

Dev Academy

Yamunanagar (Haryana)

Solutions

Class
12

Revision Notes

CHEMISTRY

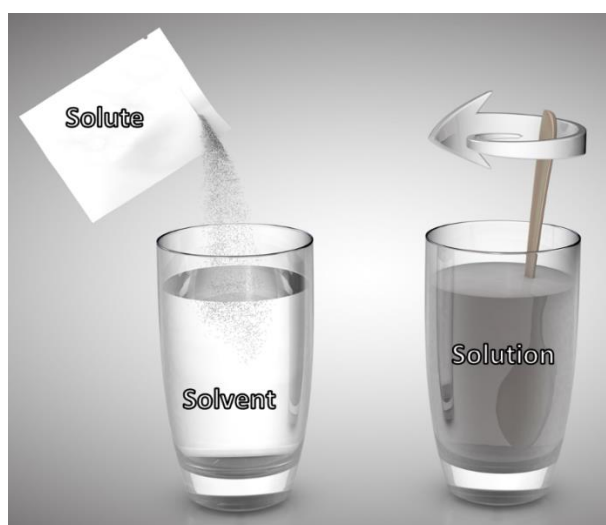
By
Mr. Hardev Singh Antal

Website: devacademy.click

Email id: support@devacademy.click

Introduction

- A solution is a **homogenous mixture** of two or more non-reacting compounds whose composition can be varied within certain limits.
- The components of binary solution are generally referred to as solute and solvent.
- The component which is present in large quantity is called **Solvent** while the component which is present in lesser quantity is called **solute**.



Types of Solution

- Depending on the physical states of solute and solvent, the solution can be of three types: (a.) Solid solutions (b.) Liquid Solutions (c.) Gaseous Solutions

Solid Solutions		
Solute	Solvent	Examples
Solid	Solid	Alloys (Brass, Bronze etc.)
Liquid	Solid	Hydrated salts and Amalgam
Gas	Solid	Dissolved gases in minerals

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Liquid Solutions		
Solute	Solvent	Examples
Solid	Liquid	Salt solution in water
Liquid	Liquid	Alcohol in water
Gas	Liquid	Oxygen in water and Carbonated beverages

Gaseous Solutions		
Solute	Solvent	Examples
Solid	Gas	Camphor in Nitrogen gas
Liquid	Gas	Humidity in air
Gas	Gas	Air

Expressing Concentration of Solution

- The concentration of a solution may be defined as the **amount of solute present in the given quantity of the solution or solvent**. The concentration of solution can be expressed in various common ways as discussed below:

(a) Mass %	(b) Volume %	(c) Mass by volume %
(d) parts per million	(e) Strength	(f) Molarity
(g) Molality	(h) Mole fraction	(i) Normality

- Points to Remember:

Conc. = $\frac{\text{Amount of Solute}}{\text{Amount of Solution}}$	Conc. = $\frac{\text{Amount of Solute}}{\text{Amount of Solvent}}$
<ul style="list-style-type: none"> Mass Percentage (w/w) Volume Percentage (v/v) Mass-Volume Percentage (w/v) Parts per million (w/w , v/v) Strength (gm/L) Molarity (mol/L) Mole fraction (mol/mol) Normality (gm eq.wt / L) 	<ul style="list-style-type: none"> Molality (mol/Kg)

- Symbols Used:

A = Solvent	B = Solute	W = Weight	M = Molar mass	V = Volume
n = Moles	Solⁿ = Solution	D = Density	Eq.wt. = Equivalent Weight	

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- **Mass Percentage (w/w)**

$$\text{Mass \% of B} = \frac{\text{Mass of B} \times 100}{\text{Total mass of solution}} = \frac{W_B \times 100}{W_{\text{sol}}} = \frac{W_B \times 100}{W_A + W_B}$$

- **Volume Percentage (v/v)**

$$\text{Volume \% of B} = \frac{\text{Volume of B} \times 100}{\text{Total volume of solution}} = \frac{V_B \times 100}{V_{\text{sol}}} = \frac{V_B \times 100}{V_A + V_B}$$

- **Mass-Volume Percentage (w/v)**

$$\text{Mass-Volume \% of B} = \frac{\text{Mass of B} \times 100}{\text{Total volume of solution}} = \frac{W_B \times 100}{V_{\text{sol}}}$$

- **Parts per million (ppm)**

(In terms of **w/w**) ppm of B = $\frac{\text{Mass of B} \times 10^6}{\text{Total Mass of solution}} = \frac{W_B \times 10^6}{W_{\text{sol}}}$

(In terms of **v/v**) ppm of B = $\frac{\text{Volume of B} \times 10^6}{\text{Total Volume of solution}} = \frac{V_B \times 10^6}{V_{\text{sol}}}$

- **Strength (gm/L)**

$$\text{Strength (S)} = \frac{\text{Mass of the solute in grams}}{\text{Volume of solution in litres}} = \frac{W_B}{V_{\text{sol in L}}} = \frac{W_B \times 1000}{V_{\text{sol in ml}}}$$

- **Molarity (mol/L)**

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Volume of the solution in Litres}} = \frac{n_B}{V_{\text{sol in L}}} = \frac{n_B \times 1000}{V_{\text{sol in mL}}}$$

$\text{Moles of solute } (n_B) = \frac{\text{Weight of solute}}{\text{Molecular mass of solute}} = \frac{W_B}{M_B}$

$$\text{Molarity (M)} = \frac{W_B \times 1000}{M_B \times V_{\text{sol in mL}}} = \frac{\text{Strength}}{M_B}$$

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- **Molality (mol/Kg)**

$$\text{Molality (m)} = \frac{\text{Number of moles of solute}}{\text{Weight of the solvent in Kg}} = \frac{n_B}{W_{A \text{ in Kg}}} = \frac{n_B \times 1000}{W_{A \text{ in g}}}$$

$$\text{Molality (m)} = \frac{W_B \times 1000}{M_B \times W_{A \text{ in g}}}$$

- **Mole Fraction (χ : Chi) (mol/mol)**

$$\text{Mole fraction of B } (\chi_B) = \frac{\text{Moles of B}}{\text{Moles of solution}} = \frac{n_B}{n_{\text{sol}}} = \frac{n_B}{n_A + n_B}$$

$$\text{Mole fraction of A } (\chi_A) = \frac{\text{Moles of A}}{\text{Moles of solution}} = \frac{n_A}{n_{\text{sol}}} = \frac{n_A}{n_A + n_B}$$

⇒ The sum of mole fraction of all components in solution is always equal to 1.

$$\chi_A + \chi_B = 1$$

⇒ So that: $\chi_A = 1 - \chi_B$ or $\chi_B = 1 - \chi_A$

- **Normality (gm equivalent/L)**

$$\text{Normality (N)} = \frac{\text{Gram equivalent weight of solute}}{\text{Volume of solution in Litre}} = \frac{\text{gm eq.wt}_B}{V_{\text{sol in L}}} = \frac{\text{gm eq.wt}_B \times 1000}{V_{\text{sol in mL}}}$$

$$\text{Gram equivalent weight of solute} = \frac{\text{Weight of solute in gm}}{\text{Equivalent mass of solute}} = \frac{W_B}{\text{Eq.wt.}_B}$$

$$\text{Normality (N)} = \frac{W_B \times 1000}{\text{Eq.wt.}_B \times V_{\text{sol in mL}}}$$

$$\text{Eq.wt. of B} = \frac{M_B}{n_{\text{factor}}}$$

$$\text{Normality (N)} = \frac{W_B \times 1000 \times n_{\text{factor}}}{M_B \times V_{\text{sol in mL}}} = \text{Molarity} \times n_{\text{factor}}$$

How to determine n_factor of solute ?

n_factor of **acid** = Basicity of the acid (or number of H⁺)

n_factor of **base** = Acidity of the base (or number of OH⁻)

n_factor of **salt** = Total cationic charge or Total anionic charge per molecule

n_factor of **oxidising or reducing agent** = No. of e_s⁻ gain/loss by a molecule

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• Points to Remember

- Molarity, Strength, and Normality change with temperature because of expansion or contraction of the liquid.
- Molality does not change with temperature because mass of the solvent does not change with change in temperature.
- Normality equation (Dilution Formula): $N_1V_1 = N_2V_2$
- Normality of a Mixture: $N_{\text{mixture}} = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$ or $\frac{N_1V_1 + N_2V_2 + \dots + N_nV_n}{V_1 + V_2 + \dots + V_n}$
- Molarity equation (Dilution Formula): $M_1V_1 = M_2V_2$
- Molarity equation (for Reacting components): $\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2}$
- Molarity of a Mixture: $M_{\text{mixture}} = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$ or $\frac{M_1V_1 + M_2V_2 + \dots + M_nV_n}{V_1 + V_2 + \dots + V_n}$
- Relationship between Molarity and Molality:
 - Molality = $\frac{\text{Molarity} \times 1000}{(\text{density} \times 1000) - (\text{Molarity} \times M_B)}$
 - Molarity = $\frac{\text{Molality} \times 1000 \times \text{density}}{1000 + (\text{Molality} \times M_B)}$

Numerical - 1

2.46 gm of NaOH is dissolved in water and the solution is made to 250 mL in the volumetric flask. Calculate the molarity of the solution.

Explanation:

- Given Values: Solute = NaOH , $M_B = 40$, $W_B = 2.46$ gm , $V_{\text{sol}} = 250$ mL
- Formula Used: Molarity (M) = $\frac{W_B \times 1000}{M_B \times V_{\text{sol in mL}}}$
- Calculations: Molarity (M) = $\frac{2.46 \times 1000}{40 \times 250} = \frac{2.46}{10} = \mathbf{0.246 \text{ mol/L}}$

Numerical - 2

Calculate the molality of a solution containing 20.7 gm of K_2CO_3 dissolved in 500 mL of the solution (assuming density of solution = 1.05 g/ml).

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Explanation:

- Given Values: Solute = K_2CO_3 , $M_B = 138$, $W_B = 20.7$ gm, $V_{sol} = 500$ mL
 $D_{sol} = 1.05$ gm/mL.

- Formula Used: Molality (m) = $\frac{W_B \times 1000}{M_B \times W_{A \text{ in } g}}$

- Let's find other values:

$$W_{sol} = D_{sol} \times V_{sol} = 1.05 \times 500 = 525 \text{ gm}$$

$$W_A = W_{sol} - W_B = 525 - 20.7 = 504.3 \text{ gm}$$

- Calculations: Molality (m) = $\frac{20.7 \times 1000}{138 \times 504.3} = \frac{20700}{69593.4} = 0.297 \text{ mol/Kg}$

Numerical - 3

Battery acid is 4.27 M H_2SO_4 and has density of 1.25 g/ml. What is the molality of H_2SO_4 in the solution?

Explanation:

- Given Values: Solute = H_2SO_4 , $M_B = 98$, $D_{sol} = 1.25$ gm/mL,
Molarity = 4.27 mol/L

- Formula Used: Molality = $\frac{\text{Molarity} \times 1000}{(\text{density} \times 1000) - (\text{Molarity} \times M_B)}$

- Calculations: Molality = $\frac{4.27 \times 1000}{(1.25 \times 1000) - (4.27 \times 98)} = 5.135 \text{ mol/Kg}$

Exercises

- If 16 gm of oxalic acid is dissolved in 750 ml of solution, what is the mass% of oxalic acid in solution? (Density of solution is 1.1 g cm^{-3}).
- A litre of public supply water contain 3×10^{-3} gm of chlorine. Calculate the mass % and ppm of chlorine.
- A litre of sea water (about 1030 gm) contains 6×10^{-3} gm of dissolved oxygen. Calculate the mass % and ppm of dissolved oxygen.
- Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile (CH_3CN) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN .

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5. Calculate the percentage composition in terms of mass of a solution obtained by mixing 300 gm of 25% and 400 gm of 40% solution by mass.
6. Calculate the molarity of a solution of CaCl_2 if on chemical analysis it is found that 500 mL of CaCl_2 solution contain 1.505×10^{23} Cl^- ions.
7. 100 ml of a solution containing 5 g of NaOH are mixed with 200 ml of M/5 NaOH solution. Calculate the molarity of the resulting solution.
8. The density of a 2.05 M acetic acid in water is 1.02 g/ml. Calculate the molality of the solution.
9. Calculate the mole fraction of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) in a solution containing 20% of $\text{C}_2\text{H}_6\text{O}_2$ by mass.
10. 2.82 gm of glucose is dissolved in 30 gm of water. Calculate (a) molality (b) mole fraction of glucose and water.
11. A solution is 25% water, 25% ethanol, and 50% acetic acid by mass. Calculate the mole fraction of each component.
12. A solution of glucose in water is labelled as 10 % (w/w). The density of the solution is 1.20 g/ml. Calculate the (a) molality (b) molarity and (c) mole fraction of each component in solution.
13. A sugar syrup of weight 214.2 gm contains 34.2 gm of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$). Calculate: (a) Molal concentration (b) mole fraction of sugar in solution.
14. A commercially available sample of sulphuric acid is 15% H_2SO_4 by weight (density = 1.10 g/mL). Calculate (a) molarity (b) normality (c) molality.
15. Concentrated sulphuric acid has a density 1.9 gm/mL and is 99% H_2SO_4 by mass. Calculate the molarity of sulphuric acid.

Factors Affecting the Solubility of a Solid in a Liquid

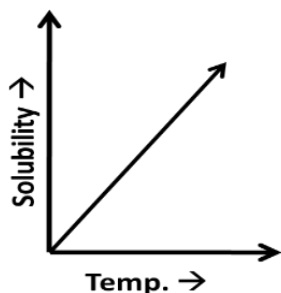
- **Nature of the solute and the solvent**

A solid dissolve in a liquid (solvent) if the intermolecular interactions are similar. This is expressed by saying "**Like dissolves like.**" This means that, non-polar substances are more likely to be soluble in non-polar solvents (i.e., benzene, CCl_4 , CS_2 etc.) while ionic (or polar) substances are more likely to be soluble in polar solvents (i.e., H_2O).

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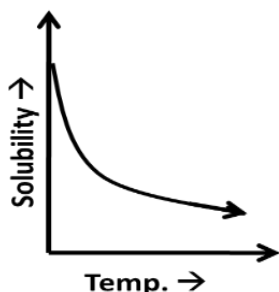
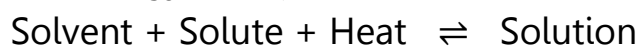
• Effect of Temperature

The solubility may increase or decrease or show irregular behaviour with increase in temperature. We observe following three behaviours:



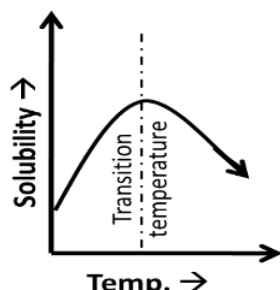
a. The solubility of solids increases with increase in temperature:

The solubility of most of substances such as NaNO_3 , NH_4Cl , KCl , AgNO_3 , NaCl , KI , and sugar etc. increases with rise in temperature. This is because the dissolution process for these substances is endothermic ($\Delta_{\text{sol}}H > 0$).



b. The solubility of solids decreases with increase in temperature:

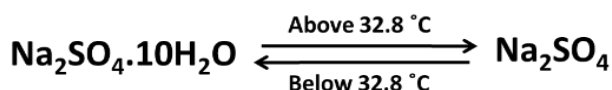
The solubility of some substances like Li_2SO_4 , $\text{Ce}_2(\text{SO}_4)_3$, Na_2CO_3 and CaO etc. decrease with rise in temperature. This is because dissolution process is exothermic ($\Delta_{\text{sol}}H < 0$).



c. The solubility shows irregular behavior with increase in temperature:

The solubility of some substances (like Na_2SO_4) increases up to a certain temperature and then decreases as the temperature is further raised. The temperature at which solubility starts decrease is called **transition temperature**.

For example, the solubility curve of Na_2SO_4 shows a sharp break at 32.8°C . This is due to change in one solid form into another solid form. Below transition temperature, only hydrated $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ exists while above this temperature, anhydrous Na_2SO_4 exists.



• Effect of Pressure

The effect of pressure on the solubility of solids in liquid is very small or insignificant. This is because solids and liquids are incompressible and practically remain unaffected by changes in pressure.

Factors Affecting the Solubility of a Gas in a Liquid

• Nature of the gas and the solvent

Gases that can react chemically or can form ions in aqueous solution are more soluble in water than in any other solvent. Example:

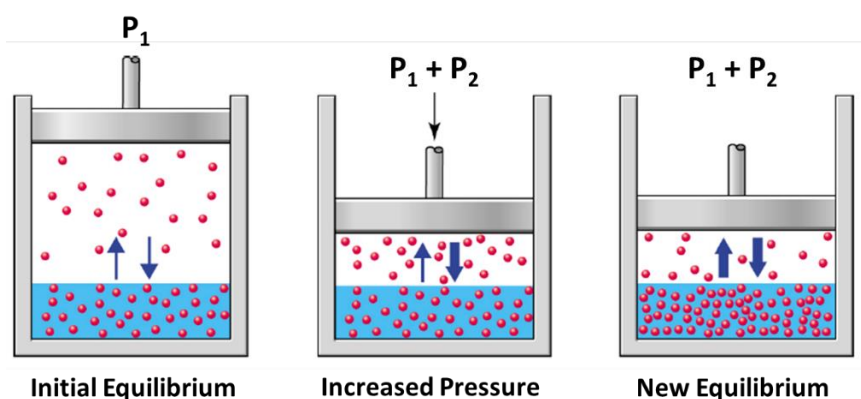
- Gases like H_2 , O_2 , N_2 etc. dissolve in H_2O in very small amounts whereas the gases like SO_2 , H_2S , HCl , NH_3 etc. are highly soluble.
- O_2 , N_2 and CO_2 are more soluble in ethyl alcohol than in H_2O while gases such as NH_3 and H_2S are more soluble in H_2O than in ethyl alcohol.

• Effect of Temperature

Gases dissolve in a liquid by **exothermic** process. Therefore, according to Le-Chatelier's principle, an increase in temperature will result in a decrease in the solubility of a gas.

• Effect of Pressure

- The solubility of gases increases with increase of pressure.
- To understand this, consider a gas in dynamic equilibrium with a solution.
- Now increase the pressure over the solution. This will increase the number of gaseous particles per unit volume over the solution.
- Hence, more molecules will dissolve and solubility of gas increase until a new equilibrium is reached.



- **William Henry** gave quantitative relationship between the solubility of a gas in a solvent and the pressure of a gas on a solution, known as Henry's law.

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❖ According to Henry's Law:

The solubility of a gas in a liquid at a particular temperature is directly proportional to the pressure of the gas on that solution at equilibrium.

- If we express the solubility of a gas in terms of mole fractions, then **Henry's law** can be written as:

$$\chi \propto p$$

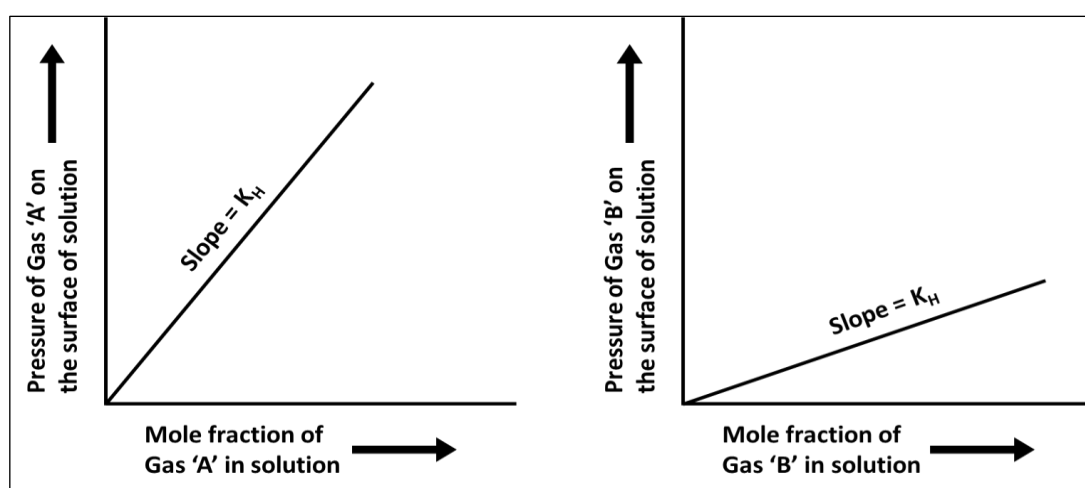
$$\chi = K' \cdot p$$

$$K_H = \frac{1}{K'}$$

So that: $p = K_H \cdot \chi$

Where K_H is called Henry's law constant.

- Thus, most used form of **Henry's law** may be defined as:
The pressure of a gas over a solution in which the gas is dissolved is directly proportional to the mole fraction of the gas dissolved in the solution at equilibrium.



❖ Mathematical Modifications to Henry's Law

- According to Henry's Law: $P_{\text{gas}} = K_H \cdot \chi_{\text{gas}}$
- As we know: $\chi_{\text{gas}} = \frac{n_{\text{gas}}}{n_{\text{solution}}} = \frac{n_{\text{gas}}}{n_{\text{solvent}} + n_{\text{gas}}}$

[Assuming that, $n_{\text{solvent}} \gg n_{\text{gas}}$, so that, $n_{\text{solvent}} + n_{\text{gas}} \approx n_{\text{solvent}}$]

- $P_{\text{gas}} = K_H \times \frac{n_{\text{gas}}}{n_{\text{solvent (A)}}} = K_H \times \frac{n_{\text{gas}} \times M_A}{W_A} = K_H \times \frac{W_{\text{gas}} \times M_A}{M_{\text{gas}} \times W_A}$

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Unit : Solutions

❖ Properties of Henry's constant (K_H)

- K_H is a function of nature of gas. Different gases have different K_H values at same temperature.
- Greater the value of K_H , lower the solubility of the gas.
- The value of K_H increases with increase in temperature.

❖ Applications of Henry's law:

➤ In the production of carbonated beverages:



To increase the solubility of CO_2 in soft drinks, soda water, beer or champagne, the bottles are sealed under high pressure. When the bottle is opened under normal atmospheric conditions, the pressure inside the bottle falls and the excess CO_2 bubbles out of the solution.

➤ In deep sea diving (Scuba diving):



Scuba divers depends upon **compressed air** for breathing under water. According to Henry's law, increased pressure increases the solubility of atmospheric gases in blood. Oxygen is used up for metabolism, but nitrogen will remain dissolved in blood. When the divers come towards the surface, the pressure gradually decreases. N_2 comes out of the body quickly forming bubbles in the blood stream. These bubbles restrict blood flow and can even burst or blocks capillaries, which cause painful and dangerous condition called the **bends** or **decompression sickness**. To avoid bends as well as the toxic effects of high concentration of nitrogen in blood, most divers these days use air diluted with helium gas (about 11.7 % He, 56.2 % N_2 and 32.1 % O_2).

➤ At high altitudes:



At high altitudes the partial pressure of O_2 is less than that of the ground level. This results in low concentration of O_2 in the blood and tissue of the climbers. They feel weak and are unable to think properly, a disease called **anoxia**.

Numerical - 1

If N_2 gas is bubbled through water at 293 K, how many milli moles of N_2 gas would dissolve in 1 litre of water. Assume that N_2 exerts a partial pressure of 0.987 bar. The K_H for N_2 at 293 K is 76.48 k bar.

Explanation:

- Given values: $P_{N_2} = 0.987$ bar , $K_H = 76.48$ k bar = 76480 bar , $M_{H_2O} = 18$

$$V_{\text{solvent}(H_2O)} = 1 \text{ Litre or } 1000 \text{ ml} \quad (D_{H_2O} = 1 \text{ gm/ml})$$

- Formula used: $n_{\text{gas}} = \frac{P_{\text{gas}} \times W_A}{K_H \times M_A}$

- Let's find other values:

$$W_A \text{ or } W_{H_2O} = D_{H_2O} \times V_{H_2O} = 1 \text{ gm/ml} \times 1000 \text{ ml} = 1000 \text{ gm} ,$$

- Calculations:

$$n_{\text{gas}} = \frac{0.987 \text{ bar} \times 1000 \text{ gm}}{76480 \text{ bar} \times 18 \text{ gm/mol}} = 7.16 \times 10^{-4} \text{ mol}$$

Now Milli moles of $N_2 = 7.16 \times 10^{-4} \times 10^3 = 7.16 \times 10^{-1} \text{ m mol}$ or **0.716 m mol**

Numerical - 2

At what partial pressure, oxygen will have solubility of 0.05 g L^{-1} in water at 293 K? Henry's constant (K_H) for O_2 in water at 293 K is 34.36 k bar. Assume the density of the solution to be same as that of the solvent.

Explanation:

- Given values: $K_H = 34.36$ k bar = 34.36×10^3 bar , $M_{H_2O} = 18$, $M_{O_2} = 32$

Solubility of gas = 0.05 g/L [i.e. 0.05 gm of O_2 in 1 L of solution]

$$W_{O_2} = 0.05 \text{ gm} \quad V_{\text{sol}} = 1 \text{ L or } 1000 \text{ ml} \quad D_{\text{sol}} = D_{H_2O} = 1 \text{ gm/ml}$$

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- Formula used: $P_{\text{gas}} = K_H \times \frac{W_{\text{gas}} \times M_A}{M_{\text{gas}} \times W_A}$
- Let's find other values:
 $W_{\text{sol}} = D_{\text{sol}} \times V_{\text{sol}} = 1000 \text{ gm}$, $W_{\text{H}_2\text{O}} = W_{\text{sol}} - W_{\text{O}_2} = 1000 - 0.05 \approx 1000$
- Calculations: $P_{\text{gas}} = \frac{34.36 \times 10^3 \times 0.05 \times 18}{32 \times 1000} = \mathbf{0.966 \text{ bar}}$

Exercises

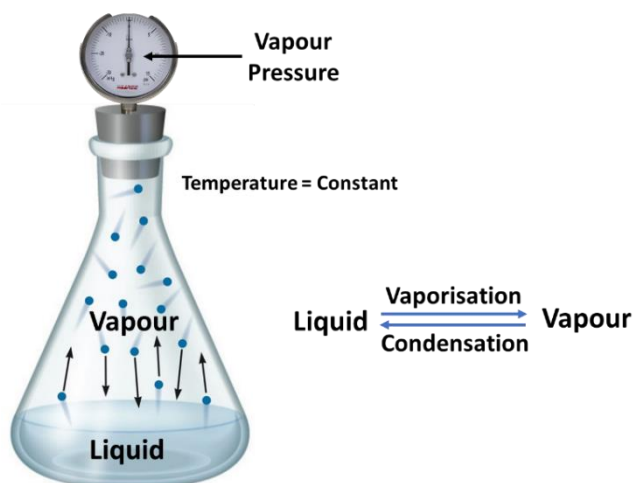
1. If nitrogen gas is bubbled through water at 293 K, how many millilitres (at STP) of nitrogen would dissolve in a litre of water? Given that the partial pressure of nitrogen is equal to 742.5 torr and K_H for nitrogen is 5.75×10^7 torr.
2. The Henry's law constant for the solubility of nitrogen gas in water at 298 K is 1×10^5 atm. The mole fraction of nitrogen in air is 0.8. What is the number of moles of nitrogen from the air dissolved in 10 moles of water at 298 K and 5 atm pressure?
3. If N_2 gas is bubbled through water at 293 K, how many milli moles of N_2 gas would dissolve in 1 litre of water. Assume that N_2 exerts a partial pressure of 0.987 bar. The K_H for N_2 at 293 K is 76.48 k bar.
4. At what partial pressure, oxygen will have solubility of 0.05 g L^{-1} in water at 293 K? Henry's constant (K_H) for O_2 in water at 293 K is 34.36 k bar. Assume the density of the solution to be same as that of the solvent.
5. Air contain O_2 and N_2 in the ratio of 1 : 4. Calculate the ratio of solubilities in term of mole fraction of O_2 and N_2 dissolved in water at atmospheric pressure and room temperature at which Henry's constant for O_2 and N_2 are 3.30×10^7 torr and 6.60×10^7 torr respectively.
6. The solubility of pure nitrogen gas at 25°C and 1 atm is 6.8×10^{-4} mole/L. What is the concentration of nitrogen dissolved in water under atmospheric conditions? The partial pressure of nitrogen gas in atmosphere is 0.78 atm.
7. If solubility of any gas in the liquid at 1 bar pressure is 0.05 mole/L. What will be its solubility at 3 bar pressure, keeping the temperature constant?
8. 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.

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9. What is the ratio of the solubilities of nitrogen and oxygen in water at 373 K, given that $K_H(N_2) = 12.6 \times 10^4$ atm and $K_H(O_2) = 7.01 \times 10^4$ atm. Assume that pressure 'P' (N_2) = 0.80 atm and pressure 'P' (O_2) = 0.20 atm.

Vapour Pressure of Liquids

- When a liquid is allowed to evaporate in a closed vessel, a part of the liquid evaporates. It fills the available space with vapours and level of liquid decreases. This process is called **vaporisation**.
- Some molecules of vapour strike the surface of liquid and get condensed. The process of **condensation** acts in opposite direction to the process of evaporation.
- Ultimately, a stage is reached when the rate of evaporation becomes equal to rate of condensation and **equilibrium** gets established between the liquid and vapour phase.
- The pressure exerted by the vapours above the liquid surface at the time of equilibrium at a given temperature is called **vapour pressure**.



❖ Factors Affecting Vapour Pressure

○ Nature of liquid:

The liquids, which have weaker intermolecular forces, have greater vapour pressure because more molecules tend to escape into vapour phase. Example: Dimethyl ether and ethyl alcohol have greater vapour

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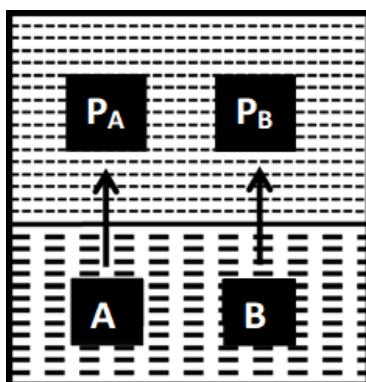
pressure than water because of weaker intermolecular forces as compared to water.

○ Temperature:

The vapour pressure of liquid increases with increase in temperature. This is because more molecules will have larger kinetic energies and escape readily into vapour phase resulting in higher vapour pressure.

Vapour Pressure of Liquid-Liquid Solutions

- When a binary solution of two volatile liquids (A and B) is placed in a closed vessel, both components would evaporate and eventually an equilibrium would be established between liquid and vapour phase.



- According to Dalton's law of partial pressures, the total vapour pressure (P_{Total}) in the container will be the sum of the partial vapour pressures (P_A and P_B) of both components of the solution.

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

- According to **Raoult's law**:

For a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to their mole fraction in solution. Then, according to Raoult's law:

$$P_A \propto \chi_A \quad \text{and} \quad P_A = P_A^\circ \cdot \chi_A$$
$$P_B \propto \chi_B \quad \text{and} \quad P_B = P_B^\circ \cdot \chi_B$$

Where :

P_A and P_B are the partial vapour pressures of components in solution.

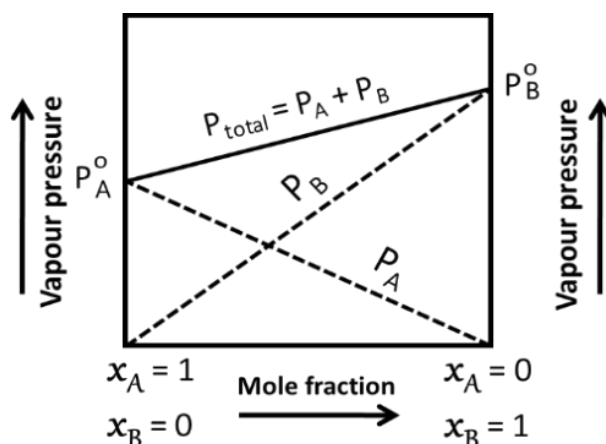
P_A° and P_B° are the vapour pressures of components in Pure state.

χ_A and χ_B are the mole fractions of components in solution

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- Substituting the values of P_A and P_B , in equation $P_{\text{Total}} = P_A + P_B$, we get

- $P_{\text{Total}} = [P_A^{\circ} \cdot \chi_A] + [P_B^{\circ} \cdot \chi_B]$

As we know, $\chi_A + \chi_B = 1$ or $\chi_A = 1 - \chi_B$

- $P_{\text{Total}} = [P_A^{\circ} (1 - \chi_B)] + [P_B^{\circ} \cdot \chi_B]$
 $= P_A^{\circ} - P_A^{\circ} \cdot \chi_B + P_B^{\circ} \cdot \chi_B$
 $= P_A^{\circ} + (P_B^{\circ} - P_A^{\circ}) \chi_B$

- The composition of **vapour phase** in equilibrium can be determined by the **partial pressure** of components. If Y_A and Y_B are the mole fractions of components A and B respectively in vapour phase then:

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

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

- Konowaloff's rule**

At any fixed temperature, mole fraction of the more volatile component is always greater in the vapour phase than in the solution phase.

- Raoult's law as a special case of Henry's Law**

If we compare the equations for Raoult's law and Henry's law.

$$P = K_H \cdot \chi_B \quad (\text{According to Henry's law})$$

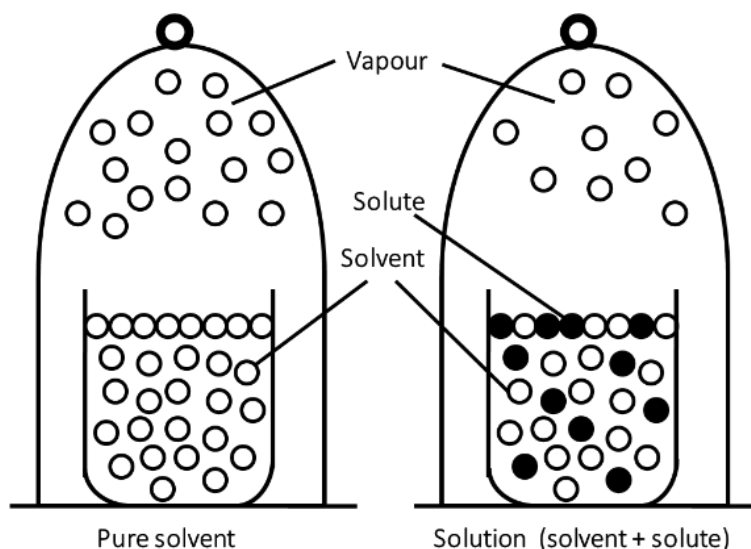
$$P_A = P_A^{\circ} \cdot \chi_A \quad (\text{According to Raoult's law})$$

The partial pressure of the volatile component or gas is directly proportional to its mole fraction in solution.

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Vapour Pressure of Solid-Liquid Solutions

- When the solute is **non-volatile**, only the solvent molecules are present in the vapour phase. Therefore, the vapour pressure of solution is due to **solvent only**. However, the vapour pressure of the solution is found to be **less** than that of the pure solvent.



- This can be explained as follows:**
 - We know that evaporation is a surface phenomenon. The vapour pressure depends on the escape of solvent molecules from the surface of the liquid.
 - In the case of solution, some of the non-volatile solute particles occupy a certain surface area. As a result, lesser number of solvent molecules will escape into vapours. Hence, there will be a lowering in vapour pressure of solution.
- The total vapour pressure of solution will be equal to the partial vapour pressure of solvent only.

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

- According to Raoult's law, the partial vapour pressure of volatile component in the solution is directly proportional to the mole fraction in it.

$$P_A = P_A^\circ \cdot \chi_A$$

Now:

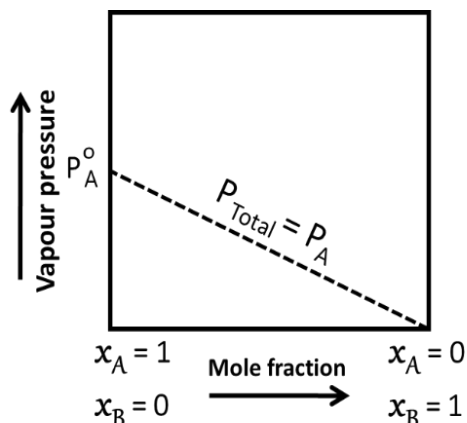
$$P_{\text{Total}} = P_A = P_A^\circ \cdot \chi_A$$

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- The above relationship may also be put forward in different ways as:



$$\begin{aligned}
 \circ P_A &= P_A^\circ \cdot \chi_A && (\because \chi_A = 1 - \chi_B) \\
 \circ P_A &= P_A^\circ (1 - \chi_B) \\
 &= P_A^\circ - P_A^\circ \chi_B \\
 \circ P_A^\circ \chi_B &= P_A^\circ - P_A \\
 \circ \chi_B &= \frac{P_A^\circ - P_A}{P_A^\circ} = \frac{\Delta P_A}{P_A^\circ}
 \end{aligned}$$

- In this expression, $P_A^\circ - P_{Total} = \Delta P_A$, expresses the **lowering of vapour pressure** while $\frac{P_A^\circ - P_{Total}}{P_A^\circ}$ is called **relative lowering in vapour pressure** and χ_B represents mole fraction of the solute in solution.
- Hence, the above expression may be expressed in words as follows:
The **relative lowering of vapour pressure** of a solution containing a non-volatile solute is equal to the **mole fraction of the solute** in the solution at a given temperature.

Ideal and Non-ideal Solutions

Ideal Solutions

- An ideal solution may be defined as the solution which **obeys Raoult's law** under all conditions of temperatures and concentrations.
- Such solutions are formed by mixing the two components which are identical in molecular size and have almost identical intermolecular forces.
- The intermolecular interactions between components A – B are of same magnitude as in pure components A – A and B – B.

The ideal solutions have the following characteristics :

- Heat change on mixing is zero ($\Delta H_{\text{mixing}} = 0$).

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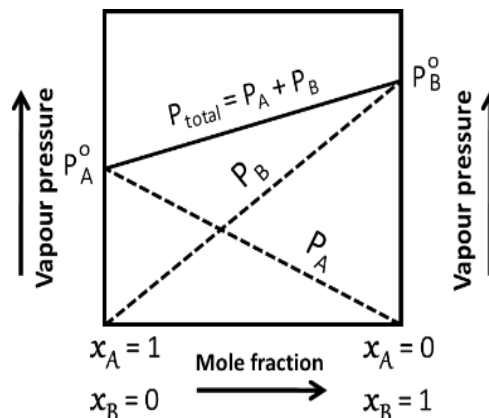
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- Volume change on mixing is zero ($\Delta V_{\text{mixing}} = 0$).
- Obeys Raoult's law ($P_A = P_A^\circ \cdot \chi_A$ and $P_B = P_B^\circ \cdot \chi_B$).

Examples of ideal solution:

- Benzene + Toluene
- n-Hexane + n-Heptane
- Ethyl chloride + Ethyl bromide
- Chlorobenzene + Bromobenzene



Non-ideal Solutions

- The solutions which **do not obey Raoult's law** under all conditions of temperatures and concentrations are called non-ideal solutions.
- Such solutions are formed by mixing the two components which are non-identical in molecular size and have non-identical intermolecular forces.

The non-ideal solutions have the following characteristics :

- Heat change on mixing is not equal to zero ($\Delta H_{\text{mixing}} \neq 0$).
- Volume change on mixing is not equal to zero ($\Delta V_{\text{mixing}} \neq 0$).
- Do not obey Raoult's law ($P_A \neq P_A^\circ \cdot \chi_A$ and $P_B \neq P_B^\circ \cdot \chi_B$).

Types of non-ideal solution :

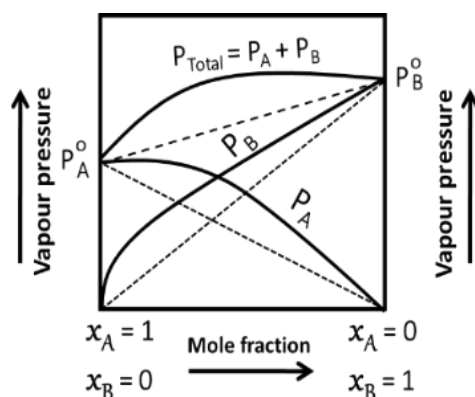
- (a) Non-ideal solution showing **positive deviations** from Raoult's law.
- (b) Non-ideal solution showing **negative deviations** from Raoult's law.

(a) Non-ideal solution showing positive deviation from Raoult's law

- When the partial pressure of components is found to be more than expected on the basis of Raoult's law. As a result, total vapour pressure of the solution is greater than expected.

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- The intermolecular interactions between components A – B are of less magnitude as in pure components A – A and B – B.
- The boiling points of such solutions are relatively lower as compared to those of pure component. The composition of such solution remains unchanged on distillation, hence behave like **minimum boiling azeotropes**.

Characteristics :

- Heat change on mixing is always positive ($\Delta H_{\text{mixing}} = \text{positive}$)
- Volume change on mixing is also always positive ($\Delta V_{\text{mixing}} = \text{positive}$)
- Partial pressure is found to be more than expected ($P_A > P_A^\circ \cdot \chi_A$)

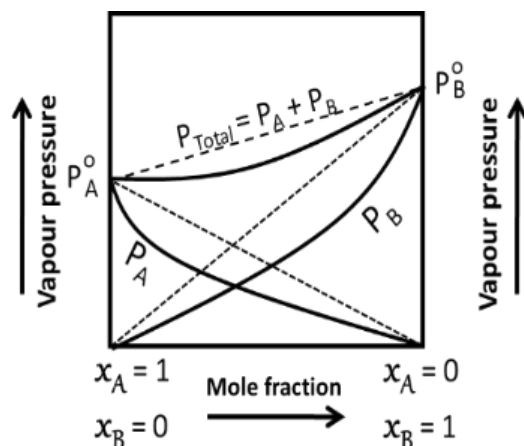
Examples :

- Acetone + Carbon disulphide
- Acetone + Ethyl alcohol
- Acetone + Benzene
- Methyl alcohol + Water

(b) Non-ideal solution showing negative deviation from Raoult's law

- When the partial pressure of components is found to be less than expected on the basis of Raoult's law. As a result, total vapour pressure of the solution is lower than expected.

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- The intermolecular interactions between components A – B are of greater magnitude as in pure components A – A and B – B.
- The boiling points of such solutions are relatively higher as compared to those of pure component, hence, behave like **maximum boiling azeotropes**.

Characteristics :

- Heat change on mixing is always negative ($\Delta H_{\text{mixing}} = \text{negative}$)
- Volume change on mixing is also always negative ($\Delta V_{\text{mixing}} = \text{negative}$)
- Partial pressure is found to be less than expected ($P_A < P_A^\circ \cdot \chi_A$)

Examples :

- Chloroform + Acetone
- Acetone + Aniline
- Chloroform + Benzene
- HCl + Water
- Chloroform + Diethyl ether

Azeotropes

- Azeotropes are the binary solution having the same composition in both liquid and vapour phase, and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation method.

There are two types of Azeotropes

- **Minimum boiling azeotropes or positive azeotropes**
 - When the boiling point of the azeotrope is **less** than the boiling points of the pure components, then it is called *minimum boiling azeotropes*.
 - Non-ideal solutions showing positive deviation from Raoult's law behave as minimum boiling azeotropes.
 - Example: 95.4 % solution of ethanol with water boil at 351.15 K
- **Maximum boiling azeotropes or negative azeotropes**
 - When the boiling point of the azeotrope is **more** than the boiling point of the pure components, then it is called *maximum boiling azeotropes*.
 - Non-ideal solutions showing negative deviation from Raoult's law behave as maximum boiling azeotropes.
 - Example: 68 % solution of nitric acid with water boil at 393.5 K.

Exercises

1. Vapour pressure of chloroform (CHCl_3) and dichloromethane (CH_2Cl_2) at 298 K are 200 mmHg and 415 mmHg respectively. Calculate the (a) Vapour pressure of the solution prepared by mixing 25.5 g of CHCl_3 and 40 g of CH_2Cl_2 at 298 K and (b) Mole fraction of each component in vapour phase.
2. In ideal solution of a non-volatile solute 'B' in solvent 'A' in 2 : 5 molar ratio and has vapour pressure 250 mmHg. If another solution in ratio 3 : 4 prepared, then calculate vapour pressure above this solution.
3. The vapour pressure of an aqueous solution of glucose is 750 mmHg at 373 K. Calculate the molality and mole fraction of glucose.
4. Methanol and ethanol form nearly an ideal solution. If the vapour pressure of pure methanol and pure ethanol at 350 K are 8.1×10^4 and $4.5 \times 10^4 \text{ Nm}^{-2}$ respectively, calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour phase if the solution contains 64 gm of methanol and 46 gm of ethanol at this temperature.

5. The vapour pressure of a dilute aqueous solution of glucose is 750 mmHg at 373 Kelvin. Calculate the mole fraction of solute if the vapour pressure of pure water is 760 mmHg at 373 K.
6. Equal moles of benzene and toluene are mixed. The vapour pressure of benzene and toluene in the pure state are 700 and 600 mmHg respectively. Calculate the mole fraction of benzene in vapour state.
7. Two liquids 'X' and 'Y' on mixing form an ideal solution. The vapour pressure of the solution containing 3 moles of 'X' and 1 mole of 'Y' is 550 mmHg. But when 4 moles of 'X' and 1 mole of 'Y' are mixed, the vapour pressure of solution thus formed is 560 mmHg. What will be the vapour pressure of the pure 'X' and pure 'Y' at this temperature.
8. Vapour pressure of CH_3Cl and CH_2Cl_2 are 540 mmHg and 402 mmHg respectively. 101 gm of CH_3Cl and 85 grams of CH_2Cl_2 are mixed together. Determine: (a) the vapour pressure at which the solution starts boiling (b) Molar ratio of solute versus solvent in vapour phase in equilibrium with solution.
9. The vapour pressure of ethyl acetate and ethyl propionate are 72.8 and 27.7 mmHg respectively. A solution is prepared by mixing 25 g of ethyl acetate and 50 g of ethyl propionate. Assuming the solution to be ideal, Calculate the vapour pressure of the solution.

Colligative Properties

- Those properties of ideal solutions which depend only on the number of solute particles but do not depend on the nature of solute are called colligative properties.
- The important colligative properties are:
 - Relative Lowering in Vapour Pressure
 - Elevation in Boiling Point
 - Depression in Freezing Point
 - Osmotic Pressure

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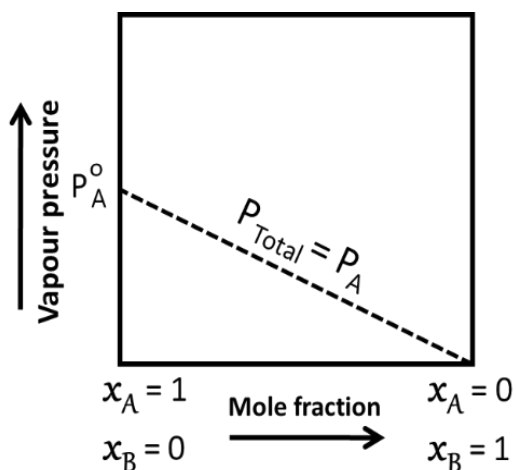
Unit : Solutions

Relative Lowering in Vapour Pressure

- The vapour pressure of solvent in solution is always less than that of pure solvent. This is because of non-volatile solute occupy some surface area; hence the vapour pressure decrease.
- When the solute is **non-volatile**, only the solvent molecules are present in the vapour phase. Therefore, vapour pressure of solution is due to **solvent only**.

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

- By Using Raoult's law:



- $P_A = P_A^{\circ} \cdot \chi_A$ ($\because \chi_A = 1 - \chi_B$)
- $P_A = P_A^{\circ} (1 - \chi_B)$
 $= P_A^{\circ} - P_A^{\circ} \chi_B$
- $P_A^{\circ} \chi_B = P_A^{\circ} - P_A$
- $\chi_B = \frac{P_A^{\circ} - P_A}{P_A^{\circ}} = \frac{\Delta P_A}{P_A^{\circ}}$

- In this expression, $P_A^{\circ} - P_{\text{Total}} = \Delta P_A$, expresses the **lowering of vapour pressure** while $\frac{P_A^{\circ} - P_{\text{Total}}}{P_A^{\circ}}$ is called **relative lowering in vapour pressure** and χ_B represents mole fraction of the solute in solution.

Determination of molar mass of solute:

- $\chi_B = \frac{P_A^{\circ} - P_A}{P_A^{\circ}}$ -----(1)

- $\chi_B = \frac{n_B}{n_A + n_B}$ -----(2)

- Compare equation (1) and (2)

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

- For a dilute solution, $n_A \gg \gg n_B$, hence, $n_A + n_B \cong n_A$,
- Now,

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

$$\frac{P_A^\circ - P_A}{P_A^\circ} = \frac{W_B \times M_A}{M_B \times W_A} \quad [\because P_A^\circ - P_A = \Delta P_A]$$

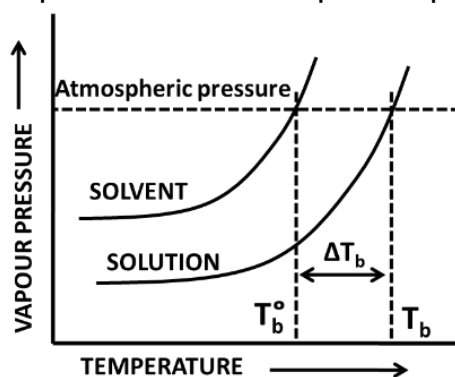
$$\frac{\Delta P_A}{P_A^\circ} = \frac{W_B \times M_A}{M_B \times W_A} \quad \text{Or} \quad M_B = \frac{W_B \times M_A \times P_A^\circ}{\Delta P_A \times W_A}$$

Exercises

1. Vapour pressure of water at 293 K is 17.51 mm. Lowering of vapour pressure of a sugar solution is 0.0614 mm. Calculate (i) Relative lowering of vapour pressure (ii) Mole fraction of water (iii) Vapour pressure of the solution.
2. The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile and non-electrolyte solid weighing 0.5 g is added to 39.0 g of benzene (molar mass 78 g/mol). The vapour pressure of the solution then is 0.845 bar. What is the molar mass of the solid substance?
3. The vapour pressure of 2.1 % of an aqueous solution of non-electrolyte at 373 K is 755 mm. Calculate the molar mass of solute. (Consider that vapour pressure of water at 373 K is 760 mm).
4. 20 g of solute was added to 100 g of water at 25 °C. The vapour pressure of water and that of the solution were 23.76 mmHg and 22.41 mmHg respectively at that temperature. Calculate the relative molecular mass of the solute.

Elevation in Boiling Point

- The boiling point of liquid is the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.



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Unit : Solutions

- It is found that the boiling point of the solution is always higher than that of pure solvent (is called elevation in boiling point).
- The elevation in boiling point (ΔT_b) depends on molal concentration (m) of solute in solution. $\Delta T_b \propto m$ or $\Delta T_b = K_b \times m$
- Where K_b is called the molal elevation constant or ebullioscopic constant and 'm' is the molality.

Solvent	K_b (K Kg/mol)
H ₂ O	0.52
C ₆ H ₆	2.53
C ₂ H ₅ OH	1.20

$$\Delta T_b = K_b \times \frac{W_B \times 1000}{M_B \times W_{\text{solvent in g}}}$$

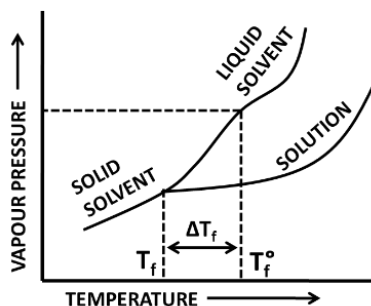
$$\Delta T_b = T_b - T_b^\circ$$

Exercises

- The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute. K_b for benzene is 2.53 K kg/mol.
- 18 g of glucose, C₆H₁₂O₆, is dissolved in 1 kg of water. At what temperature will the water boil at 1.013 bar pressure? K_b for water is 0.52 K kg/mol.
- A solution of glycerol (C₃H₈O₃), in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42 °C. What mass of glycerol was dissolved to make the solution? K_b for water = 0.52 K kg/mol.

Depression in Freezing Point

- Freezing point of a substance is the temperature at which the solid and liquid forms of the substance have same vapour pressure.



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Unit : Solutions

- It is found that the freezing point of the solution is always lower than that of pure of solvent (is called depression in freezing point).
- The depression in freezing point (ΔT_f) depends upon molal concentration (m) of solute in solution. $\Delta T_f \propto m$ or $\Delta T_f = K_f \times m$
- Where K_f is called the molal depression constant or cryoscopic constant and m is the molality.

Solvent	K_f (K Kg/mol)
H ₂ O	1.86
C ₆ H ₆	5.12
C ₂ H ₅ OH	1.99

$$\Delta T_f = K_f \times \frac{W_B \times 1000}{M_B \times W_{\text{solvent in g}}}$$

$$\Delta T_f = T_f^\circ - T_f$$

Applications of Depression of freezing point :

- In making antifreeze solutions:
 - The running of a vehicle (car or bus) in sub-zero weather even when the radiator is full of water, which has freezing point 0 °C or 273 K, has been possible due to depression in freezing point of water takes place by addition of some quantity of ethylene glycol (called antifreeze) in water.
- In melting of ice on roads:
 - In winter, where snowfall occurs heavily, the ice deposited on roads is molten by scattering common salt (NaCl) or CaCl₂ on the roads. This is because salt-ice mixture has very low freezing point and hence ice keeps on melting.

Exercises

- A solution containing 34.2 g of cane-sugar (C₁₂H₂₂O₁₁) dissolved in 500 cm³ of water froze at -0.374 °C. Calculate the K_b of water.
- 1.00 g of non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. K_f of benzene is 5.12 K kg/mol. Find Molar mass of solute.
- 45 g of ethylene glycol (C₂H₆O₂) is mixed with 600 g water. Calculate : (a) freezing point of depression (b) freezing point of solution. (K_f for H₂O = 1.86 K kg/mol)

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4. Calculate the temperature at which a solution containing 54 g of glucose in 250 g of water will freeze. (K_f for water = 1.86 K kg/mol)
5. What mass of ethylene glycol (Molecular mass = 62.0 g/mol) must be added to 5.50 kg of water to lower the freezing point of water from 0 °C to -10.0 °C. (K_f H₂O is 1.86 K kg/mol).

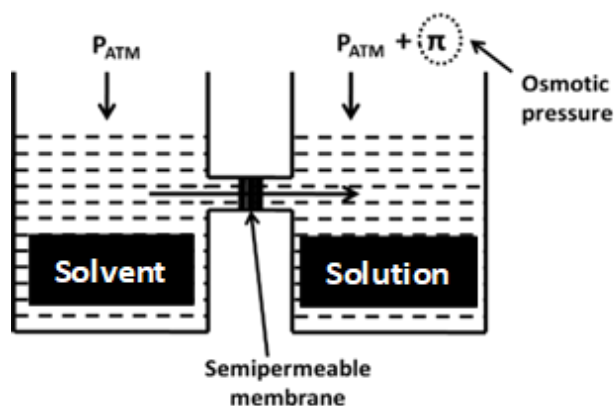
Osmotic Pressure

Osmosis and Diffusion :

- Diffusion is the spontaneous process of movement of both solute and solvent from their higher concentration to lower concentration.
- Osmosis is the spontaneous process of movement of solvent only, from its higher concentration to lower concentration through semi-permeable membrane.
 - Semi-permeable Membrane can be defined as the membrane which is selectively permeable to substances and allow solvent molecules to pass through it but do not allow solute molecule.
Common examples are: parchment membrane, cellophane membrane, copper ferrocyanide etc.

Osmotic Pressure :

- It can be defined as the additional pressure applied on the solution to prevent the entry of the solvent into the solution through semi-permeable membrane. It is represented by ' π .'



- Osmotic pressure (π) of a solution is found to be directly proportional to molar concentration (C) of the solution and its temperature (T).

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$$\pi \propto C \text{ ----- (i)}$$

$$\pi \propto T \text{ ----- (ii)}$$

- Compare the equation (i) and (ii)

$$\pi \propto CT \quad \text{or} \quad \pi = RCT$$

Where 'R' is a constant and its value is found to be same as that of the 'Gas constant'.

- The above equation is usually written as :

$$\pi = CRT \quad \text{C is molar concentration} = \frac{n}{V}$$

Where 'n' is the number of moles of solute and V is the volume of solⁿ in Litre.

- Now: $\pi = \frac{n}{V}RT$ or $\pi V = nRT$

This equation is called Van't Hoff equation for dilute solutions.

Determination of Molecular mass from Osmotic Pressure

$$\pi V = nRT$$

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

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

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

Where :- 'n' is moles of solute = $\frac{W_B}{M_B}$

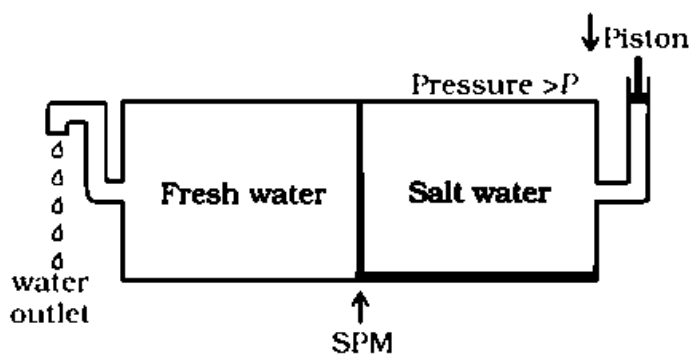
If **volume** of solution in **mL** then equation become :

$$\pi = \frac{W_B \times RT \times 1000}{M_B \times V}$$

$$M_B = \frac{W_B \times RT \times 1000}{\pi \times V}$$

Reverse Osmosis (R.O.) :

- If a pressure higher than the osmotic pressure is applied on the solution, the solvent will flow from the solution into the pure solvent through the semi-permeable membrane. The process is called reverse osmosis (RO).



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Unit : Solutions

Hypertonic, Hypotonic, and Isotonic solutions

- The solution which has high osmotic pressure with respect to another solution is called hypertonic solution. It contains relatively large quantity of solute.
- The solution which has low osmotic pressure with respect to another solution is called hypotonic solution. It contains relatively small quantity of solute.
- The solution which has same osmotic pressure with respect to another solution is called isotonic solution. It has equimolar concentration of solute.

Biological Importance of Osmosis :

- Plants absorb water from the soil through their roots due to osmosis.
- In animals, water moves into different parts of the body due to osmosis.
- Bursting of RBCs when placed in water is also due to osmosis.
- Opening and closing of stomata of plant leaves is also due to osmosis.
- Raw mangoes shrink to pickle when placed in common salt is due to osmosis.
- Wilted flowers revive when placed in fresh water is due to osmosis.

By study of osmosis, it helps us to conclude the following :

- When RBCs are placed in **hypotonic** solution, having salt concentration less than 0.9 %, they will start swell up due to endosmosis.
- When RBCs are placed in **hypertonic** solution, having salt concentration more than 0.9 %, they will start shrink due to exosmosis.
- When RBCs are placed in **isotonic** solution, having salt concentration 0.9 %, the cell never swell and nor shrink because no osmosis takes place.

Explanation of Some Phenomenon Based on Osmosis :

- People taking a lot of salt in food develop swelling of their tissues, a disease is called **edema**. This is due to retention of water in the tissue cells because of osmosis.
- Raw mangoes shrink into pickle when placed in common salt solution. This is due to outflow of water from the cells of mangoes because of osmosis.
- Wilted flower revives again when placed in fresh water. This is due to flow of water into the flower cells because of osmosis.



Turgid cell and Plasmolysed cell

- When water enters the cell, it starts swell up due to **endosmosis**, the cell wall of the cell then exert pressure to oppose the flow of water into the cell, this exerted pressure is called **turgor pressure** and the cell is called **turgid cell**.
- When water going out the cell, it starts shrink due to **exosmosis**, the protoplasm of the cell attains small spherical shape, this phenomenon is called **plasmolysis** or **crenation** and the cell is called **plasmolysed cell**.

Remember that osmosis takes place in the direction of:

- High solvent concentration to Low solvent concentration.
- Low solute concentration to high solute concentration.
- Diluted solution to concentrated solution
- Low osmotic pressure to high osmotic pressure

Exercises

1. 200 cm³ of an aqueous solⁿ of protein contains 1.26 g of protein. Osmotic pressure of this solution at 300 K is found to be 2.57×10^{-3} bar. Calculate molecular mass of protein.
2. 10 g of a substance were dissolved in water and solution was made up to 250 cm³. Osmotic pressure of solution was found to be 8×10^5 Nm⁻² at 288 K. Find molar mass of solute.
3. A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr at 25 °C. Assuming that the gene fragment is a non-electrolyte, calculate its molar mass.

Abnormal Molecular Masses

- When the molecular mass of a substance determined by studying any of the colligative properties comes out to be different than the theoretically expected value, then the substance is said to show abnormal molecular mass.

Abnormal molecular masses are observed in any one of the following cases:

- When the solute undergoes dissociation in the solution.
- When the solute undergoes association in the solution.
- When the solution is non-ideal.

Van't Hoff factor

- To calculate the extent of association or dissociation, Van't Hoff introduced a factor 'i' called Van't Hoff factor.
- It is defined as the **ratio** of the **experimental value** of the colligative property to the **calculated value** of the colligative property.

$$i = \frac{\text{Experimental or Observed colligative property}}{\text{Normal or Calculated colligative property}} = \frac{C_o}{C_c}$$

- As we know that, colligative property is inversely proportional to the molecular mass of the solute, we can also write:

$$i = \frac{\text{Normal or Calculated Molecular mass}}{\text{Experimental or Observed Molecular mass}} = \frac{M_c}{M_o}$$

Dissociation = $i > 1$
Association = $i < 1$

Modified Expressions of Colligative Properties :

- Relative Lowering in Vapour pressure:

$$\frac{\Delta P_A}{P_A^\circ} = i \frac{W_B \times M_A}{M_B \times W_A} \quad \text{OR} \quad \frac{P_A^\circ - P_A}{P_A^\circ} = i X_B$$

- Elevation in Boiling point:

$$\Delta T_b = i \times K_b \times m \quad \text{OR} \quad \Delta T_b = i \times K_b \times \frac{W_B \times 1000}{M_B \times W_{\text{solvent in g}}}$$

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- Depression in Freezing point:

$$\Delta T_f = i \times K_f \times m \quad \text{OR} \quad \Delta T_f = i \times K_f \times \frac{W_B \times 1000}{M_B \times W_{\text{solvent in g}}}$$

- Osmotic pressure:

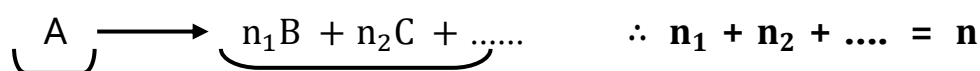
$$\pi = i \frac{W_B \times RT \times 1000}{M_B \times V}$$

Calculation of the Degree of Dissociation

- When an electrolyte is dissolved in a solvent, it dissociates into ions. The fraction of the total number of electrolyte molecules that undergoes dissociation is called **degree of dissociation**.

$$\text{Degree of dissociation } (\alpha) = \frac{\text{No of moles dissociated}}{\text{Total number of moles taken}}$$

- Consider that, A molecules dissociates in solvent to give 'n' ions



Initial conc. : 1 0 moles

Final conc. : 1 - α n α moles

- Observed colligative property = 1 + (n - 1) α
- Calculated colligative property = 1 (as 1 mole of solute 'A' was taken)

- Van't Hoff factor 'i' = $\frac{\text{Observed colligative property}}{\text{Calculated colligative property}} = \frac{1 + (n-1)\alpha}{1}$

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

- As we know that, $i' = \frac{\text{Calculated Molecular mass}}{\text{Observed Molecular mass}} = \frac{M_C}{M_O}$

- $\therefore \alpha = \frac{i-1}{n-1} = \frac{\frac{M_C}{M_O} - 1}{n-1} = \frac{M_C - M_O}{M_O (n-1)}$

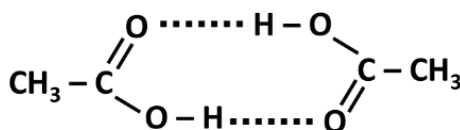
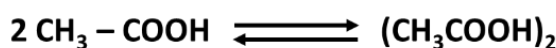
Calculation of the Degree of Association

- In some cases, 'n' molecules of the solute 'A' associate to form large associated molecule 'A_n'. The fraction of the total number of solute molecules which exist in the form of associated molecule is called **degree of association**.

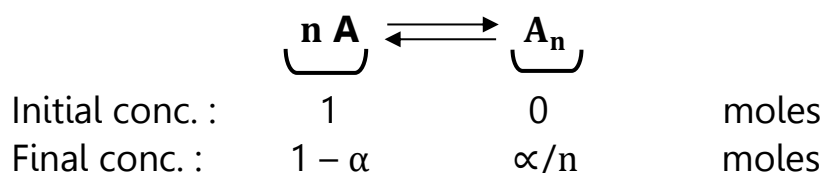
$$\text{Degree of association } (\alpha) = \frac{\text{No of moles associated}}{\text{Total number of moles taken}}$$

- Example:**

- Molecules of ethanoic acid (acetic acid) dimerise in benzene due to hydrogen bonding.
- This normally happens in solvents of low dielectric constant.
- In this case the number of particles is reduced due to dimerization.



- Consider that, 'n' number of simple molecules of solute 'A' associate to form associated molecule A_n.



- Total number of moles in solution = $(1 - \alpha) + \frac{\alpha}{n}$ (Observed C.P.)
- Total number of moles of solute was taken = 1 (Calculated C.P.)
- \therefore van't Hoff factor 'i' = $\frac{\text{Observed colligative property}}{\text{Calculated colligative property}} = \frac{(1 - \alpha) + \frac{\alpha}{n}}{1}$
- Hence, $\alpha = (1 - i) \frac{n}{n-1}$
- As we know that, 'i' = $\frac{\text{Calculated Molecular mass}}{\text{Observed Molecular mass}} = \frac{M_c}{M_o}$
- $\therefore \alpha = \left(1 - \frac{M_c}{M_o}\right) \frac{n}{n-1} = \left(\frac{M_o - M_c}{M_o}\right) \frac{n}{n-1}$

Exercises

1. 0.5 gm KCl was dissolved in 100 gm water and the solution originally at 20 °C, froze at -0.24 °C. Calculate the percentage ionization of salt. K_f for water = 1.86 K Kg mol⁻¹.
2. 0.6 mL of acetic acid having density of 1.06 gm/ml is dissolved in 1 Litre of water. The depression in freezing point observed for this strength of the acid was 0.0205 °C. Calculate the Van't Hoff factor and the dissociation constant of the acid. K_f for water = 1.86 K Kg mol⁻¹.
3. Depression in freezing point of 0.10 molal solution of HF is -0.201 °C. Calculate percentage degree of dissociation of HF. K_f for H₂O = 1.86 K Kg mol⁻¹.
4. Calculate the freezing point depression expected for 0.0711 molal aqueous solution of Na₂SO₄. If this solution freezes at -0.32 °C, what would be the value of Van't Hoff factor? K_f for water = 1.86 K Kg mol⁻¹.
5. Calculate the boiling point of a solution prepared by adding 15 gm of NaCl to 250 gm of water (K_b for water = 0.52 K Kg mol⁻¹).

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