

A solution may be defined as a Homogeneous mixtures of a single phase containing one or more of the chemical species dispersed on a molecular scale.

SOLUTE AND SOLVENT

- (a) The component whose physical state is same as that of resulting solution is called as Solvent and the other component whose physical state changes is termed as Solute. *e.g.* In a homogenous mixture of Na(s) and Hg(l) resulting in the formation of NaHg(s), Na(s) is considered as solvent and Hg(l) is termed as Solute which is contrary to the common belief that liquids are solvents.;
- (b) When both components are having the same phase as that of that the resulting solution and the relative amount of one substance in a solution is much greater than that of the other, the substance present in greater amount is generally regarded as the solvent.

METHODS OF EXPRESSING CONCENTRATIONS OF SOLUTIONS

The concentration of solutions are generally expressed in the following ways: Solute: designated as 'b' Solvent: designated as 'a'

1. Molarity (M): No. of moles of solute per litre of solution.

$$M = \frac{\text{number of moles of } \boldsymbol{b}}{\text{Volume of solution in Liter}} = \frac{n_b}{V_{(L)}} = \frac{(W_b) \times 1000}{(M_b) \times V_{(ml)}}; \text{ where, } V_{(ml)} = \text{Volume of Solution in mililitres.}$$

2. Molality (m): No. of moles of solute per kg of solvent.

 $m = \frac{\text{Number of moles of solute}}{\text{Weight of solvent in Kg}} = m = \frac{n_b}{W_a (kg)}; m = \frac{W_b \times 1000}{M_b \times W_a}; W_a = \text{Weight of solvent in gms}$

3. Normality (N) : No. of Gram equivalent of solute per litre of solution.

Gm. equivalent = $\frac{\text{Weight of solute}}{\text{Equivalent mass of solute}}$; Equivalent mass = $\frac{\text{Molar mass of solute}}{n \text{ factor}}$;

 $\mathbf{N} = \mathbf{M} \times \mathbf{n}_{f}$: Where M is the molarity and $\mathbf{n}_{f} = \mathbf{n}$ factor

4. Mole fraction (X) : Ratio of number of moles of one of the components to the total number of moles present in the solution.

$$X_{b} = \frac{n_{b}}{n_{a} + n_{b} + n_{c} + \dots}; X_{a} = \frac{n_{a}}{n_{a} + n_{b} + n_{c} + \dots}; \text{Total mole fraction of a solution is } X_{a} + X_{b} = 1.$$

- 5. Mass Percentage (w/W %) = $\frac{\text{Mass of solute (gram)}}{\text{Mass of solution (gram)}} \times 100$; A 10% aqueous NaCl solution contains 10 grams of NaCl per 100 grams of solution. Ten grams of NaCl is mixed with 90 grams of water to form 100 grams of solution.
- 6. Volume Percentage $(v/V \%) = \frac{Volume of solute (ml)}{Volume of solution (ml)} \times 100$; e.g. 10% volume percentage of aqueous solution of ethanol means 10 mL solute present in 100mL of the solution.
- 7. Mass by Volume Percentage (w/V%) = $\frac{\text{Mass of solute (gram)}}{\text{Volume of solution (mL)}} \times 100$
- 8. Parts per Million = $\frac{\text{Number of parts of the component}}{\text{Total number of parts of all the components of the solution}} \times 10^6$

Concentration in parts per million can also be expressed as mass to mass, volume to volume and mass to volume.

Hand-Out Chemistry Chapter 2 : Solution

Illustration 1:	Calculate the molality and mole fraction of the solute in aqueous solution containing 3.0 g of urea (mol. mass=60) per 250 g of water.			
Solution:	Weight of solute = 3 g ;Mol. mass (M_b) [urea] = 60 g mol ⁻¹ ; Weight of solvent = 250 g			
	m= $\frac{W_b \times 1000}{M_b \times W_a} = \frac{3 \times 1000}{60 \times 250} = 0.2$ m; n _b = $\frac{\text{Weight in gm}}{\text{molar mass}} = \frac{3}{60} = 0.05$;			
	$n_a = \frac{\text{Weight in gm}}{\text{molar mass}} = \frac{250}{18} = 13.89; \ X_b = \frac{0.05}{0.05 + 13.89} = -0.0037$			
Illustration2.	Calculate the molarity and normality of a solution containing 9.8 g of H_2SO_4 in 250 cm ³ of the solution.[Mormass (M _b) [H_2SO_4] = 98 g mol ⁻¹]			
Solution:	$M = \frac{(W_b) \times 1000}{(M_b) \times V_{(ml)}} = \frac{9.8 \times 1000}{98 \times 250} = 0.4 \text{ M; Normality} = M \times n_f; N = 0.4 \times 2 = 0.8 \text{ N}$			
Illustration 3.	Find the molarity and molality of a 15% solution of H_2SO_4 (density =1.020 g cm ⁻³).			
Solution: Let the solution be 100 g ; Weight of solute = 15 g ; Weight of solvent = 85 g				
	Volume of solution taken = $\frac{100}{1.020}$ ml; M = $\frac{(W_b) \times 1000}{(M_b) \times V_{(ml)}} = \frac{15 \times 1000}{98 \times \frac{100}{1.020}} = 1.56$ M;			
	m = $\frac{(W_b) \times 1000}{(M_b) \times W_a} = \frac{15 \times 1000}{98 \times 85} = 1.8 \text{ m}$			
Illustration 4.	A solution of ethanol in water is 1.54 molal. How much grams of it are there in 2500 g of the solvent.			
Solution:	Molality = 1.54 m; Weight of solvent = 2500 g; m = $\frac{(W_b) \times 1000}{(M_b) \times W_a} = 1.54 \frac{W_b \times 1000}{46 \times 2500}$; $W_b = 177.1$ g			
Illustration 5.	What volume of 95 % H_2SO_4 (density = 1.85 g cm ⁻³) and what mass of water must be taken to prepare 100 cm ³ of 15% solution of H_2SO_4 (density = 1.10 g cm ⁻³).			
Solution: Given solution: Let there be 100 g of solution, Weight of solute = 95 g; Density = 1.85 g c				
	Volume of solution = $\frac{\text{Mass}}{\text{Density}} = \frac{100}{1.85} = 54.04 \text{ ml}; M = \frac{(W_b) \times 1000}{(M_b) \times V_{(ml)}} = \frac{95 \times 1000}{98 \times 54.04} = 18 \text{ M}$			
	Required solution: Let there be 100 g of solution, Weight of solute = 15 g; Density = 1.10 g cm ⁻³ ;			
	Volume of solution = $\frac{\text{Mass}}{\text{Density}} = \frac{100}{1.10} = 90.91 \text{ ml}$ $M = \frac{(W_b) \times 1000}{(M_b) \times V_{(ml)}} = \frac{15 \times 1000}{98 \times 90.91} = 1.68 \text{ M}$			
Now if the required solution is to be prepared from the given solution then :				
	$M_1 n_1 V_1 = M_2 n_2 V_2; 18 \times V_1 = 1.68 \times 100$			
	$V_1 = 9.33 \text{ ml}$ [rest of volume is due to water add. = $100 - 9.33 = 90.67 \text{ ml}$]			

Vidyamandir Classes



PRACTICE QUESTION

- 1. Calculate the mole fraction of ethylene glycol (C2H6O2) in a solution containing 20% of C2H6O2 by mass. (Ans 0.068).
- 2. Calculate the molarity of a solution containing 5 g of NaOH in 450 mL solution. (0.278 mol dm⁻³)
- 3. Calculate molality of 2.5 g of ethanoic acid (CH3COOH) in 75 g of benzene. (Ans- 0.556 mol kg-1)
- Calculate (a) molality (b) molarity and (c) mole fraction of KI if the density of 20% (m/m) aqueous KI is 1.202 g mL-1.
 Ans. (a) 1.5 mol kg⁻¹ (b) 1.45 M (c) 0.0263
- 5. Calculate the molarity of each of the following solutions (a) 30 mL of 0.5 M H_2SO_4 diluted to 500 mL.

(b) 30 g of $Co(No_3)_2$.6H₂O in 4.3 L of solution.

Ans. (a) 0.03 M;(b)0.022 M

Saturated solution: The solution in which no more solute can be dissolved at the same temperature and pressure.

Solubility: The maximum amount of a solute that can be dissolved in a given volume of solution at a constant temperature and pressure is called its solubility.

FACTORS EFFECTING SOLUBILITY OF A SOLID IN LIQUID

(*i*) **Temperature :** The solubility of a solid in a liquid is significantly affected by temperature changes. This, being dynamic equilibrium, follow Le Chateliers Principle. In general, if in a nearly saturated solution, the dissolution

process is endothermic (Δ_{sol} H>0), the solubility should increase with rise in temperature and if it is exothermic

 $(\Delta_{sol} H \le 0)$ the solubility should decrease. These trends are also observed experimentally.

(*ii*) **Pressure:** Pressure does not have any significant effect on solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by change in pressure.

HENRY'S LAW

The law states that at a constant temperature the solubility of a gas in liquid is directly proportional to the pressure of the gas. The most commonly used form of the Henry's law state that "the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas(x) in the solution" and is expressed as:

 $p = K_{H}x$; Here K_{H} is the Henry's law constant.

From equation $p = K_H x$, we can say that higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid. K_H value for both N_2 and O_2 increases with an increase of temperature indicating that the solubility of gases increases with the decrease of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than in warm waters.

LIMITATIONS OF HENRY'S LAW

- (*i*) It is applicable at moderate temperature and pressure and falls when pressure used is too high and temperature used is too low.
- (*ii*) The gas should not get dissociated or associated when it is dissolved in the solvent.
- (*iii*) The solubility of the gas should not be high in the solvent NH₃, CO₂, HCl in water.
- (*iv*) The gas should not form a new species after reacting with the solvent when it is dissolved. For example, NH_3 does not follow Henry's law due to this reason.

APPLICATIONS OF HENRY'S LAW

- (*i*) In aerated soft drinks the carbon dioxide in soft drinks is sealded under high pressure to increase the solubility of CO₂ in it for desired taste.
- (ii) Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as *bends*, which are painful and dangerous to life. To avoid bends, as well as the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).
- (*iii*) At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as *anoxia*.

EFFECT OF TEMPERATURE

According to Le Chatelier's Principle, solubility should increase with the increase of temperature for endothermic processes ($\Delta_{sol} H > 0$) and should decrease with the increase of temperature for exothermic ($\Delta_{sol} H < 0$) processes. When dissolved, the gas molecules are present in liquid phase and the process can be considered similar to the condensation process. Heat is evolved in this process.

Illustration 6. H_2S , 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.

Solution: As the condition is given as STP ; \therefore p = 1 atm and Solubility = 0.195 m

$$X = \frac{m}{m + \frac{100}{Ma}} = \frac{0.195}{0.195 + \frac{1000}{18}} = \frac{0.195}{0.195 + 55.5} = \frac{0.195}{55.70} = 3.5 \times 10^{-3} = K_{\rm H} \times 3.5 \times 10^{-3};$$

$$K_{\rm H} = \frac{1}{3.5} \times 10^3 = 2.86 \times 10^2$$

Illustration 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 per ml of soda water when packed under 2.5 atm CO₂ pressure at 298K.

Solution:

1 atm = 101325 pa; \therefore 1.67 × 10⁸ pa = 1648.123 atm; K_{H} = 1.648 × 10³; $P = K_{H}X$; 2.5 = 1.648 × 10³ X;

$$X = \frac{2.5}{1.648 \times 10^3} = 1.5 \times 10^{-3}; X = \frac{\text{moles of CO}_2}{\text{moles of CO}_2 + \frac{1}{18}}; 1.5 \times 10^{-3} = \frac{\text{moles}}{\text{mol} + 0.055};$$

moles $= \frac{0.055}{665.67} = 8.3 \times 10^{-5} \text{ moles};$
Mass of CO₂ = $8.3 \times 10^{-5} \times 44 = 3.6 \times 10^{-3} \text{ g}$

PRACTICE QUESTIONS

- 1. If N_2 is bubbled through water at 293 K, how many milli moles of N₂ gas would dissolve in 1 litre of water. Assume N₂ exerts a partial pressure of 0.987 bar. Given the Henry's law constant for N₂ at 293 K is 76.48 kbar. Ans. 7.17 × 10⁻⁸
- 2. Calculate the concentration of CO_2 in a soft drink that is bottled with a partial pressure CO_2 of 4 atm over the liquid at 25°C. The Henry's law constant for CO_2 in water at 25°C is 3.1×10^{-2} mol/litre atm. Ans. 129 M
- 3. The Henry's law constant for oxygen dissolved in water is 4.34×10^4 atm at 25°C. If the partial pressure of oxygen in air is 0.2 atm under atmospheric conditions, calculate the concentration of dissolved oxygen in water in equilibrium with air at 25°C. Ans. Mole fraction of $O_2 = 4.6 \times 10^{-6}$ & Molar is 2.56 × 10⁻⁴ M
- 4. Calculate the solubility of H_2 in water at 25°C if its partial pressure above the solution is 1 bar. Given that Henry's constant for H_2 in water at 25°C is 71.18 kbar. Ans. 1.40 × 10⁻⁵
- 5. Henry's law constant for the molarity of methane in benzene at 298 K is 4.27×10^5 mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg. Ans. 1.78×10^{-3}

VAPOUR PRESSURE OF LIQUID SOLUTIONS

It is the Pressure exerted by vapours of the liquid on its liquid surface at equilibrium. Following are the important points regarding vapour presseure.

- 1. More volatile is the substance more will be the vapour pressure.
- 2. Lesser is the inter-molecular force of attraction between liquid molecules higher is the vapour pressure (as there is more volatile nature)
- **3.** Vapour Pressure of liquid is not considered as surface phenomenon. Although evaporation is a surface phenomenon and condensation occurs at surface.
- 4. Vapour pressure of liquid doesn't depend on size or shape of vessel.
- 5. Vapour Pressure of liquid depends on temperature. As the temperature increases the vapour pressure increases.

Let the total vapour pressure at this stage be p_{total} and p_1 and p_2 be the partial vapour pressures of the two component

1 and 2 respectively. These partial pressures are related to the mole fractions x_1 and x_2 of the two components 1 and 2 respectively. The quantitative relationship between them, known as the **Raoult's law**, states:

"For a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction."

Thus for component 1 $p_1 \propto x_1$ and $p_1 = p_1^0 x_1$ (Where $p_1^0 =$ Saturated vapour pressure.)

Similarly, for component 2 $p_2 = p_2^0 x_2$ (Where p_2^0 Saturated vapour pressure.)

According to Dalton's law of partial pressures $P_{total} = p_1 + p_2$

Substituting the values of p_1 and p_2 , we get $P_{total} = p_1 + p_2 = (1 - x_2) p_1^0 + x_2 p_2^0 = p_1^0 + (p_2^0 - p_1^0) x_2$ The composition of vapour phase in equilibrium with the solution is determined by the partial pressures of the components.

If y_1 and y_2 are the mole fractions of the components 1 and 2 respectively in the vapour phase, then using Dalton's law of partial pressures: $p_1 = y_1 p_{total}$; $p_2 = y_2 p_{total}$; In general $p_i = y_i p_{total}$

RAOULTS'S LAW AS A SPECIAL CASE OF HENRY'S LAW

If we compare the equations for Raoult's Law $(p_i = y p_{total})$ and Henry's law $(p = K_H x)$, we see that the partial pressure of the volatile component of gas is directly proportional to its mole fraction in solution. Only the proportionality constant K_H

differs from p_1^0 . Thus, Raoult's law becomes a special case of Henry's law in which $K_{\rm H}$ becomes equal to p_1^0 only if the solution is ideal and thats why Raoult's Law is applicable only to Ideal Solution whereas Henry's law is applicable to Non-ideal Solutions as well. A plot between the vapour pressure and the mole fraction of the solvent is linear.

Illustration 8. Benzene (C_6H_6) and Toluene (C_7H_8) form an ideal solution at 313K. The vapour pressures of pure Benzene and Toluene are 160 mmHg and 60 mmHg respectively. Calculate the partial pressures of Benzene and Toluene and total pressure over the following solutions:

- (*i*) Containing equal weights of benzene and toluene.
- (*ii*) Containing 1 mole of benzene and 4 moles of toluene
- (iii) Containing equal molecules of benzene and toluene.

Solution:

Illustration 9. The vapour pressure of benzene and toluene at 293 K are 75 mm and 22 mmHg respectively. 23.4 g of benzene and 64.4 g of toluene are mixed. If the two form an ideal solution, calculate the mole fraction of benzene in the vapour phase assuming that the vapour are in equilibrium with the liquid mixture at this temperature.

Solution:

Weight of Benzene = 23.4 g

(do it yourselft)

 $P_{\rm B}^{\circ} = 75 \, \rm mmHg$

Mol. Mass of Benzene = 78 g mol^{-1}

$$n_{\rm B} = \frac{\text{Weight in gm}}{\text{Molar mass}} = \frac{23.4}{78} = 0.3$$

$$X_{B} = \frac{n_{B}}{n_{B} + n_{T}} = \frac{0.3}{0.3 + 0.7} = 0.3$$

$$P_{B} = P_{B}^{\circ} \cdot X_{B} = 75 \times 0.3 = 22.5 \text{ mmHg}$$

$$P_{\text{total}} = P_{B} + P_{T} = 22.5 + 15.4 = 37.9 \text{ mmHg}$$

$$y_{B} = \frac{P_{B}}{P_{\text{total}}} = \frac{22.5}{37.9} = 0.59$$

Weight of Toluene = 64.4 gMol. Mass of Toluene = 92 g mol^{-1}

 $P_{T}^{\circ} = 22 \text{ mmHg}$

$$n_{T} = \frac{\text{Weight in gm}}{\text{Molar mass}} = \frac{64.4}{92} = 0.7$$

$$X_{T} = \frac{n_{T}}{n_{B} + n_{T}} = \frac{0.7}{0.3 + 0.7} = 0.7$$
$$P_{T} = P_{T}O. X_{T} = 22 \times 0.7 = 15.4 \text{ mmHg}$$

$$y_A = \frac{P_A}{P_{total}} = \frac{15.4}{37.9} = 0.41$$

IDEAL AND NON-IDEAL SOLUTIONS

Ideal Solutions : The solution which obey Raoult's law over the entire range of concentration are known as ideal solution. The ideal solutions have two other important properties. The heat of mixing of the pure component to form the solution is zero and the volume of mixing is also zero, *i.e.*, $\Delta_{mix} H = 0$; $\Delta_{mix} V = 0$

Non-ideal Solutions : When a solution does not obey Raoult's law over the entire range of concentration then it is called non-ideal solution. The vapour pressure of such a solution is either higher or lower than that predicted by Raoult's law. If it is higher, the solution exhibits positive deviation and if it is lower, it exhibits negative deviation from Raoult's law. If $p_{\text{solution}} > p_{\text{solvent}}$, the solution shows **positive deviation** and if $p_{\text{solution}} < p_{\text{solvent}}$, the solutions shows **negative deviation** from Raoult's law.

In case of positive deviation, solute-solvent (A–B) intermolecular forces are weaker than solvent-solvent (A–A) and solute-solute (B–B) intermolecular forces. So it is easier for solution (A–B) to escape than in pure state. This increases the vapour pressure and result in positive deviation. For example: Mixtures of ethanol and acetone, carbon disulphide and acetone, acetone-benzene, methyl alcohol-water, ethyl alcohol-water, carbon tetrachloride-chloroform, carbon tetrachloride-toluene show positive deviation.



In case of negative deviations from Raoult's law, the intermolecular attractive forces, between solvent-solvent (A-A) and solute-solute (B-B) are weaker than those between solvent-solute (A-B) and lead to negative deviations.

For examples: Mixtures of phenol-aniline, chloroform-diethyl ether, acetone-aniline, HCl-water, HNO₃-water, acetic acid-pyridine, etc.

AZEOTROPES

Some liquid mixtures, having definite composition, boil like pure liquid and are called azeotropic mixtures or azeotropes or constant boiling mixtures. The components of these mixtures can not be separated by fractional distillation.

- (*i*) **Minimum Boiling Azeotropes**: The solutions that show large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition, *e.g.* ethanol-water mixture containing a 95.4% ethanol boils at 351.5 K, chloroform-ethanol mixture with 6.8% ethanol, etc.
- (*ii*) Maximum Boiling Azeotropes: The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition, *e.g.* 68% nitric acid and 32% water by mass, with a boiling point 393.5 K, water-ethanol with 20.3% HCl.

COLLIGATIVE PROPERTIES

The properties of dilute solutions which are induced on addition of Non-volatile solute to a volatile solvent are called Colligative Properties. The properties that depend on the number of solute particles irrespective of their nature are relative to the total number of particles present in the solution.

- (*i*) Lowering of vapour pressure
- (*ii*) Depression in freezing point
- (*iii*) Elevation in boiling point
- (iv) Osmotic pressure

RELATIVE LOWERING OF VAPOUR PRESSURE

The vapour pressure of the solvent in solution is less than that of the pure solvent. The relation between vapour pressure of the solution, mole fraction and vapour pressure of the solvent is $p_1 = x_1 p_1^0$

 p_1 = vapour pressure of the solution; x_1 = mole fraction of the solute; p_1^0 = vapour pressure of the solvent

 $\frac{\Delta p_1}{p_1^0} = \frac{p_1^0 - p_1}{p_1^0} = x_2 = \frac{n_2}{n_1 + n_2} \cdot \frac{\Delta p_1}{p_1^0}$ is called relative lowering of vapour pressure and is equal to the mole fraction of the

 $\frac{w_{\scriptscriptstyle 2} \times M_{\scriptscriptstyle 1}}{M_{\scriptscriptstyle 2} \times w_{\scriptscriptstyle 1}}\,;$

ELEVATION OF BOILING POINT

It is seen that for dilute solutions the elevation of boiling point (T_b) is directly proportional to the molal concentration of the solute in a solution. Thus, $\Delta T_b \propto m$; $\Delta T_b = K_b m$

K_b is called Boiling Point Elevation Constant or Molal Elevation Constant. The unit of K_b is K kg mol⁻¹.

$$m = \frac{1000 \times w_2}{M_2 \times w_1} ; \quad \Delta \mathbf{T}_{\mathbf{b}} = \frac{\mathbf{K}_{\mathbf{b}} \times 1000 \times w_2}{\mathbf{M}_2 \times w_1}$$

DEPRESSION OF FREEZING POINT

A solution freezes when its vapour pressure equals the vapour pressure of the pure solid solvent. According to Raoult's law, when a non-volatile solid is added to the solvent its vapour pressure decreases and would become equal to that of solid solvent at lower temperature. Thus, the freezing point of the solvent decreases. Depression of freezing point $(T_{\rm f})$ for dilute solution (ideal solution) is directly proportional to molality *m* of the solution.

Or $T_{\rm f} \propto {\rm m}$; Or $T_{\rm f} = K_{\rm f} {\rm m}$; $\Delta T_{\rm f}^0 = T_{\rm f}^0 - T_{\rm f}$

The proportionality constant K_{t} , which depends on the nature of the solvent is known as **Freezing point depression** constant or Molal depression constant or Cryoscopic constant. The unit of K_t is K kg mol⁻¹.

$$\Delta T_{f} = \frac{K_{f} \times w_{2} \times 1000}{M_{2} \times w_{1}}; \qquad \qquad K_{f} = \frac{R \times M_{1} \times T_{f}^{2}}{1000 \times \Delta_{fis}H}; \qquad \qquad K_{b} = \frac{R \times M_{1} \times T_{b}^{2}}{1000 \times \Delta_{vap}H}$$

Here *R* and M_1 are the gas constant and molar mass of the solvent, respectively and T_f and T_b denote the freezing point and the boiling point of the pure solvent respectively in Kelvin. $\Delta_{fus}H$ and $\Delta_{vap}H$ are the enthalpies for the fusion and vapourisation of the solvent, respectively.

OSMOSIS AND OSMOTIC PRESSURE

When a solution is separated from the pure solvent by a semi-permeable membrane, it is observed that the solvent flows from the region of pure solvent into solution. The passage of solvent from pure solvent or from solution of lower concentration into solution of higher concentration through a semi-permeable membrane is called osmosis. The **osmotic pressure** of the solution at a given temperature may be defined as the excess hydrostatic pressure that builds up when the solution is separated from the solvent by a semi-permeable membrane. It is denoted by π .



DETERMINATION OF MOLAR MASS FROM OSMOTIC PRESSURE

In order to determine the molar mass of an unknown non-volatile compound, a known mass (say wg) of the compound is dissolved to prepare a known volume (say V litre) of solution and the osmotic pressure of the solution is determined. From this, the molecular mass of the compound is calculated as follows: According to Van't Hoff equation, M = wRT

 πV

CONDITIONS FOR GETTING ACCURATE VALUE OF MOLECULAR MASS

- (*i*) The solute must be non-volatile.
- (*ii*) The solution must be dilute. The solute should not undergo dissociation or association in the solution.

REVERSE OSMOSIS

If the pressure applied on the solution is greater than the osmotic pressure, then solvent starts passing from solution into solvent. This is called **reverse osmosis**, generally used for purification of sea water or hard water.





 w_1 = weight of solvent, M_1 = molar mass of solvent, w_2 = weight of solute, M_2 = molar mass of solute, R = Gas constant

ABNORMAL MOLAR MASSES

- Abnormal molar masses are observed when the solution is non-ideal, *i.e.* solution is not dilute.
- When the solution undergoes Dissociation/association in the solution.



Van't Hoff factor *i*, which accounts for the extent of association or dissociation, is the ratio of the experimental value of the colligative property to the calculated value of the colligative property.

i=	Normal molar mass	Observed colligative property	No. of moles of particles after association / dissociation
	Abnormal molar mass	Calculated colligative property	No. of moles of particles before association / dissociation

PRACTICE PROBLEM

- 1. An aqueous solution freezes at -0.186 °C ($K_{\rm f} = 1.86$ °; $K_{\rm h} = 0.512$ °). What is the elevation in boiling point? Ans. 0.051 °C
- 2. Calculate the amount of NaCl that must be added to one kilogram of water so that the freezing point is depressed by 3 K. (Given K_c for water = 1.86 K/m). Ans. 94.35 g
- 3. Ethylene glycol (molar mass = 62 g mol⁻¹) is a common automobile antifreeze. Calculate the freezing point of a solution containing 12.4 g of this substance in 100 g of water. Would it be advisable to keep this substance in the car radiator during summer? Given: K_r for water =1.86 K kg/mol, K_h for water =0.512 K kg/mol. Ans. -3.72°C
- Boiling point of water at 750mm Hg is 96.63°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. 23.44 mm Hg
- 5. A solution of a non-volatile solute in water freezes at -0.30° C. The vapour pressure of pure water at 298 K is 23.51 mm Hg and $K_{\rm f}$ for water is 1.86 degree/molal. Calculate the vapour pressure of this solution at 298 K. Ans.1.108 kg

SOLVED EXAMPLES

- 1. Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.
- Sol. 30% of benzene in carbon tetrachloride by mass means that Mass of benzene in the solution = 30g Mass of solution = 100g ;Mass of carbon tetrachloride = 100–30 g = 70 g ;Molar mass of benzene (C_cH_c) = 78 g mol⁻¹

Molar mass of CCl₄ = $12 + 4 \times 35.5 = 154$ g mol⁻¹; No of moles of benzene = $\frac{30}{78 \text{ g m o } l^{-1}} = 0.385$

No. of moles of CCI $_{4} = \frac{7 \ 0 \ g}{1 \ 5 \ 4 \ m \ m \ o \ l^{-1}} = 0 \ .4 \ 5 \ 5$; Mole fraction of benzene = 0.458

- 2. H_2S , toxic gas with rotten egg like smell, is used for qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant.
- Sol. Solubulity of H₂S gas = 0.195 m i.e. 0.195 mole in 1 kg of the solvent (water)

1 kg of the solvent (water) =
$$1000g = \frac{1000}{18g \text{ mol}^{-1}} = 55.55 \text{ moles}$$

. Mole fraction of H₂S gas in the solution
$$(x) = \frac{0.195}{0.195 + 55.55} = \frac{0.195}{55.745} = 0.0035$$

Pressure at STP = 0.987 bar; Applying Henry's law, $P_{H_2S} = K_H \times x_{H_2S}$ or $K_H = \frac{p_{H_2S}}{x_{H_2S}} = \frac{0.987 \text{ bar}}{0.0035} = 282 \text{ bar}.$

- 3. 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 CO₂ pressure at 298 K.
- **Sol.** $K_{H} = 1.67 \times 10^{8} Pa$, $p_{CO_{2}} = 2.5 atm = 2.5 \times 101325 Pa$; Applying Henry's law, $p_{CO_{2}} = K_{H} \times x_{CO_{2}}$

$$\therefore \qquad x_{\rm CO_2} = \frac{p_{\rm CO_2}}{K_H} = \frac{2.5 \times 101325 \, Pa}{1.67 \times 10^8 \, Pa} = 1.517 \times 10^{-3}, \quad i.e., \frac{n_{CO_2}}{n_{H_2O} + n_{CO_2}} \simeq \frac{n_{CO_2}}{n_{H_2O}} = 1.517 \times 10^{-3}$$

For 500 mL of soda water, water present $\simeq 500 mL = 500 g = \frac{500}{18} = 27.78$ mole; *i.e.*, $n_{H_2O} = 27.78$ mole

$$\therefore \frac{n_{CO_2}}{27.78} = 1.517 \times 10^{-3} \text{ or } n_{CO_2} = 42.14 \times 10^{-3} \text{ mole} = 42.14 = 42.14 \times 10^{-3} \times 44 \text{ g} = 1.854 \text{ g}.$$

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

Sol.
$$p_A = x_A \times p_A^0$$
; $p_B = x_B \times p_B^0 = (1 - x_A) p_B^0$; $P_{\text{Total}} = p_A + p_B = x_A p_A^0 + (1 - x_A) p_B^0 = p_B^0 + (p_A^0 - p_B^0) x_A$

Substituting the given values, we get $600 = 700 + (450 - 700)x_A$ or $250x_A = 100$ or $x_A = \frac{100}{250} = 0.40$

Thus, composition the liquid mixture will be x_A (mole fraction of A) =0.45, x_B (mole fraction of B)= 1-0.40 = 0.60

:.
$$p_A = x \times p_A^{0} = 0.40 \times 450 mm = 180 mm$$
, $p_B = x_B \times p_B^{0} = 0.60 \times 700 mm = 420 mm$ Mole fraction of A in the vapour phase $= \frac{p_A}{p_A + p_B} = \frac{180}{180 + 420} = 0.30$; Mole fraction of B in the vapour phase $= 1 - 0.30 = 0.70$.

- 5. Boilling point of water at 750 mm Hg is 96.63°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.
- Sol. Elevation in boiling point required (ΔT_b) = 100 –96.63°=3.37°Applying the formula, $M_2 = \frac{1000K_b w_2}{w_2 \Delta T_b}$ Ans- 1108.2
- 6. Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolved 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C.

Sol.
$$\pi = CRT = \frac{\pi}{V}RT$$
; $\pi = \frac{1}{185,000} \text{mol} \times \frac{1}{0.45L} \times 8.314 \times 10^3 \text{ Pa } \text{LK}^{-1} \text{mol}^{-1} \times 310 \text{K} = 30.96 \text{ Pa}.$

- 7. The partial pressure of ethane over a saturated solution containing 6.56×10^{-2} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial pressure of the gas ?
- **Sol.** Applying the relationship $m = K_{H} \times p$; In the first case, $6.56 \times 10^{-2} \text{ g} = K_{H} \times 1 \text{ bar or } K_{H} = 6.56 \times 10^{-2} \text{ g bar}^{-1}$

In the second case, 5.00×10^{-1} g = $(6.56 \times 10^{-2} \text{ g bar}^{-1}) \times \text{p or } \text{p} = \frac{5.00 \times 10^{-2} \text{g}}{6.56 \times 10^{-2} \text{g bar}^{-1}} = 0.762$ bar.

Chemistry/Class XII

- 8. An aqueous solution of 2% non volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent, What is the molecular mass of the solute ?
- Sol. Vapour pressure of pure water at the boiling point $(p^0) = 1$ atm = 1.013 bar; Vapour pressure of solution $(p_s) = 1.004$ bar

$$\frac{p^{\circ} - p_s}{p^{\circ}} = \frac{n_2}{n_1 + n_2} \simeq \frac{n_2}{n_1} = \frac{w_2 / M_2}{w_1 / M_1} = \frac{w_2}{M_2} \times \frac{M_1}{w_1} \quad \therefore \frac{(1.013 - 1.004)}{1.013 bar} = \frac{2g}{M_2} \times \frac{18g \text{ mol}^{-1}}{98g} \text{ or } M_2 = 41.35 \text{ g mol}^{-1}$$

- 9. Heptane and octane form ideal solution . At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa respectively . What will be the vapour pressure of a mixture of 26.0 g of heptane and 35.0 g of octane ?
- **Sol.** x (octane) = 1 0.456 = 0.544
- 10. The vapour pressure of water is 12.3 k Pa at 300 K. Calculate the vapour pressure of 1 molal solution of a solute in it .

Sol. ... Mol fraction of solute
$$=\frac{1}{1+55.5} = 0.0177$$
; Now, $\frac{p^{\circ}-p_s}{p^{\circ}} = x_2$, *i.e.*, $\frac{12.3-p_s}{12.3} = 0.0177$ or $p_s = 12.08$ k Pa.

- 11. Calculate the mass of a non volatile solute (molar mass 40 g mol⁻¹) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%. Ans- 73.43 kPa.
- 12. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K. Calculate the freezing point of a 5% glucose in water if freezing point of pure water is 273.15 K. Ans 269.06 K
- 13. Two elements A and B form compounds having molecular formula AB_2 and AB_4 . When dissolved in 20 g of benzene (C_6H_6), 1 g of AB_2 lowers the freezing point by 2.3 K whereas 1.0 g of AB_4 lowers it by 1.3 K. The molal depression constant for benzene is 5.1 K kg mol⁻¹. Calculate atomic masses of A and B.

Sol.
$$M_2 = \frac{1000K_f w_2}{w_1 \times \Delta_c}$$
; $M_{AB_2} = \frac{1000 \times 5.1 \times 1}{20 \times 2.3} = 110.87 \text{ g mol}^{-1}$, $M_{AB_4} = \frac{1000 \times 5.1 \times 1}{20 \times 1.3} = 196.15 \text{ g mol}^{-1}$

Suppose atomic masses of A and B are 'a' and 'b' respectively. Then Molar mass of $AB_2 = a + 2 b = 110.87 \text{ g mol}^{-1}$

Molar mass of AB₄ = $a + 4b = 196.15 \text{ g mol}^{-1}$; Thus, Atomic mass of A = 25.59 u, atomic mass of B = 42.64 u

- 14. Based on solute-solvent interactions, arrange the following in order of increasing solubility in noctane and explain. Cyclohexane, KCI, CH₃OH,CH₃CN
- Sol. (i) Cyclohexane and n-octane both are non-polar. Hence, they mix completely in all propotions.
 - (ii) KCI is an ionic compound while n-octane is non-polar. Hence, KCI will not dissolve at all in *n*-octane (iii) CH₃OH and CH₃CN both are polar but CH₃CN is less polar than CH₃OH. As the solvent is non-polar, CH₃CN will dissolve more than CH₃OH in *n*-octane. Thus, the order of solubility will be KCI < CH₃OH < CH₃CN < Cyclohexane.
- 15. If the solubility product of CuS is 6×10^{-16} , calculate the maximum molarity of CuS in aqueous solution.
- Sol. Maximum molarity of CuS in aqueous solution = Solubility of CuS in mol L^{-1} . If S is the solubility of CuS in mol L^{-1} ,

then
$$\operatorname{CuS} \rightleftharpoons Cu^{2+} + S_s^{2-}, K_{sp} = [Cu^{2+}][S^{2-}] = S \times S = S^2, S = \sqrt{6 \times 10^{-16}} = 2.45 \times 10^{-8} \operatorname{mol} \mathrm{L}^{-1}.$$

- 16. The depression in freezing point of water observed for the same amount of acetic acid trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.
- Sol. The depression in freezing points are in the order :
 - acetic acid < trichloroacetic acid < trifluoroacetic acid

Fluorine, being most electronegative, has the highest electron withdrawing inductive effect. Consequently, Trifluoroacetic acid is the strongest acid while acetic acid is the weakest acid. Hence, trifluoroacetic acid ionizes to the largest extent while acetic acid ionizes to the minimum extent to give ions in their sloutions in water. Greater the ions produced, greater is the depression in freezing point. Hence, the depression in freezing point is maximum for the fluroacetic acid amd minimum for acetic acid.

Hand-Out Chemistry Chapter 2 : Solution



17. Calculate the depression in the freezing point of water when 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water. $K_a = 1.4 \times 10^{-3}$, $K_r = 1.86$ K kg mole⁻¹.

Sol. Molality of the solution
$$(m) = \frac{8.16 \times 10^{-2} mole}{250g} \times 1000g = 0.3264$$

If α is the degree of dissociation of CH₃CH₂CHClCOOH, then

1

 $CH_{3}CH_{2}CHCICOOH \rightleftharpoons CH_{3}CH_{2}CHCICOO^{-} + H^{+}$ Initial conc. C mol L⁻¹ 0 0 At eqm. C (1-\alpha) C \alpha C \alpha

:
$$K_a = \frac{C\alpha.C\alpha}{C(1-\alpha)} \simeq C \alpha^2 \text{ or } \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} = 0.065$$

$$CH_3CH_2CHCICOOH \implies CH_3CH_2CHCICOO^- + H^+$$

Initial moles

Moles at eqm. $1 - \alpha$ α Total = 1 + α

:.
$$i = \frac{1+\alpha}{1} = 1+\alpha = 1+.065 = 1.065$$
; $\Delta T_f = i K_f m = (1.065)(1.86)(0.3264) = 0.65^\circ$.

- 18. 19.5 g of CH₂FCOOH is dissolved in 500 g of water. The depression in the freezing point observed is 1.0°C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid. K_{ℓ} for water is 1.86 K kg mol⁻¹.
- **19.** Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water. Ans- 17.44 mm.
- 20. Henry's law constant for the molarity of methane in benezene at 298 K is 4.27×10^5 mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg. Ans- 1.78×10^{-3} .
- 21. 100 g of liquid A (molar mass 140 g mol⁻¹) was dissolved in 1000 g of liquid B (molar mass 180 g mol⁻¹)

The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liqued A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 torr. Ans- 32 torr.

- 22. Benzene and toluene form ideal solution over the entire range of composition. The vapour pressures of pure benzene and toluene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in the vapour phase if 80 g of benzene is mixed with 100 g of toluene. Ans- 0.60
- 23. The air is a mixture of a number of gases. The major components are oxygen and nitrgen with approximate proportion of 20% is to 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K, if the Henry's law constants for oxygen and nitrogen are 3.30×10^7 mm and 6.51×10^7 mm respectively, calculate the composition of these gases in water.
- Sol. Total pressure of air in equilibrium with water = 10 atm; As air contains 20% oxygen and 79 nitrogen by volume,

$$\therefore \text{ Partial pressure of oxygen } (Po_2) = \frac{20}{100} \times 10 \text{ atm} = 2 \text{ atn} = 2 \times 760 \text{ mm} = 1520 \text{ mm}$$

Partial pressure of nitrogen $(p_{N_2}) = \frac{79}{100} \times 10 \text{ atm} = 7.9 \text{ atm} = 7.9 \times 760 \text{ mm} = 6004 \text{ mm}$

$$p_{O_2} = K_H \times x_{O_2}$$
 or $x_{O_2} = \frac{p_{O_2}}{K_H} = \frac{1520 \text{mm}}{3.30 \times 10^7 \text{mm}} = 4.61 \times 10^{-5}$; $x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{6004 \text{mm}}{6.51 \times 10^7 \text{mm}} = 9.22 \times 10^{-5}$.

Chemistry/Class XII

- 24. Determine the amount of $CaCl_2$ (i = 2.47) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27° C. Ans- 3.42 g.
- 25. Determine the osmotic pressure of a solution prepared by dissolved 25 mg of K_2SO_4 in 2 litre of water at 25°C, assuming that it is completely dissociated.
- **Sol.** As K_2SO_4 dissociates completely as $K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$; *i.e.*, ions produced = 3, $\therefore i = 3$

:.
$$\pi = i \text{ CRT} = i \frac{n}{V} RT = i \times \frac{w}{M} \times \frac{1}{V} RT = 3 \times \frac{0.025 \text{g}}{174 \text{g mol}^{-1}} \times \frac{1}{2L} \times 0.0821 \text{ L atm } \text{K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} = 5.27 \times 10^{-3} \text{ atm}$$

PREVIOUS YEAR QUESTIONS 2012

- 1. (a) Define the following terms:
 - (i) Mole fraction;
 - (ii) Ideal solution.
 - (b) 15.0 g of an unknown molecular material is dissolved in 450 g of water. The resulting solution freezes at -0.34 °C. What is the molar mass of the material? (K_c for water = 1.86 K kg mol⁻¹)

OR

- (a) Explain the following:
 - (i) Henry's law about dissolution of a gas in a liquid.
 - (ii) Boiling point elevation constant for a solvent.
- (b) A solution of glycerol ($C_3H_8O_3$) 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 if glycerol was dissolved to make this solution? (Kb for water = 0.512 K kg mol⁻¹)

2011

- 1. (i) Raoult's law in its general from in reference to solutions. (ii) Henry's law about partial pressure of a gas in a mixture.
- 2. What mass of NaCl must be dissolved in 65.0 g of water to lower the freezing point of water by 7.50°C? The freezing point depression constant (K_p) for water is 1.86° C/m. Assume Van't Hoff factor for NaCl is 1.87. (Molar mass of NaCl = 58.5 g)

2010

- 1. Define the terms, 'osmosis' and 'osmotic pressure'. What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of molar masses of solutes in solutions?
- 2. Describe the role of the following : (*i*) NaCN in the extraction of silver from a silver ore (*ii*) Iodine in the refining of titanium (*iii*) Cryolite in the metallurgy of aluminium.

2009

- 1. Differentiate between molality and molarity of a solution. What is the effect of change in temperature of a solution on its molality and molarity.
- 2. 100 mg of a protein is dissolved in just enough water to make 10.0 mL of solution. If this solution has an osmotic pressure of 13.3 mm Hg at 25° C, what is the molar mass of the protein. (R = 0.0821 L atm mol⁻¹ K⁻¹ and 760 mm Hg = 1 atm.)
 Ans. 13980

2008

- 1. State Henry's law correlating the pressure of a gas and its solubility in a solvent and mention two applications of the law. (2 marks)
- 2. Calculate the temperature at which a solution 54 g of glucose, $(C_6H_{12}O_6)$, in 250 g of water will freeze. (K_f for water = 1.86 K mol⁻¹kg). (2 marks)

Hint:
$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1}$$
 Ans: 102.23°C.

Chemistry/Class XII