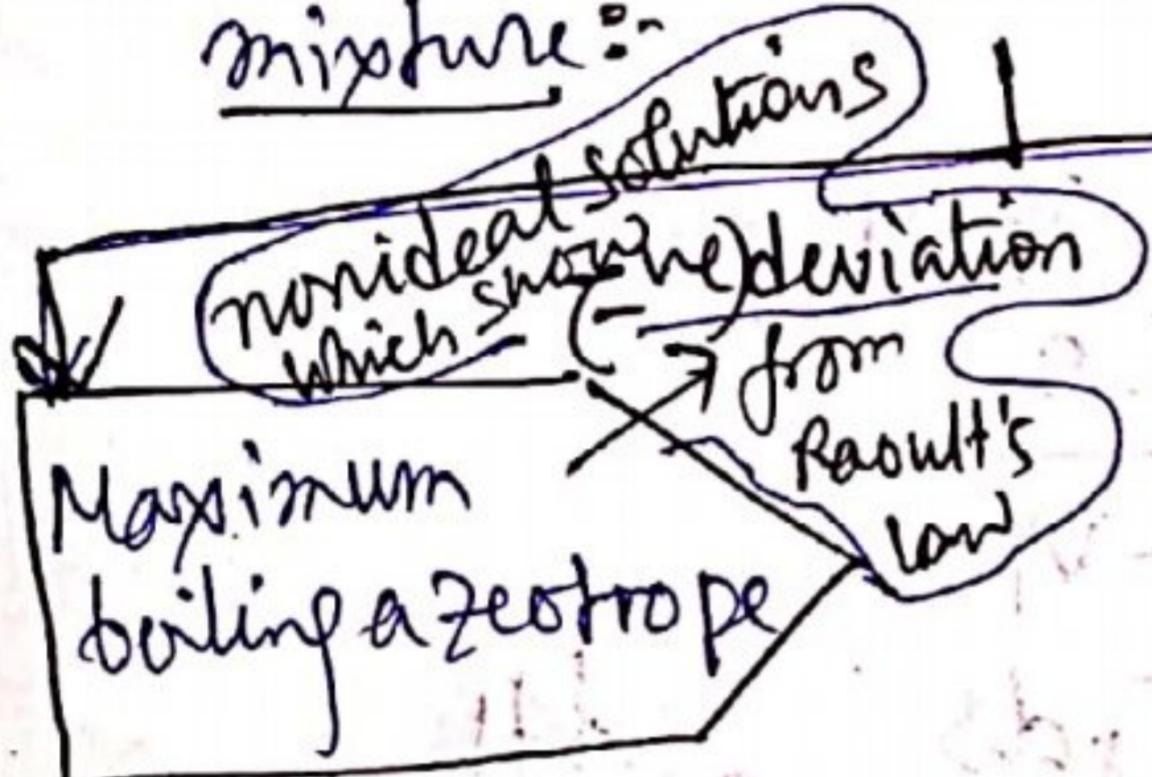
It is an example of -ve deviation & the nature of the components are polar substance

31/03/19

What is azeotropic mixture?

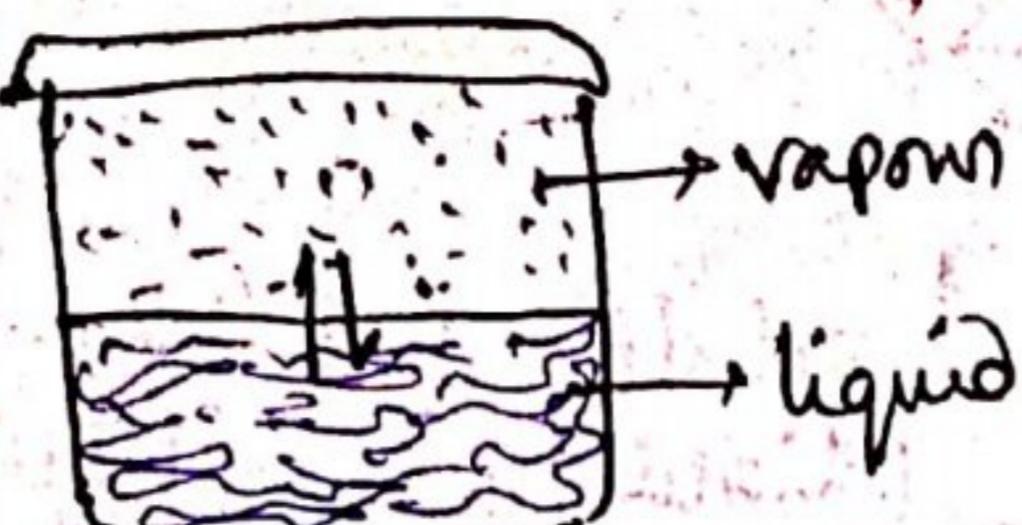
- (1) It is - binary solution - 1 solute + 1 solvent
(liquid) (liquid)
- (2) It must have a fixed composition
such as - $\alpha_A \neq y_A$ and $\alpha_B \neq y_B$
deviation of Raoult's law
- (3) It is a constant boiling mixture because $x_A = y_A$ & $x_B = y_B$
- (4) It can't be separated by ~~any~~ simple method like -
Fractional Distillation.

- (5) There are 2 types of azeotropic mixture:-



more the vapor pressure = minimum boiling point
less the vapor pressure = maximum boiling point

Relation between Temp. and Vap.
pressure of
a soln.



Let G_1 and G_2 be the free energies of a liquid and its vapour phase in a closed system forming an equilibrium. Now imagine a virtual change that a small amount of liquid is converted into vapour as a result of which the drop in free energy of liquid is $-\Delta G_1$ and the gain in free energy of its vapour is ΔG_2 . As the system is in equilibrium, the net $\Delta G = 0$

$$-\Delta G_1 + \Delta G_2 = 0$$

$$\Delta G_1 = \Delta G_2$$

$$G = H - TS$$

$$\Delta G = U + PV - TS$$

$$\Delta G = dU + PdV + VdP - TdS - SdT$$

For a reversible mechanical process applying 1st law of T.D.

$$dQ = dU + PdV = TdS$$

$$\Delta S = \frac{dQ_{rev}}{T}$$

$$\Delta Q = TdS + VdP - TdS - SdT$$

$$\Delta Q = VdP - SdT$$

$$V_1 \Delta P - S_1 \Delta T = V_2 \Delta P - S_2 \Delta T$$

$$\frac{\Delta P}{\Delta T} = \frac{S_2 - S_1}{V_2 - V_1}$$

$$\frac{dp}{dT} = \frac{T dS}{T(V_2 - V_1)} = \frac{L}{T(V_2 - V_1)}$$

where L = latent heat of the change of pure solvent per gram mole.

If $L = +ve$ & $V_2 > V_1$, then

$\frac{dp}{dT}$ is a +ve quantity

$$\boxed{\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)}}$$

This is known as Clapeyron Clausius eqn which expresses the relation

between vap pressure of a solution is directly proportional to the temp.

For a liquid-vapour system, V_g = volume of vapour (or gas in system)
 V_l = volume of liquid

$$\frac{dp}{dT} = \frac{L}{T(V_g - V_l)} \quad \text{if } V_g > V_l \text{ then } (V_g - V_l) \approx V_g$$

or $\frac{dp}{dT} = \frac{L}{T \times V_g}$ and if the vap. behaves like an ideal gas then applying ideal gas equation $P V_g = RT$ when $n=1$ mole

$$V_g = \frac{RT}{P}$$

$$\therefore \frac{dp}{dT} = \frac{L}{T} \left(\frac{RT}{P} \right)$$

$$\frac{dp}{dT} = \frac{L}{RT^2} \cdot P \Rightarrow \frac{dp}{P} = \frac{L}{R} \cdot \frac{dT}{T^2}$$

By integration $\int d\ln P = -\frac{L}{RT} + Z$

again By taking lower range P_1 & upper range P_2 while initial temp. T_1 & higher temp. T_2 on integration we'll get

$$\int_{P_1}^{P_2} \frac{d\ln P}{P} = \int_{T_1}^{T_2} \frac{L}{R} \cdot \frac{dT}{T^2}$$

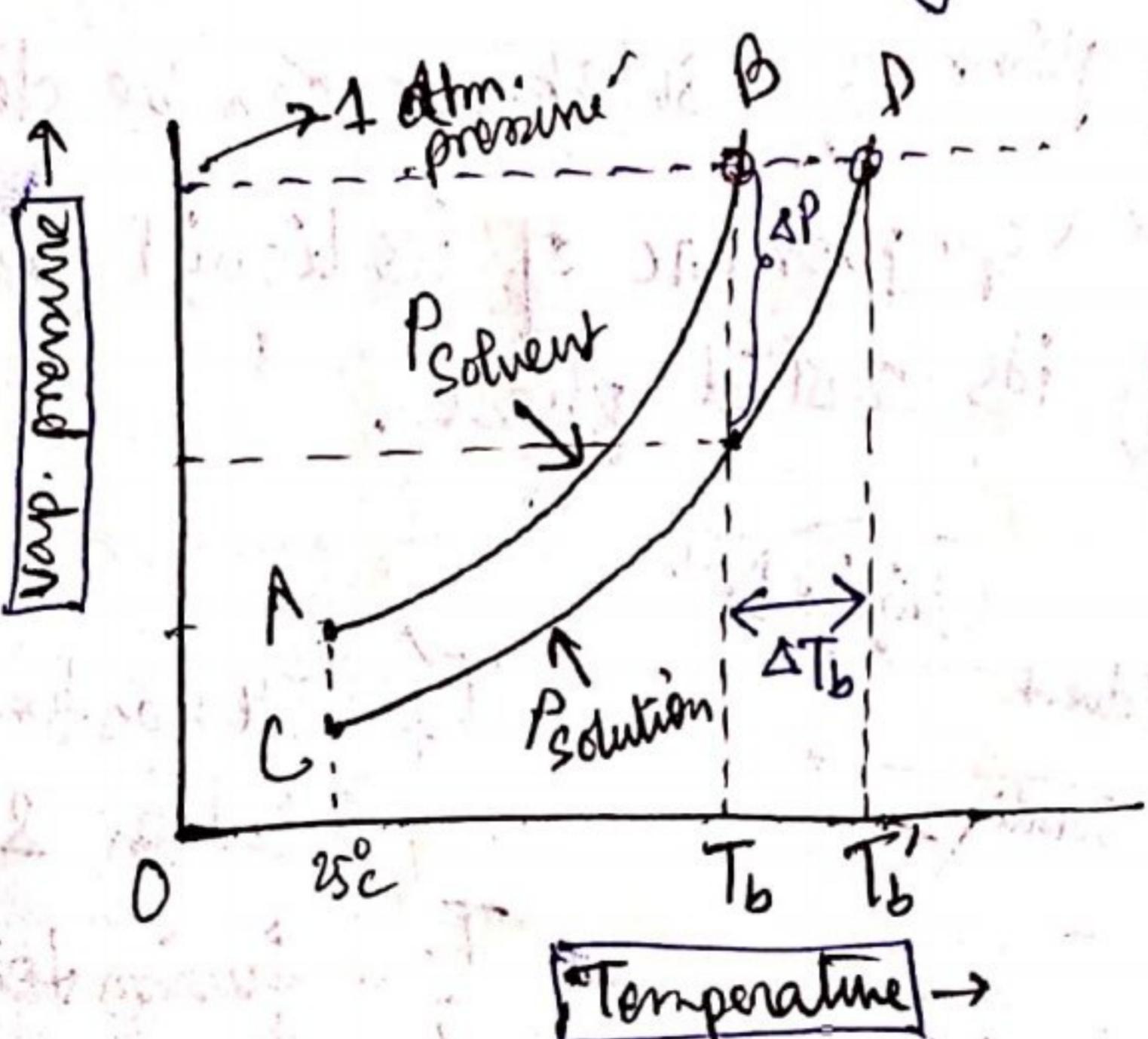
$$\log \frac{P_2}{P_1} = \frac{L}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

This is the integral form of Clapeyron-Claussius equation:

$$\log \frac{P_2}{P_1} = \frac{L}{2.303RT_1T_2} (T_2 - T_1)$$

Elevation in boiling point of a liquid when a nonvolatile solute is added into it.

Definition of boiling point: Boiling point of a liquid can be defined as a temperature at which the vapour pressure of the liquid equals to the 1 atm is known as boiling point of that liquid.



T_b & T_b' are the boiling points of pure solvent & solution

AB and CD are representing the vapour pressure curve for pure solvent & solution respectively

$$T_b' > T_b$$

$$(BD) = \Delta T_b = T_b' - T_b = +ve \\ = \text{elevation in boiling}$$

is directly proportional to the [solute], active mass of solute i.e.

$$\Delta T_b \propto [\text{solute}] \rightarrow \text{This concen must be same in both}$$

$$\Delta T_b \propto m$$

m = molality of solution in moles/kg

$$\Delta T_b = K_b m$$

where K_b = molar elevation in boiling point or

Ebullioscopic constant

which can be defined as -

When $m = 1$ mole/kg then

$$m = \frac{n_2}{\text{per kg weight of solvent}}$$

$$= \frac{W_2 \times 1000}{M_2 \times \text{per gm weight of solvent}}$$

$$m = \frac{W_2 \times 1000}{M_2 \times W_1}$$

$\Delta T_b = K_b \Rightarrow$ "The elevation in boiling point for addition of 1 mole of nonvolatile solute per kg of the solvent".

$$K_b = \frac{RT_b}{1000 \times l_v}$$

l_v = latent heat of vapourisation of pure solvent per gm.

$$\therefore \Delta T_b = K_b \times \frac{W_2 \times 1000}{M_2 \times W_1}$$

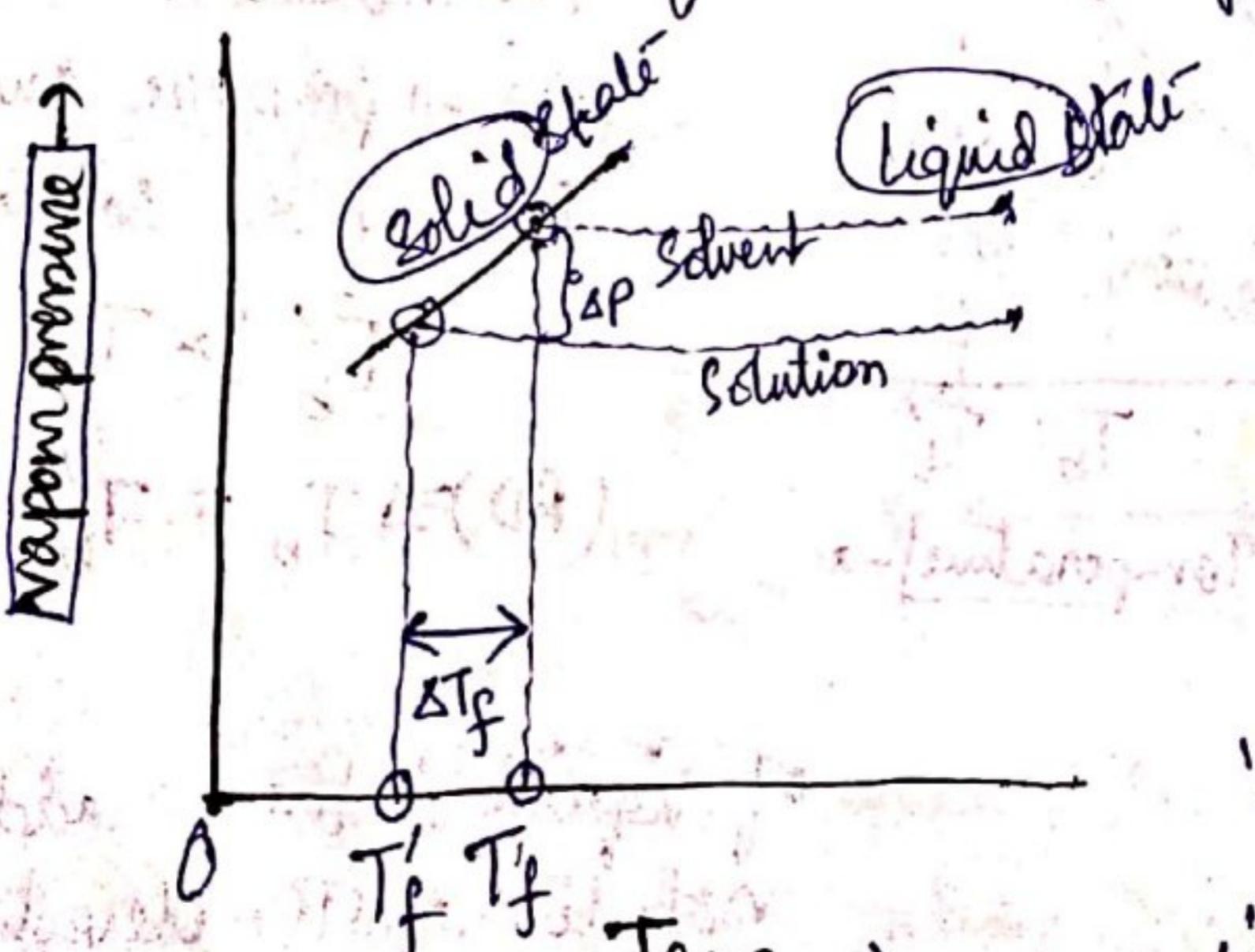
$$M_2 = \frac{K_b \times W_2 \times 1000}{\Delta T_b \times W_1}$$

we can determine the molar mass of solute

for water, the value of $K_b = 0.52^\circ\text{C} \text{ mole}^{-1}$ or $0.52 \text{ K kg mole}^{-1}$

Freezing point

freezing point of a substance can be defined as the temp. at which the vap. pressure of its liquid phase equals to the vap. pressure of its solid phase.



T'_f = fusion temp. of solution &

T_f = fusion temp. of pure solvent

$\because T'_f < T_f$

$\therefore T'_f - T_f = -\Delta T_f$

where ΔT_f = depression in freezing point due to addition of nonvolatile solute

freezing point of a liquid is due to addition of nonvolatile solute

Since $\Delta T_f \propto [\text{solute}]$ \rightarrow the temp. independent concentration terms

$$\Delta T_f = k_f m$$

$$\Delta T_f = k_f \times \frac{w_2 \times 1000}{M_2 \times w_1}$$

Molecular mass of unknown solute

$$M_2 = \frac{k_f \times w_2 \times 1000}{\Delta T_f \times w_1}$$

Where k_f = molal depression in freezing point or cryoscopic constant

$$k_f = \frac{RT_f}{1000 \times l_f}$$

where l_f = latent heat of fusion of pure solvent per gm.

For water, the value of $k_f = 1.86^\circ\text{C mole}^{-1}$ or $1.86 \text{ K kg mole}^{-1}$

- for any liquid the value of $k_f > k_b$ always.

This is because — The value of $l_f > l_v$

$$k_b = \frac{RT_b}{l_v \times 1000}$$

$$k_b \propto \frac{1}{l_v}$$

$$k_f = \frac{RT_f}{1000 \times l_f}$$

for any liquid

$$k_f \propto \frac{1}{l_f}$$

Osmotic pressure
Van't Hoff factor:

Osmotic pressure

Osmotic pressure is
the excess pressure
applied on the

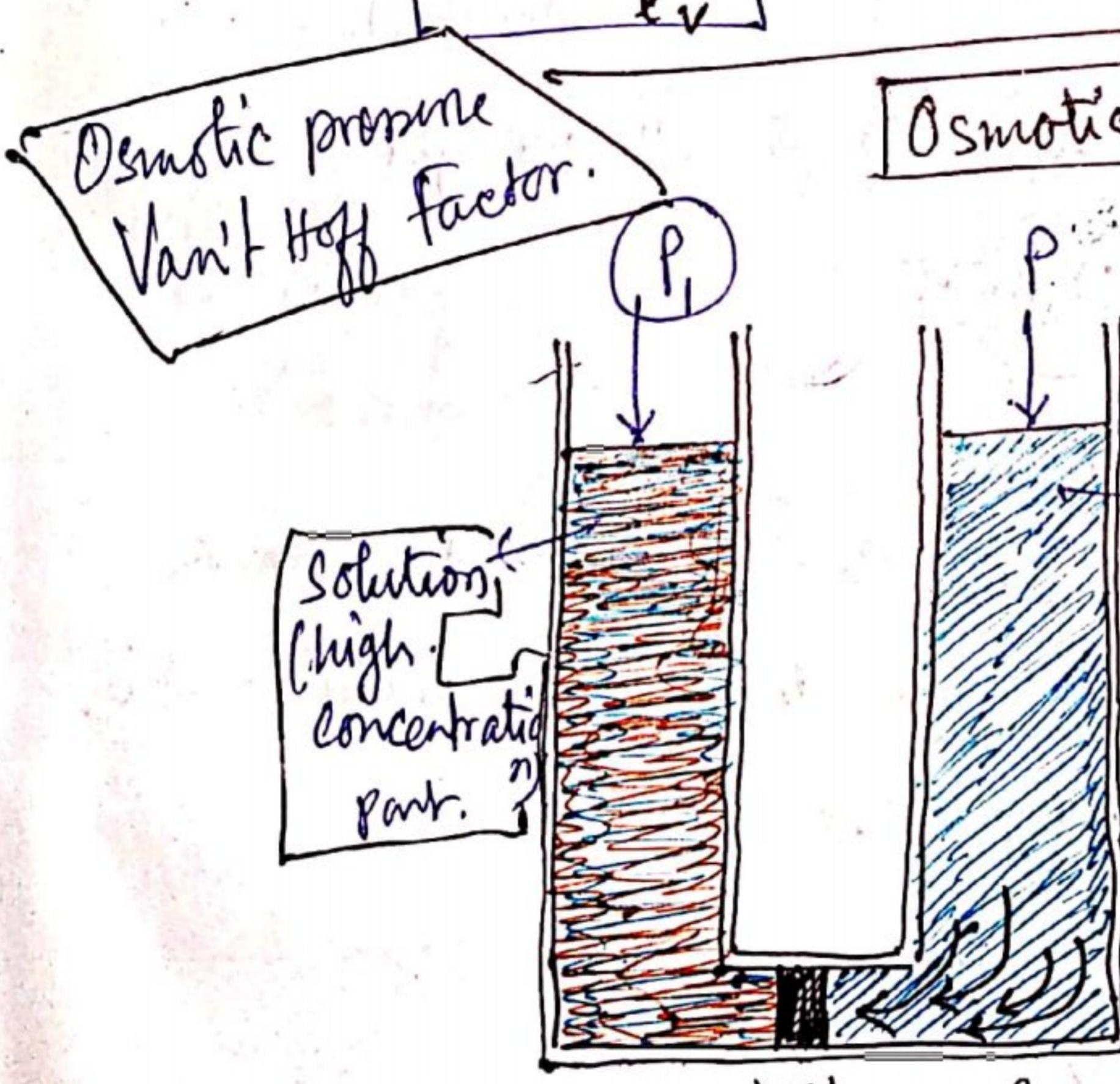
solution part
required to
stop the natural

flow of solvent from
solvent (low concentration) part
to solution chamber (higher
concentration part) through

a semipermeable membrane ('x'),

$$\Pi = P_i - P$$

Osmotic pressure can be defined as the hydrostatic pressure i.e. $\Pi = h \rho g$ where ρ = density of soln, g = acceleration due to gravity &



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$h = \text{depth of the solution which is required to stop}$
 $\text{the natural flow of solvent from solvent} \rightarrow \text{solution}$
 through 'X' (SPM)

$K_4[Fe(N)_6]$, $Cu_2(Po_4)_2$ — all these chemicals can be used as
 SPM in laboratory.

1st Law of Osmotic pressure Keeping temp. in Kelvin scale constant
 osmotic pressure of the solution (Π) is directly proportional to the
 concentration (c) in molarity of solution.

$\Pi \propto c$ when T in K is kept constant.

a) $\Pi = K_1 c$ Where K_1 is the proportionality constant.

$$\frac{\Pi}{V} = K_1$$

If V litre be the dilution of solution,
 then $c \propto \frac{1}{V}$

a) $\Pi V = K_1 \quad \text{(i)}$

2nd law of Osmotic pressure Keeping concentration (c) constant of a solution osmotic pressure is directly proportional to the temp (T) in Kelvin scale. i.e. $\Pi \propto T$ whence c is kept fixed.

a) $\Pi = K_2 T \quad \text{(ii)}$ K_2 is the proportionality constant.

On combining equation (i) & (ii) we get

$$\Pi = K_1 \times K_2 c T$$

$$\Pi = K c T$$

Where the new constant $K = K_1 \times K_2$ can be replaced by R

Where n = no. of moles of solute & R = universal ideal solution constant.

$$\boxed{\Pi = n R T}$$

or $\Pi = \frac{n R T}{V}$

a) $\Pi = \frac{W \cdot RT}{M \cdot V}$

W = mass of solute
 M = Molecular mass of solute

$$\boxed{\Pi = \frac{d R T}{M}}$$

d = density of solution

Reverse Osmosis
& its application?

Isotonic/Iso osmotic pressure

conditions to be isotonic
concentrations of 2 solutions
must be same.

Hypotonic
solution

Hypertonic
solution

$$\text{for 2 } \xrightarrow{\text{isotonic solutions}} \Pi = C_1 RT, \quad \Pi = C_2 RT$$

$$C_1 RT = C_2 RT$$

$$\frac{n_1}{V_1} = \frac{n_2}{V_2}$$

$$\Pi \propto \Delta T_b \propto \Delta T_f$$

$$\frac{w_1}{M_1 V_1} = \frac{w_2}{M_2 V_2}$$

Vant Hoff factor (*i*) The cause of abnormal behaviors of a solution.

In most cases the experimental values of colligative properties differ from the theoretical or calculated values of them because

- of → (i) Highly concentrated solution.
(ii) Due to ionisation/ dissociation or association of solute in solution.

To avoid the above anomalies Vant Hoff introduced a factor '*i*' in his equation (known as Vant Hoff equation) used to measure the Osmotic pressure i.e. $\Pi = i CRT$ where

$$\left(i = \frac{N}{M} \right) i = \frac{\text{Normal or theoretical molar mass of solute}}{\text{Observed or experimental molar mass of solute due to dissociation/ association}}$$

or $i = \frac{\text{Observed/experimental colligative properties due to ionisation/association}}{\text{Normal/theoretical colligative properties without any ionisation/ association}}$

$$\text{Colligative property} \propto \frac{1}{\text{molecular mass.}}$$

After introducing van't Hoff factor the corrected or modified values of colligative properties are as follows:-

$$(i) \Pi = iCRT \quad (ii) \Delta T_b = ik_b m$$

$$(iii) \Delta T_f = ik_f m \quad (iv) \frac{P_i^0 - P_i}{P_i^0} = i \frac{w_2 M_1}{M_2 w_1}$$

During ionisation

$$i > 1$$

If α be the degree of ionisation then

$$\alpha = \frac{i-1}{n-1}$$

During association

$$i < 1$$

If α' be the degree of association then

$$\alpha' = \frac{1-i}{1-\frac{1}{n}}$$