LIQUID SOLUTION

Osmosis

Spontaneous flow of solvent molecules through a semipermeable membrane from a pure solvent to the solution (or from a dilute solution to a concentrated solution) is termed as osmosis.



Osmotic Pressure (π): The hydrostatic pressure built up on the solution which just stops osmosis. Alternatively, it may be defined as the pressure which must be applied to the concentrated solution in order to stop osmosis.

For dilute solutions $\pi = CRT = h\rho g$ (hydrostatic pressure)

Where C is the total molar concentration of all the free species present in the solution, h is the height developed by the column of the concentrated solution and ρ is the density of the solution in the column. On the basis of osmotic pressure, *the solutions can be classified in three classes*.

- (a) Hypertonic solution: When two solutions are being compared, then the solution with higher osmotic pressure is termed as hypertonic.
- (b) Hypotonic solution: When two solutions are being compared, then the solution with lower osmotic pressure is termed as hypertonic.
- (c) Isotonic solutions: Two solutions having same osmotic pressures at same temperature. (This implies $C_1 = C_2$).
- **Note:**-Osmotic pressures can be determined quite accurately, hence it is used in the determination molecular weights of large proteins and similar substances.
- **Reverse Osmosis:** If a pressure greater than the osmotic pressure is applied on the concentrated solution, the solvent starts to flow from concentrated solution to dilute solution (or pure solvent). This is reverse osmosis. One of its chief uses is desalination of sea water to get pure drinking water.

Examole: Calculate osmotic pressure of 5% solution of cane sugar (sucrose) at 15°C.

Solution: $m = \text{mol. mass of sucrose } (C_{12}H_{22}O_{11}) = 342$ w = 5g V = -100 mL = 0.1 litre S = 0.082, T = (15 + 273) = 288 KApplying the equation $PV = \frac{W}{m} \text{ ST}$, $P = \frac{5}{342} \times \frac{1}{0.1} = 0.082 \times 288 = 3.453$] Example: Consider a vertical tube of corss-sectional area of 1cm². The bottom of the tube is closed with a semipermeable membrane and 1 g glucose is placed in the tube. The closed end of the tube is immersed in pure water. What will be the height of the liquid level in the tube at equilibrium? The density of solution may be taken as 1g/cm². What is the osmotic pressure at equilibrium at 25°C? Assume negligible depth of immersion of tube.

 $= 1 \text{ cm}^2$

Solution: Let height in tube = h cm

$$V = (h \times 1) \text{ cm}^{3} \qquad \Box \text{ Cross-sectional area}$$

$$\pi V = nRT$$

$$\pi \times \left(\frac{h \times 1}{1000}\right) = \frac{1}{180} \times 0.0821 \times 298$$

$$\pi = \frac{134.92}{h} \text{ atm}$$

$$\pi = h \times d \times g$$

$$\frac{134.92}{h} = \frac{h \times 1}{100} \times \frac{9.8}{101.325} \qquad 1 \text{ atm} = 101.325 \text{ KP}_{a}$$

$$h = 375 \text{ cm} = 3.75 \text{ m}$$

$$\pi = h \times d \times g = 3.75 \times 1 \times 9.8 \qquad = 36.7 \text{ KP}_{a}$$
[Ans. 3.75 m; 36.7 KP_a]

Example: A 5% soltuion of cane sugar is isotonic with 0.877% soltuion of urea. Calculate the molecular mass of urea if molecular mass of cansugar is 342.

Solution: Let the molecular mass of urea be m₂

Molarity of sugar = $\frac{w_1}{m_1 \times V_1} = \frac{5}{342 \times 0.1}$ Molarity of urea = $\frac{w_2}{m_2 \times V_2} = \frac{0.877}{m_2 \times 0.1}$

For isotonic solutions,

$$\frac{w_1}{m_1 \times V_1} = \frac{w_2}{m_2 \times V_2} \implies \frac{5}{342 \times 0.1} = \frac{0.877}{m_2 \times 0.1}$$
$$m_2 = \frac{0.877 \times 342}{5} = 59.987$$

Practice Problem I

- Q.1 A solution containing 4 gm of a non-volatile organic solute per 100 ml was found to have an osmotic pressure equal to 500 cm of mercury at 27°C. The molecular weight of solute is (A) 14.97 (B) 29.44 (C) 149.7 (D) 137.2
 Q.2 The osmotic pressure of decimolar solution of glucose at 30°C is -
- (A) 24.88 atm (B) 2.48 atm (C) 12.44 atm (D) 124.4 atm

Q.3	A solution containing 8.6 gm urea in one litre was found to be isotonic with a 5% (wt/vol) solution of an organic volatile solute. The molecular weight of solute is -						
	(A) 348.9	(B) 34.89	(C) 861.2	(D) 86.12			
Q.4	The osmotic pressure and 50 ml of 1.6% se (A) 10.56 atm	e of a solution containin olution (w/v) of cane-s (B) 8.98 atm	ng 100 ml of 3.4% solu sugar (m. wt 342) at 27 (C) 17.06 atm	tion (w/v) of urea (m. wt. 60) ^o C is - (D) 9.70 atm			
Q.5	Two solutions each in 100 mL having 4 g glucose and 10 g sucrose respectively. How much urea should be added to one of them in order to make them isotonic ?(A) 0.4218 g urea in glucose solution (C) 0.72 g urea in sucrose solution(B) 0.77 g urea in glucose solution (D) 0.421 g urea in sucrose solution						
Q.6	5 g of a polymer of molecular weight 50kg mol ⁻¹ is dissolved in 1 dm ³ solution. If the density of this solution is 0.96 kg dm ⁻³ at 300 K, the height of solution that will represent this pressure is						
	(A) 28.13 mm	(B) 20.85 mm	(C) 26.52 mm	(D) 24.94 mm			
Q.7	100 mL aqueous solution of glucose with osmotic pressure 1.2 atm at 25°C is mixed with 300 mL aqueous solution of urea at 2.4 atm at 25°C. Osmotic pressure of the mixture is - (A) 1.37 atm (B) 2.59 atm (C) 1.85 atm (D) 2.13 atm						
Q.8	10 g of solute A and 20 g of solute B are present in 500 mL of solution. The solution has the same osmotic pressure as 6.67 g of A and 30 g of B present in same volume of solution at same temperature. The ratio of molar masses of solute A and B will be - (A) 0.25 (B) 0.66 (C) 0.33 (D) 0.75						
Q.9	At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Find out the extent of dilution (A) 5 (B) 2.5 (C) 1.25 (D) 6.5						
Q.10	The relation ship between osmotic pressure at 273 K, when 10 gm glucose (P_1), 10 gm urea (P_2) and 10 gm sucrose (P_3) are dissolved in 250 ml of water is						
0.11	$(\mathbf{r}_{1})_{1} - \mathbf{r}_{2} - \mathbf{r}_{3} = (\mathbf{r}_{1})_{1} - \mathbf{r}_{2} = (\mathbf{r}_{1})_{2} - \mathbf{r}_{1} - \mathbf{r}_{3} = (\mathbf{r}_{1})_{1} - \mathbf{r}_{3} = (\mathbf{r}_$						
Q.11	what oshiouc pressure would the 1.25 motal sucrose solution exhibit at 25° C? The density of this solution is 1.34 g/mL.						
	(A) 28.70 atm	(B) 30.22 atm	(C) 21.72 atm	(D) 24.55 atm			
Q.12	The osmotic pressure of blood is 8.21 atm at 37°C. How much glucose is used per lit for an intravenous injection that is to isotonic with blood ? (A) 180 gm (B) 342 gm (C) 58.06 gm (D) 55.55 gm						
Q.13	Osmotic pressure of insulin solution at 298 K is found to be 0.0072 atm. Hence, height of water column due to this pressure is [given d (Hg) = 13.6 g/mL] – (A) 0.760 mm (B) 70.28 mm (C) 74 mm (D) 760 mm						
Q.14	At certain temperature, the osmotic pressure of an aqueous solution of urea was found to be 405 mm. How many times the solution should be diluted in order to exhibit the osmotic pressure of 81 mm at the same temperature ?						
0.15	If democratics ' C						
Q.15	It depression in freezing point is 0.93° C then the osmotic pressure of aqueous solution of the given non-electrolyte at 27°C is - [Given : K _f for water = 1.86 K kg mol ⁻¹ & molality is equal to molarity] (A) 12.3 atm (B) 1.23 atm (C) 6.15 atm (D) 2.46 atm						

Abnormal Molecular Mass

Vapour pressure lowering, boiling point elevation, freezing point depression and osmotic pressure are colligative properties which depend upon the fraction of solute and solvent particles in solution and not upon the chemical nature of the solute. If solute molecules dissociates in solution, there are more particles in solution and therefore, lowering of vapour pressure shows an increased effect.

 $\operatorname{NaCl}_{(s)} \rightleftharpoons \operatorname{Na}_{(aq)}^{+} + \operatorname{Cl}_{(aq)}^{-}$

If the solute molecules associates in solution, there are less particles in solution, and therefore lowering of vapour pressure shows a decreased effect.

 $nAB \rightleftharpoons (AB)_n$ $2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$

- **The molecular mass of a solute is inversely proportional to its molality.** If colligative molality is 2 m, the calculated molecular mass is one-half of the actual molecular mass of the solute. If colligative molality is 3 m, the calculated molecular mass is one third of the actual molecular mass of the solute. The molecular mass of benzoic acid is 122 g/mol. But the molecular mass of benzoic acid dissolved in benzene is found to be 244 g/mol by using a colligative property. Benzoic acid associates to form a dimer and therefore its colligative molality is one-half of the molality of benzoic acid. As molecular mass of a solute is inversely proportional to molality, the molecular mass of benzoic acid determined using a colligative property is double the actual molecular mass of benzoic acid. We can summarize the results as:
- 1. **The extent of dissociation and colligative property.** A solute dissociates completely or partially in solution makes available more particles than would otherwise be present in solution and therefore, a colligative property shows an increased effect. For example, molecular masses obtained of strong acids, bases and salts are much less than their normal values. As an example, one particle of potassium chloride on dissociation in water gives two particles, K⁺ and Cl⁻ and therefore, the molecular mass obtained by a colligative property is half of its normal molecular mass.

$$\underset{\substack{l \text{ mol}}{K^+Cl^-_{(s)}}+nH_2O \longrightarrow K^+_{(aq)}+Cl^-_{(aq)}$$

- 2. The extent of association and colligative property: A solute that associates in solution provides less particles that would otherwise be present in solution and therefore, the colligative property shows the decreased effect. For example, benzoic acid in benzene is found to have molecular mass which is just twice its normalmolecular mass.
- It is found that compounds which are capable of forming hydrogen bonds, e.g., phenols, carboxylic aids, alcohols: because of association show decreased effect of colligative property.



Van't Hoff Factor

In 1886, Van't Hoff, Jacobus Henricus (Dutch chemist, 1859,-1911) introduced a factor 'i' known as Van't Hoff factor to express the extent to association or dissociation of a solute in solution. It can be calculated as:

number of solute particles dissolved

 $= \frac{\text{Observed colligative property}}{\text{normal colligative property}} = \frac{\text{observed molality}}{\text{normal molality}} = \frac{\text{normal molecular weight of solute}}{\text{observed molecular weight of solute}}$

The Van't Hoff factor for a solute can be calculated by the following modified equations:

(i)
$$\frac{P_A^0 - P_A}{P_A^0} = i X_B$$
 (ii) $\Delta T_f = i K_f m$ (iii) $\Delta T_b = i K_b m$ (iv) $\pi = i CRT$

where C is molarity of the solution.

Note: For non-electrolytes; i = 1

For electrolytes; i > 1 (If solute particles undergo Dissociation in the solution) i < 1 (If solute particles undergo Association in the solution)

Application of Van't Hoff Factor:

i) Calculation of Degree of Dissociation of solute particles:

A_n	, mA	
No. of moles dissolved	1 mol	0
No. of moles after dissociation	$1-\alpha$	nα
Total number of moles present in solution	$=(1-\alpha)+n\alpha$	

Van't Hoff factor, $i = \frac{Moles \text{ of solute actually present in solution}}{Moles \text{ of solute dissolved}}$

$$=\frac{(1-\alpha)+n\alpha}{1}=1+(n-1)\alpha \quad \text{or} \quad \alpha=\frac{i-1}{n-1}$$

ii) Calculation of Degree of Association of solute particles: Let n moles of the solute, A, associate to form (A)_n. If α is the degree of association.

$nA \iff A_n$		
No. of moles dissolved	1 mol	0
No. of moles after dissociation	$1 - \alpha$	α/n

Total number of moles present in solution $= (1 - \alpha) + \alpha/n$

$$i = \left[1 - \alpha \left(1 - \frac{1}{n}\right)\right]$$
 Hence $\alpha = \frac{i-1}{\frac{1}{n}-1} = (i-1) \times \frac{n}{1-n}$

Example: A solution is prepared by dissolving 26.3g of $CdSO_4$ in 1000g water. The depression in freezing point of solution was found to be 0.284K. Calculate the Van't Hoff factor. The cryoscopic constant of water is 1.86K kg solvent mol⁻¹- solute.

Solution: Molecular mass $CdSO_4 = 112.4 + 32 + 4 \times 16 = 208.4 \text{ g/mol}$

> Mass CdSO₄ $Molality CdSO_4 = \overline{Molecular mass CdSO_4 \times Mass solvent in kg}$

$$=\frac{26.3g}{(208.4g/mol)\times\left(\frac{1000}{1000}kg\right)}=0.216m$$

$$\Delta T_{f} = iK_{f}m$$
 or $i = \frac{\Delta T_{f}}{K_{f}m} = \frac{0.284K}{1.86K/m \times 0.126m} = 1.21$

Example. Three particles of a solute, A, associate in benzene to form species A, Calculate the freezing point of 0.25 molal solution. The degree of association of solute A is found to be 0.80. the freezing point of benzene and its cryoscopic constant are 5.5°C and 5.12 Km⁻¹ respectively.

Solution:

$$\begin{array}{cccc} 3A & \longrightarrow & A_{3} \\ \text{No. of moles dissolved} & 3 & 0 \\ \text{No. of moles after dissociation} & m(1-\alpha) & m\alpha/3 \\ \text{Total moles present after dissociation} \end{array}$$

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$$= m(1-\alpha) + m\frac{\alpha}{3} = m\left(1-\alpha + \frac{\alpha}{3}\right) = m\left(1-\frac{2\alpha}{3}\right) = 0.25m\left\lfloor\frac{3-2\times0.8}{3}\right\rfloor = 0.177m$$

$$\Delta T_{f} = K_{f}m \quad \text{or} \quad T_{f}^{0} - T_{f} = 5.12 \text{ Km}^{-1} \times 0.117 \text{ m} = 0.6$$

$$T_{f}^{0} = T_{f}^{0} - 0.6^{\circ}\text{C} = 5.5^{\circ}\text{C} - 0.6^{\circ}\text{C} = 4.9^{\circ}\text{C}$$

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Practice Problem II

Q.1 A pentimolal solution of potassium chloride freezes at -0.68°C. If K, for H₂O is 1.86, the degree of dissociation of KCl is -(A) 75% (B) 83% (C) 65% (D) 92% Q.2 The depressions in freezing point of 1 M urea, 1 M glucose and 1 M NaCl are in the ratio : (A) 1 : 2 : 3 (B) 3 : 2 : 2 (C) 1 : 1 : 2 (D) none of these **Q.3** An electrolyte A gives 3 ions and B is a non-electrolyte. If 0.1 M solution of B produces an osmotic pressure P, then 0.05 M solution of A will produce an osmotic pressure, assuming that the electrolyte is completely ionised. (B) P (C) 0.5 P (D) 0.75 P (A) 1.5 P 0.4 Which is the correct relation between osmotic pressure of 0.1 M NaCl solution and 0.1 M Na_2SO_4 solution ? (A) the osmotic pressure of Na₂SO₄ is less than NaCl solution the osmotic pressure of Na₂SO₄ is more than NaCl solution **(B)** (C) both have same osmotic pressures none of the above (D) **Q.5** Which one of the following pairs of solutions will be expected to be isotonic under the same temperature? (A) 0.1 M urea and 0.1 M NaCl (B) 0.1 M urea and 0.2 M MgCl₂ (C) 0.1 M NaCl and 0.1 M Na_2SO_4 (D) 0.1 M Ca(NO₃)₂ and 0.1 M Na₂SO₄

(A) 0.95 (B) 0.97 (C) 0.94 (D) 0.96 Q.7 What is the freezing point of a solution containing 8.1 g HBr in 100 g water, to be 90% ionised. ? $[K_r$ for water = 1.86 K kg mol ⁻¹]	assuming the acid					
Q.7 What is the freezing point of a solution containing 8.1 g HBr in 100 g water, to be 90% ionised. ? [K _f for water = $1.86 \text{ K kg mol}^{-1}$]	assuming the acid					
(A) 0.85° C (B) -3.53° C (C) 0° C (D) -0.35°						
Q.8 The molal freezing point constant for water is 1.86 K kg mol ⁻¹ . Therefore, th	e freezing point of					
$\begin{array}{c} 0.1 \text{ M NaCl solution in water is expected to be :} \\ (A) -1.86^{\circ}\text{C} \\ (B) -0.186^{\circ}\text{C} \\ (C) -0.372^{\circ}\text{C} \\ (D) +372^{\circ}\text{C} \\ (D)$	2ºC					
 Q.9 Select correct statement : (A) b. p. of 1 molal NaCl solution is twice that of 1 molal sucrose solution (B) b. p. elevation of 1 molal glucose solution is half of the 1 molal KCl (C) b.p. is a colligative property (D) all of the above 	on solution					
Q.10 Two solution of KNO ₃ and CH ₃ COOH are prepared separately molarity of osmotic pressure are $P_1 \& P_2$. The correct relationship between the osmotic p	both in 0.1 M and pressure is -					
(A) $P_2 > P_1$ (B) $P_1 > P_2$ (C) $P_1 = P_2$ (D) $\frac{P_1}{P_1 + P_2}$	$\frac{P_2}{P_2} + \frac{P_2}{P_1 + P_2}$					
Q.11 A 5.8% wt/vol. NaCl solution will exert an osmotic pressure closest to which o	ne of the following					
 (A) 5.8% (wt/vol) sucrose solution (B) 5.8% (wt/vol) glucose solution (C) 2 molal sucrose solution (D) 1 molal glucose solution 	tion					
Q.12 How many grams of NaBr must be added to270 gm of water to lower the v 3.125 mm Hg at temperature at which vapour pressure of water is 50 mm Hg. Assur of NaBr	vapour pressure by me 100% ionisation					
(A) 51.5 gm (B) 103 gm (C) 75 gm (D) 37.5	gm					
Q.13 Sea water is found to contain NaCl & MgCl ₂ . If NaCl is 80% ionised and Mg then van't Hoff factor is - (A) 1.3 (B) 5.0 (C) 3.3 (D) 3.8	Cl_2 is 50% ionised					
O 14 The f p of a 0.08 molal solution of NaHSO is -0.372° C. The dissociation const	ant for the reaction					
$HSO_4^{-} \longrightarrow H^+ + SO_4^{2-} ; \text{ is - } [K_f \text{ for water} = 1.86^{\circ}C]$						
(A) 2×10^{-4} (B) 4×10^{-4} (C) 2×10^{-2} (D) 4×10^{-2}	10-2					
Q.15 If the observed and normal osmotic pressures of a 1% NaCl solution are 5.75 degree of dissociation of NaCl is – (A) 0.9 (B) 1.0 (C) 0.57 (D) 0.3	If the observed and normal osmotic pressures of a 1% NaCl solution are 5.75 and 3.00 atm, the degree of dissociation of NaCl is $-$					
 Q.16 0.01 M solution of KCl and BaCl₂ are prepared in water. The freezing point of -2°C. What freezing point would you expect for BaCl₂ solution – 	0.01 M solution of KCl and BaCl ₂ are prepared in water. The freezing point of KCl is found to be -2° C. What freezing point would you expect for BaCl ₂ solution –					
(A) -5° C (B) -4° C (C) -3° C (D) -2° C						
Q.17 The elevation in boiling point of a solution of 10 g of a binary electrolyte (mo in 100 of water is ΔT_{b} . The value of K_{b} for water is –	olecular mass 100)					
(A) $\frac{\Delta T_{b}}{2}$ (B) 10 (C) $10\Delta T_{B}$ (D) $\frac{\Delta T_{b}}{10}$	-					
Q.18 Van't Hoff factors are x, y, z in the case of association, dissociation and no ch Increasing order is - (A) $x < y < z$ (B) $x = y = z$ (C) $y < x < z$ (D) $x < z$	nange respectively. z < y					

Q.19	1 mole each of following solutes are taken in 5 moles water,(i) NaCl(ii) K_2SO_4 (iii) Na_3PO_4 (iv) glucoseAssuming 100% ionisation of the electrolyte, relative decrease in V. P. will be in order(A) i < ii < iii < iv(B) iv < iii < ii < i(C) iv < i < ii < iii(D) equal					der			
Q.20	A 0.002 molar solution of NaCl having degree of dissociation of 90% at 27°C has osmotic pressure								
	(A) 0.94	bar	(B) 9.4 bar	(C) 0.09	4 bar	(D) 9.4×10^{-4} ba	ar		
Q.21	At 20°C, the vapour pressure of 0.1 M solution of urea is 0.0311 mm less than that of water and the vapour pressure of 0.1 M solution of KCl is 0.0574 mm less than that of water. The apparent degree of dissociation of KCl at this dilution is -								
Q.22	The freezing point of a solution of 20.5 g NH_4Br in 100 g of water is -6.2°C. The freezing p a solution of 3.42 g cane-sugar in 100 g of water is -0.185°C. The degree of ionisation of s (A) 80% (B) 30% (C) 60% (D) 40%				eezing point of ion of salt is -				
Q.23	A 1.2% solution (wt./ volume) of NaCl is isotonic with 7.2% solution (wt. /volume) of glucose. Degree of ionisation and van't Hoff factor of NaCl is - (A) $\alpha = 95\%$, $i = 1.95$ (B) $\alpha = 90\%$, $i = 1.90$ (C) $\alpha = 85\%$, $i = 1.85$ (D) $\alpha = 75\%$, $i = 1.75$								
Q.24	1 g of monobasic acid in 100 g of water lowers the freezing point by 0.168°. If 0.2 g of same acid requires 15.1 mL of N/10 alkali for complete neutralization, degree of dissociation of acid will be - $[K_f \text{ for H}_2 \text{O is } 1.86 \text{ K mol}^{-1} \text{ kg}]$ (A) 16.8% (B) 22.4% (C) 19.6% (D) 26.2%						ne acid requires e -		
Q.25The molal depression of the freezing point in 1000 g of water is 1.86. What would be the depression of freezing point of water when :(i) 120 g of urea is dissolved in 1000 gm of water.(A) 1.86°C(B) $8.26°C$ (C) 7.87°C(D) $3.72°C$ (ii) 117 g of sodium chloride is dissolved in 1000 gm of water (Assuming sodium chloride is fully ionised)(A) 7.44°C(B) $3.72°C$ (C) 11.16°C(D) $6.18°C$ (iii) 488.74 g of BaCl ₂ .2H ₂ O have been dissolved in 1000 g of water. (Assuming barium chloride is fully ionised)(A) 7.44°C(B) 11.16°C(C) $3.72°C$ (D) $5.87°C$									
Practice Sheet I									
1.	(C)	2. (B)	3. (A)	4. (D)	5. (A)	6. (C)	7. (D)		
8.	(C)	9. (A)	10. (C)	11. (A)	12. (C)	13. (C)	14. (B)		
1:	5. (A)								
Practice Sheet II									
1.	(B)	2. (C)	3. (A)	4. (B)	5. (D)	6. (A)	7. (B)		
8.	(C)	9. (B)	10. (D)	11. (C)	12. (A)	13. (C)	14. (D)		
15	5. (A)	16. (C)	17. (A)	18. (D)	19. (C)	20. (C)	21. (B)		
22	2. (C)	23. (A)	24. (C)	25. (i) (D)	(ii) (A) (i	ii) (B)			

SOLVED PROBLEMS

SUBJECTIVE

Problem 1: Calculate the molecular weight of cellulose acetate if its 0.5% (wt./vol) solution in acetone (sp. gr. = 0.9) shows an osmotic rise of 23 mm against pure acetone at 27°C.

Solution: 0.5% (wt. / vol) solution means 0.5 gm of cellulose acetate is dissolved in 100 ml solution. Osmotic pressure = 23 mm of pure acetone

 $\pi = 2.3$ Cm of pure acetone $= \frac{2.3 \times 0.9}{13.6}$ cm of Hg = 0.1522 cm of Hg $\pi = \frac{0.1522}{76}$ atm = 0.002 atm

Let the molecular weight of the cellulose acetate be M \Rightarrow n_{cellulose acetate} = $\frac{0.5}{M}$

Volume = v = 100 ml = 0.1 lit R = 0.082 lit atm mol⁻¹ K⁻¹, T = (27 + 273) = 300 K $\pi = \frac{n}{v} \times RT \Rightarrow 0.002 = \frac{0.5}{M} \times \frac{1}{0.1} \times 0.0821 \times 300$ \therefore M = 61575

Problem 2: 1kg of an aqueous solution of Sucrose is cooled and maintained at -4° C. How much ice will be separated out if the molality of the solution is 0.75? $K_{f}(H_{2}O) = 1.86 \text{ Kg mol}^{-1}$ K.

Solution: Since molality of solution is .75, hence .75 moles of sucrose are present in 1000 g of solvent (i.e. water) \Box m_{solution} = m_{water} + m_{sucrose} = 1000 + .75 × 342 = 1256.5 gm \therefore m_{sucrose} (in kg) = $\frac{256.5}{1256.5}$ × 1000 = 204.14 gm , m_{water} = 1000 - 204.14 = 795.86 gm \Box Δ T_f = K_f × m \Rightarrow 4 = 1.86 × $\frac{204.14/342}{W/1000}$ \Rightarrow w = 277.15 \therefore amount of ice = 795.86 - 277.15 = 518.31 gm

Problem 3: River water is found to contain 11.7% NaCl, 9.5% $MgCl_2$, and 8.4%. NaHCO₃ by weight of solution. Calculate its normal boiling point assuming 90% ionization of NaCl, 70% ionization of MgCl, and 50% ionization of NaHCO₃ (K_b for water = 0.52)

Solution: $n_{NaCl} = \frac{11.7}{58.5} = 0.2$, $n_{MgCl_2} = \frac{9.5}{95} = 0.1$, $n_{NaHCO_3} = \frac{8.4}{84} = 0.1$ $i_{NaCl} = 1 + \alpha = 1 + 0.9 = 1.9$, $i_{MgCl_2} = 1 + 2\alpha = 1 + 0.7 \times 2 = 2.4$, $i_{NaHCO_3} = 1 + 2\alpha = 1 + 0.5 \times 2 = 2.0$ Weight of solvent = 100 - (11.7 + 9.5 + 8.4) = 70.4 g $\Delta T_b = \frac{(i_{NaCl} \times n_{NaCl} + i_{MgCl_2} \times n_{MgCl_2} + i_{NaHCO_3} \times n_{NaHCO_3}) \times K_b \times 1000}{Weight of solvent}$ $= \frac{(1.9 \times 0.2 + 2.4 \times 0.1 + 2 \times 0.1) \times 0.52 \times 1000}{70.4} = 5.94^{\circ}C$ \therefore Boiling point of solution = 100 + 5.94 = 105.95^{\circ}C **Problem 4:** An aqueous solution containing 288 gm of a non-volalite compound having the stochiometric composition $C_x H_{2x} O_x$ in 90 gm water boils at 101.24°C at 1.00 atmospheric pressure. What is the molecular formula?

 $K_{b}(H,O) = 0.512 \text{ K mol}^{-1} \text{ kg } T_{b}(H,O) = 100^{\circ}C$

Solution: Elevation in B.P. = 101.24 - 100 = 1.24°C

 $\Delta T_{b} = K_{b} \times i \times \text{molality} \qquad \Rightarrow 1.24 = 0.512 \times \frac{288}{m} \times \frac{1000}{90} \quad (\therefore i = 1)$ $\therefore m = 1321.2 \text{ gm mol}^{-1}$ $\text{molar mass of } C_{x}H_{2x}O_{x} = 12x + 1 \times 2x + 16x = 30x$ $\therefore 30x = 1321.2 \qquad \therefore x = 44 \qquad \text{Hence the molecular formula is} = C_{44}H_{88}O_{44}$

Problem 5: 30 ml of CH₃OH (d = 0.7980 gm Cm⁻³) and 70 ml of H₂O (d = 0.9984 gm cm⁻³) are mixed at 25°C to form a solution of density 0.9575 gm cm⁻³. Calculate the freezing point of the solution. K_f (H₂O) is 1.86 Kg mol⁻¹ K. Also calculate its molarity

Solution: Weight of $CH_3OH(w_1) = 30cm^3 \times 0.7980 \text{ gm/cm}^3 = 23.94 \text{ gm}$ Weight of solvent (H₂O) (w₂) = 70 cm³ × 0.9984 gm cm³ = 69.888 gm

 $m = \frac{23.94}{32} \times \frac{1000}{69.88} = 10.7046 \text{ molal}$

 $\therefore \Delta T_{f} = K_{f} \times i \times \text{molality}, \quad (\text{for CH}_{3}\text{OH}, i = 1)$ $\Delta T_{f} = 1.86 \times 10.7046^{\circ}\text{C} = 19.91^{\circ}\text{C}$ Freezing point of the solution = 0– 19.91°C = -19.91°C Weight of solution = weight of solute + weight of solvent = 23.94 + 69.888 = 93.828 gm

volume of the solution = $\frac{\text{wt. of the solution}}{\text{density of the solution}} = \frac{93.828}{0.95751} = 97.99 \text{ ml}$

M (molarity) = $\frac{23.94}{32} \times \frac{1000}{97.99}$ mol lit⁻¹ = 7.63 M

Problem 6: A complex is represented as $CoCl_s xNH_s$. Its 0.1 m solution in aqueous solution shows $\Delta T_f = 0.558^{\circ} K_f(H_2O) = 1.86 \text{ mol}^{-1} \text{ K}$ and assume 100% ionization and co-ordination number of Co(III) is six. What is the complex?

 $\therefore i = \frac{0.558}{0.186} = 3$

or, i \approx 3 indicates that complex ionize to form three ions since co-ordination number is 6 hence x = 5

i.e., $CoCl_3.5NH_3 \longrightarrow [Co(NH_3)_5Cl]^{++} + 2Cl^{-}$ $\downarrow \qquad \downarrow \qquad \downarrow$ 1 Cation 2 anions So, the complex is [Co(NH) Cl]Cl

So, the complex is $[Co(NH_3)_5Cl]Cl_2$

Problem 7: A solution comprising 0.1 mol of naphthalene and 0.9 mol of benzene is cooled until some benzene freezes out. The solution is then decanted off from the solid and warmed to 353 K, where its vapour pressure is found to be 670 torr. The freezing and normal boiling point of benzene are 278.5 K and 353 K, respectively. Calculate the temperature to which the solution was cooled originally and the amount of benzene that must have frozen out. Assume conditions of ideal solution. K_c for benzene = 5K kg mole⁻¹.

Solution: Molality of the resulting solution (i.e. after the benzene freezes out) can be determined on the basis Raoult's law.

$$m = \frac{X_{naph} \times 1000}{X_{benzene} \times 78} = \frac{\frac{(760 - 670)}{760}}{0.88 \times 78} = 1.72 \text{ mol kg}^{-1}.$$

Weight of benzene in the resulting solution $=\left(\frac{1000}{1.72} \times 0.1\right) = 58.1 \text{ g}$

Amount of benzene frozen = $0.9 \times 78 - 58.1 = 12.1$ g

 $\Delta T_{f} = K_{f}m = 5 \times 1.72 = 8.60 \text{ K}$

Hence the temp to which the solution was cooled = 278.5 - 8.60 = 269.9 K

Problem 8: Find K_a , the ionization constant of tartaric acid if a 0.100 molal aqueous solution of tartaric acid freezes at -0.205° C. Assume that only the first ionization is of importance and that 0.1 m = 0.1M. $K_f = 1.86 \text{ kg mol}^{-1} \text{ K}$.

Solution: Assuming that the tartaric acid be a monobasic as AH. It ionizes as

 $\begin{array}{ccccc} AH & \rightleftharpoons & A^{\Theta} & + & H^{+} \\ \text{Initially conc.} & C & 0 & 0 \\ \text{Conc. after dissociation} & C(1-\alpha) & C\alpha & C\alpha, \\ \text{Here, } i = \frac{C(1-\alpha) + C\alpha + C\alpha}{C}, \text{ where } \alpha = \text{degree of dissociation} = \frac{C(1+\alpha)}{C} = 1+\alpha \\ \text{Molal concentration} = 0.1 \\ \Delta T_{f} = K_{f} \times C_{m} \times i & \Longrightarrow & 0.205 = 1.86 \times 0.1 \times (1+\alpha) & \therefore \alpha = 0.1 \\ K_{a} = \frac{[A^{-}][H^{+}]}{[AH]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{\alpha^{2}C}{1-\alpha} \qquad K_{a} = \frac{(0.1)^{2} \times 0.1}{1-0.1} = 1.11 \times 10^{-3} \\ \therefore K_{a} = 1.11 \times 10^{-3} \end{array}$

Problem 9: The freezing point depression of a 0.109 M aq. solution of formic acid is $-0.21^{\circ}C$. Calculate the equilibrium constant for the reaction, $HCOOH(aq) \Longrightarrow H^{+}(aq) + HCOO^{-}(aq)$

 $K_{f} for water = 1.86 \ kg \ mol^{-1} \ K$ Solution: Initially moles Moles after dissociation $i = \frac{(1-\alpha) \times C + \alpha \times C + \alpha \times C}{1 \times C} = 1 + \alpha,$ $\Delta T_{f} = K_{f} \times i \times C_{m}$ $0.21 = 1.86 \times (1+\alpha) \times 0.109 \ (\text{ for dilute solution molality} \approx \text{molarity})$ $\therefore 1+\alpha = \frac{0.21}{1.86 \times 0.109} = 1.0358 \implies \alpha = 0.0358 = 0.036$ $K_{a} = \frac{[H^{+}][HCOO^{-}]}{[HCOOH]} = \frac{C\alpha^{2}}{(1-\alpha)} = \frac{0.109 \times (0.036)^{2}}{0.964} = 1.41 \times 10^{-5}$ **Problem 10:** The freezing point of a solution of acetic acid (mole fraction is 0.02) in benzene 277.4 K. Acetic acid exists partly as a dimer $2A \Longrightarrow A_2$. Calculate equilibrium constant for dimerisation. Freezing point of benzene is 278.4 k and (K_t for benzene is 5)

Solution: 2A Α, 1 initially moles 0 $1-\alpha$ $\alpha/2$ moles after dimer is formed $\therefore i = \frac{(1-\alpha) + \alpha/2}{1} = 1 - \alpha/2$ $X_{A} = 0.02, \qquad X_{B} = 0.98$ Molality of A in B = $\frac{X_A}{m_B} \times \frac{1000}{X_B} = \frac{0.02}{78} \times \frac{1000}{0.98} = 0.262 \text{ mol kg}^{-1}$ of Benzene $278.4-277.4 = 5 \times i \times 0.262$ Since, $\Delta T_f = K_f \times i \times molality$ or, $1 = 5 \times i \times 0.262$, $i = \frac{1}{5 \times 0.262} = 0.763$, $1 - \alpha/2 = 0.763 \implies \alpha = 0.47$ Hence the molality of A after dimer is formed = $(1-\alpha) \times$ initial molality $= (1 - 0.48) \times \text{initial molality} = 0.52 \times 0.262$ Molality of A_2 after dimer is formed

$$= \frac{\alpha}{2} \times \text{molality} = \frac{0.48}{2} \times 0.262 = 0.24 \times 0.26 = 0.06288$$

The equilibrium constant $K_{eq} = \frac{[A_2]}{[A]^2} = \frac{0.06288}{(0.13624)^2} = 3.39 \text{ kg mol}^{-1}$

<u>EXERCISE I</u>

Raoult's law

- Q.1 At 25°C, the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of CH_3OH in a solution in which the (partial) vapor pressure of CH_3OH is 23.0 torr at 25°C?
- Q.2 The vapour pressure of pure liquid solvent A is 0.80 atm. When a nonvolatile substance B is added to the solvent its vapour pressure drops to 0.60 atm. What is the mole fraction of component B in the solution?
- Q.3 The vapour pressure of pure water at 26°C is 25.21 torr. What is the vapour pressure of a solution which contains 20.0 glucose, $C_6H_{12}O_6$, in 70 g water?
- Q.4 The vapour pressure of pure water at 25°C is 23.76 torr. The vapour pressure of a solution containing 5.40 g of a nonvolatile substance in 90.0 g water is 23.32 torr. Compute the molecular weight of the solute.

Raoult's law in combinaton with Dalton's law of P.P. and V.P. lowering

- Q.5 The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is prepared at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate total vapour pressure of the solution.
- Q.6 Calculate the mole fraction of toluene in the vapour phase which is in equilibrium with a solution of benzene and toluene having a mole fraction of toluene 0.50. The vapour pressure of pure benzene is 119 torr; that of toluene is 37 torr at the same temperature.
- Q.7 What is the composition of the vapour which is in equilibrium at 30°C with a benzene-toluene solution with a mole fraction of benzene of 0.40? With a mole fraction of benzene of 0.60?

 $P_b^{\circ} = 119$ torr and $P_t^{\circ} = 37$ torr

- Q.8 At 90°C, the vapour pressure of toluene is 400 torr and that of σ -xylene is 150 torr. What is the composition of the liquid mixture that boils at 90°C, when the pressure is 0.50 atm? What is the composition of vapour produced?
- Q.9 Two liquids A and B form an ideal solution at temperature T. When the total vapour pressure above the solution is 400 torr, the mole fraction of A in the vapour phase is 0.40 and in the liquid phase 0.75. What are the vapour pressure of pure A and pure B at temperature T?
- Q.10 Calculate the relative lowering in vapour pressure if 100 g of a nonvolatile solute (mol.wt.100) are dissolved in 432 g water.
- Q.11 What weight of the non-volatile solute, urea needs to be dissolved in 100 g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution?
- Q.12 The vapour pressure of an aqueous solution of glucose is 750 mm Hg at 373 K. Calculate molality and mole fraction of solute.

- Q.13 The vapour pressure of pure benzene at 25° C is 639.7 mm of Hg and the vapour pressure of a solution of a solute in C₆H₆ at the same temperature is 631.7 mm of Hg. Calculate molality of solution.
- Q.14 The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A nonvolatile nonelectrolyte solid weighing 2.175 g is added to 39.0 of benzene. The vapour pressure of the solution is 600 mm of Hg. What is molecular weight of solid substance?
- Q.15 The vapour pressure of water is 17.54 mm Hg at 293 K. Calculate vapour pressure of 0.5 molal solution of a solute in it.
- Q.16 Benzene and toluene form two ideal solution A and B at 313 K. Solution A (total pressure P_A) contains equal mole of toluene and benzene. Solution B contains equal masses of both (total pressure P_B). The vapour pressure of benzene and toluene are 160 and 60 mm Hg respectively at 313 K. Calculate the value of P_A/P_B .

Boiling point elevation and freezing point depression

- Q.17 When 10.6 g of a nonvolatile substance is dissolved in 740 g of ether, its boiling point is raised 0.284°C. What is the molecular weight of the substance? Molal boiling point constant for ether is 2.11°C⋅kg/mol.
- Q.18 A solution containing 3.24 of a nonvolatile nonelectrolyte and 200 g of water boils at 100.130°C at 1atm. What is the molecular weight of the solute? (K_b for water 0.513°C/m)
- Q.19 The molecular weight of an organic compound is 58.0 g/mol. Compute the boiling point of a solution containing 24.0 g of the solute and 600 g of water, when the barometric pressure is such that pure water boils at 99.725°C.
- Q.20 An aqueous solution of a nonvolatile solute boils at 100.17°C. At what temperature will this solution freeze? [K_f for water 1.86°C/m]
- Q.21 Pure benzene freeze at 5.45°C. A solution containing 7.24 g of C₂H₂Cl₄ in 115.3 g of benzene was observed to freeze at 3.55°C. What is the molal freezing point constant of benzene?
- Q.22 A solution containing 6.35 g of a nonelectrolyte dissolved in 500 g of water freezes at -0.465° C. Determine the molecular weight of the solute.
- Q.23 The freezing point of a solution containing 2.40 g of a compound in 60.0 g of benzene is 0.10°C lower than that of pure benzene. What is the molecular weight of the compound? (K_f is 5.12°C/m for benzene)
- Q.24 The elements X and Y form compounds having molecular formula XY_2 and XY_4 . When dissolved in 20 gm of benzene, 1 gm XY_2 lowers the freezing point by 2.3°, whereas 1 gm of XY_4 lowers the freezing point by 1.3°C. The molal depression constant for benzene is 5.1. Calculate the atomic masses of X and Y.
- Q.25 Calculate the molal elevation constant, K_b for water and the boiling of 0.1 molal urea solution. Latent heat of vaporisation of water is 9.72 kcal mol⁻¹ at 373.15 K.
- Q.26 Calculate the amount of ice that will separate out of cooling a solution containing 50g of ethylene glycol in 200 g water to -9.3° C. (K_f for water = 1.86 K mol⁻¹ kg)

- Q.27 A solution of 0.643 g of an organic compound in 50ml of benzene (density ; 0.879 g/ml) lowers its freezing point from 5.51°C to 5.03°C. If K_f for benzene is 5.12 K, calculate the molecular weight of the compound.
- Q.28 The cryoscopic constant for acetic acid is 3.6 K kg/mol. A solution of 1 g of a hydrocarbon in 100 g of acetic acid freezes at 16.14°C instead of the usual 16.60°C. The hydrocarbon contains 92.3% carbon. What is the molecular formula?

Osmotic pressure

- Q.29 Find the freezing point of a glucose solution whose osmotic pressure at 25°C is found to be 30 atm. $K_{f}(water) = 1.86 \text{kg.mol}^{-1}$.K.
- Q.30 At 300 K, two solutions of glucose in water of concentration 0.01 M and 0.001 M are separated by semipermeable membrane. Pressure needs to be applied on which solution, to prevent osmosis? Calculate the magnitude of this applied pressure.
- Q.31 At 10°C, the osmotic pressure of urea solution is 500 mm. The solution is diluted and the temperature is raised to 25°C, when the osmotic pressure is found to be105.3 mm. Determine extent of dilution.
- Q.32 The osmotic pressure of blood is 7.65 atm at 37°C. How much glucose should be used per L for an intravenous injection that is to have the same osmotic pressure as blood?
- Q.33 What would be the osmotic pressure at 17°C of an aqueous solution containing 1.75 g of sucrose $(C_{12}H_{22}O_{11})$ per 150 cm³ of solution?
- Q.34 A 250 mL water solution containing 48.0 g of sucrose, $C_{12}H_{22}O_{11}$, at 300 K is separated from pure water by means of a semipermeable membrane. What pressure must be applied above the solution in order to just prevent osmosis?
- Q.35 A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g in 125 cm³ of an aqueous medium. At 4°C an osmotic pressure rise of 2.6 mm of the solution was observed. The solution had a density of 1.00 g/cm³. Determine the molecular weight of the protein.
- Q.36 The osmotic pressure of a solution of a synthetic polyisobutylene in benzene was determined at 25°C. A sample containing 0.20 g of solute/100 cm³ of solution developed a rise of 2.4 mm at osmotic equilibrium. The density of the solution was 0.88 g/cm³. What is the molecular weight of the polyisobutylene?
- Q.37 A 5% solution (w/v) of cane-sugar (Mol. weight = 342) is isotonic with 0.877% (w/v) of urea solution. Find molecular weight of urea.
- Q.38 10 gm of solute A and 20 gm of solute B are both dissolved in 500 ml water. The solution has the same osmotic pressure as 6.67 gm of A and 30 gm of B dissolved in the same amount of water at the same temperature. What is the ratio of molar masses of A and B?

Van't Hoff factor & colligative properties

Q.39 A storage battery contains a solution of H_2SO_4 38% by weight. What will be the Van't Hoff factor if the $\Delta T_{f(experiment)}$ in 29.08. [Given $K_f = 1.86 \text{ mol}^{-1} \text{ Kg}$]

- Q.40 A certain mass of a substance, when dissolved in 100 g C_6H_6 , lowers the freezing point by 1.28°C. The same mass of solute dissolved in 100g water lowers the freezing point by 1.40°C. If the substance has normal molecular weight in benzene and is completely ionized in water, into how many ions does it dissociate in water? K_f for H_2O and C_6H_6 are 1.86 and 5.12K kg mol⁻¹.
- Q.41 2.0 g of benzoic acid dissolved in 25.0g of benzene shows a depression in freezing point equal to 1.62K. Molal depression constant (K_f) of benzene is 4.9 K.kg.mol⁻¹. What is the percentage association of the acid?
- Q.42 A decimolar solution of potassium ferrocyanide is 50% dissociated at 300K. Calculate the osmotic pressure of the solution. (R=8.314 JK⁻¹ mol⁻¹)
- Q.43 The freezing point of a solution containing 0.2 g of acetic acid in 20.0g of benzene is lowered by 0.45°C. Calculate the degree of association of acetic acid in benzene. (K_f for benzene = 5.12 K mol⁻¹ kg)
- Q.44 0.85 % aqueous solution of NaNO₃ is apparently 90% dissociated at 27°C. Calculate its osmotic pressure. (R= 0.082 *l* atm K⁻¹ mol⁻¹)
- Q.45 A 1.2% solution (w/v) of NaCl is isotonic with 7.2% solution (w/v) of glucose. Calculate degree of ionization and Van't Hoff factor of NaCl.

<u>ANSWER</u>	
EXERCISE I	

Q.1	0.24	Q.2	0.25	Q.3	24.5 torr	Q.4	57.24 g/mol
Q.5	66.13 mm Hg	Q.6	0.237	Q.7	0.682, 0.318; 0.829, 0.171		
Q.8	92 mol% toluene; 96.8 mol % toluene			Q.9 $P_A^\circ = 213.33$ torr, $P_B^\circ = 960.0$ torr			
Q.10	0.04	Q.11	111.1g, 18.52	molal	Q.12 0.741 m, 0		0.741 m, 0.013
Q.13	0.162 m	Q.14	65.25	Q.15	17.38	Q.16	0.964
Q.17	106 g/mol	Q.18	64.0 g/mol	Q.19	100.079°C	Q.20	- 0.62°C
Q.21	5.08°C/m	Q.22	50.8 g/mol	Q.23	2050 g/mol	Q.24	x = 25.6, y = 42.6
Q.25	$K_b = 0.512 \text{ kg mol } K^{-1}, T_b = 373.20 \text{ K}$			Q.26 38.71	g	Q.27 156.06	
Q.28	C_6H_6	Q.29	$T_{f} = -2.28^{\circ}C$	Q.30	P = 0.2217 atm should be applied		d be applied
Q.31	$(V_{final} = 5.V_{original})$	Q.32	54.2 g	Q.33	0.81 atm	Q.34	13.8 atm
Q.35	$5.4 \times 10^5 \text{ g/mol}$	Q.36	$2.4 \times 10^5 \text{ g/m}$	ol	Q.37 59.99		59.99
Q.38	$M_{A}/M_{B} = 0.33$	Q.39	i = 2.5	Q.40	3 ions	Q.41	$\alpha = 99.2\%$
Q.42	$7.482 \times 10^5 \text{ Nm}^{-2}$	Q.43	94.5 %	Q.44	4.64 atm	Q.45	0.95; 1.95