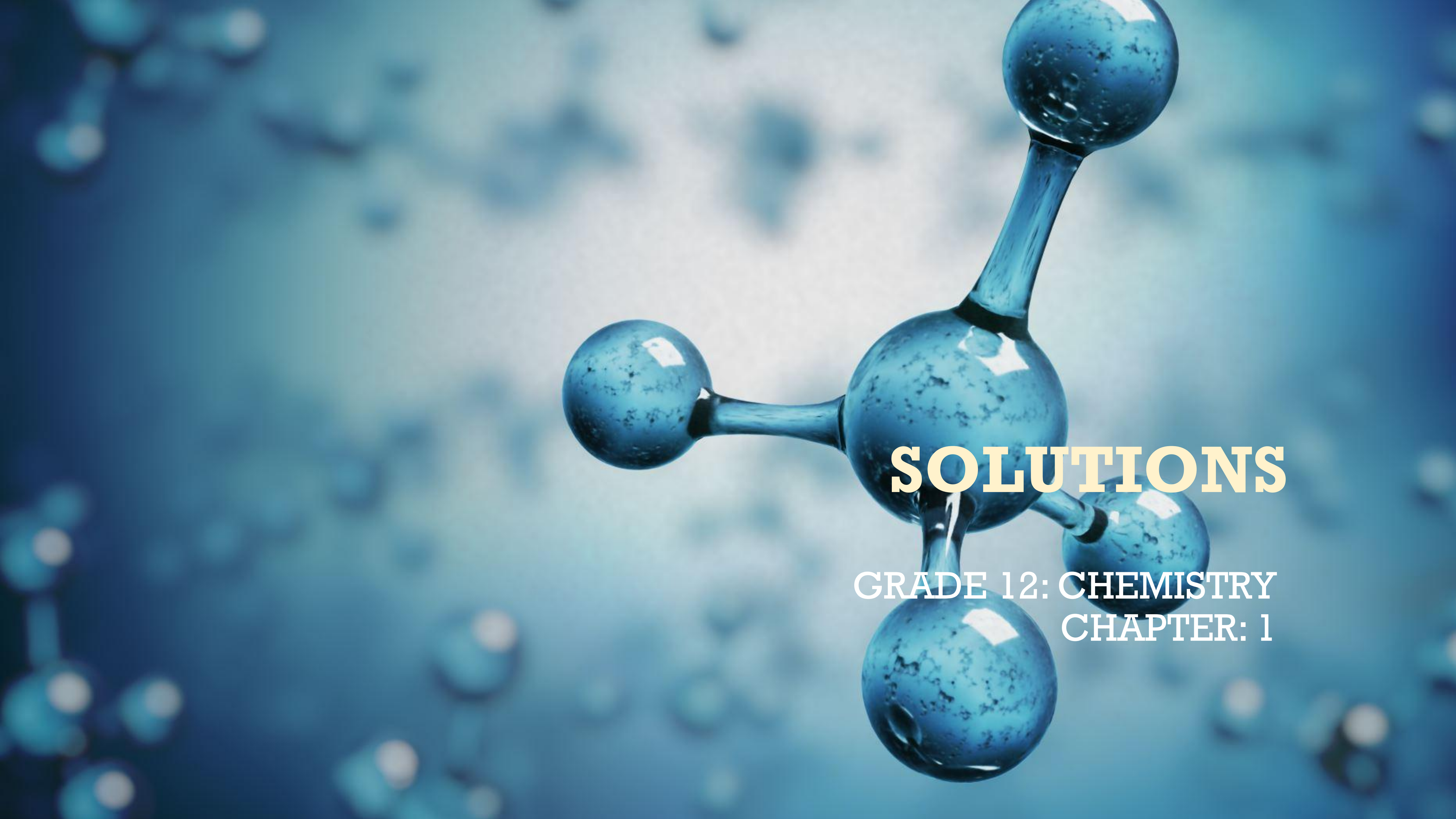


SOLUTIONS

GRADE 12: CHEMISTRY
CHAPTER: 1

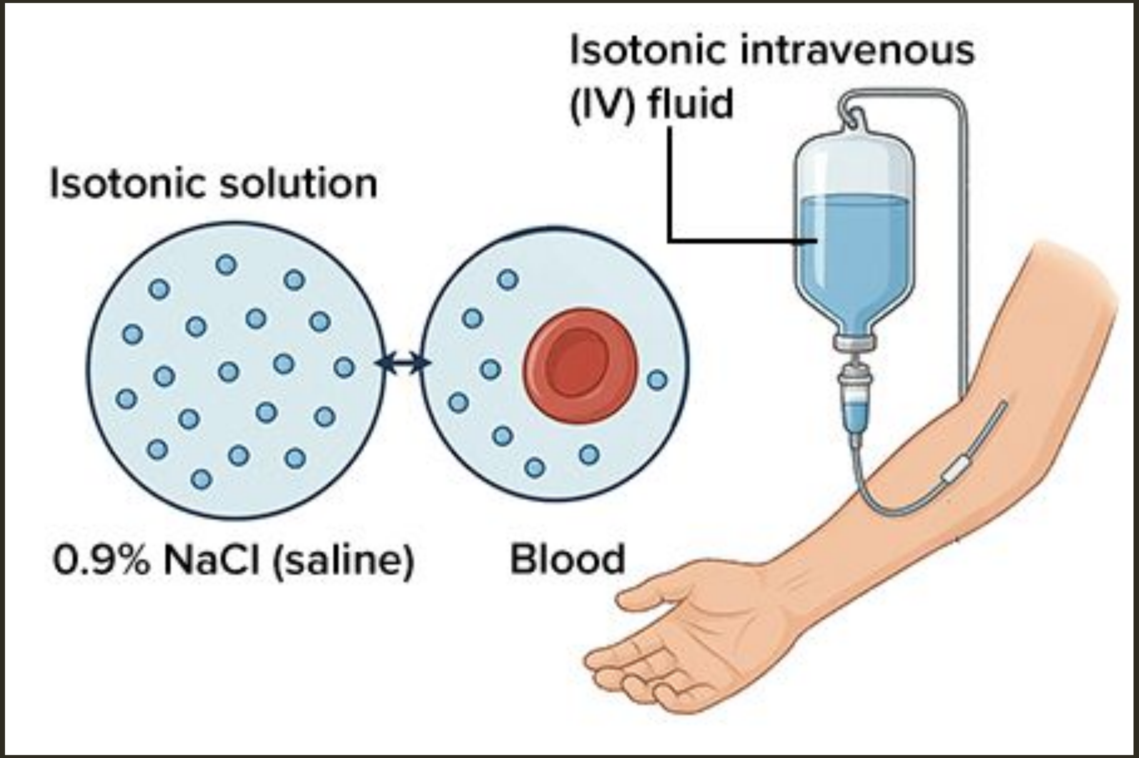
Human body is 70% water.

Why is the water in the body not frozen when outside temperature falls below 0^0C?

Freezing temperatures outside must damage the internals of a car as the coolants may freeze and burst because volume of ice is more than water.

Antifreeze keeps car engines from freezing in winter by lowering the freezing point.


But why us???



Adding salt to water raises its boiling point, allowing food to cook faster at a higher temperature.

Intravenous fluids are designed with specific osmotic pressure (isotonic) to be compatible with human blood cells.

“Life itself runs on solutions”:

In our body and around us, **nothing important happens in the solid state**. Almost all life processes happen when substances are **dissolved in liquids**.

- **Blood** is a solution
  Oxygen, glucose, salts, hormones — all are **dissolved** and transported.
- **Digestion** happens in solution
  Food nutrients must dissolve before they can be absorbed.
- **Medicines** work only when they dissolve in body fluids.
- **Plants** absorb minerals from soil **as aqueous solutions**.
- Even **sea water, soft drinks, IV fluids** — all are solutions.

WHY?

“When we study the chapter ‘Solutions’, we are not studying mixing — we are studying how life, technology, and chemistry function at the molecular level.”

LIST OF CONCEPTS TO MASTER:

- 1.1: Types of solutions
- 1.2: Expressing Concentration of Solutions
- 1.3: Solubility
  - Solubility of a Solid in a Liquid
  - Solubility of a Gas in a Liquid
- 1.4: Vapour Pressure of Liquid Solutions
  - Raoult’s Law
  - Henry’s Law
- 1.5: Ideal and Non-ideal Solutions
- 1.6: Colligative Properties and Determination of Molar Mass
  - Relative lowering of vapour pressure
  - Elevation of boiling point
  - Depression of freezing point
  - Osmosis & Osmotic Pressure
- 1.7: Abnormal Molar Masses
  - van’t Hoff factor

KEYWORDS:

- Homogeneous mixture
- Binary solution
- Concentration
- Mole fraction
- Molarity & Molality
- Solubility
- Dissolution & Crystallisation
- Exothermic & Endothermic reaction
- Partial pressure
- Vapour pressure
- Bends
- Anoxia
- Volatile & Non - Volatile
- Ideal & Non ideal solutions
- +ve & -ve deviation
- Azeotropes
- Minimum & Maximum boiling azeotrope
- Colligative properties
- Relative lowering of vapour pressure
- Elevation of boiling point
- Molal elevation constant
- Depression of freezing point
- Molal depression constant
- Semi permeable membrane
- Osmosis
- Osmotic pressure
- Abnormal molar mass
- van’t Hoff factor

1.1 TYPES OF SOLUTIONS

ACTIVITY

TYPES	**SOLVENT**	**SOLUTE**	**EXAMPLES**

TYPES	SOLVENT	SOLUTE	EXAMPLES
GASEOUS SOLUTION	**GAS**	GAS	Mixture of different air
	GAS	LIQUID	Humidity; Fog; Chloroform in N_2
	GAS	SOLID	Smoke; I_2 in N_2; Camphor in N_2
LIQUID SOLUTION	**LIQUID**	GAS	O_2 in H_2O; CO_2 in H_2O
	LIQUID	LIQUID	Ethanol in H_2O
	LIQUID	SOLID	Salt in H_2O; Sugar in H_2O
SOLID SOLUTION	**SOLID**	GAS	H_2 gas in Platinum/ Palladium/ Nickel
	SOLID	LIQUID	Amalgam of liquid Mercury (Hg) with solid Sodium metal (Na)
	SOLID	SOLID	Alloy of Copper in gold etc.

SOLUTIONS:

- ***Homogeneous*** mixture of two or more components
- ’***Like dissolves like***’ - polar - polar / non polar - non polar

BINARY SOLUTIONS:

- Homogeneous mixture of two components

Solute:

- Present in lesser amount
- May or may not change its physical state on mixing with solvent

Solvent:

- Present in higher amount
- Never changes its physical state and decides the state of the solution

1.2 EXPRESSING CONCENTRATION OF SOLUTIONS

CONCENTRATION OF A SOLUTION:

- ***Amount of solute*** present in a ***given amount of solution*** at a ***definite temperature***

CONCENTRATION TERMS:

- Mass % (m/m):

$$\frac{\text{Mass of Solute}}{\text{Mass of Solution}} \times 100$$

- Volume % (v/v):

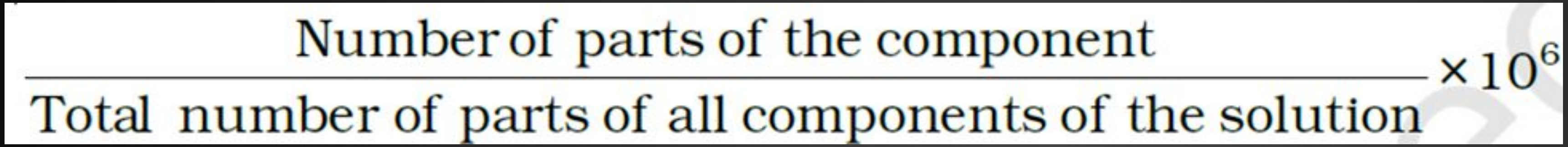
$$\frac{\text{Volume of Solute}}{\text{Volume of Solution}} \times 100$$

- Mass by volume % (m/v):

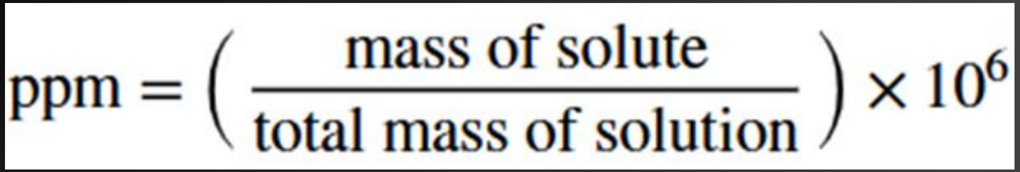
$$\frac{\text{Mass of solute (in g)}}{\text{Volume of solution (in mL)}} \times 100$$

CONCENTRATION TERMS:

- Parts per million (ppm): This unit is used when a solute is present in ***trace*** quantities



$$\frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$



$$\text{ppm} = \left(\frac{\text{mass of solute}}{\text{total mass of solution}}\right) \times 10^6$$

LEARNING CHECK

If concentration by mass of 600 g NaCl solution is 40 %, find the amount of solute by mass in this solution.

LEARNING CHECK

If concentration by mass of 600 g NaCl solution is 40 %, find the amount of solute by mass in this solution.

Ans: 240 g

LEARNING CHECK

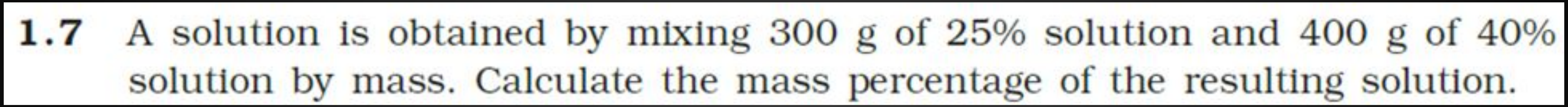
If we add 68 g sugar and 272 g water to 160 g solution having concentration 20 %, find final concentration of this solution.

LEARNING CHECK

If we add 68 g sugar and 272 g water to 160 g solution having concentration 20 %, find final concentration of this solution.

Ans: 20%

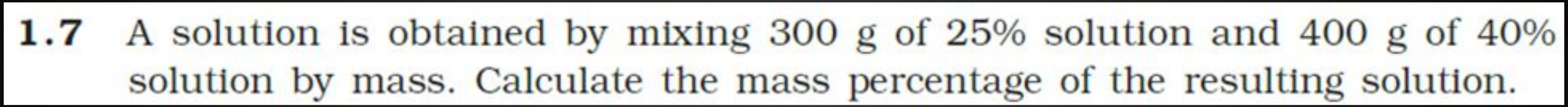
LEARNING CHECK



1.7 A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.

Ans:

LEARNING CHECK



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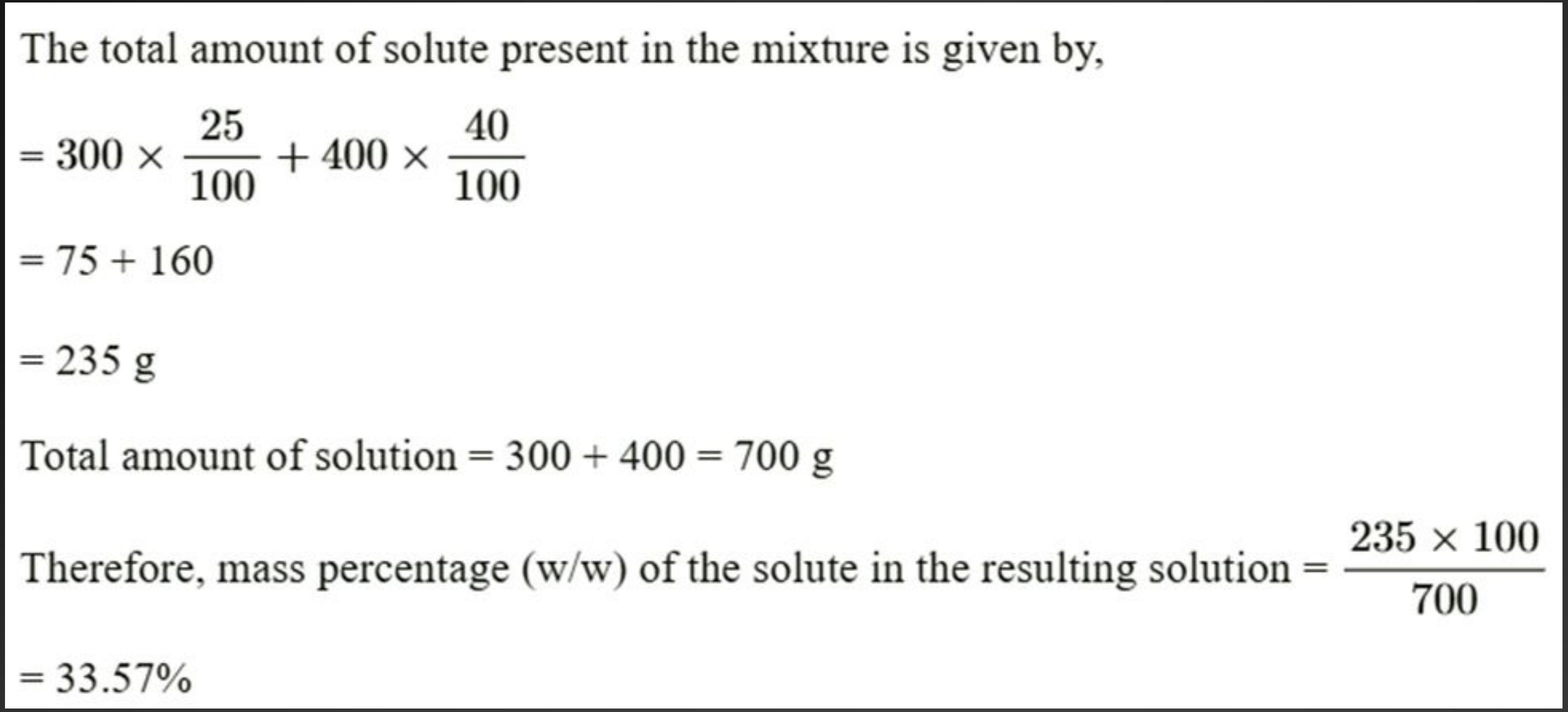


The total amount of solute present in the mixture is given by,

$$= 300 \times \frac{25}{100} + 400 \times \frac{40}{100}$$

$= 75 + 160$

$= 235$ g

Total amount of solution = $300 + 400 = 700$ g

Therefore, mass percentage (w/w) of the solute in the resulting solution $= \dfrac{235 \times 100}{700}$

$= 33.57\%$

CONCENTRATION TERMS:

Mole fraction (x):

- ***Independent*** of ***temperature*** and ***pressure***, ensuring consistency during thermodynamic calculations
- ***NO UNIT***
- ***Sum of the mole fraction*** of all the components is ***always 1***

$$\frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}}$$

$$x_i = \frac{n_i}{n_1 + n_2 + \ldots\ldots + n_i} = \frac{n_i}{\sum n_i}$$

NOTE: $\text{Moles } (n) = \frac{\text{Mass of substance (g)}}{\text{Molar Mass (g/mol)}}$

LET'S SOLVE

A mixture of gases at equilibrium contains 20 moles of SO_2 gas, 40 moles of O_2 gas and 40 moles of SO_3 gas. What is the mole fraction of SO_2 at equilibrium?

LET’S SOLVE

A mixture of gases at equilibrium contains 20 moles of SO_2 gas, 40 moles of O_2 gas and 40 moles of SO_3 gas. What is the mole fraction of SO_2 at equilibrium?

Ans: 0.2

LET'S SOLVE

5.85 g of NaCl are dissolved in 90 g of water. Calculate the mole fraction of NaCl.

LET’S SOLVE

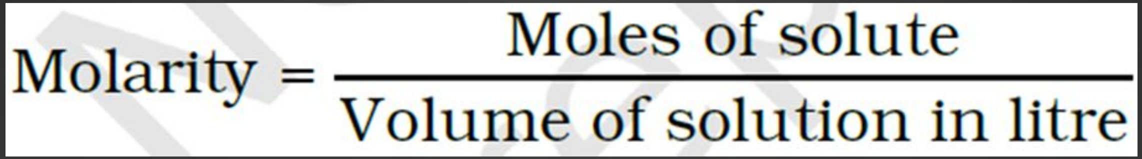
5.85 g of NaCl are dissolved in 90 g of water. Calculate the mole fraction of NaCl.

Ans: 0.0196

CONCENTRATION TERMS:

- Molarity (M / mol L^{-1}):
  - → Volume being temperature dependent, ***molarity changes with temperature***
  - → For dilution: $M_1V_1 = M_2V_2$
  - → For mixing two solutions (of same substance) of different concentrations:

    $M_{final} = (M_1V_1 + M_2V_2) / V_{final}$



$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

LET’S SOLVE

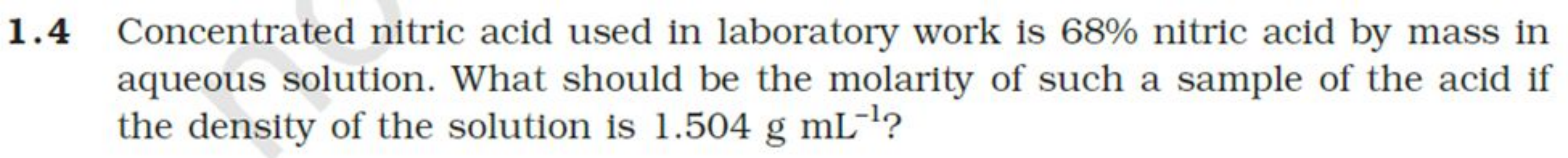
What is the molarity of a solution that was prepared by dissolving 14.2 g of $NaNO_3$ (molar mass = 85.0 g/mol) in enough water to make 350 mL of solution?

LET'S SOLVE

What is the molarity of a solution that was prepared by dissolving 14.2 g of $NaNO_3$ (molar mass = 85.0 g/mol) in enough water to make 350 mL of solution?

Ans: 0.477 M

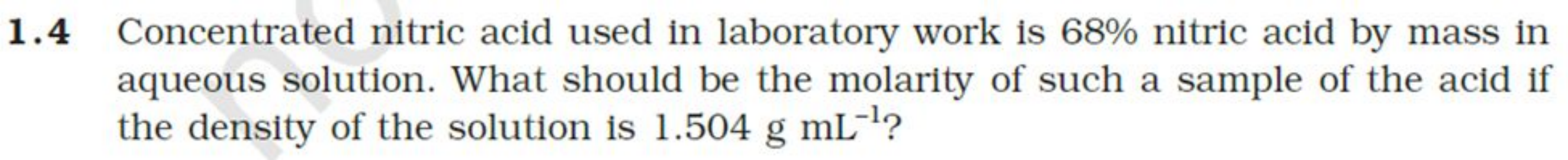
LET'S SOLVE



1.4 Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g mL^{-1}?

Ans:

LET’S SOLVE



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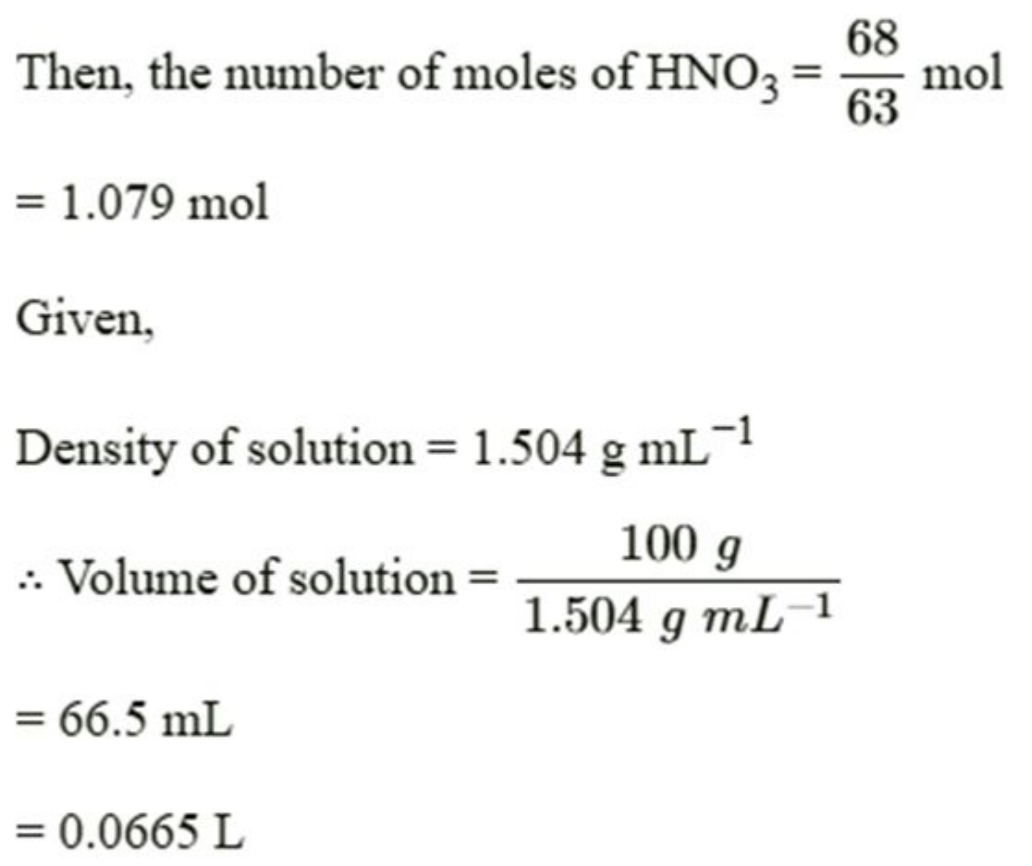
Ans:



Then, the number of moles of $HNO_3 = \frac{68}{63}$ mol

$= 1.079$ mol

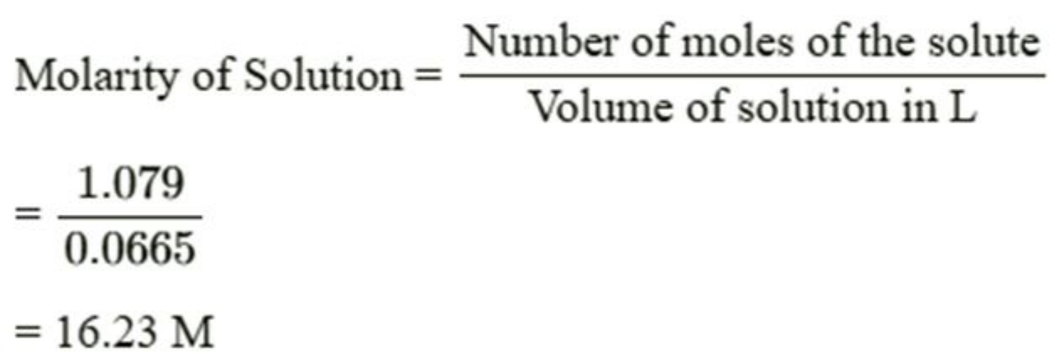
Given,

Density of solution $= 1.504\ g\ mL^{-1}$

$\therefore$ Volume of solution $= \frac{100\ g}{1.504\ g\ mL^{-1}}$

$= 66.5$ mL

$= 0.0665$ L



Molarity of Solution $= \frac{\text{Number of moles of the solute}}{\text{Volume of solution in L}}$

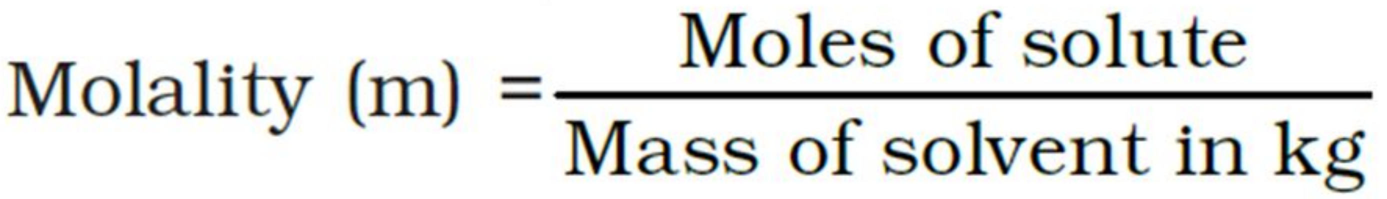
$= \frac{1.079}{0.0665}$

$= 16.23$ M

CONCENTRATION TERMS:

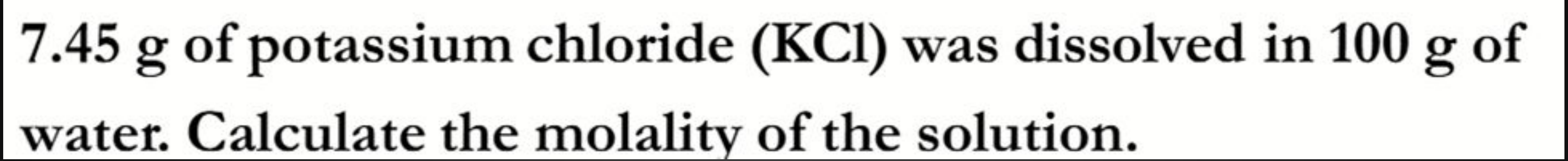
- Molality (m / mol kg^{-1}):

  → ***Molality is temperature independent***



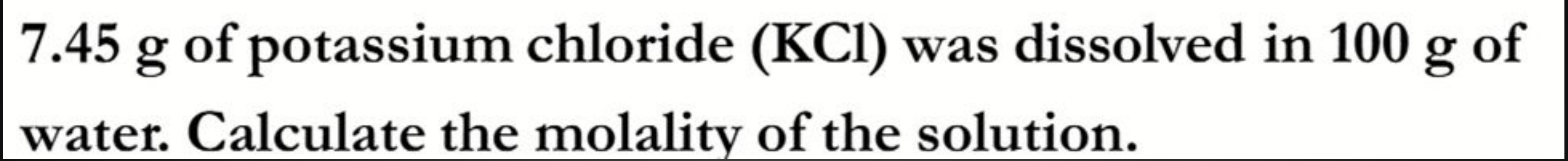
$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

LET’S SOLVE



7.45 g of potassium chloride (KCl) was dissolved in 100 g of water. Calculate the molality of the solution.

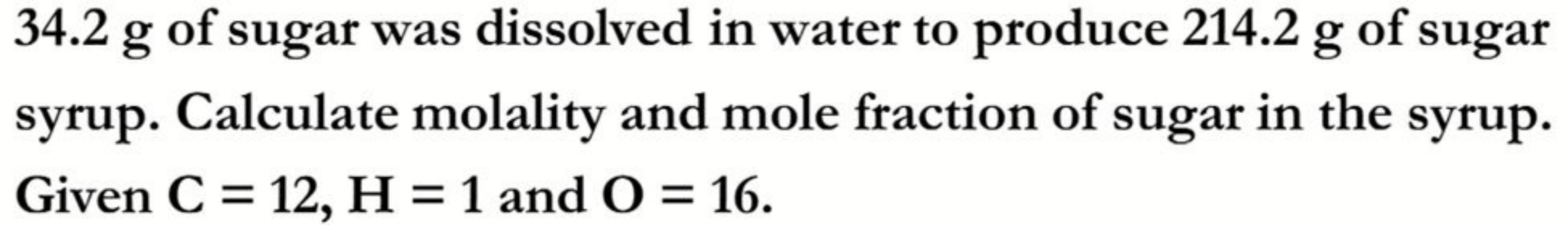
LET’S SOLVE



7.45 g of potassium chloride (KCl) was dissolved in 100 g of water. Calculate the molality of the solution.

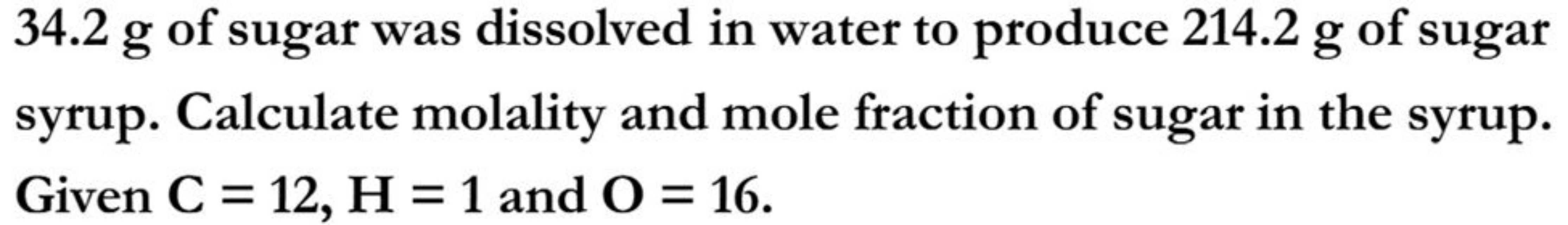
Ans: 1 mol kg^{-1}

LET’S SOLVE



34.2 g of sugar was dissolved in water to produce 214.2 g of sugar syrup. Calculate molality and mole fraction of sugar in the syrup. Given C = 12, H = 1 and O = 16.

LET'S SOLVE



34.2 g of sugar was dissolved in water to produce 214.2 g of sugar syrup. Calculate molality and mole fraction of sugar in the syrup. Given C = 12, H = 1 and O = 16.

Ans: Molality = 0.5556 mol kg^{-1} & mole fraction = 0.0099

CONCENTRATION TERMS:

- Temperature independent units: Mass %, ppm, mole fraction and molality
- Temperature dependent unit: molarity

  → This is because ***volume depends on temperature*** and the ***mass does not***.

1.3 SOLUBILITY

SOLUBILITY:

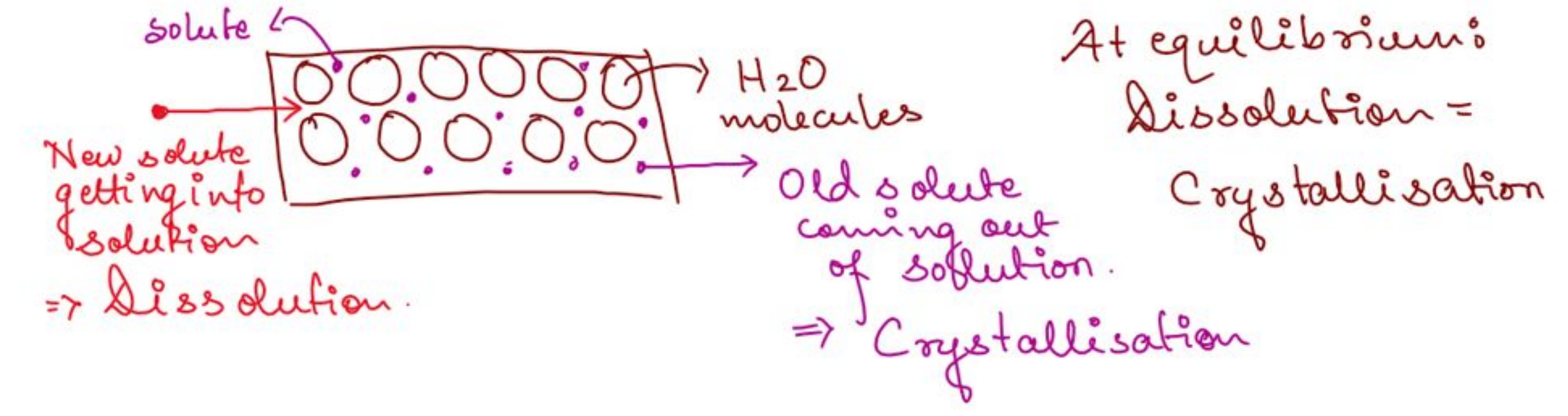
- ***Maximum*** amount of a ***solute*** that can be dissolved ***in*** a ***specified amount*** of ***solvent*** at a ***specified temperature***.

- Factors affecting the solubility: nature of solute and solvent, temperature and pressure.

SOLUBILITY OF A SOLID IN A LIQUID:

- A solute dissolves in a solvent if the intermolecular interactions are similar in the two or we may say ***like dissolves like***.

$$\text{Solute} + \text{Solvent} \rightleftharpoons \text{Solution}$$



At equilibrium: Dissolution = Crystallisation

SOLUBILITY OF A SOLID IN A LIQUID:

$$\text{Solute} + \text{Solvent} \rightleftharpoons \text{Solution}$$

CRYSTALLISATION	DISSOLUTION
● Dissolved solute forms solid crystals, ***reducing concentration*** in the solution. ● Generally an ***exothermic*** process (releases heat) as new bonds are formed. ● Often achieved by cooling a saturated solution or evaporating the solvent.	● Solute dissolves into the solvent, ***increasing*** the ***concentration*** ● Generally an ***endothermic*** process (absorbs heat) as it requires energy to break bonds. ● Often favored by higher temperatures.

SOLUBILITY OF A SOLID IN A LIQUID:

◪Effect of Temperature:

→ For exothermic reactions: $\Delta H_{sol} < 0$; solubility ↓ when temperature ↑

→ For endothermic reactions: $\Delta H_{sol} > 0$; solubility ↑ when temperature ↑

SOLUBILITY OF A SOLID IN A LIQUID:

◪Effect of Pressure:

→ ***no*** significant ***effect***

→ ***solids*** and ***liquids*** are highly ***incompressible***

→ remain ***unaffected by*** changes in ***pressure***.

SOLUBILITY OF A GAS IN A LIQUID:

◪Effect of Temperature:

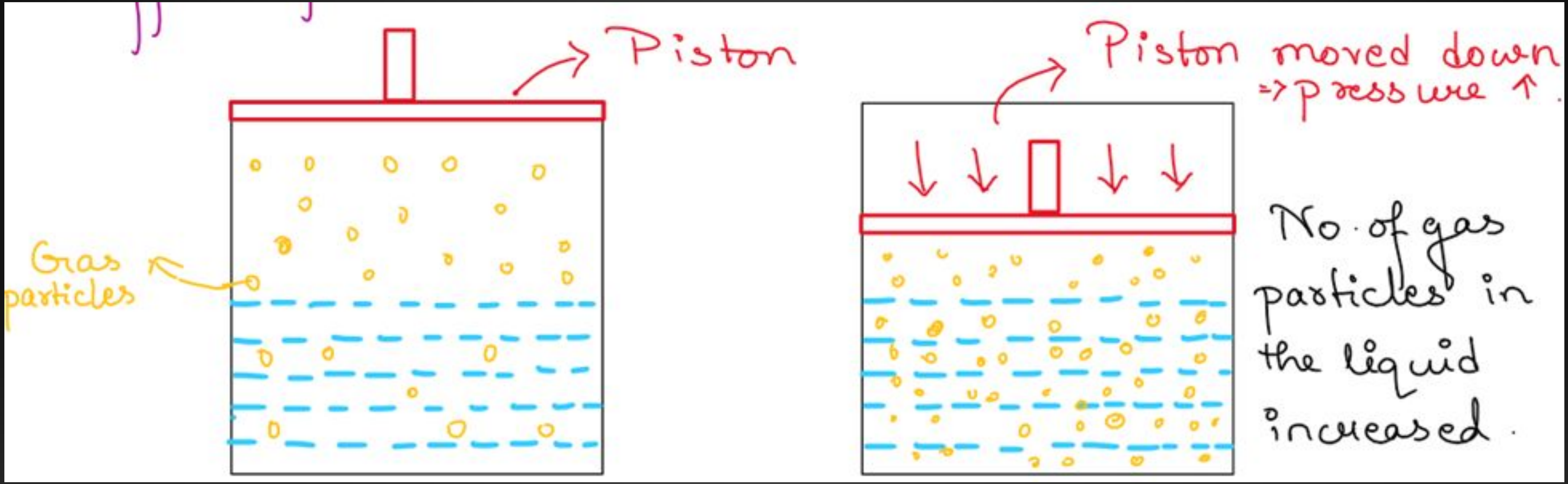
→ Gases on dissolving changes to liquid phase

→ Energy is released & becomes exothermic process

→ For exothermic reactions: $\Delta H_{sol} < 0$; ***solubility*** ↓ when ***temperature*** ↑

SOLUBILITY OF A GAS IN A LIQUID:

- Effect of Pressure: **Henry's Law**



SOLUBILITY OF A GAS IN A LIQUID:

- Effect of Pressure: **Henry's Law**

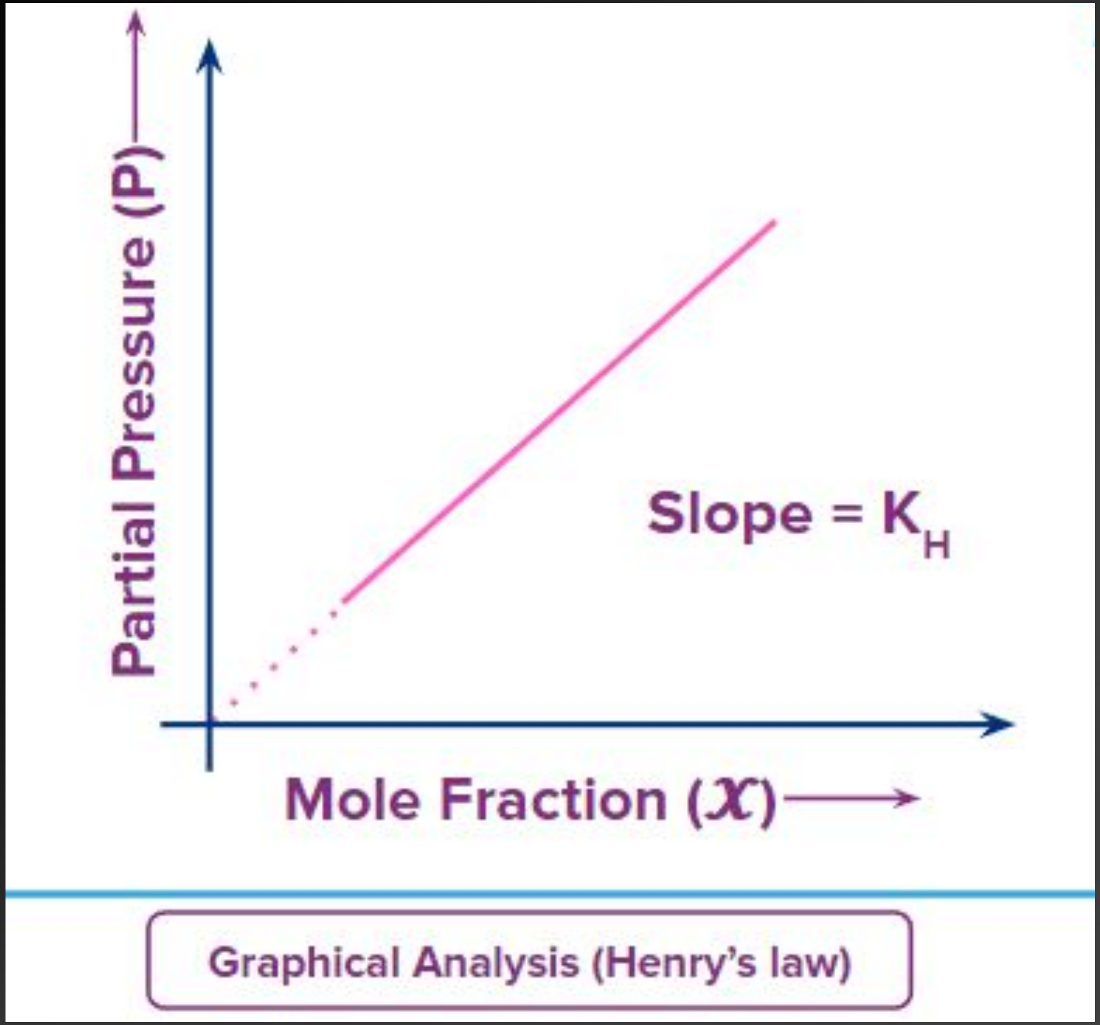
STATEMENT 1: At a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

STATEMENT 2: The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.

$$p = K_H\, x;\ K_H = \text{Henry's Law Constant}$$

- Different gases have different K_H values at the same temperature. This suggests that ***K_H*** is a ***function of the nature of the gas.***
- ***Higher*** the value of ***K_H*** at a given pressure, the ***lower*** is the ***solubility*** of the gas in the liquid.

SOLUBILITY OF A GAS IN A LIQUID:



LIMITATION OF HENRY'S LAW:

→ Not followed at very high pressure or very low temperature

→ Not followed if there is chemical reaction/ association / dissociation of solute and solvent

SOLUBILITY OF A GAS IN A LIQUID:

APPLICATION OF HENRY’S LAW:

→ aquatic species are more comfortable in cold waters rather than in warm waters

→ To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure

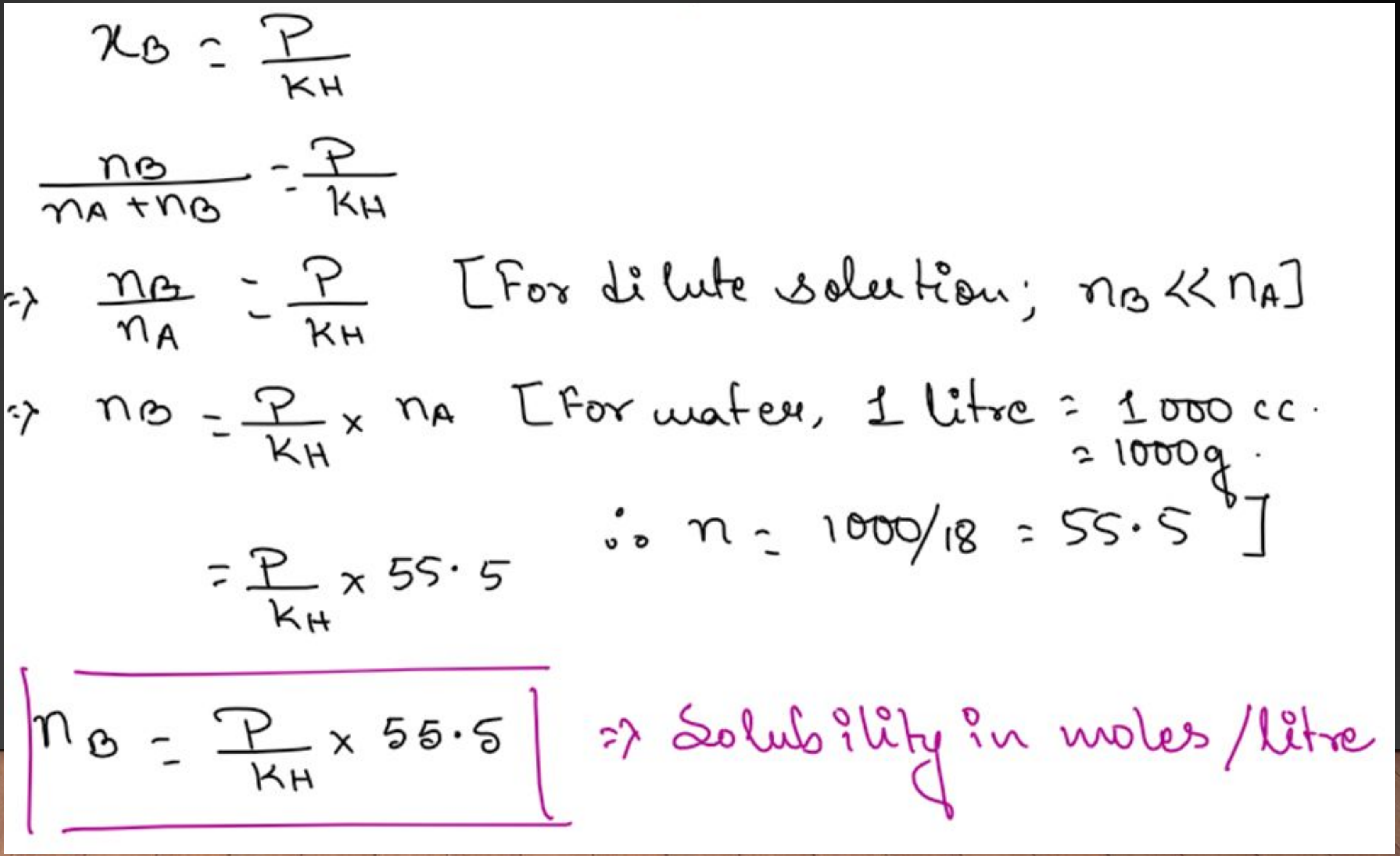
→ **BENDS:** While deep water diving, the pressure increases under water which in turn increases the solubility of N_2 in blood. While coming up when pressure decreases, these dissolved gases will try to come out of the capillaries causing painful conditions called ***BENDS***. To avoid bends composition maintained in oxygen cylinder is: 11.7% He, 56.2% N_2 and 32.1% O_2

→ **ANOXIA:** At high altitude the pressure ↓, as a result O_2 level in blood also ↓ which causes different health problems like weakness, fatigue etc.

HENRY’S LAW FORMULA LIST:

If solubility is asked in:

- Mole fraction: $x_B = p/K_H$
- Moles/litre or molarity:



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

$$\frac{n_B}{n_A + n_B} = \frac{P}{K_H}$$

$$\Rightarrow \frac{n_B}{n_A} = \frac{P}{K_H}$$ [For dilute solution; $n_B << n_A$]

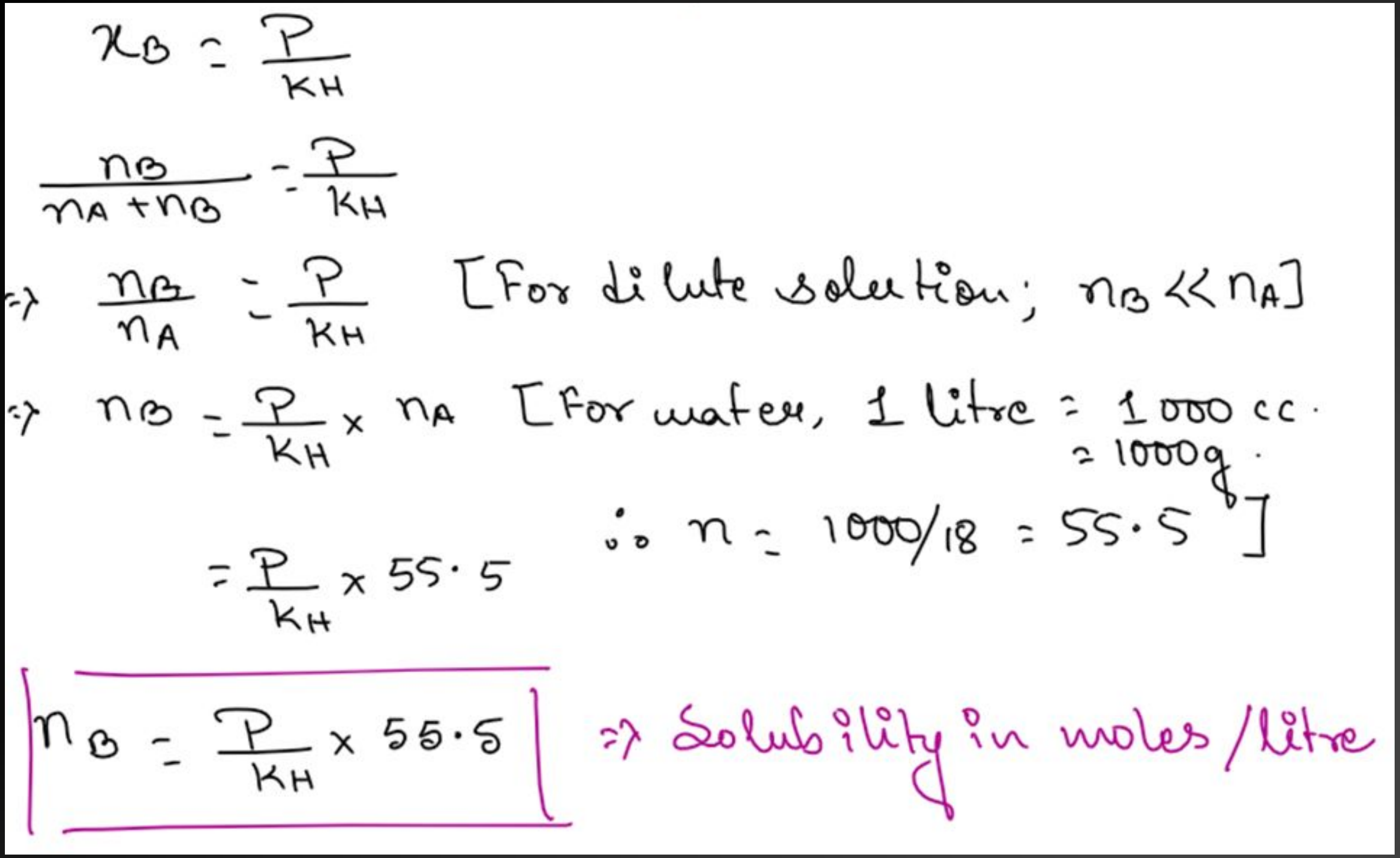
$$\Rightarrow n_B = \frac{P}{K_H} \times n_A$$ [For water, 1 litre = 1000 cc. = 1000g. $\therefore n = 1000/18 = 55.5$]

$$= \frac{P}{K_H} \times 55.5$$

$$\boxed{n_B = \frac{P}{K_H} \times 55.5}$$ ⇒ Solubility in moles/litre

- Millimoles/litre:

  (Moles/litre) x 1000



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= 1000g.
∴ n = 1000/18 = 55.5]

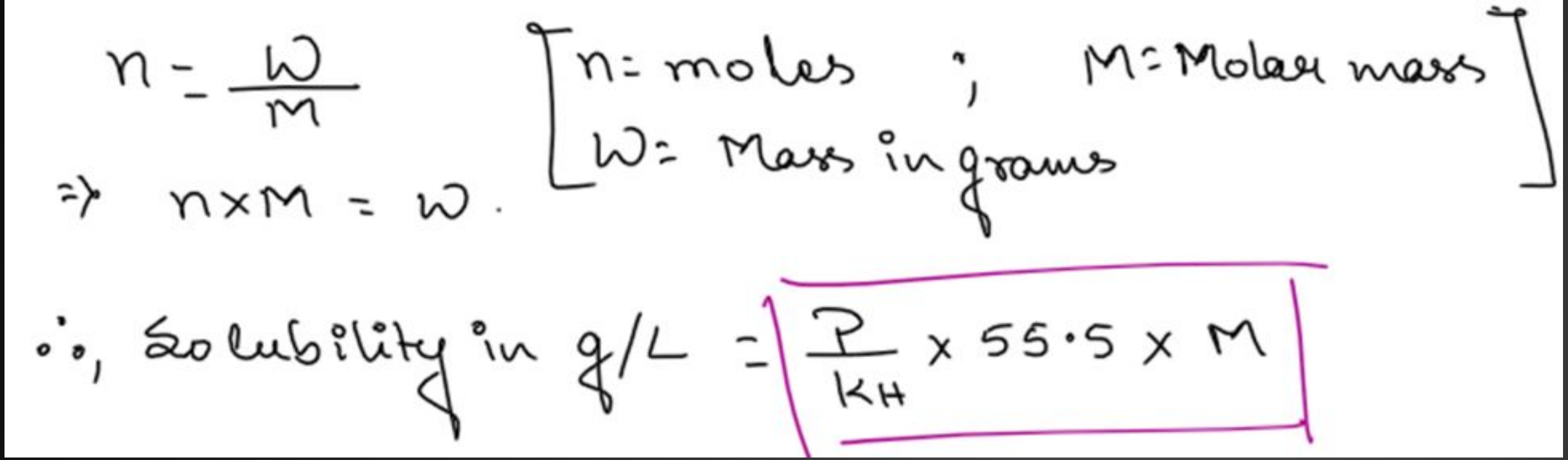
$$= \frac{P}{K_H} \times 55.5$$

$$\boxed{n_B = \frac{P}{K_H} \times 55.5}$$ ⇒ Solubility in moles/litre

HENRY’S LAW FORMULA LIST:

If solubility is asked in:

- Grams/litre:

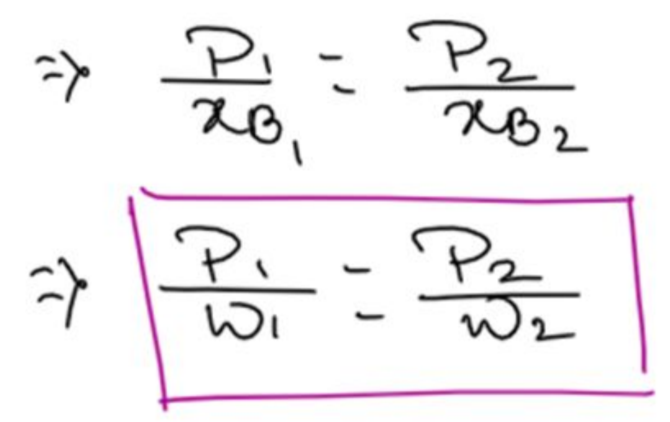


$n = \frac{W}{M}$ $\left[\begin{array}{l} n = \text{moles} \; ; \quad M = \text{Molar mass} \\ W = \text{Mass in grams} \end{array}\right]$

$\Rightarrow n \times M = W.$

$\therefore$, Solubility in g/L $= \boxed{\frac{P}{K_H} \times 55.5 \times M}$

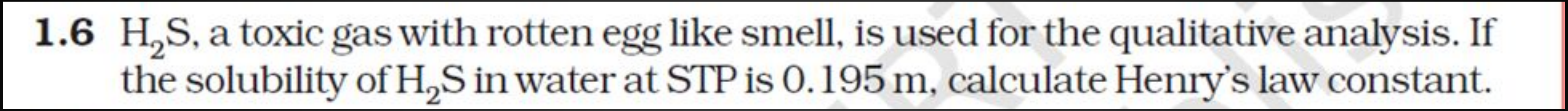
- p/x_B = K_H = constant



$$\Rightarrow \frac{P_1}{x_{B_1}} = \frac{P_2}{x_{B_2}}$$

$$\Rightarrow \boxed{\frac{P_1}{W_1} = \frac{P_2}{W_2}}$$

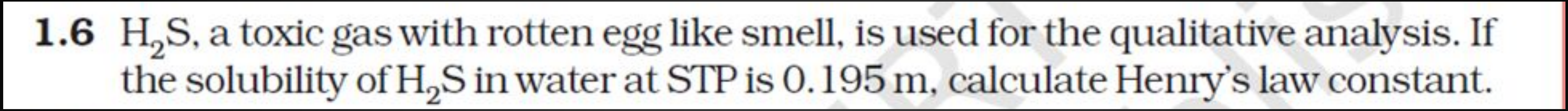
LEARNING CHECK



1.6 H_2S, a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant.

Ans:

LEARNING CHECK



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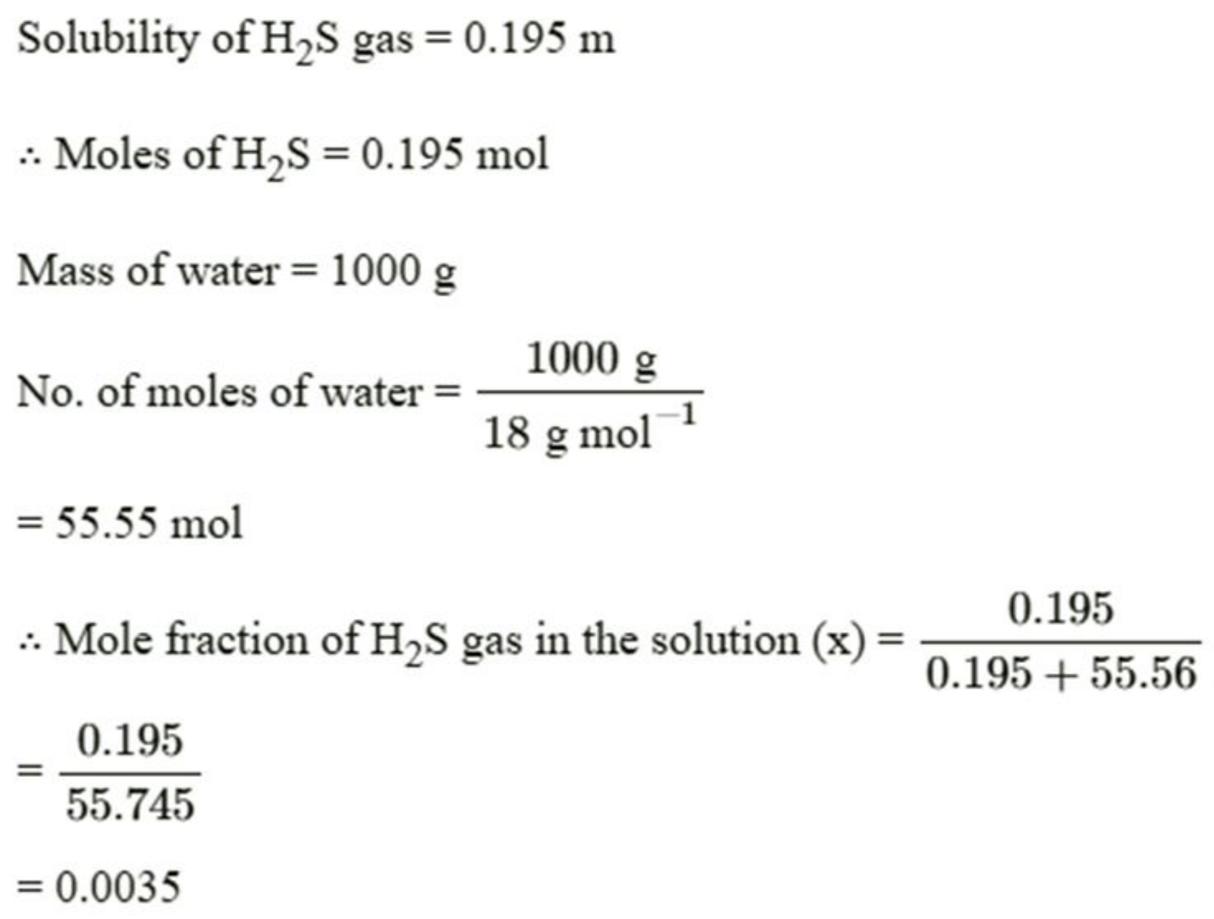


Solubility of H_2S gas = 0.195 m

$\therefore$ Moles of H_2S = 0.195 mol

Mass of water = 1000 g

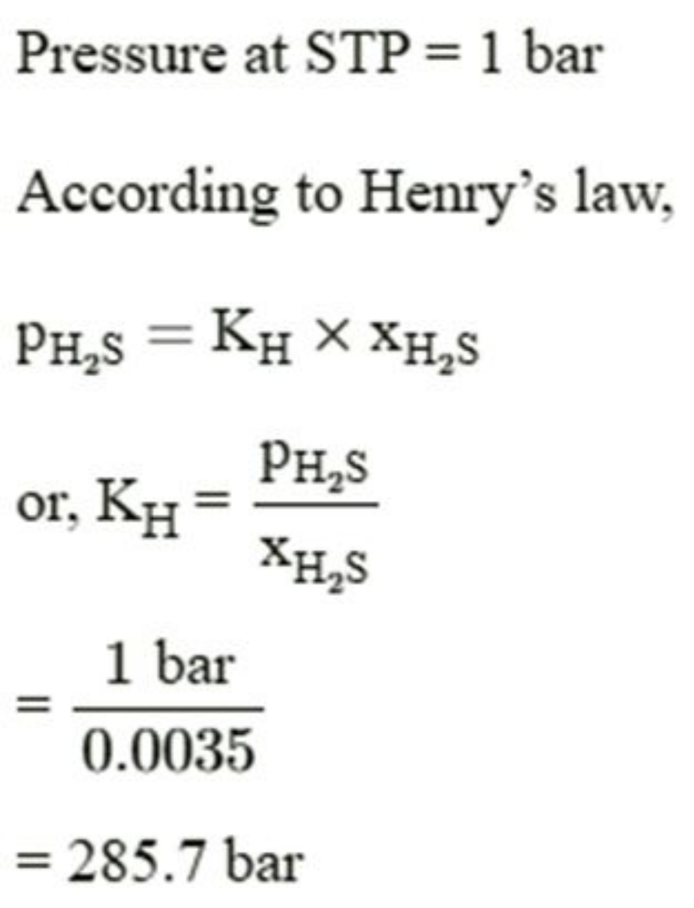
$$\text{No. of moles of water} = \frac{1000\ \text{g}}{18\ \text{g mol}^{-1}}$$

= 55.55 mol

$$\therefore \text{Mole fraction of } H_2S \text{ gas in the solution } (x) = \frac{0.195}{0.195 + 55.56}$$

$$= \frac{0.195}{55.745}$$

= 0.0035



Pressure at STP = 1 bar

According to Henry's law,

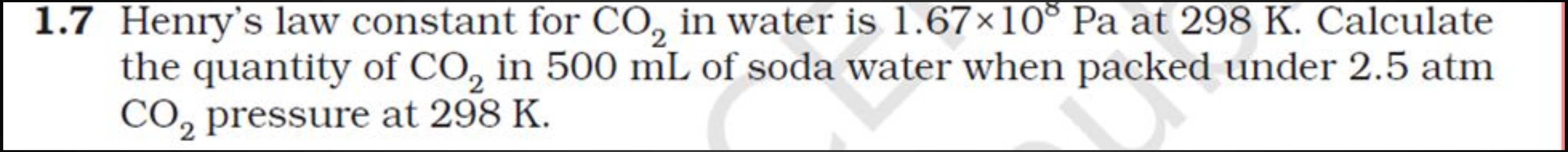
$$p_{H_2S} = K_H \times x_{H_2S}$$

$$\text{or, } K_H = \frac{p_{H_2S}}{x_{H_2S}}$$

$$= \frac{1\ \text{bar}}{0.0035}$$

= 285.7 bar

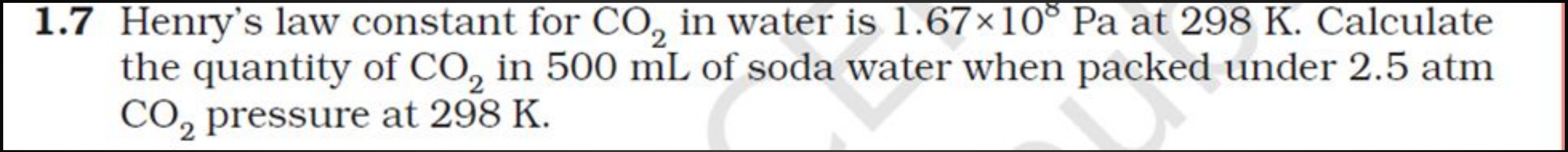
LEARNING CHECK



1.7 Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

Ans:

LEARNING CHECK



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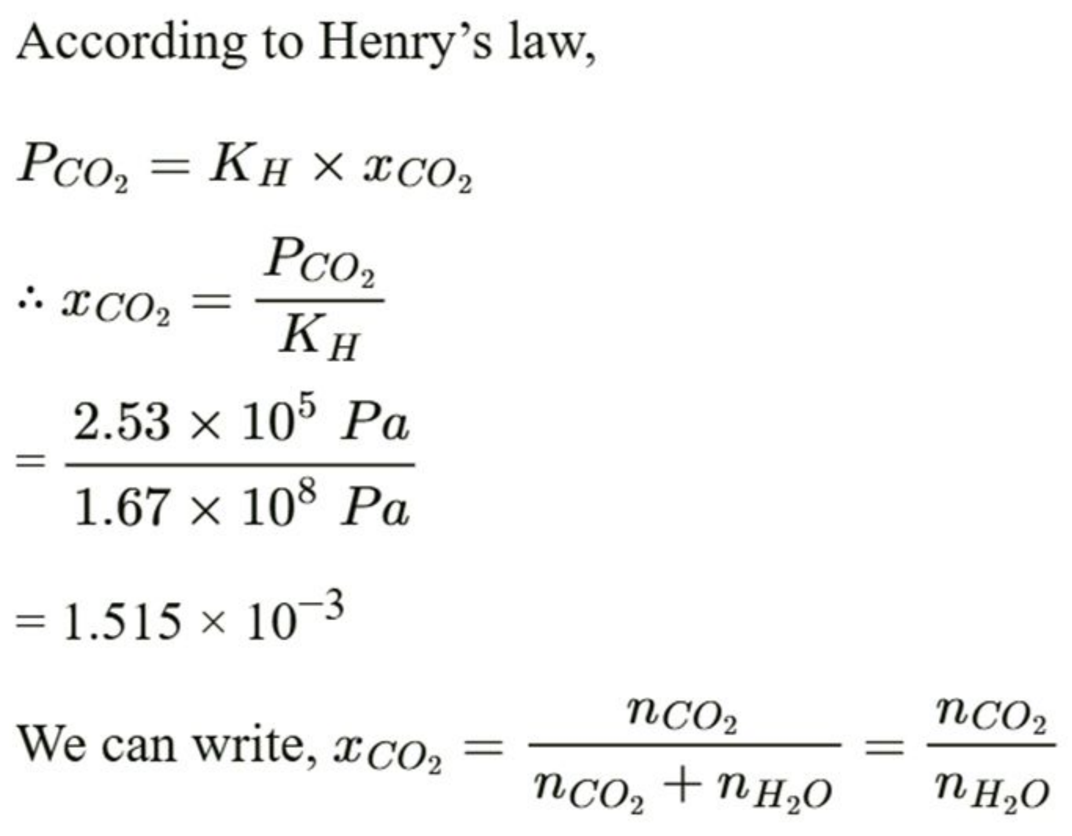


According to Henry's law,

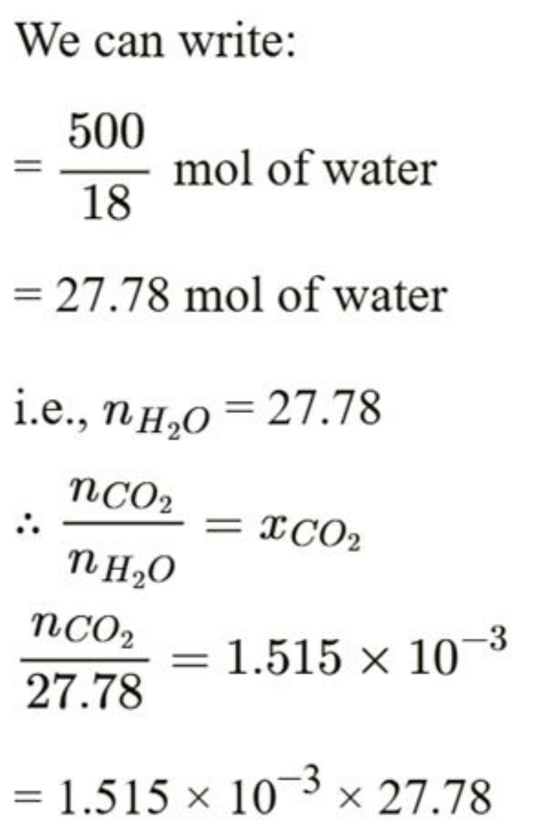
$$P_{CO_2} = K_H \times x_{CO_2}$$

$$\therefore x_{CO_2} = \frac{P_{CO_2}}{K_H}$$

$$= \frac{2.53 \times 10^5\ Pa}{1.67 \times 10^8\ Pa}$$

$$= 1.515 \times 10^{-3}$$

We can write, $x_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{H_2O}} = \frac{n_{CO_2}}{n_{H_2O}}$



We can write:

$$= \frac{500}{18} \text{ mol of water}$$

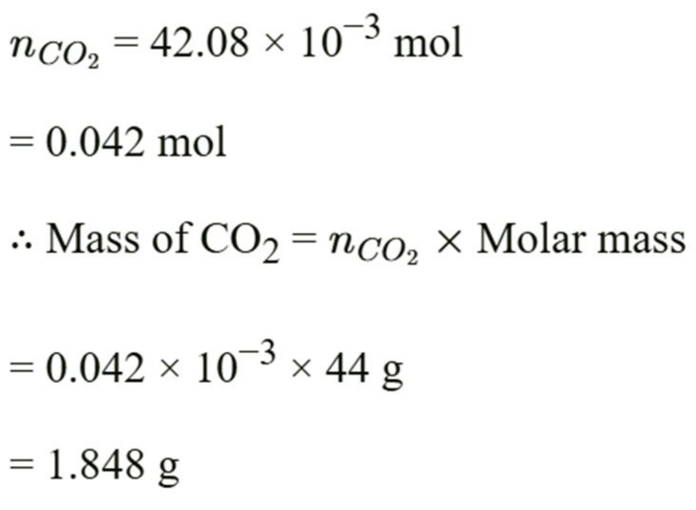
$$= 27.78 \text{ mol of water}$$

i.e., $n_{H_2O} = 27.78$

$$\therefore \frac{n_{CO_2}}{n_{H_2O}} = x_{CO_2}$$

$$\frac{n_{CO_2}}{27.78} = 1.515 \times 10^{-3}$$

$$= 1.515 \times 10^{-3} \times 27.78$$



$n_{CO_2} = 42.08 \times 10^{-3}$ mol

$= 0.042$ mol

$\therefore$ Mass of $CO_2 = n_{CO_2} \times$ Molar mass

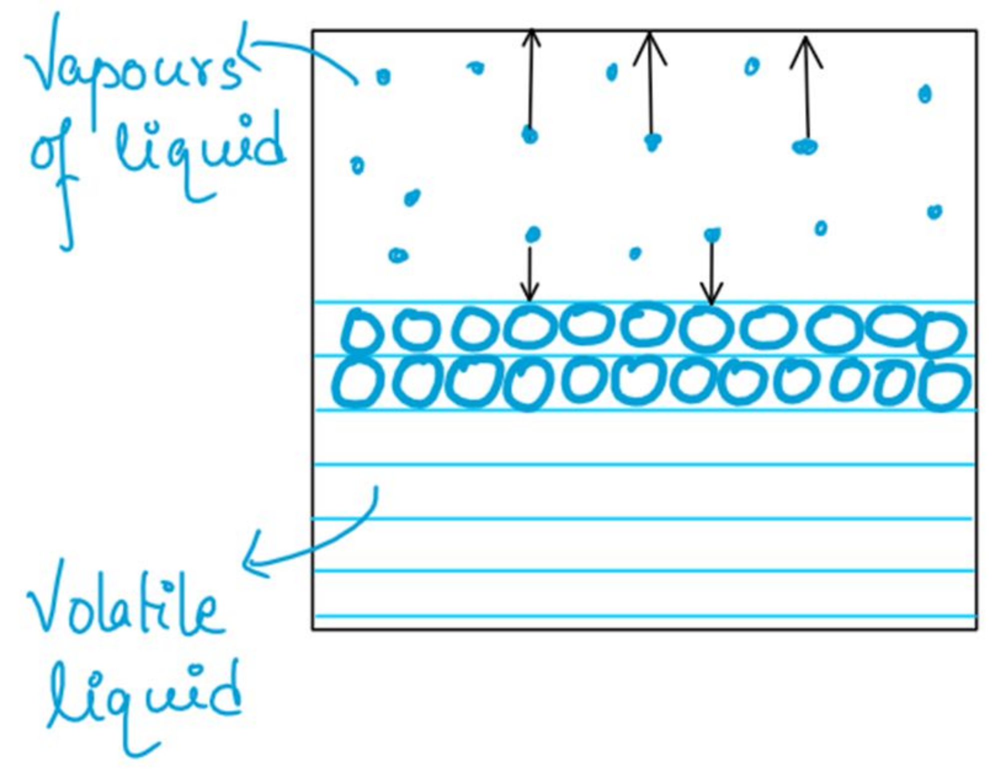
$= 0.042 \times 10^{-3} \times 44$ g

$= 1.848$ g

1.4 VAPOUR PRESSURE OF LIQUID SOLUTIONS

VAPOUR PRESSURE OF LIQUID SOLUTIONS:

LIQUID - LIQUID SOLUTIONS: RAOULT'S LAW



Vapour pressure: Pressure exerted by a vapour in thermodynamic equilibrium with its condensed phases (liquid or solid) in a closed system at a specific temperature.

- Evaporation → surface phenomenon → more surface → more vapour → more vapour pressure

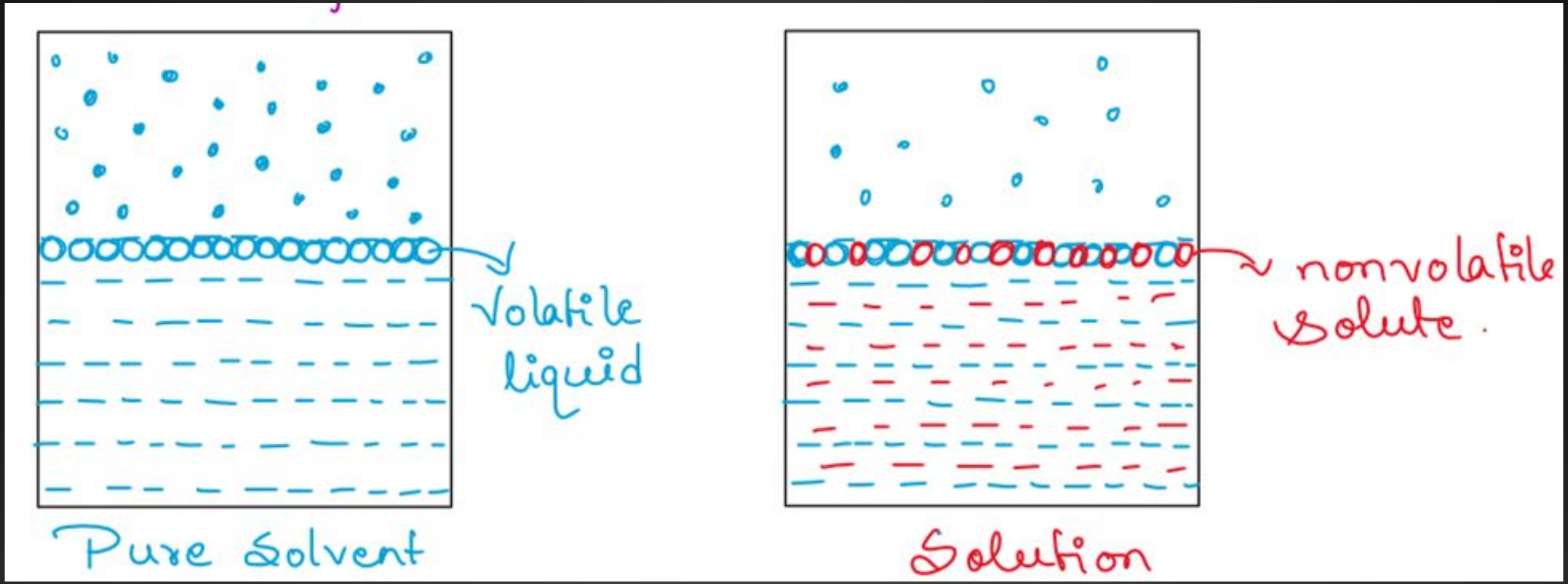
- When only solvent is present: $p_A = p_A^0$

Raoult's law for volatile liquids: For a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution, $p_A = p_A^0 x_A$

VOLATILE: That can form vapours easily due to evaporation

VAPOUR PRESSURE OF LIQUID SOLUTIONS:

RAOULT'S LAW FOR NON VOLATILE SOLUTE

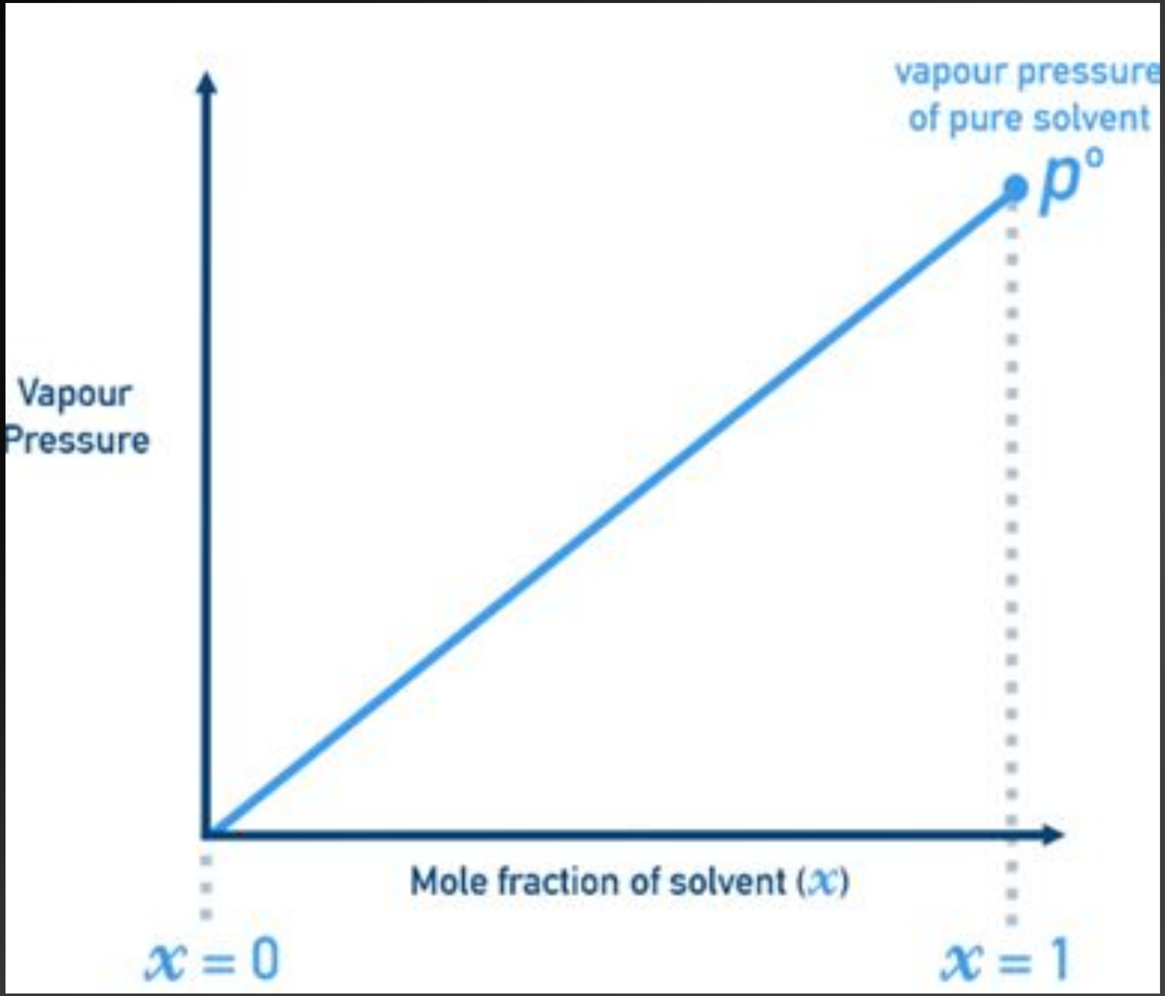


$p_A \propto x_A$

$p_A = p_A^0 x_A \Rightarrow$ **Raoult's Law for non volatile solute** $[p_A < p_A^0]$

VAPOUR PRESSURE OF LIQUID SOLUTIONS:

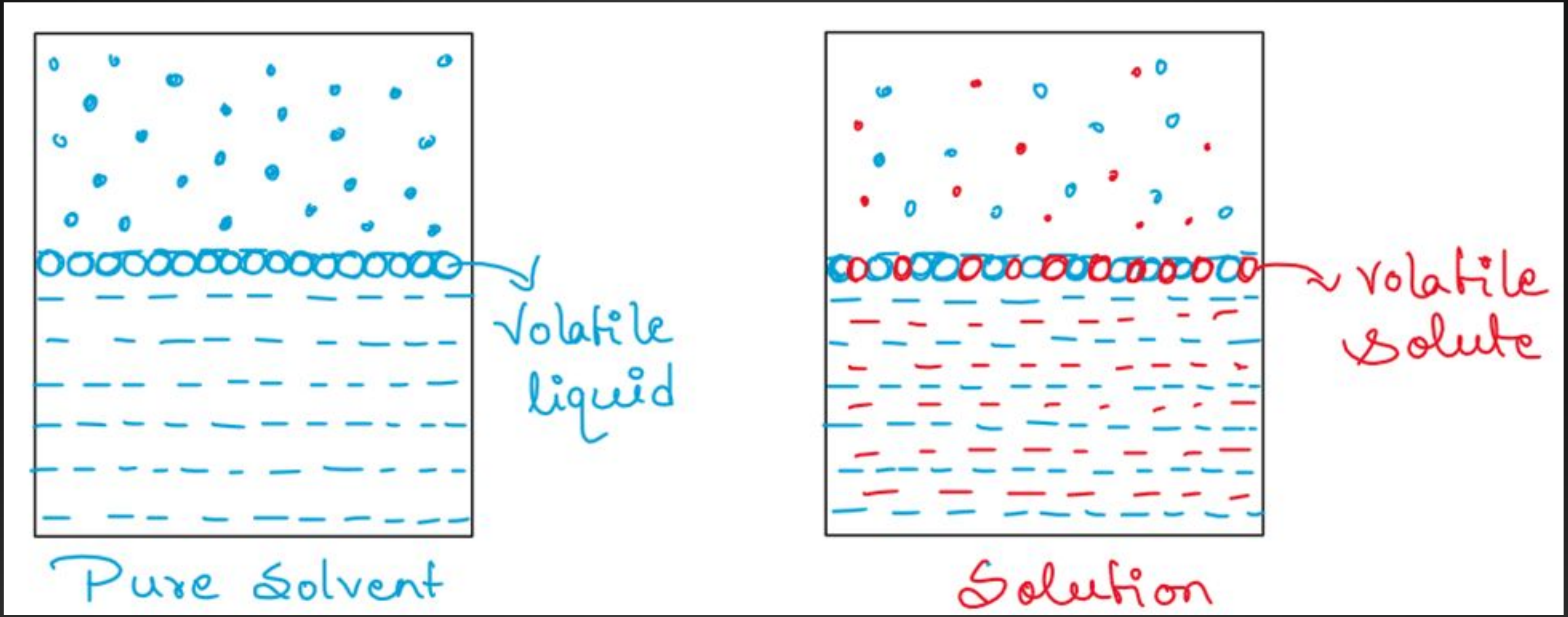
GRAPH OF RAOULT'S LAW FOR NON VOLATILE SOLUTE



Vapour pressure lowers as effective surface of evaporation decreases

VAPOUR PRESSURE OF LIQUID SOLUTIONS:

RAOULT'S LAW FOR VOLATILE SOLUTE

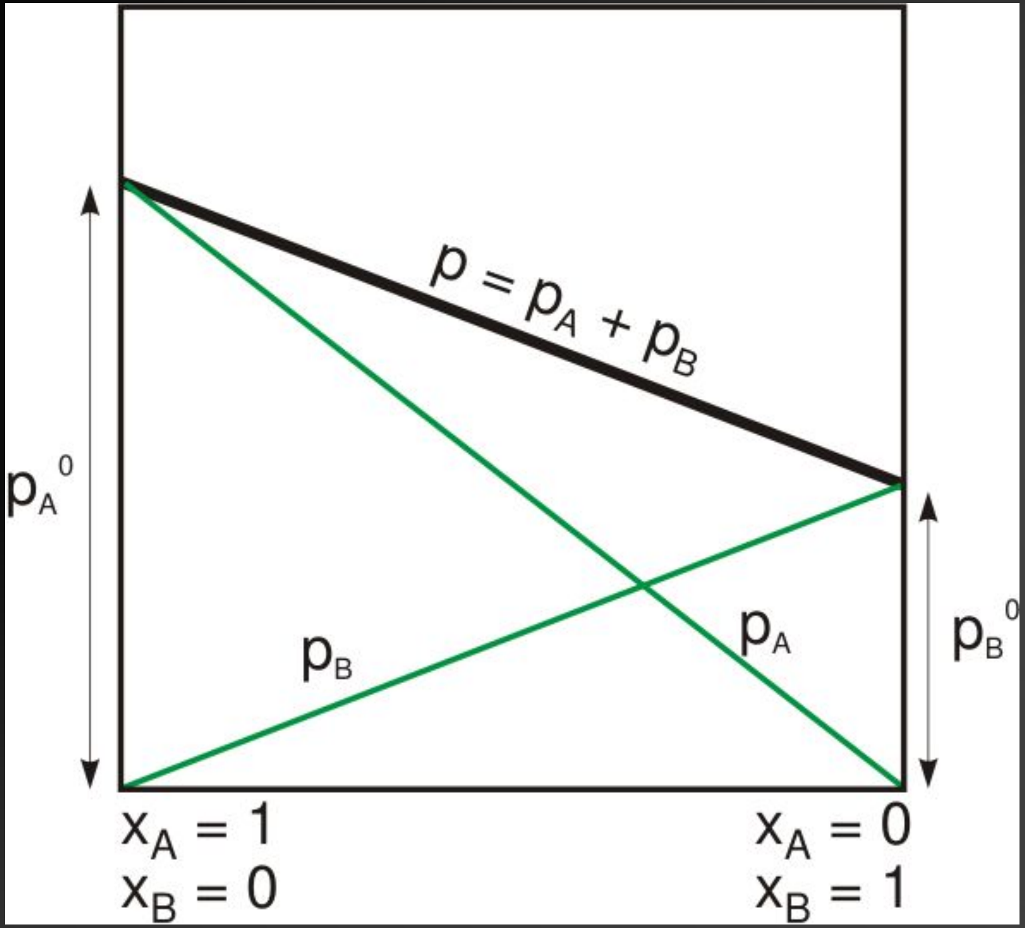


$p_A \propto x_A$ $p_B \propto x_B$ Total pressure: $p_T = p_A + p_B$

$p_A = p_A^0 x_A$ $p_B = p_B^0 x_B$ $p_T = p_A^0 x_A + p_B^0 x_B \Rightarrow$ **Raoult's Law for volatile solute**

VAPOUR PRESSURE OF LIQUID SOLUTIONS:

GRAPH OF RAOULT'S LAW FOR VOLATILE SOLUTE



→The component having higher p^0 is more volatile in nature.

→At equilibrium, vapour phase will always be rich in the component which is more volatile.

→The graph is always tilted , never straight because two different substances in their pure state can't have same vapour pressure

VAPOUR PRESSURE OF LIQUID SOLUTIONS:

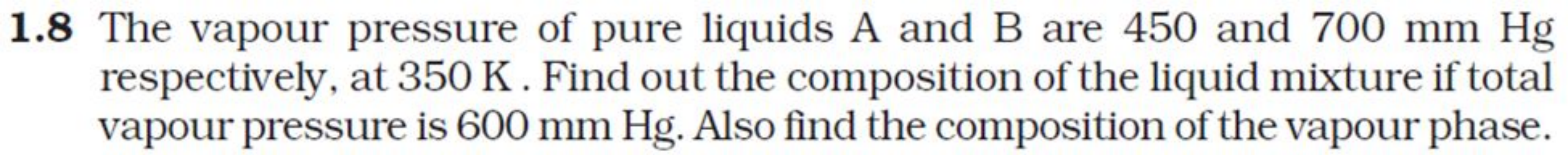
COMPOSITION IN VAPOUR PHASE

y_A & y_B ⇒ composition of component A & B in vapour phase respectively

$y_A + y_B = 1$

$y_A = p_A/p_T$ & $y_B = p_B / p_T$

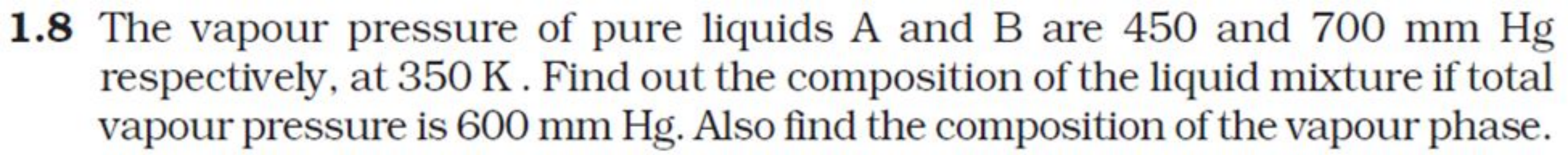
LEARNING CHECK



1.8 The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K . Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.

Ans:

LEARNING CHECK



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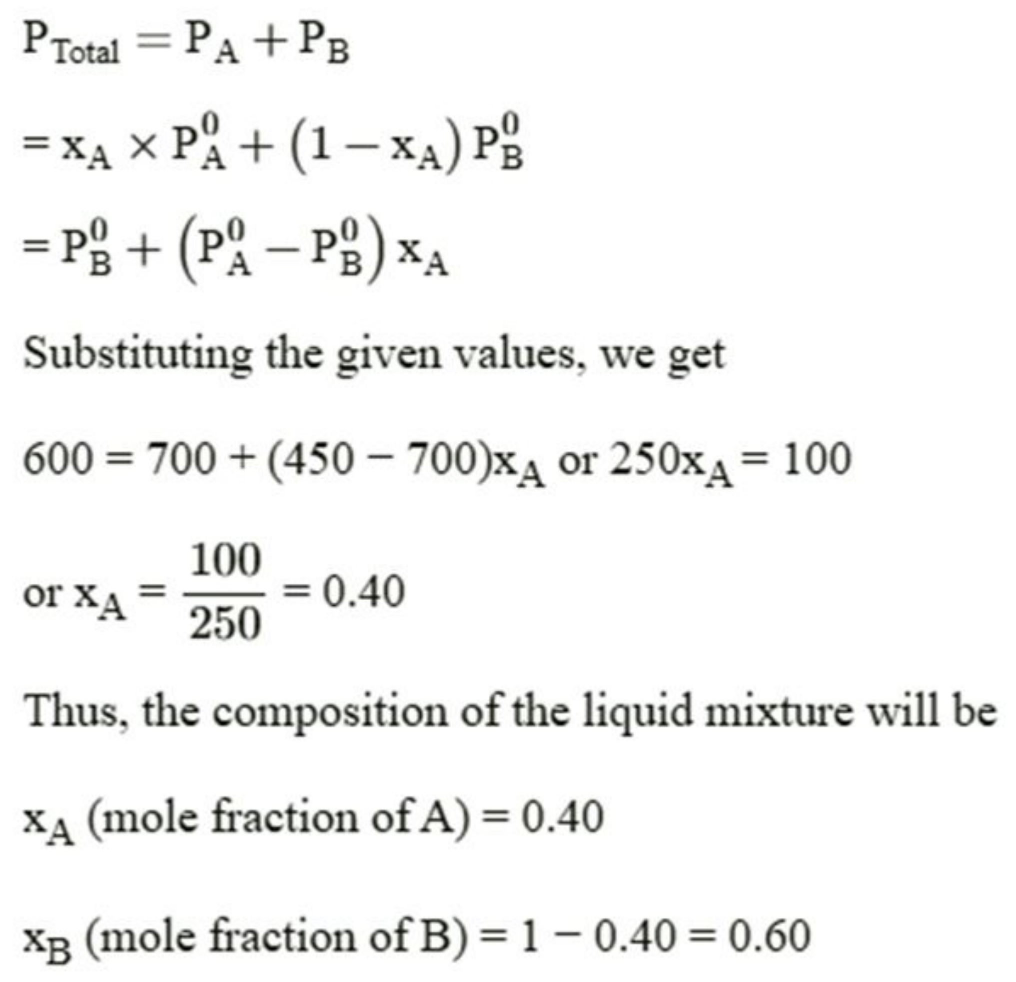
Ans:



$P_{Total} = P_A + P_B$

$= x_A \times P_A^0 + (1 - x_A)\, P_B^0$

$= P_B^0 + \left(P_A^0 - P_B^0\right) x_A$

Substituting the given values, we get

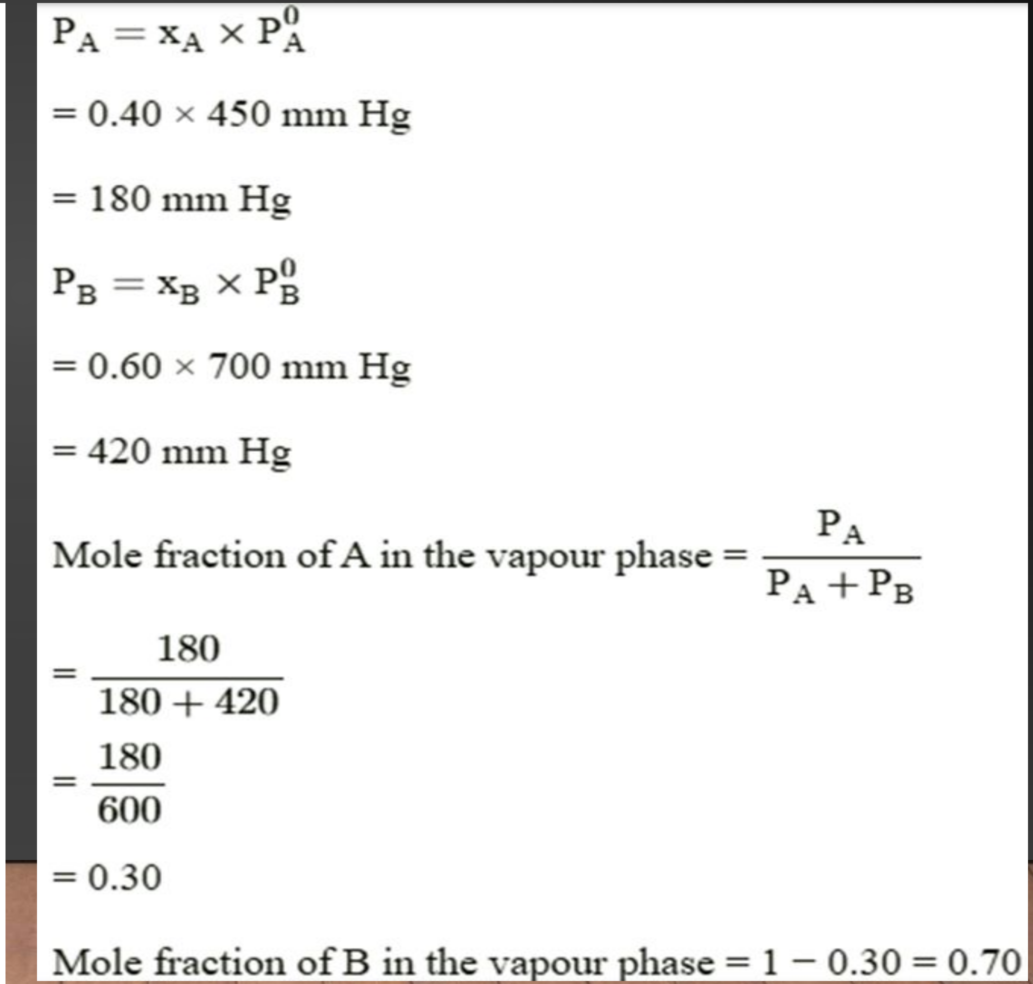
$600 = 700 + (450 - 700)x_A$ or $250x_A = 100$

or $x_A = \dfrac{100}{250} = 0.40$

Thus, the composition of the liquid mixture will be

x_A (mole fraction of A) = 0.40

x_B (mole fraction of B) = 1 − 0.40 = 0.60



$P_A = x_A \times P_A^0$

$= 0.40 \times 450$ mm Hg

$= 180$ mm Hg

$P_B = x_B \times P_B^0$

$= 0.60 \times 700$ mm Hg

$= 420$ mm Hg

Mole fraction of A in the vapour phase $= \dfrac{P_A}{P_A + P_B}$

$= \dfrac{180}{180 + 420}$

$= \dfrac{180}{600}$

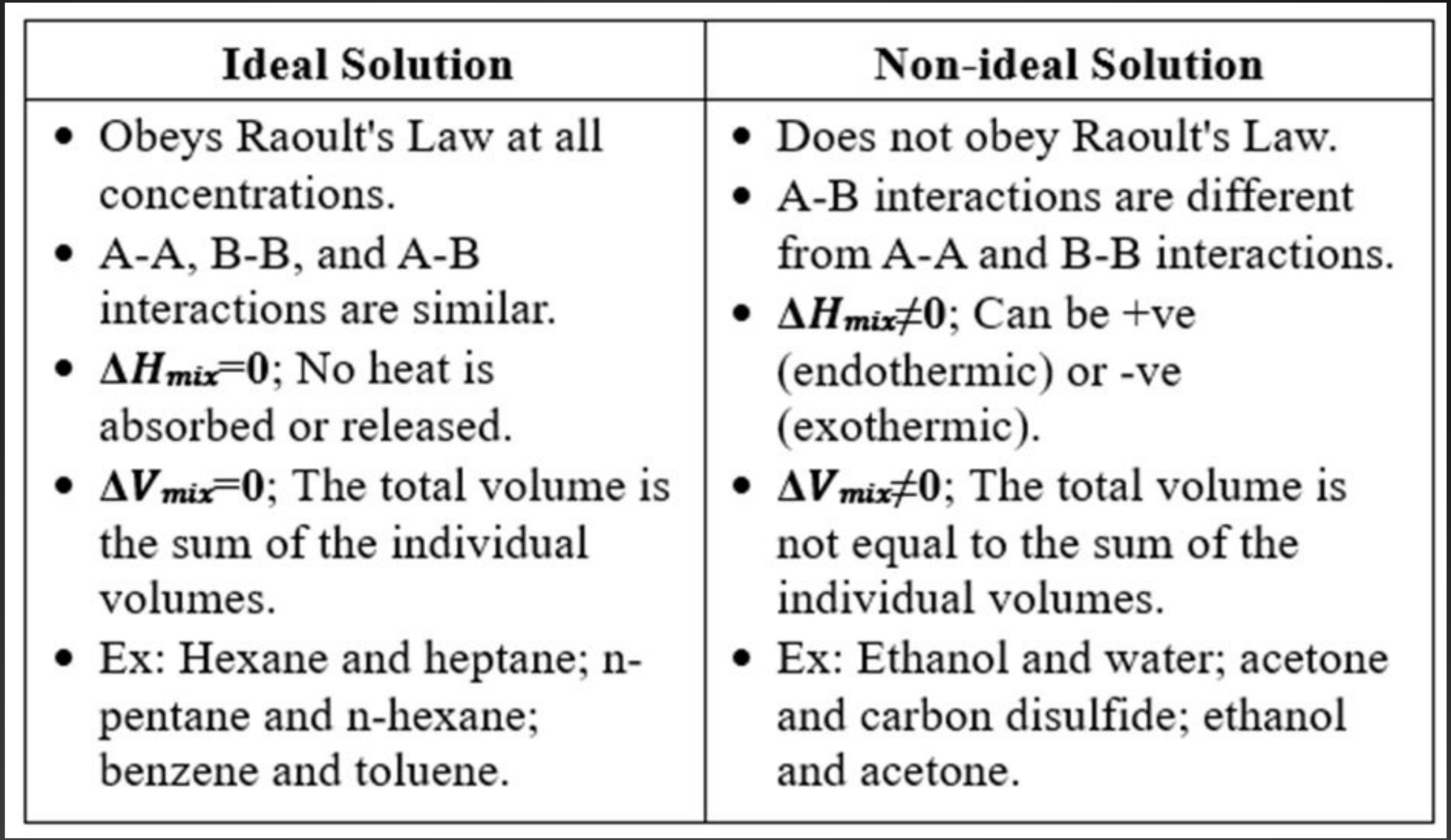
$= 0.30$

Mole fraction of B in the vapour phase = 1 − 0.30 = 0.70

1.5 IDEAL AND NON-IDEAL SOLUTIONS

VAPOUR PRESSURE OF LIQUID SOLUTIONS:

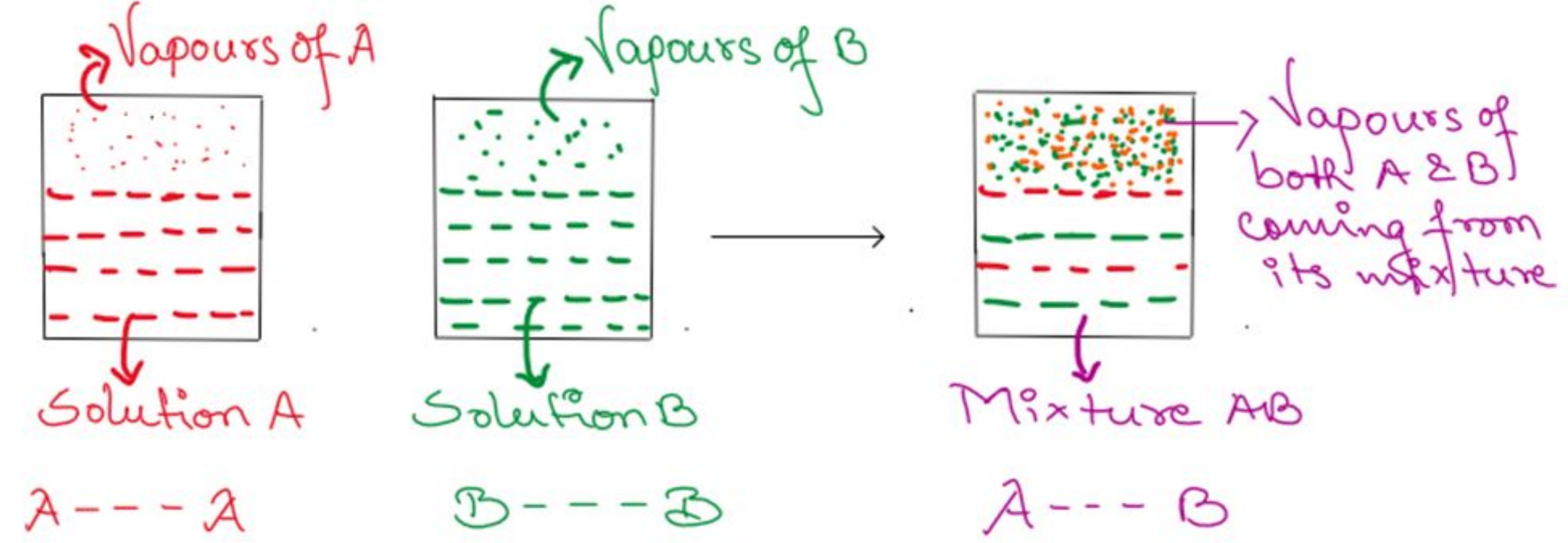
IDEAL vs NON-IDEAL SOLUTION



Ideal Solution	Non-ideal Solution
• Obeys Raoult's Law at all concentrations. • A-A, B-B, and A-B interactions are similar. • $\Delta H_{mix}=0$; No heat is absorbed or released. • $\Delta V_{mix}=0$; The total volume is the sum of the individual volumes. • Ex: Hexane and heptane; n-pentane and n-hexane; benzene and toluene.	• Does not obey Raoult's Law. • A-B interactions are different from A-A and B-B interactions. • $\Delta H_{mix}\neq0$; Can be +ve (endothermic) or -ve (exothermic). • $\Delta V_{mix}\neq0$; The total volume is not equal to the sum of the individual volumes. • Ex: Ethanol and water; acetone and carbon disulfide; ethanol and acetone.

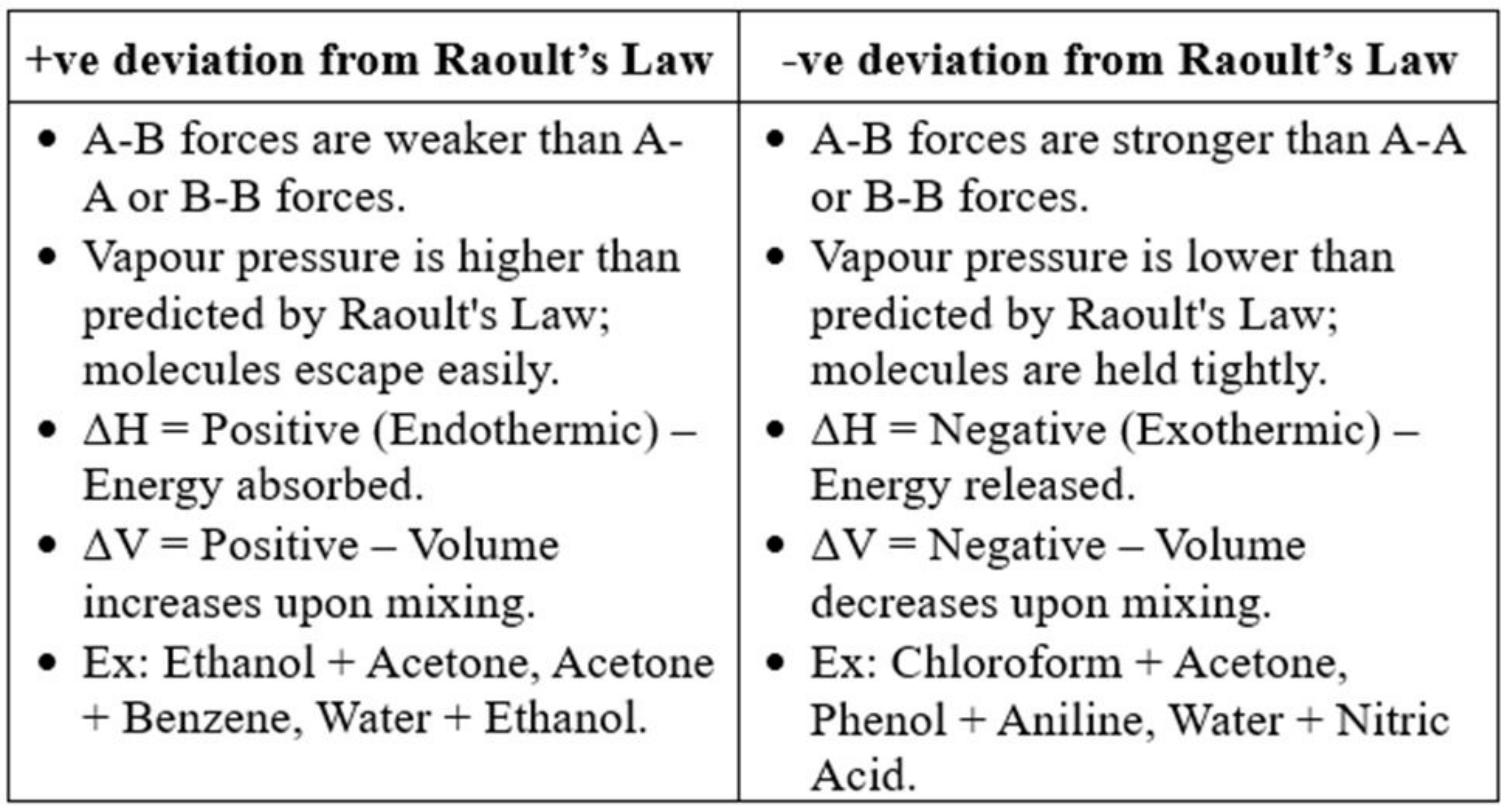
VAPOUR PRESSURE OF LIQUID SOLUTIONS:

DEVIATION FROM IDEAL BEHAVIOUR



VAPOUR PRESSURE OF LIQUID SOLUTIONS:

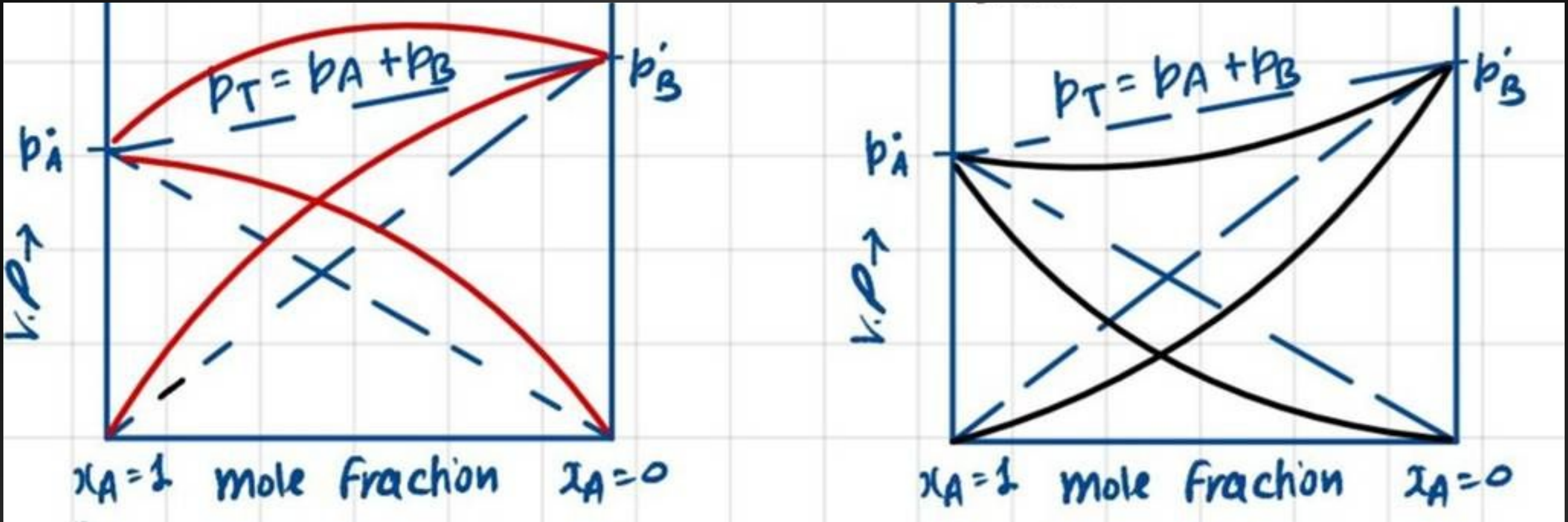
+VE *vs* -VE DEVIATION FROM IDEAL BEHAVIOUR



+ve deviation from Raoult’s Law	**-ve deviation from Raoult’s Law**
• A-B forces are weaker than A-A or B-B forces. • Vapour pressure is higher than predicted by Raoult's Law; molecules escape easily. • ΔH = Positive (Endothermic) – Energy absorbed. • ΔV = Positive – Volume increases upon mixing. • Ex: Ethanol + Acetone, Acetone + Benzene, Water + Ethanol.	• A-B forces are stronger than A-A or B-B forces. • Vapour pressure is lower than predicted by Raoult's Law; molecules are held tightly. • ΔH = Negative (Exothermic) – Energy released. • ΔV = Negative – Volume decreases upon mixing. • Ex: Chloroform + Acetone, Phenol + Aniline, Water + Nitric Acid.

VAPOUR PRESSURE OF LIQUID SOLUTIONS:

+VE *vs* -VE DEVIATION FROM IDEAL BEHAVIOUR



VAPOUR PRESSURE OF LIQUID SOLUTIONS:

AZEOTROPES

Binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature which cannot be separated by fractional distillation.

MINIMUM BOILING AZEOTROPES:

→ Liquid pairs showing large +ve deviation

→ At the azeotropic composition their vapour pressure is highest & boiling point is minimum & it is lower than either of the components.

MAXIMUM BOILING AZEOTROPES:

→ Liquid pairs showing large -ve deviation

→ At the azeotropic composition their vapour pressure is lowest & boiling point is maximum & it is higher than either of the components.

1.6 COLLIGATIVE PROPERTIES AND DETERMINATION OF MOLECULAR MASS

COLLIGATIVE PROPERTIES

→ depend on the ***number of solute particles*** irrespective of their nature relative to the total number of particles present in the solution.

→ studied only in case of solution containing ***non volatile solute***

→ studied for ***dilute solutions***

RELATIVE LOWERING OF VAPOUR PRESSURE

Acc to Raoult's Law;

$\mathbf{p_A \propto x_A}$

$\Rightarrow \mathbf{p_A = p_A{}^0\, x_A}$

$\Rightarrow \mathbf{p_A = p_A{}^0\, (1 - x_B)}$

$\Rightarrow \mathbf{p_A{}^0\, x_B = \boxed{p_A{}^0 - p}}$

$\Rightarrow \mathbf{x_B = \boxed{[p_A{}^0 - p] / p_A{}^0}}$

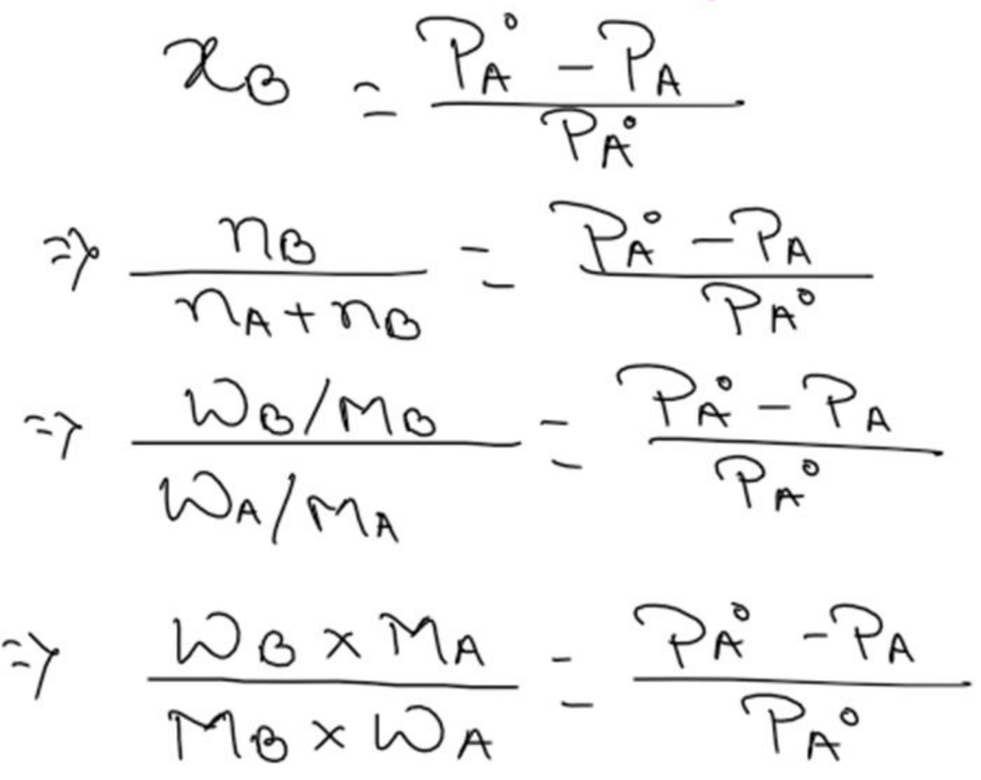
$p_A{}^0 - p$ = Lowering of vapour pressure

$[p_A{}^0 - p] / p_A{}^0$ = Relative lowering of vapour pressure

Thus, relative lowering of vapour pressure $\propto$ no. of particles of solute

RELATIVE LOWERING OF VAPOUR PRESSURE

Determination of molar mass (g mol^{-1}):



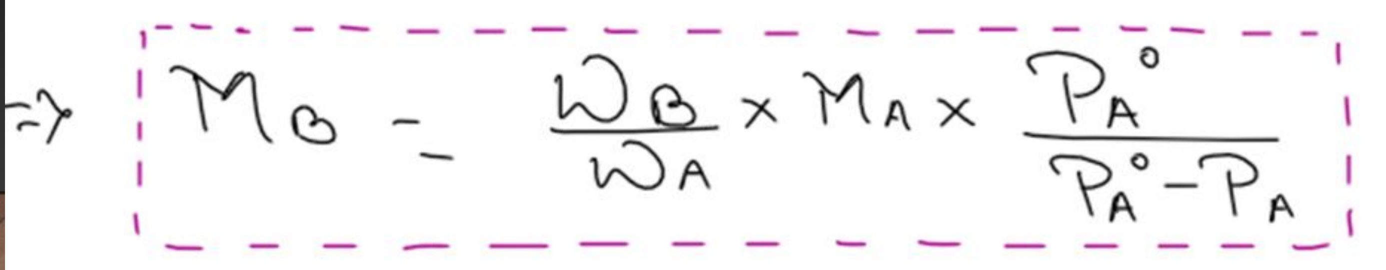
$$x_B = \frac{P_A^\circ - P_A}{P_A^\circ}$$

$$\Rightarrow \frac{n_B}{n_A + n_B} = \frac{P_A^\circ - P_A}{P_A^\circ}$$

$$\Rightarrow \frac{W_B/M_B}{W_A/M_A} = \frac{P_A^\circ - P_A}{P_A^\circ}$$

$$\Rightarrow \frac{W_B \times M_A}{M_B \times W_A} = \frac{P_A^\circ - P_A}{P_A^\circ}$$

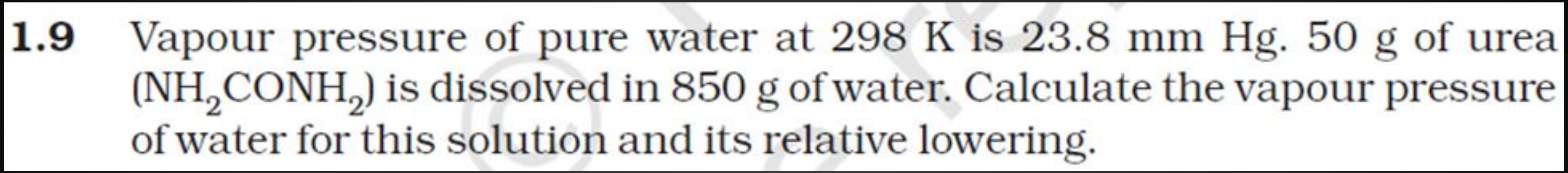
As solution is dilute, thus $n_A >> n_B$ so n_B can be ignored w.r.t addition



$$\Rightarrow \boxed{M_B = \frac{W_B}{W_A} \times M_A \times \frac{P_A^\circ}{P_A^\circ - P_A}}$$

p_A^0 - p is also written as Δp

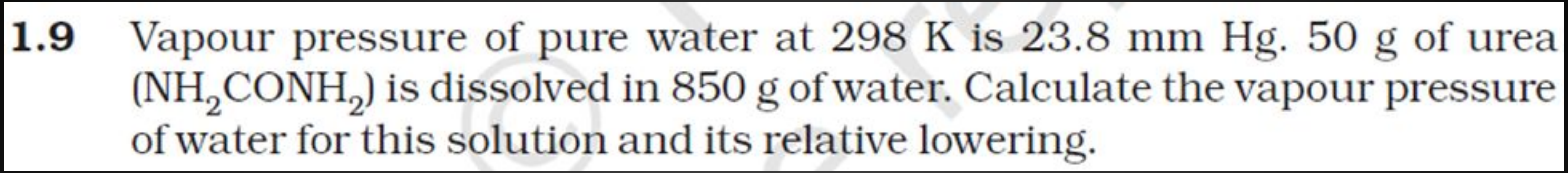
LEARNING CHECK



1.9 Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea (NH_2CONH_2) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.

Ans:

LEARNING CHECK



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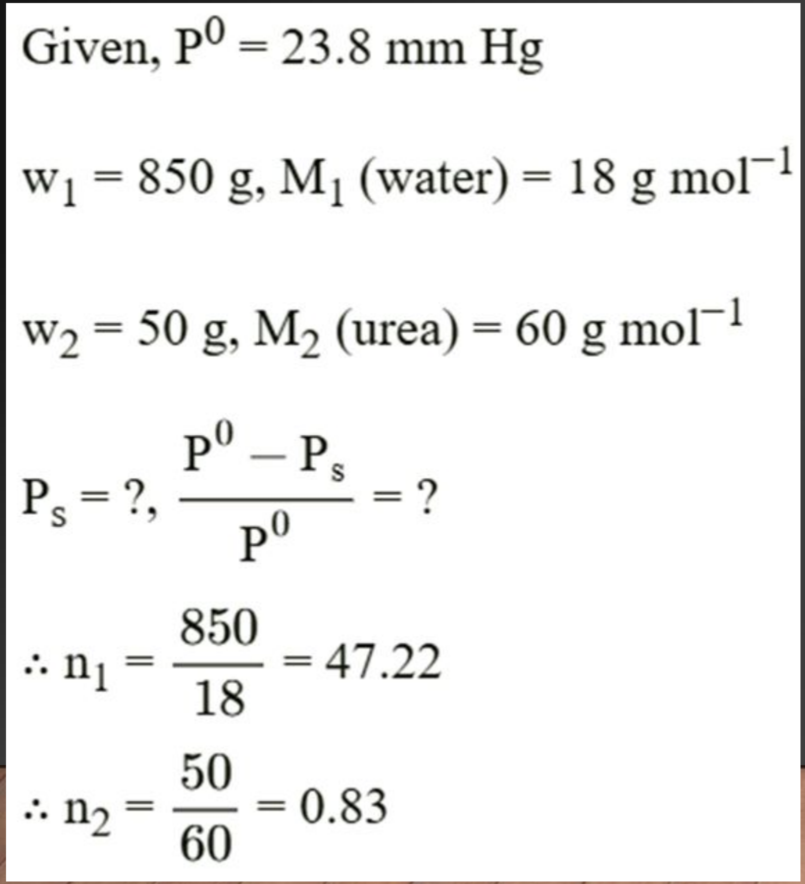


Given, $P^0 = 23.8$ mm Hg

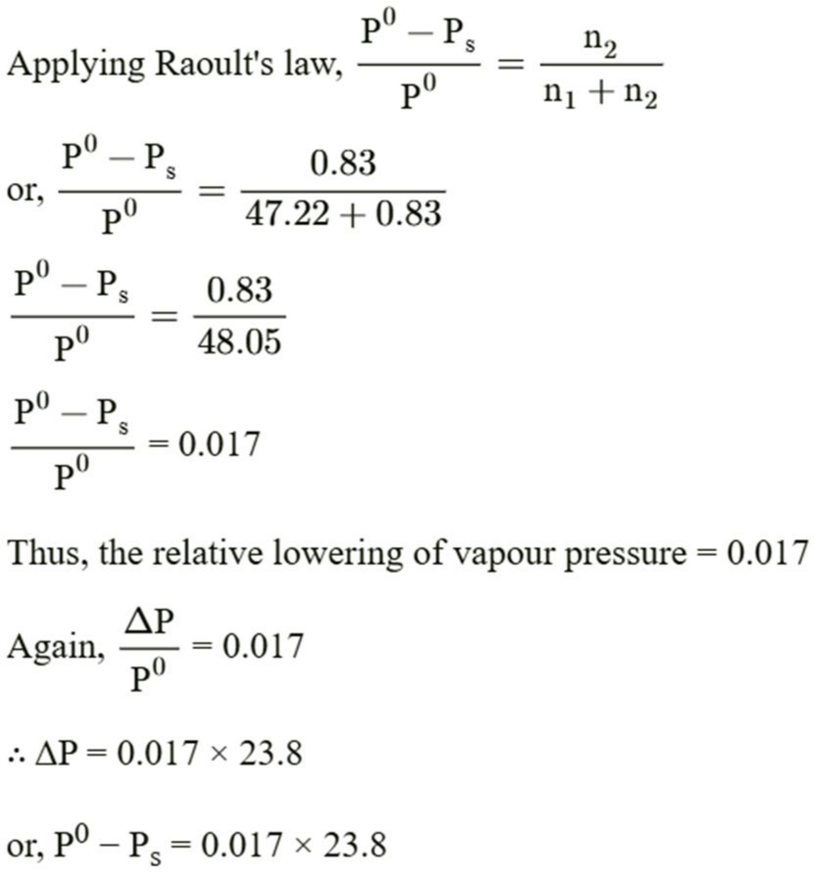
$w_1 = 850$ g, M_1 (water) $= 18$ g mol^{-1}

$w_2 = 50$ g, M_2 (urea) $= 60$ g mol^{-1}

$P_s = ?, \dfrac{P^0 - P_s}{P^0} = ?$

$$\therefore n_1 = \frac{850}{18} = 47.22$$

$$\therefore n_2 = \frac{50}{60} = 0.83$$



Applying Raoult's law, $\dfrac{P^0 - P_s}{P^0} = \dfrac{n_2}{n_1 + n_2}$

or, $\dfrac{P^0 - P_s}{P^0} = \dfrac{0.83}{47.22 + 0.83}$

$$\frac{P^0 - P_s}{P^0} = \frac{0.83}{48.05}$$

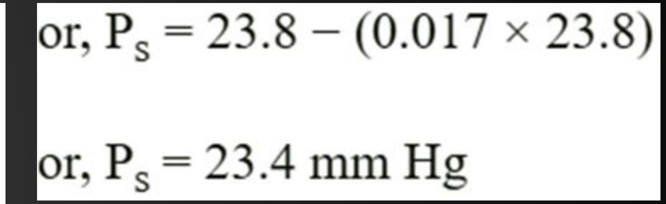
$$\frac{P^0 - P_s}{P^0} = 0.017$$

Thus, the relative lowering of vapour pressure = 0.017

Again, $\dfrac{\Delta P}{P^0} = 0.017$

$\therefore \Delta P = 0.017 \times 23.8$

or, $P^0 - P_s = 0.017 \times 23.8$

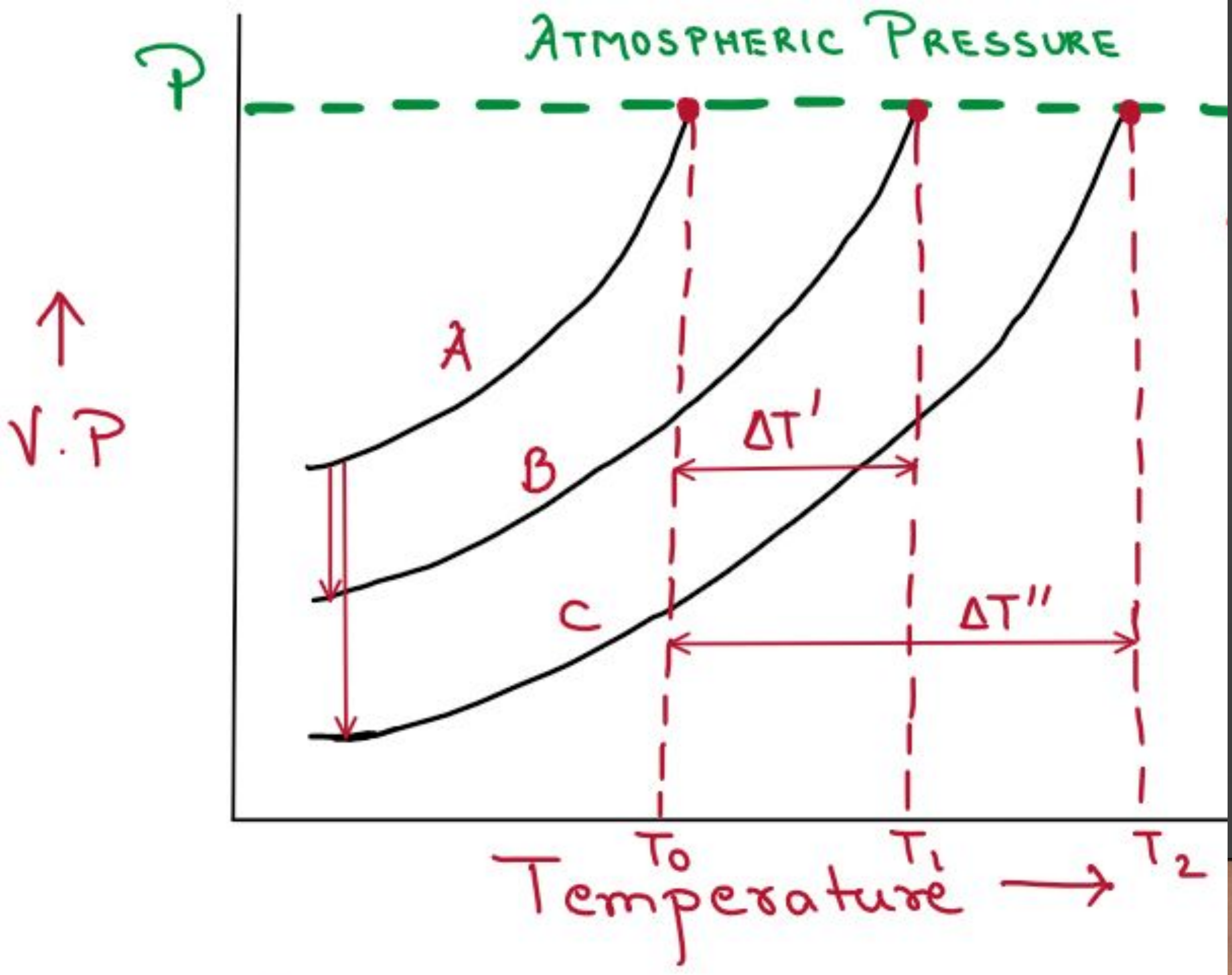


or, $P_s = 23.8 - (0.017 \times 23.8)$

or, $P_s = 23.4$ mm Hg

ELEVATION OF BOILING POINT

Boiling point: Temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.



Plot A: Pure solvent
Plot B & C: Solution

$\Delta T' = T_1 - T_0$ = Elevation in b.p
$\Delta T'' = T_2 - T_0$ = Elevation in b.p

Lowering of v.p $\propto$ amount of solute added
$\therefore$ elevation in b.p $\propto$ amount of solute added

ELEVATION OF BOILING POINT

Determination of molar mass:

$$\Delta T_b \propto x_B$$

$$\Rightarrow \Delta T_b = K \cdot x_B$$

$$\Rightarrow \Delta T_b = K \cdot \frac{n_B}{n_A + n_B}$$

$$\Rightarrow \Delta T_b = K \frac{n_B}{n_A}$$

$$\Rightarrow \Delta T_b = K \cdot \frac{W_B / M_B}{W_A / M_A}$$

$$\Rightarrow \Delta T_b = K \cdot \frac{W_B \cdot M_A}{W_A \cdot M_B}$$

For dilute solution, $n_B << n_A$

$\therefore$, $n_A + n_B \approx n_A$

ELEVATION OF BOILING POINT

Determination of molar mass:

$$\Rightarrow \Delta T_b = k_b \cdot \frac{W_B}{W_A \cdot M_B}$$

$$\Rightarrow \boxed{M_B = \frac{k_b \cdot W_B}{\Delta T_b \cdot W_A(kg)}}$$

For a particular solvent M_A is constant.
∴, $k \times M_A = K_b$

K_b = Molal Elevation Constant / Ebullioscopic constant

$$\Delta T_b = k_b \cdot \frac{W_B}{M_B \cdot W_A}$$

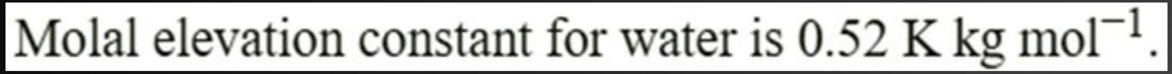
$$\Delta T_b = k_b \cdot \frac{n_B}{W_A(kg)} \quad [\because, W_B/M_B = n_B]$$

$$\boxed{\Delta T_b = k_b \cdot m}$$

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap} H}$$

LEARNING CHECK

1.10 Boiling point of water at 750 mm Hg is 99.63°C. How much sucrose is to be added to 500 g of water such that it boils at 100°C.



Molal elevation constant for water is 0.52 K kg mol^{-1}.

Ans:

LEARNING CHECK

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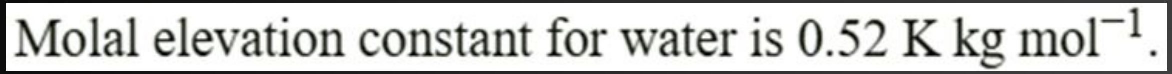
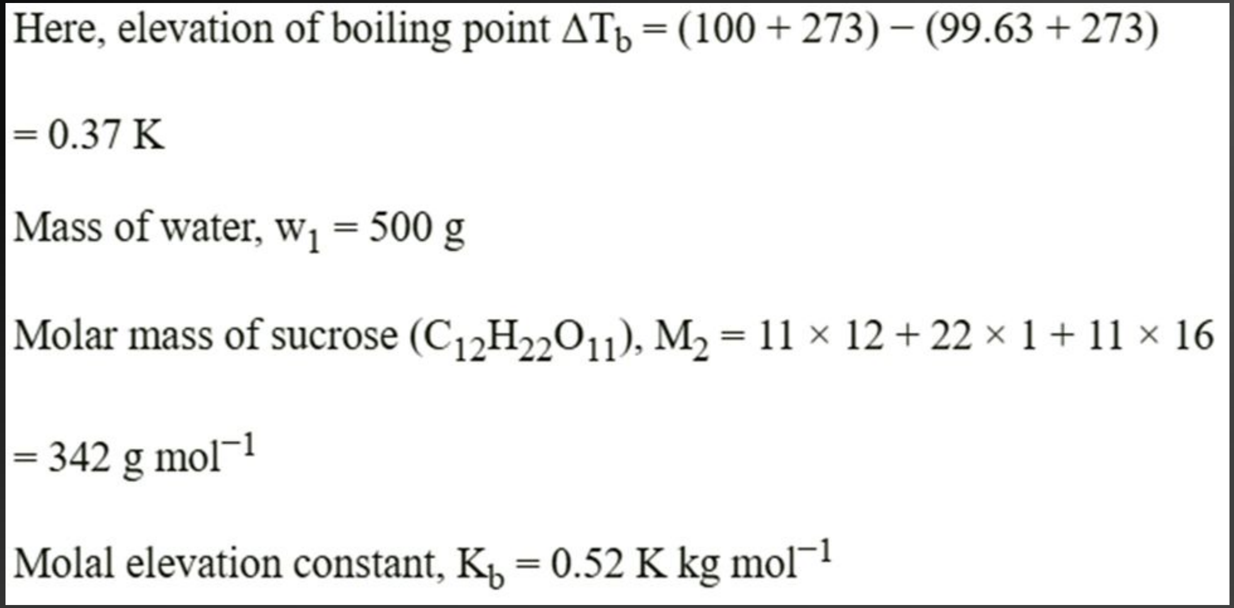


Molal elevation constant for water is 0.52 K kg mol^{-1}.

Ans:



Here, elevation of boiling point $\Delta T_b = (100 + 273) - (99.63 + 273)$

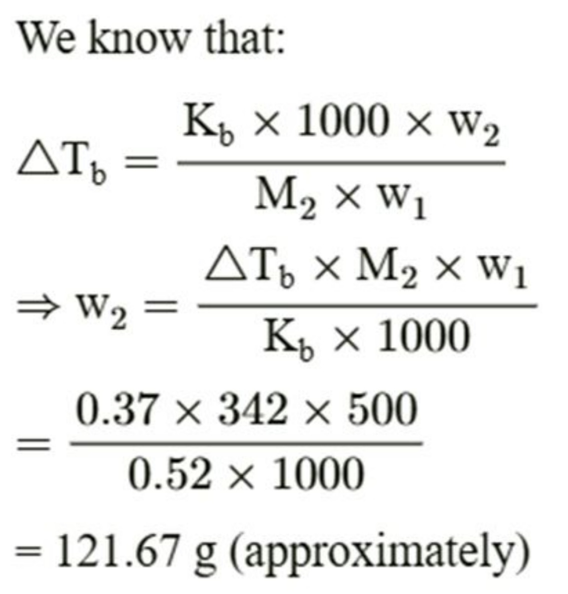
$= 0.37$ K

Mass of water, $w_1 = 500$ g

Molar mass of sucrose ($C_{12}H_{22}O_{11}$), $M_2 = 11 \times 12 + 22 \times 1 + 11 \times 16$

$= 342$ g mol^{-1}

Molal elevation constant, $K_b = 0.52$ K kg mol^{-1}



We know that:

$$\triangle T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

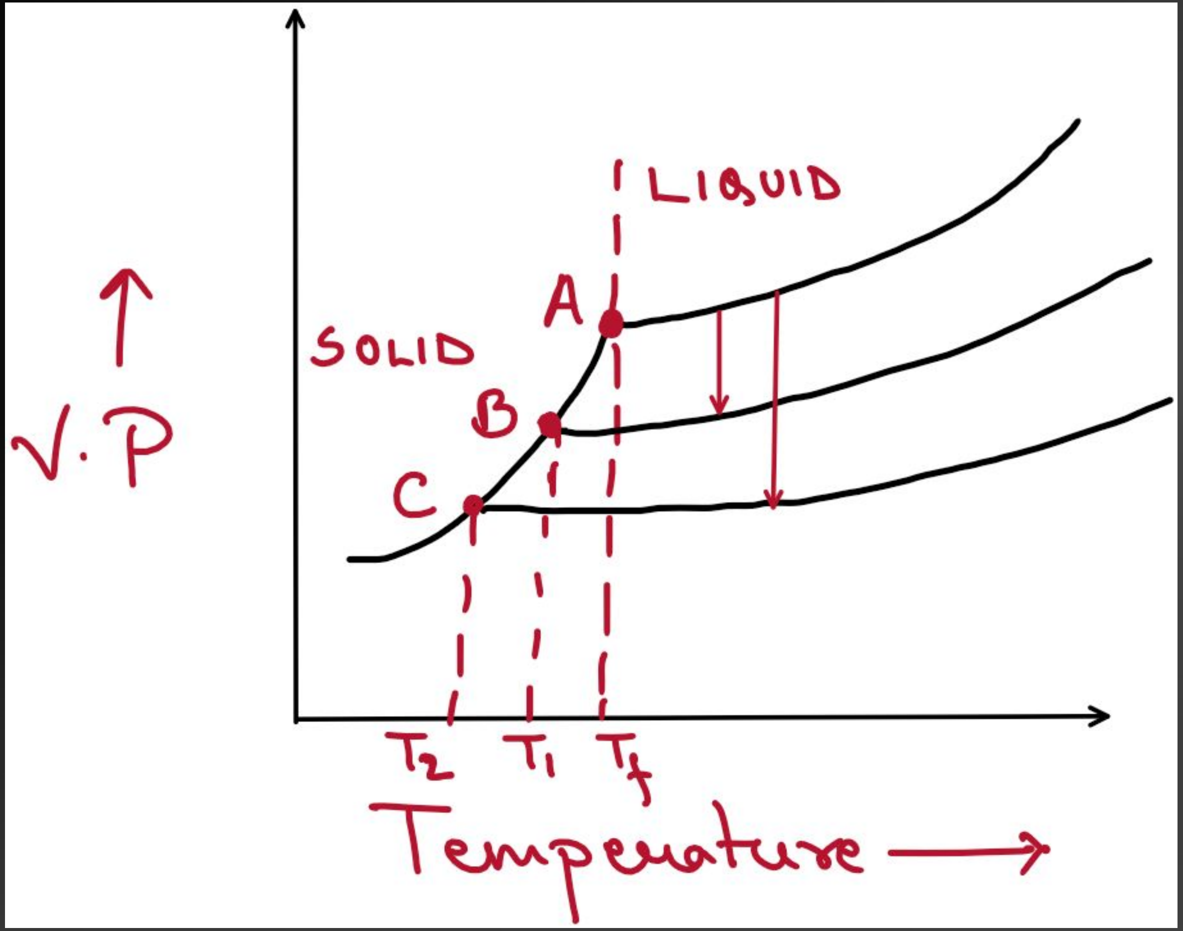
$$\Rightarrow w_2 = \frac{\triangle T_b \times M_2 \times w_1}{K_b \times 1000}$$

$$= \frac{0.37 \times 342 \times 500}{0.52 \times 1000}$$

= 121.67 g (approximately)

DEPRESSION OF FREEZING POINT

Freezing point: Temperature at which a particular solution is in equilibrium with solid solvent



Plot A: Pure solvent
Plot B & C: Solution

T_f = Actual freezing point
T_1 & T_2 = Freezing point after depression

Lowering of v.p $\propto$ amount of solute added
$\therefore$ depression in f.p $\propto$ amount of solute added

DEPRESSION OF FREEZING POINT

Determination of molar mass:

$$\Delta T_f \propto x_B$$

$$\Delta T_f = K \cdot x_B$$

$$\Rightarrow \Delta T_f = K \cdot \frac{n_B}{n_A + n_B}$$

$$\Rightarrow \Delta T_f = K \cdot \frac{n_B}{n_A}$$

$$\Rightarrow \Delta T_f = K \cdot \frac{W_B \times M_A}{M_B \times W_A}$$

For dilute solution, $n_B << n_A$

$\therefore$, $n_A + n_B \approx n_A$

DEPRESSION OF FREEZING POINT

Determination of molar mass:

$$\Delta T_f = K_f \cdot \frac{W_B}{M_B \times W_A}$$

$$\Rightarrow \boxed{M_B = \frac{k_f \times W_B}{\Delta T_f \times W_A(kg)}}$$

For a particular solvent M_A is constant.
$\therefore$, k x $M_A = K_f$

K_f = Molal Depression Constant / Cryoscopic constant

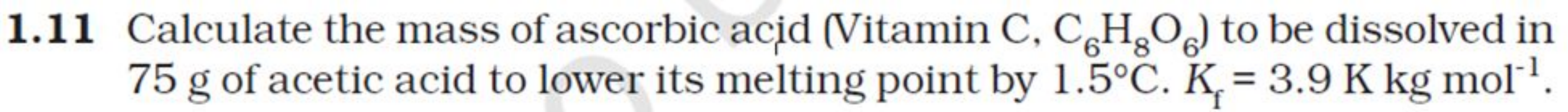
$$\Delta T_f = k_f \cdot \frac{W_B}{M_B \cdot W_A}$$

$$\Delta T_f = k_f \cdot \frac{n_B}{W_A(kg)} \quad [\because, W_B/M_B = n_B]$$

$$\boxed{\Delta T_f = k_f \cdot m}$$

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus}H}$$

LEARNING CHECK



1.11 Calculate the mass of ascorbic acid (Vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5°C. $K_f = 3.9 \text{ K kg mol}^{-1}$.

Ans:

LEARNING CHECK

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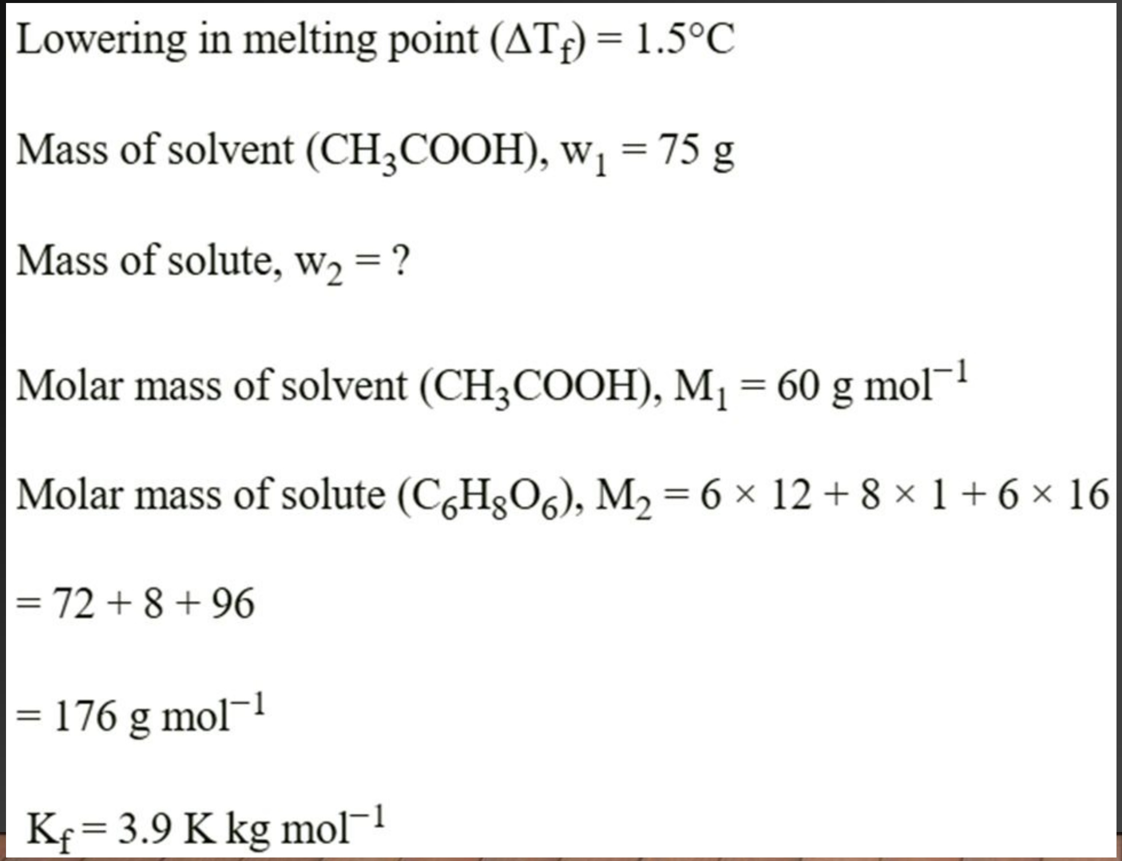
Ans:



Lowering in melting point (ΔT_f) = 1.5°C

Mass of solvent (CH_3COOH), $w_1 = 75$ g

Mass of solute, $w_2 = ?$

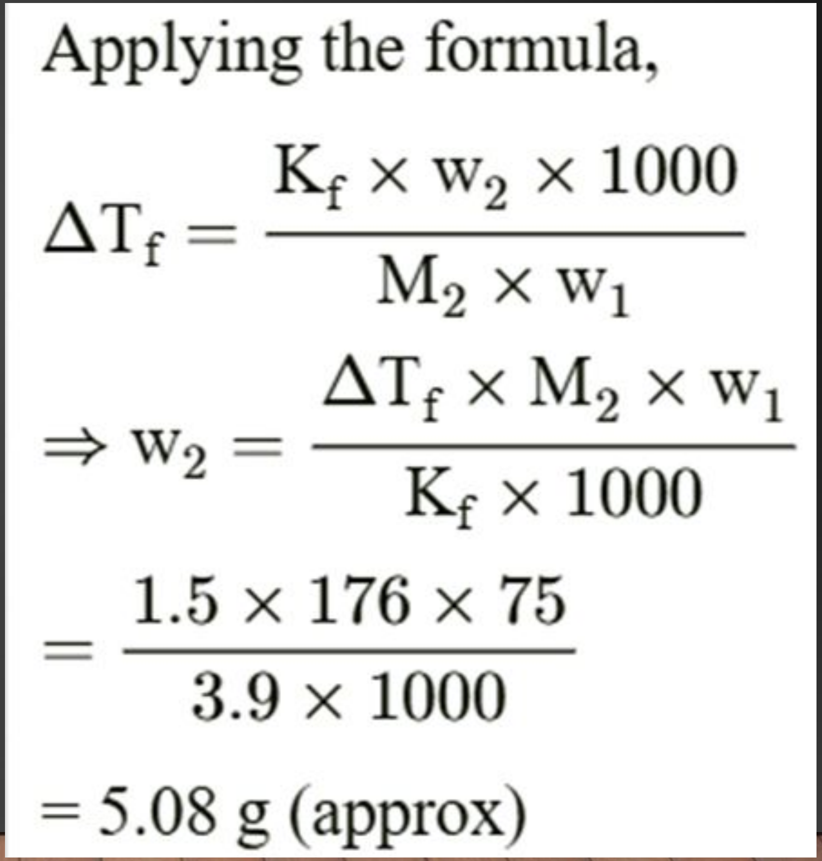
Molar mass of solvent (CH_3COOH), $M_1 = 60 \text{ g mol}^{-1}$

Molar mass of solute ($C_6H_8O_6$), $M_2 = 6 \times 12 + 8 \times 1 + 6 \times 16$

$= 72 + 8 + 96$

$= 176 \text{ g mol}^{-1}$

$K_f = 3.9 \text{ K kg mol}^{-1}$



Applying the formula,

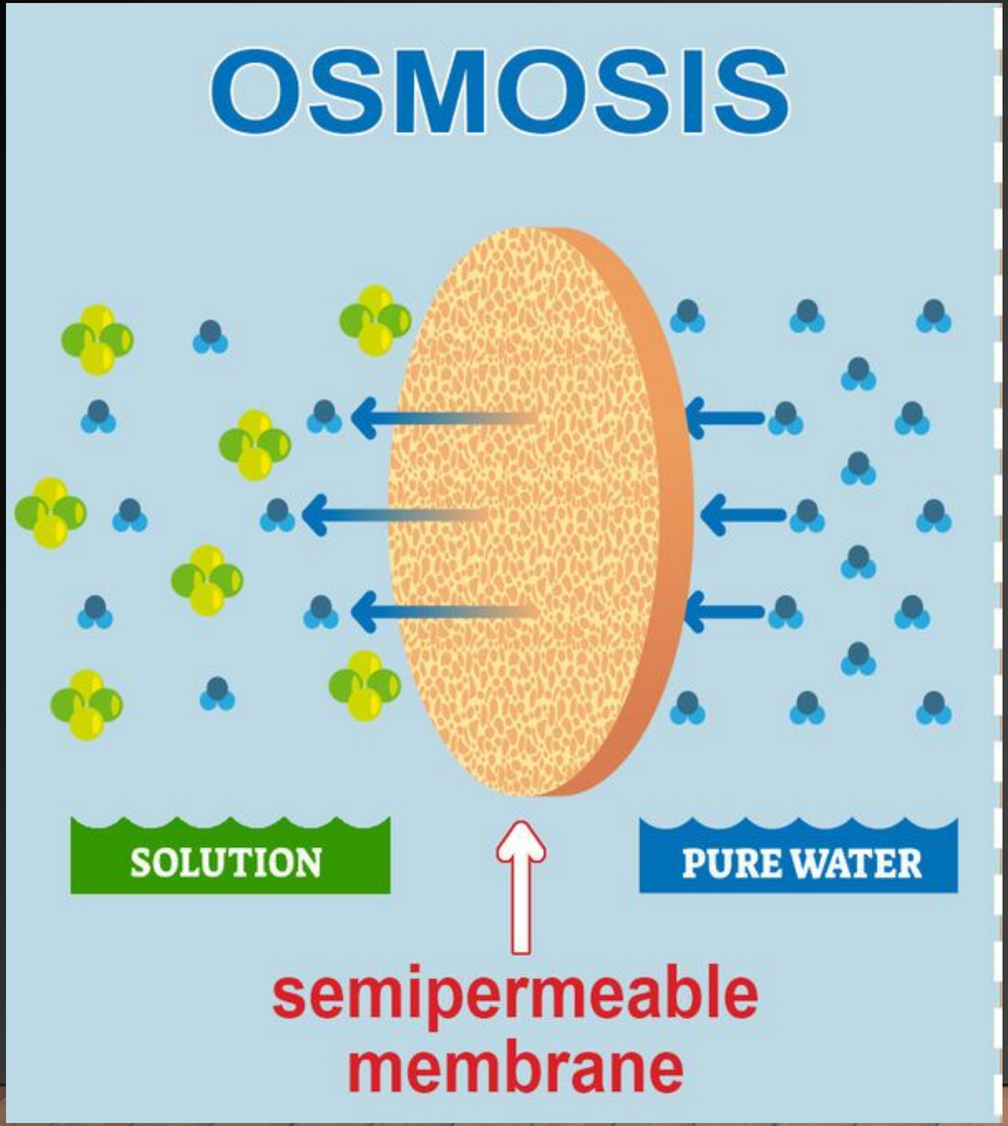
$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1}$$

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

$$= \frac{1.5 \times 176 \times 75}{3.9 \times 1000}$$

$= 5.08$ g (approx)

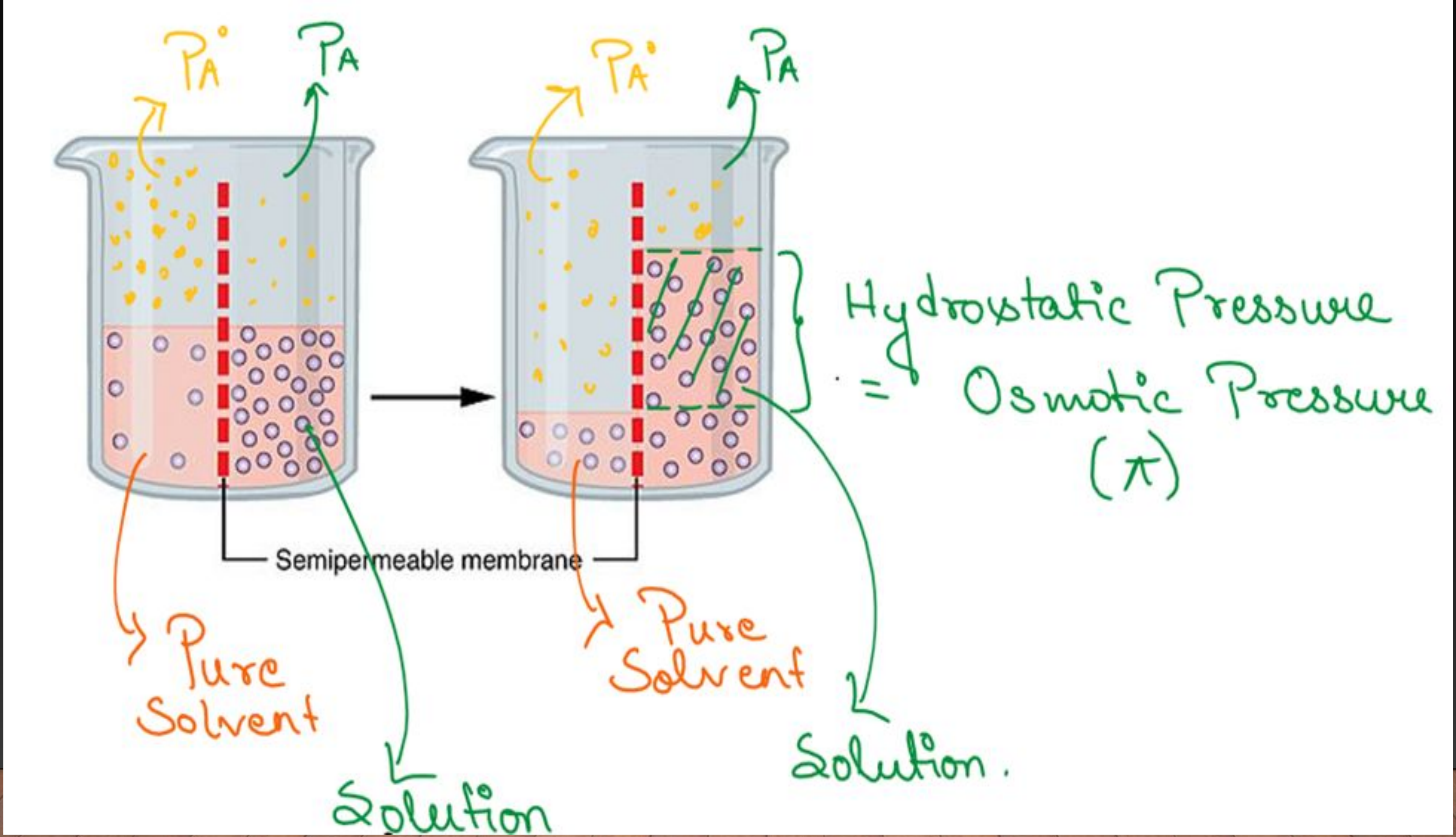
OSMOSIS & OSMOTIC PRESSURE



Semi permeable membrane (SPM):
→ Sheet or film that contains network of submicroscopic pores or holes
→ ***Only solvent*** molecules are allowed to pass through

Osmosis: Spontaneous flow of solvent molecule from solvent side to solution side or from solution of low concentration to solution of high concentration side through a SPM.

OSMOSIS & OSMOTIC PRESSURE



OSMOSIS & OSMOTIC PRESSURE

Osmotic Pressure (π):
→ The ***minimum pressure*** required to ***stop*** the ***inward flow of*** pure ***solvent*** across a SPM into a solution.

Determination of molar mass:
It has been found experimentally that osmotic pressure is proportional to the molarity, C of the solution at a given temperature T.

$$\pi = CRT$$

$$\pi = \frac{n_B RT}{V}$$

$$\pi = \frac{W_B RT}{M_B V}$$

$$\boxed{M_B = \frac{W_B RT}{\pi V}}$$

OSMOSIS & OSMOTIC PRESSURE

Determination of molar mass:

Osmotic pressure method has advantage over the other methods for determining molar mass because:

- it is measured around room temperature
- molarity is used instead of molality
- it has large magnitude even for dilute solutions gives more accurate results

→ It is useful for ***biomolecules (proteins)*** as they are generally ***not stable at higher temperatures*** and ***polymers*** have ***poor solubility***.

OSMOSIS & OSMOTIC PRESSURE

Isotonic Solution:

→ Two solutions having ***same osmotic pressure*** at a given temperature.

→ ***No osmosis*** takes place when these are separated by SPM.

Hypertonic Solution:

→ Solution with ***higher concentration*** (more solute & less solvent)

Hypotonic Solution:

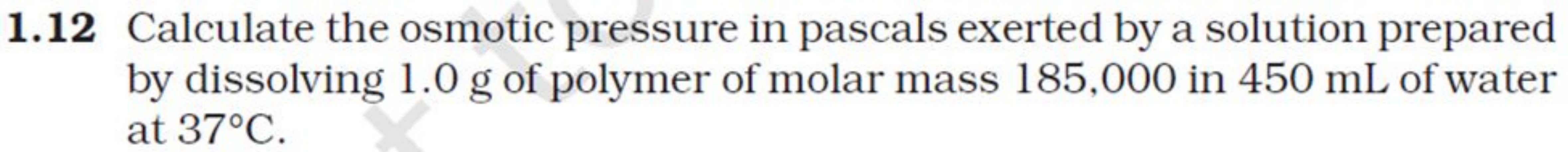
→ Solution with ***lower concentration*** (less solute & more solvent)

Reverse Osmosis:

→ Phenomenon by which ***pure solvent flows out of the solution*** through the SPM by applying a ***pressure higher than the osmotic pressure*** to the solution side.

→ It is used in desalination of seawater.

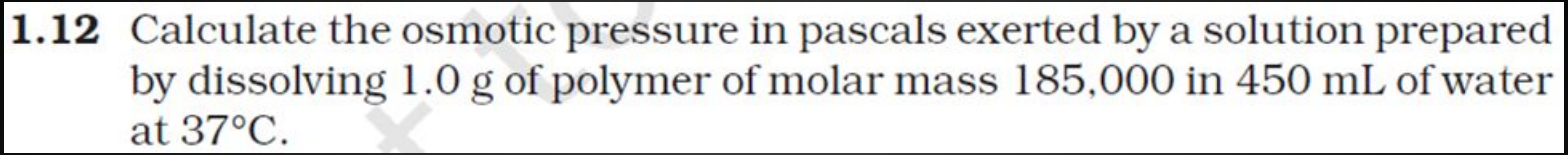
LEARNING CHECK



1.12 Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C.

Ans:

LEARNING CHECK



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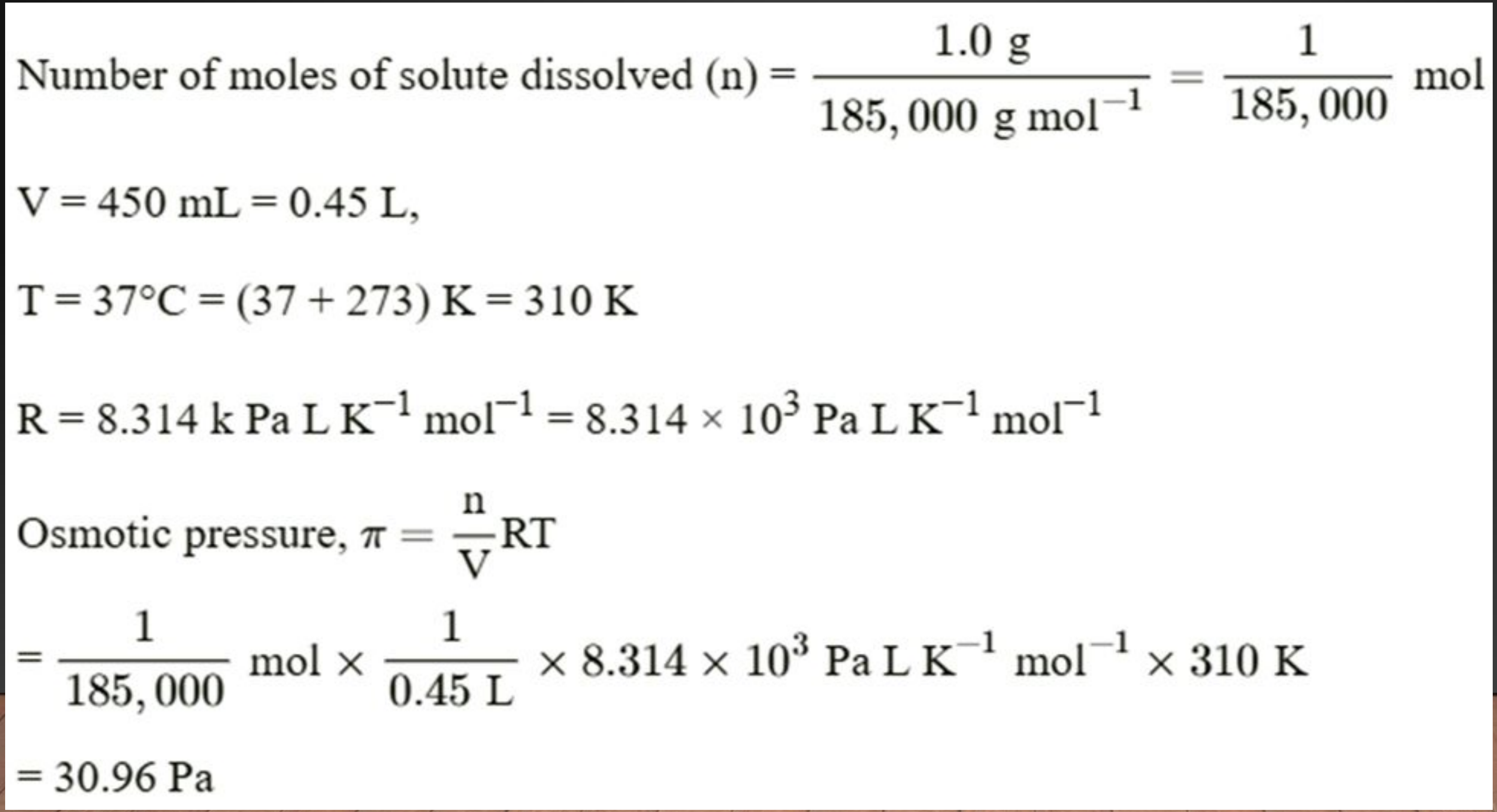


Number of moles of solute dissolved (n) = $\frac{1.0\ \text{g}}{185,000\ \text{g mol}^{-1}} = \frac{1}{185,000}$ mol

V = 450 mL = 0.45 L,

T = 37°C = (37 + 273) K = 310 K

$R = 8.314\ \text{k Pa L K}^{-1}\ \text{mol}^{-1} = 8.314 \times 10^3\ \text{Pa L K}^{-1}\ \text{mol}^{-1}$

Osmotic pressure, $\pi = \frac{n}{V}RT$

$= \frac{1}{185,000}\ \text{mol} \times \frac{1}{0.45\ \text{L}} \times 8.314 \times 10^3\ \text{Pa L K}^{-1}\ \text{mol}^{-1} \times 310\ \text{K}$

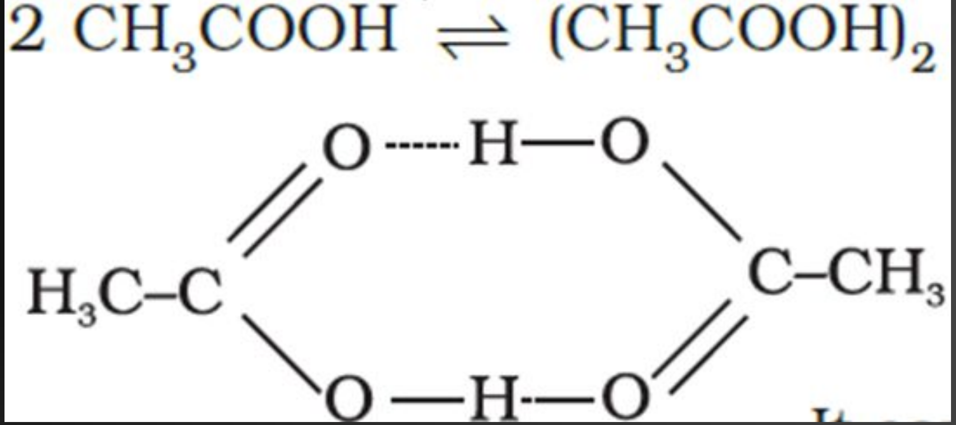
= 30.96 Pa

1.7 ABNORMAL MOLAR MASS

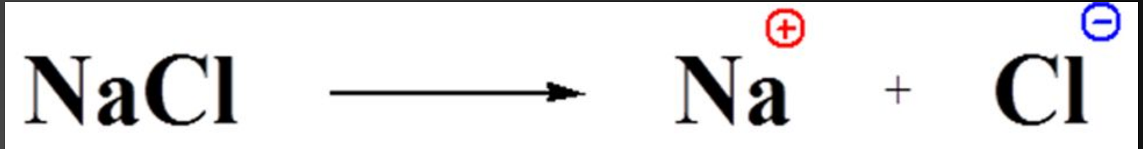
ABNORMAL MOLAR MASS & van't Hoff FACTOR

Abnormal molar mass: Molar mass that is either lower or higher than the expected or normal value.

Colligative properties ∝ no. of solute particles

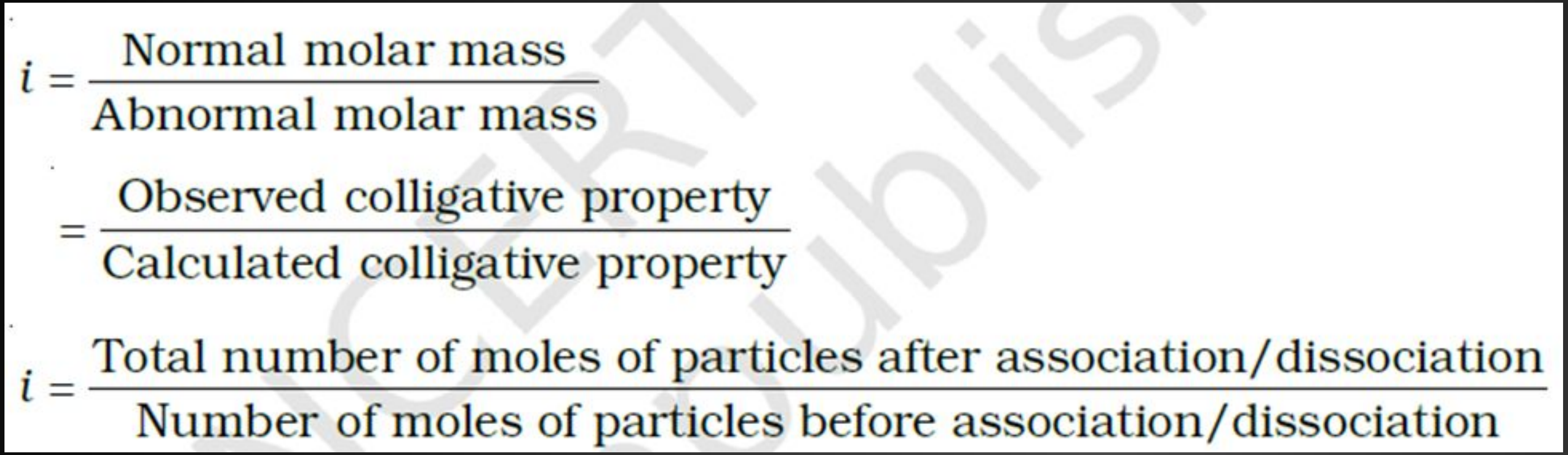


$$2\ CH_3COOH \rightleftharpoons (CH_3COOH)_2$$



$$NaCl \longrightarrow Na^{\oplus} + Cl^{\ominus}$$

ABNORMAL MOLAR MASS & van’t Hoff FACTOR



$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

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

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociation}}$$

Comparison of molecular state of solute:

- If $i = 1$; solute is a non-electrolyte i.e., no association or dissociation
- If $i \neq 1$; solute is an electrolyte i.e., association or dissociation has taken place
- If $i > 1$; solute being an electrolyte has undergone dissociation
- If $i < 1$; solute being an electrolyte has undergone association

ABNORMAL MOLAR MASS & van’t Hoff FACTOR

Inclusion of van’t Hoff factor modifies the equations for colligative properties as follows:

→ Relative lowering of vapour pressure of solvent:

$$\frac{p_1^\circ - p_1}{p_1^\circ} = i.\frac{n_2}{n_1}$$

→ Depression of Freezing point:

$$\Delta T_f = i \; K_f \; \mathrm{m}$$

→ Elevation of Boiling point:

$$\Delta T_b = i \; K_b \; \mathrm{m}$$

→ Osmotic pressure of solution:

$$\Pi = i \; n_2 \; R \; T \; / \; V$$

Relationship between degree of dissociation / association (α) with van’t Hoff factor (i):

For dissociation:

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

For association:

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

VARIATION OF van’t Hoff FACTOR WITH CONCENTRATION

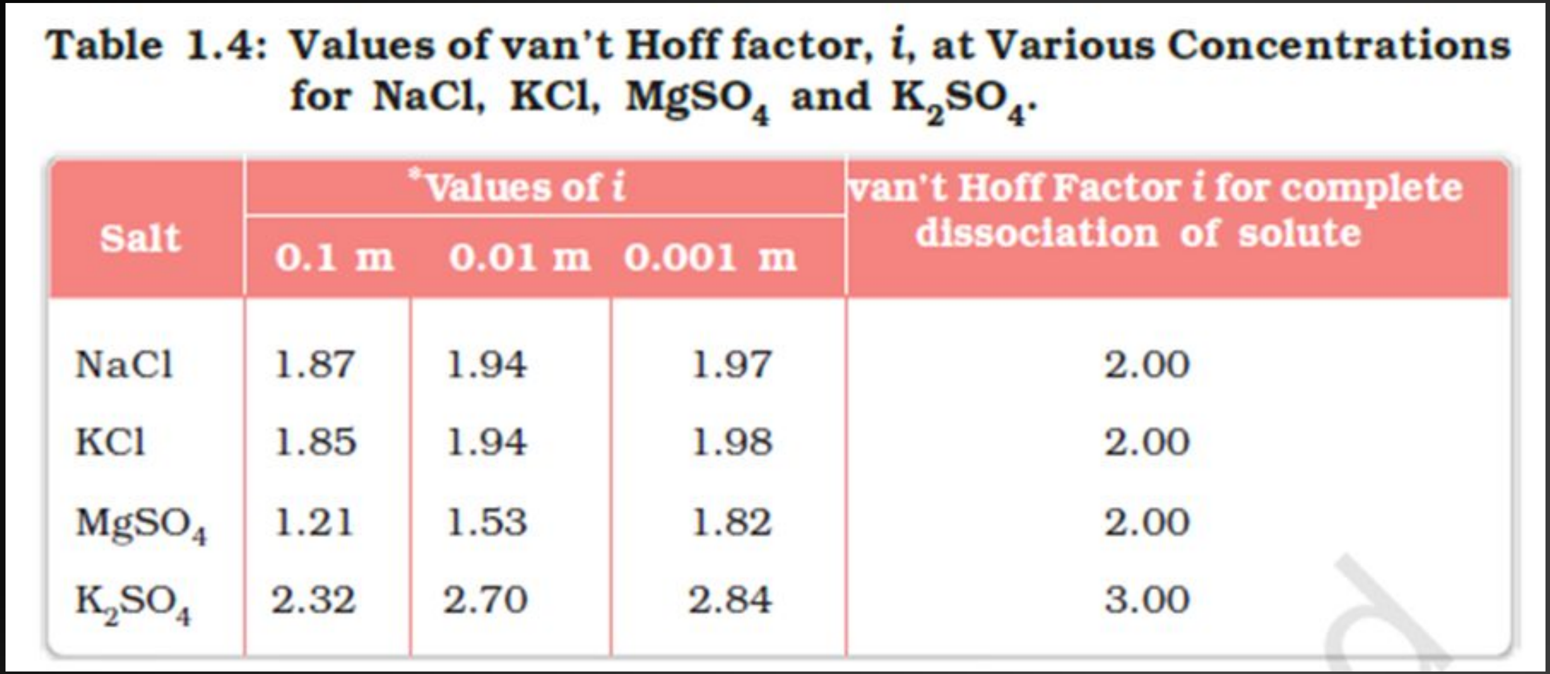


Table 1.4: Values of van't Hoff factor, *i*, at Various Concentrations for NaCl, KCl, $MgSO_4$ and K_2SO_4.

Salt	*Values of *i*			van't Hoff Factor *i* for complete dissociation of solute
	0.1 m	0.01 m	0.001 m	
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
$MgSO_4$	1.21	1.53	1.82	2.00
K_2SO_4	2.32	2.70	2.84	3.00

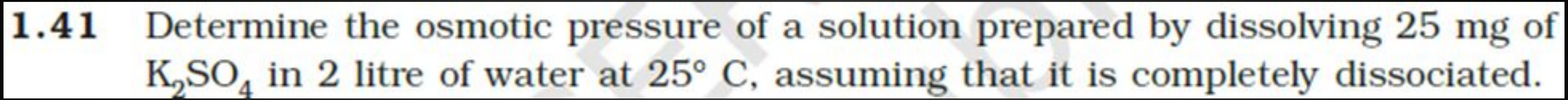
At **very dilute solutions**:

- Electrolytes dissociate almost completely
- *i* is close to the **theoretical value**

At **higher concentrations**:

- Ions attract each other (ion pairing)
- Effective number of particles decreases
- **i becomes smaller than expected**

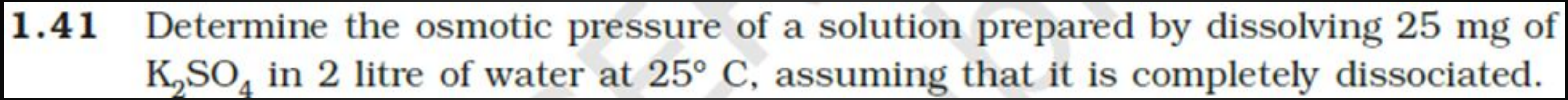
LEARNING CHECK



1.41 Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litre of water at 25° C, assuming that it is completely dissociated.

Ans:

LEARNING CHECK



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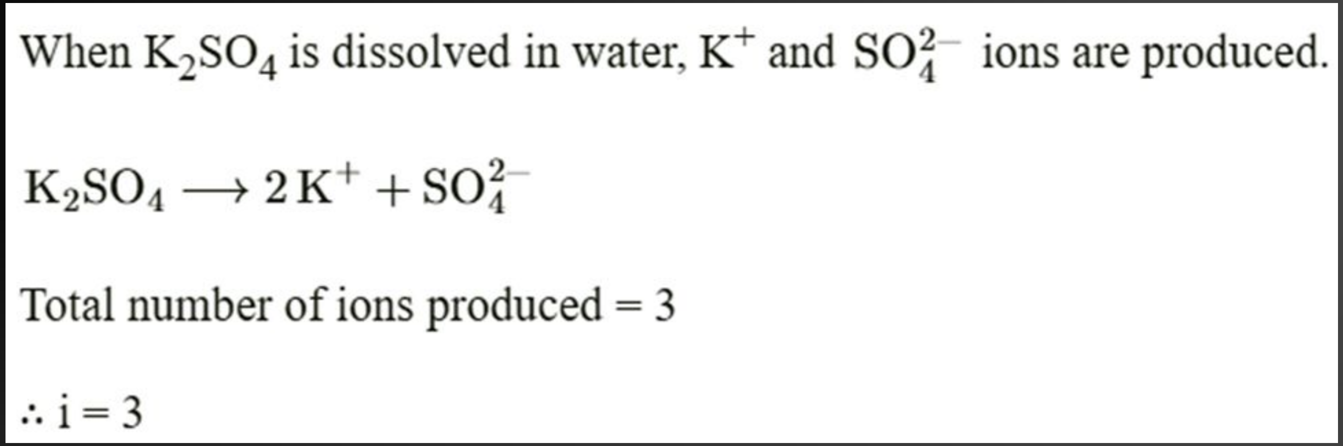
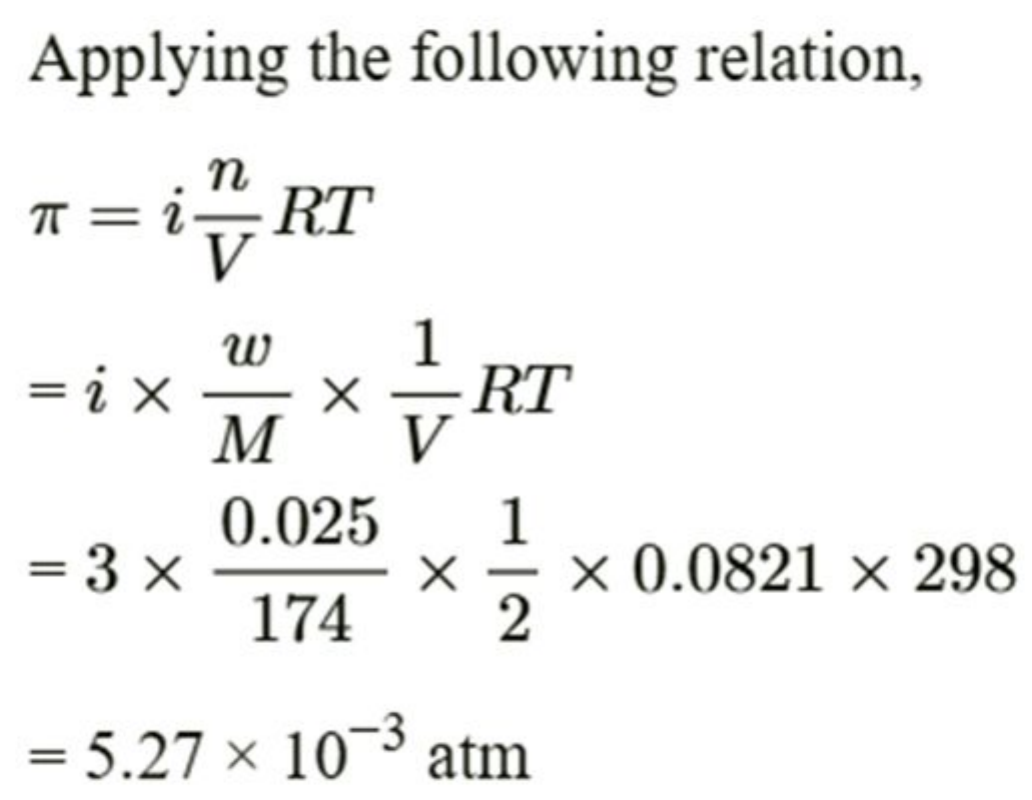


When K_2SO_4 is dissolved in water, K^+ and SO_4^{2-} ions are produced.

$$K_2SO_4 \longrightarrow 2K^+ + SO_4^{2-}$$

Total number of ions produced = 3

$\therefore i = 3$



Applying the following relation,

$$\pi = i\frac{n}{V}RT$$

$$= i \times \frac{w}{M} \times \frac{1}{V}RT$$

$$= 3 \times \frac{0.025}{174} \times \frac{1}{2} \times 0.0821 \times 298$$

$$= 5.27 \times 10^{-3} \text{ atm}$$