## 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 ( $\pi$ ): 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 $\pi=\mathrm{CRT}=\mathrm{h} \rho \mathrm{g}$ (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 $\rho$ 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 $\mathrm{C}_{1}=\mathrm{C}_{2}$ ).

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 $15^{\circ} \mathrm{C}$.

Solution: $m=$ mol. mass of sucrose $\left(\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}\right)=342$

$$
\begin{array}{ll}
w=5 \mathrm{~g} & V=-100 \mathrm{~mL}=0.1 \text { litre } \\
S=0.082, & T=(15+273)=288 \mathrm{~K}
\end{array}
$$

Applying the equation $P V=\frac{w}{m} \mathrm{ST}$,

$$
\left.P=\frac{5}{342} \times \frac{1}{0.1}=0.082 \times 288=3.453\right]
$$

Example: Consider a vertical tube of corss-sectional area of $1 \mathrm{~cm}^{2}$. 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 $1 \mathrm{~g} / \mathrm{cm}^{2}$. What is the osmotic pressure at equilibrium at $25^{\circ}$ C? Assume negligible depth of immersion of tube.
Solution: Let height in tube $=h \mathrm{~cm}$

$$
\begin{aligned}
V=(h \times 1) \mathrm{cm}^{3} & \square \text { Cross-sectiona } \\
\pi V & =\mathrm{nRT} \\
\pi \times\left(\frac{\mathrm{h} \times 1}{1000}\right) & =\frac{1}{180} \times 0.0821 \times 298 \\
\pi & =\frac{134.92}{h} \mathrm{~atm} \\
\pi & =h \times d \times \mathrm{g} \\
\frac{134.92}{h} & =\frac{h \times 1}{100} \times \frac{9.8}{101.325} \quad 1 \mathrm{~atm}=101.325 \mathrm{KP}_{a} \\
\mathrm{~h} & =375 \mathrm{~cm}=3.75 \mathrm{~m} \\
\pi & =h \times d \times \mathrm{g}=3.75 \times 1 \times 9.8 \quad=36.7 \mathrm{KP}_{a}
\end{aligned}
$$

[Ans. $3.75 \mathrm{~m} ; 36.7 \mathrm{KP}_{a}$ ]
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 $\mathrm{m}_{2}$
Molarity of sugar $=\frac{\mathrm{w}_{1}}{\mathrm{~m}_{1} \times \mathrm{V}_{1}}=\frac{5}{342 \times 0.1}$
Molarity of urea $=\frac{\mathrm{w}_{2}}{\mathrm{~m}_{2} \times \mathrm{V}_{2}}=\frac{0.877}{\mathrm{~m}_{2} \times 0.1}$
For isotonic solutions,

$$
\begin{aligned}
& \frac{\mathrm{w}_{1}}{\mathrm{~m}_{1} \times \mathrm{V}_{1}}=\frac{\mathrm{w}_{2}}{\mathrm{~m}_{2} \times \mathrm{V}_{2}} \Rightarrow \frac{5}{342 \times 0.1}=\frac{0.877}{\mathrm{~m}_{2} \times 0.1} \\
& \mathrm{~m}_{2}=\frac{0.877 \times 342}{5}=59.987
\end{aligned}
$$

## 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 $27^{\circ} \mathrm{C}$. 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 $30^{\circ} \mathrm{C}$ 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 $5 \%$ ( $\mathrm{wt} / \mathrm{vol}$ ) 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 of a solution containing 100 ml of $3.4 \%$ solution (w/v) of urea (m. wt. 60) and 50 ml of $1.6 \%$ solution ( $\mathrm{w} / \mathrm{v}$ ) of cane-sugar ( $\mathrm{m} . \mathrm{wt} 342$ ) at $27^{\circ} \mathrm{C}$ is -
(A) 10.56 atm
(B) 8.98 atm
(C) 17.06 atm
(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
(B) 0.77 g urea in glucose solution
(C) 0.72 g urea in sucrose solution
(D) 0.421 g urea in sucrose solution
Q. 65 g of a polymer of molecular weight $50 \mathrm{~kg} \mathrm{~mol}^{-1}$ is dissolved in $1 \mathrm{dm}^{3}$ solution. If the density of this solution is $0.96 \mathrm{~kg} \mathrm{dm}^{-3}$ 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. $7 \quad 100 \mathrm{~mL}$ aqueous solution of glucose with osmotic pressure 1.2 atm at $25^{\circ} \mathrm{C}$ is mixed with 300 mL aqueous solution of urea at 2.4 atm at $25^{\circ} \mathrm{C}$. Osmotic pressure of the mixture is -
(A) 1.37 atm
(B) 2.59 atm
(C) 1.85 atm
(D) 2.13 atm
Q. $8 \quad 10 \mathrm{~g}$ 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 $10^{\circ} \mathrm{C}$, the osmotic pressure of urea solution is 500 mm . The solution is diluted and the temperature is raised to $25^{\circ} \mathrm{C}$, 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 $\left(\mathrm{P}_{1}\right), 10 \mathrm{gm}$ urea $\left(\mathrm{P}_{2}\right)$ and 10 gm sucrose $\left(\mathrm{P}_{3}\right)$ are dissolved in 250 ml of water is
(A) $\mathrm{P}_{1}>\mathrm{P}_{2}>\mathrm{P}_{3}$
(B) $P_{3}>P_{1}>P_{2}$
(C) $P_{2}>P_{1}>P_{3}$
(D) $\mathrm{P}_{2}>\mathrm{P}_{3}>\mathrm{P}_{1}$
Q. 11 What osmotic pressure would the 1.25 molal sucrose solution exhibit at $25^{\circ} \mathrm{C}$ ? The density of this solution is $1.34 \mathrm{~g} / \mathrm{mL}$.
(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 $37^{\circ} \mathrm{C}$. 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 $\mathrm{d}(\mathrm{Hg})=13.6 \mathrm{~g} / \mathrm{mL}$ ] -
(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?
(A) 2 times
(B) 4 times
(C) 8 times
(D) 5 times
Q. 15 If depression in freezing point is $0.93^{\circ} \mathrm{C}$ then the osmotic pressure of aqueous solution of the given non-electrolyte at $27^{\circ} \mathrm{C}$ is -
[Given : $\mathrm{K}_{\mathrm{f}}$ for water $=1.86 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1} \&$ 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.

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

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

$$
\begin{aligned}
\mathrm{nAB} & \rightleftharpoons(\mathrm{AB})_{\mathrm{n}} \\
2 \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH} & \rightleftharpoons\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}\right)_{2}
\end{aligned}
$$

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 $122 \mathrm{~g} / \mathrm{mol}$. But the molecular mass of benzoic acid dissolved in benzene is found to be $244 \mathrm{~g} / \mathrm{mol}$ by using a colligative property. Benzoic acid associates to form a dimer and therefore its colligative molality is onehalf 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, $\mathrm{K}^{+}$and $\mathrm{Cl}^{-}$and therefore, the molecular mass obtained by a colligative property is half of its normal molecular mass.

$$
\underset{1 \mathrm{~mol}}{\mathrm{~K}_{(\mathrm{s})}^{+} \mathrm{Cl}_{-}^{-}}+\mathrm{nH}_{2} \mathrm{O} \longrightarrow \underset{\substack{\text { (mol }}}{\mathrm{K}_{1}^{+}}+\underset{1 \mathrm{~mol}}{\mathrm{Cl}_{\text {(aq) }}^{-}}
$$

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.


A dimer of benzoic acid

## 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:
$\boldsymbol{i}=\frac{\text { number of solute particles actually present in solution }}{\text { number of solute particles dissolved }}$
$=\frac{\text { Observed colligative property }}{\text { normal colligative property }}=\frac{\text { observed molality }}{\text { normal molality }}=\frac{\text { normal molecular weight of solute }}{\text { observed molecular weight of solute }}$
The Van't Hoff factor for a solute can be calculated by the following modified equations:
(i) $\frac{\mathrm{P}_{\mathrm{A}}^{0}-\mathrm{P}_{\mathrm{A}}}{\mathrm{P}_{\mathrm{A}}^{0}}=i \mathrm{X}_{\mathrm{B}}$
(ii) $\Delta \mathrm{T}_{\mathrm{f}}=\mathrm{i} \mathrm{K}_{\mathrm{f}} \mathrm{m}$
(iii) $\Delta T_{b}=i K_{b} m$
(iv) $\pi=\mathrm{iCRT}$
where C is molarity of the solution.
Note: For non-electrolytes; $i=1$
For electrolytes; $\quad i>1$ ( 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:

No. of moles dissolved
$A_{n} \rightleftharpoons n A$
No. of moles after dissociation $1-\alpha \quad \mathrm{n} \alpha$
Total number of moles present in solution $=(1-\alpha)+n \alpha$
Van't Hoff factor, $i=\frac{\text { Moles of solute actually present in solution }}{\text { Moles of solute dissolved }}$

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

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

$$
\mathrm{nA} \rightleftharpoons \mathrm{~A}_{\mathrm{n}}
$$

No. of moles dissolved $1 \mathrm{~mol} \quad 0$
No. of moles after dissociation $\quad 1-\alpha \quad \alpha / \mathrm{n}$
Total number of moles present in solution $=(1-\alpha)+\alpha / n$

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

Example: A solution is prepared by dissolving 26.3 g of $\mathrm{CdSO}_{4}$ in 1000 g water. The depression in freezing point of solution was found to be 0.284 K . Calculate the Van't Hoff factor. The cryoscopic constant of water is 1.86 K kg solvent $\mathrm{mol}^{-1}$ - solute.

Solution: $\quad$ Molecular mass $\mathrm{CdSO}_{4}=112.4+32+4 \times 16=208.4 \mathrm{~g} / \mathrm{mol}$
M olality $\mathrm{CdSO}_{4}=\frac{{\mathrm{Mass} \mathrm{CdSO}_{4}}^{\text {Molecular mass } \mathrm{CdSO}_{4} \times \text { Mass solvent in } \mathrm{kg}}}{\text { Mat }}$
$=\frac{26.3 \mathrm{~g}}{(208.4 \mathrm{~g} / \mathrm{mol}) \times\left(\frac{1000}{1000} \mathrm{~kg}\right)}=0.216 \mathrm{~m}$
$\Delta \mathrm{T}_{\mathrm{f}}=\mathrm{i} \mathrm{K}_{\mathrm{f}} \mathrm{m} \quad$ or $\mathrm{i}=\frac{\Delta \mathrm{T}_{\mathrm{f}}}{\mathrm{K}_{\mathrm{f}} \mathrm{m}}=\frac{0.284 \mathrm{~K}}{1.86 \mathrm{~K} / \mathrm{m} \times 0.126 \mathrm{~m}}=1.21$
Example. Three particles of a solute, A, associate in benzene to form species $A_{3}$. 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 $5.5^{\circ} \mathrm{C}$ and $5.12 \mathrm{Km}^{-1}$ respectively.
Solution:
$\begin{array}{lllll}\text { No. of moles dissolved } & 3 \mathrm{~A} & \longrightarrow & \mathrm{~A}_{3} & \\ & & 3 & & 0\end{array}$
No. of moles after dissociation $\quad \mathrm{m}(1-\alpha) \quad \mathrm{m} \alpha / 3$
Total moles present after dissociation

$$
\begin{aligned}
& =\mathrm{m}(1-\alpha)+\mathrm{m} \frac{\alpha}{3}=\mathrm{m}\left(1-\alpha+\frac{\alpha}{3}\right)=\mathrm{m}\left(1-\frac{2 \alpha}{3}\right)=0.25 \mathrm{~m}\left[\frac{3-2 \times 0.8}{3}\right]=0.177 \mathrm{~m} \\
& \Delta \mathrm{~T}_{\mathrm{f}}=\mathrm{K}_{\mathrm{f}} \mathrm{~m} \quad \text { or } \quad \mathrm{T}_{\mathrm{f}}^{0}-\mathrm{T}_{\mathrm{f}}=5.12 \mathrm{Km}^{-1} \times 0.117 \mathrm{~m}=0.6 \\
& \\
& \mathrm{~T}_{\mathrm{f}}=\mathrm{T}_{\mathrm{f}}^{0}-0.6^{\circ} \mathrm{C}=5.5^{\circ} \mathrm{C}-0.6^{\circ} \mathrm{C}=4.9^{\circ} \mathrm{C}
\end{aligned}
$$

## Practice Problem II

Q. 1 A pentimolal solution of potassium chloride freezes at $-0.68^{\circ} \mathrm{C}$. If $\mathrm{K}_{\mathrm{f}}$ for $\mathrm{H}_{2} \mathrm{O}$ 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.
(A) 1.5 P
(B) P
(C) 0.5 P
(D) 0.75 P
Q. 4 Which is the correct relation between osmotic pressure of 0.1 M NaCl solution and 0.1 M $\mathrm{Na}_{2} \mathrm{SO}_{4}$ solution?
(A) the osmotic pressure of $\mathrm{Na}_{2} \mathrm{SO}_{4}$ is less than NaCl solution
(B) the osmotic pressure of $\mathrm{Na}_{2} \mathrm{SO}_{4}$ is more than NaCl solution
(C) both have same osmotic pressures
(D) none of the above
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 $0.2 \mathrm{M} \mathrm{MgCl}_{2}$
(C) 0.1 M NaCl and $0.1 \mathrm{M} \mathrm{Na}_{2} \mathrm{SO}_{4}$
(D) $0.1 \mathrm{M} \mathrm{Ca}\left(\mathrm{NO}_{3}\right)_{2}$ and $0.1 \mathrm{M} \mathrm{Na}_{2} \mathrm{SO}_{4}$
Q. 6 The van't Hoff factor of a 0.005 M aqueous solution of KCl is 1.95 . The degree of ionisation of KCl is-
(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, assuming the acid to be $90 \%$ ionised. ? $\left[\mathrm{K}_{\mathrm{f}}\right.$ for water $\left.=1.86 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}\right]$
(A) $0.85^{\circ} \mathrm{C}$
(B) $-3.53^{\circ} \mathrm{C}$
(C) $0^{\circ} \mathrm{C}$
(D) $-0.35^{\circ} \mathrm{C}$
Q. 8 The molal freezing point constant for water is $1.86 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}$. Therefore, the freezing point of 0.1 M NaCl solution in water is expected to be :
(A) $-1.86^{\circ} \mathrm{C}$
(B) $-0.186^{\circ} \mathrm{C}$
(C) $-0.372^{\circ} \mathrm{C}$
(D) $+372^{\circ} \mathrm{C}$
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 solution
(C) b.p. is a colligative property
(D) all of the above
Q. 10 Two solution of $\mathrm{KNO}_{3}$ and $\mathrm{CH}_{3} \mathrm{COOH}$ are prepared separately molarity of both in 0.1 M and osmotic pressure are $\mathrm{P}_{1} \& \mathrm{P}_{2}$. The correct relationship between the osmotic pressure is -
(A) $\mathrm{P}_{2}>\mathrm{P}_{1}$
(B) $\mathrm{P}_{1}>\mathrm{P}_{2}$
(C) $\mathrm{P}_{1}=\mathrm{P}_{2}$
(D) $\frac{\mathrm{P}_{1}}{\mathrm{P}_{1}+\mathrm{P}_{2}}+\frac{\mathrm{P}_{2}}{\mathrm{P}_{1}+\mathrm{P}_{2}}$
Q. 11 A $5.8 \% \mathrm{wt} / \mathrm{vol}$. NaCl solution will exert an osmotic pressure closest to which one of the following -
(A) $5.8 \%(\mathrm{wt} / \mathrm{vol})$ sucrose solution
(B) $5.8 \%(\mathrm{wt} / \mathrm{vol})$ glucose solution
(C) 2 molal sucrose solution
(D) 1 molal glucose solution
Q. 12 How many grams of NaBr must be added to 270 gm of water to lower the vapour pressure by 3.125 mm Hg at temperature at which vapour pressure of water is 50 mm Hg . Assume $100 \%$ ionisation of NaBr
(A) 51.5 gm
(B) 103 gm
(C) 75 gm
(D) 37.5 gm
Q. 13 Sea water is found to contain $\mathrm{NaCl} \& \mathrm{MgCl}_{2}$. If NaCl is $80 \%$ ionised and $\mathrm{MgCl}_{2}$ is $50 \%$ ionised then van't Hoff factor is -
(A) 1.3
(B) 5.0
(C) 3.3
(D) 3.8
Q. 14 The f.p of a 0.08 molal solution of $\mathrm{NaHSO}_{4}$ is $-0.372^{\circ} \mathrm{C}$. The dissociation constant for the reaction, $\mathrm{HSO}_{4}^{-} \longrightarrow \mathrm{H}^{+}+\mathrm{SO}_{4}{ }^{2-}$; is $-\left[\mathrm{K}_{\mathrm{f}}\right.$ for water $\left.=1.86^{\circ} \mathrm{C}\right]$
(A) $2 \times 10^{-4}$
(B) $4 \times 10^{-4}$
(C) $2 \times 10^{-2}$
(D) $4 \times 10^{-2}$
Q. 15 If the observed and normal osmotic pressures of a $1 \% \mathrm{NaCl}$ solution are 5.75 and 3.00 atm , the degree of dissociation of NaCl is -
(A) 0.9
(B) 1.0
(C) 0.57
(D) 0.3
Q. $16 \quad 0.01 \mathrm{M}$ solution of KCl and $\mathrm{BaCl}_{2}$ are prepared in water. The freezing point of KCl is found to be $-2^{\circ} \mathrm{C}$. What freezing point would you expect for $\mathrm{BaCl}_{2}$ solution -
(A) $-5^{\circ} \mathrm{C}$
(B) $-4^{\circ} \mathrm{C}$
(C) $-3^{\circ} \mathrm{C}$
(D) $-2^{\circ} \mathrm{C}$
Q. 17 The elevation in boiling point of a solution of 10 g of a binary electrolyte (molecular mass 100) in 100 of water is $\Delta \mathrm{T}_{\mathrm{b}}$. The value of $\mathrm{K}_{\mathrm{b}}$ for water is -
(A) $\frac{\Delta \mathrm{T}_{\mathrm{b}}}{2}$
(B) 10
(C) $10 \Delta \mathrm{~T}_{\mathrm{B}}$
(D) $\frac{\Delta \mathrm{T}_{\mathrm{b}}}{10}$
Q. 18 Van't Hoff factors are $\mathrm{x}, \mathrm{y}, \mathrm{z}$ in the case of association, dissociation and no change respectively. Increasing order is -
(A) $\mathrm{x}<\mathrm{y}<\mathrm{z}$
(B) $x=y=z$
(C) y $<$ x $<$ z
(D) $\mathrm{x}<\mathrm{z}<\mathrm{y}$
Q. 191 mole each of following solutes are taken in 5 moles water,
(i) NaCl
(ii) $\mathrm{K}_{2} \mathrm{SO}_{4}$
(iii) $\mathrm{Na}_{3} \mathrm{PO}_{4}$
(iv) glucose

Assuming $100 \%$ 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
Q. 20 A 0.002 molar solution of NaCl having degree of dissociation of $90 \%$ at $27^{\circ} \mathrm{C}$ has osmotic pressure equal to -
(A) 0.94 bar
(B) 9.4 bar
(C) 0.094 bar
(D) $9.4 \times 10^{-4} \mathrm{bar}$
Q. 21 At $20^{\circ} \mathrm{C}$, 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 -
(A) $92.1 \%$
(B) $84.6 \%$
(C) $68.4 \%$
(D) $54.1 \%$
Q. 22 The freezing point of a solution of $20.5 \mathrm{~g} \mathrm{NH}_{4} \mathrm{Br}$ in 100 g of water is $-6.2^{\circ} \mathrm{C}$. The freezing point of a solution of 3.42 g cane-sugar in 100 g of water is $-0.185^{\circ} \mathrm{C}$. The degree of ionisation of salt is -
(A) $80 \%$
(B) $30 \%$
(C) $60 \%$
(D) $40 \%$
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. 241 g of monobasic acid in 100 g of water lowers the freezing point by $0.168^{\circ}$. If 0.2 g of same acid requires 15.1 mL of $\mathrm{N} / 10$ alkali for complete neutralization, degree of dissociation of acid will be [ $\mathrm{K}_{\mathrm{f}}$ for $\mathrm{H}_{2} \mathrm{O}$ is $1.86 \mathrm{~K} \mathrm{~mol}^{-1} \mathrm{~kg}$ ]
(A) $16.8 \%$
(B) $22.4 \%$
(C) $19.6 \%$
(D) $26.2 \%$
Q. 25 The 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) $1.86^{\circ} \mathrm{C}$
(B) $8.26^{\circ} \mathrm{C}$
(C) $7.87^{\circ} \mathrm{C}$
(D) $3.72^{\circ} \mathrm{C}$
(ii) 117 g of sodium chloride is dissolved in 1000 gm of water (Assuming sodium chloride is fully ionised)
(A) $7.44^{\circ} \mathrm{C}$
(B) $3.72^{\circ} \mathrm{C}$
(C) $11.16^{\circ} \mathrm{C}$
(D) $6.18^{\circ} \mathrm{C}$
(iii) 488.74 g of $\mathrm{BaCl}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}$ have been dissolved in 1000 g of water. (Assuming barium chloride is fully ionised)
(A) $7.44^{\circ} \mathrm{C}$
(B) $11.16^{\circ} \mathrm{C}$
(C) $3.72^{\circ} \mathrm{C}$
(D) $5.87^{\circ} \mathrm{C}$

## Practice Sheet I

| 1. (C) | 2. $(\mathrm{B})$ | 3. (A) | 4. (D) | 5. (A) | 6. (C) | 7. (D) |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 8. (C) | 9. (A) | 10. (C) | 11. (A) | 12. (C) | 13. (C) | 14. (B) |

15. (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. (A) | 16. (C) | 17. (A) | 18. (D) | 19. (C) | 20. (C) | 21. (B) |
| 22. (C) | 23. (A) | 24. (C) | 25. (i) (D) | (ii) (A) | (iii) (B) |  |

## SOLVED PROBLEMS

## SUBJECTIVE

Problem 1: Calculate the molecular weight of cellulose acetate if its $0.5 \%$ (wt./vol) solution in acetone ( $\mathrm{sp} . \mathrm{gr} .=0.9$ ) shows an osmotic rise of 23 mm against pure acetone at $27^{\circ} \mathrm{C}$.
Solution: $\quad 0.5 \%(\mathrm{wt} . / \mathrm{vol})$ solution means 0.5 gm of cellulose acetate is dissolved in 100 ml solution. Osmotic pressure $=23 \mathrm{~mm}$ of pure acetone
$\pi=2.3 \mathrm{Cm}$ of pure acetone $=\frac{2.3 \times 0.9}{13.6} \mathrm{~cm}$ of $\mathrm{Hg}=0.1522 \mathrm{~cm}$ of Hg
$\pi=\frac{0.1522}{76} \mathrm{~atm}=0.002 \mathrm{~atm}$
Let the molecular weight of the cellulose acetate be M

$$
\Rightarrow \mathrm{n}_{\text {cellulose acetate }}=\frac{0.5}{\mathrm{M}}
$$

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

Problem 2: 1 kg of an aqueous solution of Sucrose is cooled and maintained at $-4^{\circ} \mathrm{C}$. How much ice will be separated out if the molality of the solution is $0.75 ? K_{f}\left(\mathrm{H}_{2} \mathrm{O}\right)=1.86 \mathrm{Kg} \mathrm{mol}^{-1} \mathrm{~K}$.
Solution: Since molality of solution is 75 ,
hence .75 moles of sucrose are present in 1000 g of solvent (i.e. water)
$\square \mathrm{m}_{\text {solution }}=\mathrm{m}_{\text {water }}+\mathrm{m}_{\text {sucrose }}=1000+.75 \times 342=1256.5 \mathrm{gm}$
$\therefore \mathrm{m}_{\text {sucrose }}($ in kg$)=\frac{256.5}{1256.5} \times 1000=204.14 \mathrm{gm}, . \quad \mathrm{m}_{\text {watrer }}=1000-204.14=795.86 \mathrm{gm}$ $\square \Delta \mathrm{T}_{\mathrm{f}}=\mathrm{K}_{\mathrm{f}} \times \mathrm{m} \quad \Rightarrow 4=1.86 \times \frac{204.14 / 342}{\mathrm{~W} / 1000} \quad \Rightarrow \mathrm{w}=277.15$
$\therefore$ amount of ice $=795.86-277.15=518.31 \mathrm{gm}$
Problem 3: River water is found to contain $11.7 \% \mathrm{NaCl}, \mathbf{9 . 5 \%} \mathrm{MgCl}_{2}$, and $8.4 \% . \mathrm{NaHCO}_{3}$ by weight of solution. Calculate its normal boiling point assuming $\mathbf{9 0 \%}$ ionization of $\mathrm{NaCl}, \mathbf{7 0 \%}$ ionization of $\mathrm{MgCl}_{2}$ and $\mathbf{5 0 \%}$ ionization of $\mathrm{NaHCO}_{3}\left(\mathrm{~K}_{b}\right.$ for water $\left.=0.52\right)$
Solution: $\quad n_{\mathrm{NaCl}}=\frac{11.7}{58.5}=0.2, \quad \mathrm{n}_{\mathrm{MgCl}_{2}}=\frac{9.5}{95}=0.1, \quad \mathrm{n}_{\mathrm{NaHCO}_{3}}=\frac{8.4}{84}=0.1$
$\mathrm{i}_{\mathrm{NaCl}}=1+\alpha=1+0.9=1.9, \quad \mathrm{i}_{\mathrm{MgCl}_{2}}=1+2 \alpha=1+0.7 \times 2=2.4$,
$i_{\mathrm{NaHCO}_{3}}=1+2 \alpha=1+0.5 \times 2=2.0$
Weight of solvent $=100-(11.7+9.5+8.4)=70.4 \mathrm{~g}$

$=\frac{(1.9 \times 0.2+2.4 \times 0.1+2 \times 0.1) \times 0.52 \times 1000}{70.4}=5.94^{\circ} \mathrm{C}$
$\therefore$ Boiling point of solution $=100+5.94=105.95^{\circ} \mathrm{C}$

Problem 4: An aqueous solution containing 288 gm of a non-volalite compound having the stochiometric composition $C_{x} H_{2 x} O_{x}$ in 90 gm water boils at $101.24^{\circ} \mathrm{C}$ at 1.00 atmospheric pressure. What is the molecular formula?
$K_{b}\left(\mathrm{H}_{2} \mathrm{O}\right)=0.512 \mathrm{~K} \mathrm{~mol}^{-1} \mathrm{~kg} \mathrm{~T}_{b}\left(\mathrm{H}_{2} \mathrm{O}\right)=100^{\circ} \mathrm{C}$
Solution: Elevation in B.P. $=101.24-100=1.24^{\circ} \mathrm{C}$
$\Delta \mathrm{T}_{\mathrm{b}}=\mathrm{K}_{\mathrm{b}} \times \mathrm{i} \times$ molality $\quad \Rightarrow 1.24=0.512 \times \frac{288}{\mathrm{~m}} \times \frac{1000}{90} \quad(\therefore \mathrm{i}=1)$
$\therefore \mathrm{m}=1321.2 \mathrm{gm} \mathrm{mol}^{-1}$
molar mass of $\mathrm{C}_{\mathrm{x}} \mathrm{H}_{2 \mathrm{x}} \mathrm{O}_{\mathrm{x}}=12 \mathrm{x}+1 \times 2 \mathrm{x}+16 \mathrm{x}=30 \mathrm{x}$
$\therefore 30 \mathrm{x}=1321.2 \quad \therefore \mathrm{x}=44 \quad$ Hence the molecular formula is $=\mathrm{C}_{44} \mathrm{H}_{88} \mathrm{O}_{44}$
Problem 5: 30 ml of $\mathrm{CH}_{3} \mathrm{OH}\left(d=0.7980 \mathrm{gm} \mathrm{Cm}^{-3}\right)$ and 70 ml of $\mathrm{H}_{2} \mathrm{O}(d=0.9984 \mathrm{gm}$ $\mathrm{cm}^{-3}$ ) are mixed at $25^{\circ} \mathrm{C}$ to form a solution of density $0.9575 \mathrm{gm} \mathrm{cm}^{-3}$. Calculate the freezing point of the solution. $K_{f}\left(\mathrm{H}_{2} \mathrm{O}\right)$ is $1.86 \mathrm{Kg} \mathrm{mol}^{-1} \mathrm{~K}$. Also calculate its molarity
Solution: Weight of $\mathrm{CH}_{3} \mathrm{OH}\left(\mathrm{w}_{1}\right)=30 \mathrm{~cm}^{3} \times 0.7980 \mathrm{gm} / \mathrm{cm}^{3}=23.94 \mathrm{gm}$
Weight of solvent $\left(\mathrm{H}_{2} \mathrm{O}\right)\left(\mathrm{w}_{2}\right)=70 \mathrm{~cm}^{3} \times 0.9984 \mathrm{gm} \mathrm{cm}^{3}=69.888 \mathrm{gm}$
$\mathrm{m}=\frac{23.94}{32} \times \frac{1000}{69.88}=10.7046 \mathrm{molal}$
$\therefore \Delta \mathrm{T}_{\mathrm{f}}=\mathrm{K}_{\mathrm{f}} \times \mathrm{i} \times$ molality, $\quad\left(\right.$ for $\left.\mathrm{CH}_{3} \mathrm{OH}, \mathrm{i}=1\right)$
$\Delta \mathrm{T}_{\mathrm{f}}=1.86 \times 10.7046^{\circ} \mathrm{C}=19.91^{\circ} \mathrm{C}$
Freezing point of the solution $=0-19.91^{\circ} \mathrm{C}=-19.91^{\circ} \mathrm{C}$
Weight of solution $=$ weight of solute + weight of solvent $=23.94+69.888=93.828 \mathrm{gm}$
volume of the solution $=\frac{\text { wt. of the solution }}{\text { density of the solution }}=\frac{93.828}{0.95751}=97.99 \mathrm{ml}$
$\mathrm{M}($ molarity $)=\frac{23.94}{32} \times \frac{1000}{97.99} \mathrm{~mol} \mathrm{lit}{ }^{-1}=7.63 \mathrm{M}$
Problem 6: A complex is represented as $\mathrm{CoCl}_{3} . x \mathrm{NH}_{3}$. Its 0.1 m solution in aqueous solution shows $\Delta T_{f}=0.558^{\circ} K_{f}\left(\mathrm{H}_{2} \mathrm{O}\right)=1.86 \mathrm{~mol}^{-1} \mathrm{~K}$ and assume $100 \%$ ionization and co-ordination number of Co(III) is six. What is the complex?
Solution: $\quad \Delta \mathrm{T}_{\mathrm{f}}=\mathrm{i} \times \mathrm{K}_{\mathrm{f}} \times \mathrm{m}, \quad \Rightarrow 0.558=1.86 \times 0.1 \times \mathrm{i}$
$\therefore \mathrm{i}=\frac{0.558}{0.186}=3$
or, $\mathrm{i} \approx 3$ indicates that complex ionize to form three ions since co-ordination number is 6 hence $\mathrm{x}=5$
i.e., $\mathrm{CoCl}_{3} .5 \mathrm{NH}_{3} \longrightarrow\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right]^{++} \underset{\substack{+ \\ \text { 1 Cation }}}{ } \quad+\quad 2 \mathrm{Cl}^{-} \underset{ }{\downarrow}{ }^{\downarrow}{ }^{\downarrow}$ anions

So, the complex is $\left[\mathrm{Co}\left(\mathrm{NH}_{3}\right)_{5} \mathrm{Cl}\right] \mathrm{Cl}_{2}$
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. $K_{f}$ for benzene $=5 \mathrm{~K} \mathrm{~kg}$ mole ${ }^{-1}$.

Solution: Molality of the resulting solution (i.e. after the benzene freezes out) can be determined on the basis Raoult's law.
$\mathrm{m}=\frac{\mathrm{X}_{\text {naph }} \times 1000}{\mathrm{X}_{\text {benzene }} \times 78}=\frac{\frac{(760-670)}{760}}{0.88 \times 78}=1.72 \mathrm{~mol} \mathrm{~kg}$.
Weight of benzene in the resulting solution $=\left(\frac{1000}{1.72} \times 0.1\right)=58.1 \mathrm{~g}$
Amount of benzene frozen $=0.9 \times 78-58.1=12.1 \mathrm{~g}$ $\Delta \mathrm{T}_{\mathrm{f}}=\mathrm{K}_{\mathrm{f}} \mathrm{m}=5 \times 1.72=8.60 \mathrm{~K}$
Hence the temp to which the solution was cooled $=278.5-8.60=269.9 \mathrm{~K}$
Problem 8: Find $K_{d^{\prime}}$, the ionization constant of tartaric acid if a 0.100 molal aqueous solution of tartaric acid freezes at $-0.205^{\circ} \mathrm{C}$. Assume that only the first ionization is of importance and that $0.1 \mathrm{~m}=0.1 \mathrm{M} . K_{f}=1.86 \mathrm{~kg} \mathrm{~mol}^{-1} \mathrm{~K}$.
Solution: Assuming that the tartaric acid be a monobasic as AH. It ionizes as

|  |  | AH | $\rightleftharpoons$ | $\mathrm{A}^{\Theta}$ | + | $\mathrm{H}^{+}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Initially conc. | C | 0 |  | 0 |  |  |
| Conc. after dissociation | $\mathrm{C}(1-\alpha)$ | $\mathrm{C} \alpha$ |  | $\mathrm{C} \alpha$, |  |  |

Here, $i=\frac{C(1-\alpha)+\mathrm{C} \alpha+\mathrm{C} \alpha}{\mathrm{C}}$, where $\alpha=$ degree of dissociation $=\frac{\mathrm{C}(1+\alpha)}{\mathrm{C}}=1+\alpha$
Molal concentration $=0.1$
$\Delta \mathrm{T}_{\mathrm{f}}=\mathrm{K}_{\mathrm{f}} \times \mathrm{C}_{\mathrm{m}} \times \mathrm{i} \quad \Rightarrow \quad 0.205=1.86 \times 0.1 \times(1+\alpha) \quad \therefore \alpha=0.1$
$\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{A}^{-}\right]\left[\mathrm{H}^{+}\right]}{[\mathrm{AH}]}=\frac{\mathrm{C} \alpha \times \mathrm{C} \alpha}{\mathrm{C}(1-\alpha)}=\frac{\alpha^{2} \mathrm{C}}{1-\alpha} \quad \mathrm{K}_{\mathrm{a}}=\frac{(0.1)^{2} \times 0.1}{1-0.1}=1.11 \times 10^{-3}$
$\therefore \mathrm{K}_{\mathrm{a}}=1.11 \times 10^{-3}$
Problem 9: The freezing point depression of a 0.109 M aq. solution of formic acid is $-0.21^{\circ} \mathrm{C}$.
Calculate the equilibrium constant for the reaction,
$\mathrm{HCOOH}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{HCOO}^{-}(\mathrm{aq})$
$K_{f}$ for water $=1.86 \mathrm{~kg} \mathrm{~mol}^{-1} \mathrm{~K}$
Solution: $\quad \mathrm{HCOOH}(\mathrm{aq}) \rightleftharpoons \mathrm{H}^{+}(\mathrm{aq})+\mathrm{HCOO}^{-}(\mathrm{aq})$
Initially moles
C
Moles after dissociation

$$
(1-\alpha) \mathrm{C}
$$

0
$\mathrm{i}=\frac{(1-\alpha) \times \mathrm{C}+\alpha \times \mathrm{C}+\alpha \times \mathrm{C}}{1 \times \mathrm{C}}=1+\alpha$,
$\Delta \mathrm{T}_{\mathrm{f}}=\mathrm{K}_{\mathrm{f}} \times \mathrm{i} \times \mathrm{C}_{\mathrm{m}}$
$0.21=1.86 \times(1+\alpha) \times 0.109$ ( for dilute solution molality $\approx$ molarity $)$
$\therefore 1+\alpha=\frac{0.21}{1.86 \times 0.109}=1.0358 \Rightarrow \alpha=0.0358=0.036$
$\mathrm{K}_{\mathrm{a}}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{HCOO}^{-}\right]}{[\mathrm{HCOOH}]}=\frac{\mathrm{C}^{2}}{(1-\alpha)}=\frac{0.109 \times(0.036)^{2}}{0.964}=1.41 \times 10^{-5}$

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 $2 A \rightleftharpoons A_{2}$. Calculate equilibrium constant for dimerisation. Freezing point of benzene is $278.4 k$ and ( $K_{f}$ for benzene is 5)
Solution: $\begin{array}{rl}2 \mathrm{~A} & \mathrm{~A}_{2} \\ 1 & 0 \\ 1-\alpha & \alpha / 2 \\ \therefore \mathrm{i}=\frac{(1-\alpha)+\alpha / 2}{1}= & 1-\alpha / 2\end{array}$
$X_{A}=0.02, \quad X_{B}=0.98$
Molality of $A$ in $B=\frac{\mathrm{x}_{\mathrm{A}}}{\mathrm{m}_{\mathrm{B}}} \times \frac{1000}{X_{\mathrm{B}}}=\frac{0.02}{78} \times \frac{1000}{0.98}=0.262 \mathrm{~mol} \mathrm{~kg}^{-1}$ of Benzene
Since, $\Delta \mathrm{T}_{\mathrm{f}}=\mathrm{K}_{\mathrm{f}} \times \mathrm{i} \times$ molality $\quad 278.4-277.4=5 \times \mathrm{i} \times 0.262$
or, $1=5 \times \mathrm{i} \times 0.262, \mathrm{i}=\frac{1}{5 \times 0.262}=0.763, \quad 1-\alpha / 2=0.763 \Rightarrow \alpha=0.47$
Hence the molality of A after dimer is formed $=(1-\alpha) \times$ initial molality $=(1-0.48) \times$ initial molality $=0.52 \times 0.262$
Molality of $\mathrm{A}_{2}$ after dimer is formed
$=\frac{\alpha}{2} \times$ molality $=\frac{0.48}{2} \times 0.262=0.24 \times 0.26=0.06288$
The equilibrium constant $\quad \mathrm{K}_{\mathrm{eq}}=\frac{\left[\mathrm{A}_{2}\right]}{[\mathrm{A}]^{2}}=\frac{0.06288}{(0.13624)^{2}}=3.39 \mathrm{~kg} \mathrm{~mol}^{-1}$

## EXERCISE I

## Raoult's law

Q. $1 \quad$ At $25^{\circ} \mathrm{C}$, the vapour pressure of methyl alcohol is 96.0 torr. What is the mole fraction of $\mathrm{CH}_{3} \mathrm{OH}$ in a solution in which the (partial) vapor pressure of $\mathrm{CH}_{3} \mathrm{OH}$ is 23.0 torr at $25^{\circ} \mathrm{C}$ ?
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 $26^{\circ} \mathrm{C}$ is 25.21 torr. What is the vapour pressure of a solution which contains 20.0 glucose, $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}$, in 70 g water?
Q. 4 The vapour pressure of pure water at $25^{\circ} \mathrm{C}$ 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
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 $30^{\circ} \mathrm{C}$ with a benzene-toluene solution with a mole fraction of benzene of 0.40 ? With a mole fraction of benzene of 0.60 ?
$\mathrm{P}_{\mathrm{b}}^{\circ}=119$ torr and $\mathrm{P}_{\mathrm{t}}^{\circ}=37$ torr
Q. 8 At $90^{\circ} \mathrm{C}$, the vapour pressure of toluene is 400 torr and that of $\sigma$-xylene is 150 torr. What is the composition of the liquid mixture that boils at $90^{\circ} \mathrm{C}$, 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 $25^{\circ} \mathrm{C}$ is 639.7 mm of Hg and the vapour pressure of a solution of a solute in $\mathrm{C}_{6} \mathrm{H}_{6}$ 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 $\mathrm{P}_{\mathrm{A}}$ ) contains equal mole of toluene and benzene. Solution $B$ contains equal masses of both (total pressure $\mathrm{P}_{\mathrm{B}}$ ). The vapour pressure of benzene and toluene are 160 and 60 mm Hg respectively at 313 K . Calculate the value of $\mathrm{P}_{\mathrm{A}} / \mathrm{P}_{\mathrm{B}}$.

## 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 $0.284^{\circ} \mathrm{C}$. What is the molecular weight of the substance? Molal boiling point constant for ether is $2.11^{\circ} \mathrm{C} \cdot \mathrm{kg} / \mathrm{mol}$.
Q. 18 A solution containing 3.24 of a nonvolatile nonelectrolyte and 200 g of water boils at $100.130^{\circ} \mathrm{C}$ at 1 atm . What is the molecular weight of the solute? ( $\mathrm{K}_{\mathrm{b}}$ for water $0.513^{\circ} \mathrm{C} / \mathrm{m}$ )
Q. 19 The molecular weight of an organic compound is $58.0 \mathrm{~g} / \mathrm{mol}$. 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 $99.725^{\circ} \mathrm{C}$.
Q. 20 An aqueous solution of a nonvolatile solute boils at $100.17^{\circ} \mathrm{C}$. At what temperature will this solution freeze? $\left[\mathrm{K}_{\mathrm{f}}\right.$ for water $1.86^{\circ} \mathrm{C} / \mathrm{m}$ ]
Q. 21 Pure benzene freeze at $5.45^{\circ} \mathrm{C}$. A solution containing 7.24 g of $\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{Cl}_{4}$ in 115.3 g of benzene was observed to freeze at $3.55^{\circ} \mathrm{C}$. 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 $-0.465^{\circ} \mathrm{C}$. 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 $0.10^{\circ} \mathrm{C}$ lower than that of pure benzene. What is the molecular weight of the compound? ( $\mathrm{K}_{\mathrm{f}}$ is $5.12^{\circ} \mathrm{C} / \mathrm{m}$ for benzene)
Q. 24 The elements X and Y form compounds having molecular formula $\mathrm{XY}_{2}$ and $\mathrm{XY}_{4}$. When dissolved in 20 gm of benzene, $1 \mathrm{gm} \mathrm{XY}{ }_{2}$ lowers the freezing point by $2.3^{\circ}$, whereas 1 gm of $\mathrm{XY}_{4}$ lowers the freezing point by $1.3^{\circ} \mathrm{C}$. The molal depression constant for benzene is 5.1. Calculate the atomic masses of X and Y.
Q. 25 Calculate the molal elevation constant, $\mathrm{K}_{\mathrm{b}}$ for water and the boiling of 0.1 molal urea solution. Latent heat of vaporisation of water is $9.72 \mathrm{kcal} \mathrm{mol}^{-1}$ at 373.15 K .
Q. 26 Calculate the amount of ice that will separate out of cooling a solution containing 50 g of ethylene glycol in 200 g water to $-9.3^{\circ} \mathrm{C}$. $\left(\mathrm{K}_{\mathrm{f}}\right.$ for water $\left.=1.86 \mathrm{~K} \mathrm{~mol}^{-1} \mathrm{~kg}\right)$
Q. 27 A solution of 0.643 g of an organic compound in 50 ml of benzene (density; $0.879 \mathrm{~g} / \mathrm{ml}$ ) lowers its freezing point from $5.51^{\circ} \mathrm{C}$ to $5.03^{\circ} \mathrm{C}$. If $\mathrm{K}_{\mathrm{f}}$ for benzene is 5.12 K , calculate the molecular weight of the compound.
Q. 28 The cryoscopic constant for acetic acid is $3.6 \mathrm{~K} \mathrm{~kg} / \mathrm{mol}$. A solution of 1 g of a hydrocarbon in 100 g of acetic acid freezes at $16.14^{\circ} \mathrm{C}$ instead of the usual $16.60^{\circ} \mathrm{C}$. 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 $25^{\circ} \mathrm{C}$ is found to be 30 atm . $\mathrm{K}_{\mathrm{f}}($ water $)=1.86 \mathrm{~kg} \cdot \mathrm{~mol}^{-1} . \mathrm{K}$.
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 $10^{\circ} \mathrm{C}$, the osmotic pressure of urea solution is 500 mm . The solution is diluted and the temperature is raised to $25^{\circ} \mathrm{C}$, when the osmotic pressure is found to be 105.3 mm . Determine extent of dilution.
Q. 32 The osmotic pressure of blood is 7.65 atm at $37^{\circ} \mathrm{C}$. 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 $17^{\circ} \mathrm{C}$ of an aqueous solution containing 1.75 g of sucrose $\left(\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}\right)$ per $150 \mathrm{~cm}^{3}$ of solution?
Q. 34 A 250 mL water solution containing 48.0 g of sucrose, $\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}$, 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 $125 \mathrm{~cm}^{3}$ of an aqueous medium. At $4^{\circ} \mathrm{C}$ an osmotic pressure rise of 2.6 mm of the solution was observed. The solution had a density of $1.00 \mathrm{~g} / \mathrm{cm}^{3}$. Determine the molecular weight of the protein.
Q. 36 The osmotic pressure of a solution of a synthetic polyisobutylene in benzene was determined at $25^{\circ} \mathrm{C}$. A sample containing 0.20 g of solute $/ 100 \mathrm{~cm}^{3}$ of solution developed a rise of 2.4 mm at osmotic equilibrium. The density of the solution was $0.88 \mathrm{~g} / \mathrm{cm}^{3}$. What is the molecular weight of the polyisobutylene?
Q. 37 A 5\% solution (w/v) of cane-sugar (Mol. weight $=342$ ) is isotonic with $0.877 \%(\mathrm{w} / \mathrm{v})$ of urea solution. Find molecular weight of urea.
Q. 3810 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 $\mathrm{H}_{2} \mathrm{SO}_{4} 38 \%$ by weight. What will be the Van't Hoff factor if the $\Delta \mathrm{T}_{\mathrm{f}(\text { experiment })}$ in 29.08 . [Given $\mathrm{K}_{\mathrm{f}}=1.86 \mathrm{~mol}^{-1} \mathrm{Kg}$ ]
Q. 40 A certain mass of a substance, when dissolved in $100 \mathrm{~g} \mathrm{C}_{6} \mathrm{H}_{6}$, lowers the freezing point by $1.28^{\circ} \mathrm{C}$. The same mass of solute dissolved in 100 g water lowers the freezing point by $1.40^{\circ} \mathrm{C}$. If the substance has normal molecular weight in benzene and is completely ionized in water, into how many ions does it dissociate in water? $\mathrm{K}_{\mathrm{f}}$ for $\mathrm{H}_{2} \mathrm{O}$ and $\mathrm{C}_{6} \mathrm{H}_{6}$ are 1.86 and $5.12 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}$.
Q. 412.0 g of benzoic acid dissolved in 25.0 g of benzene shows a depression in freezing point equal to 1.62 K . Molal depression constant $\left(\mathrm{K}_{\mathrm{f}}\right)$ of benzene is $4.9 \mathrm{~K} . \mathrm{kg} . \mathrm{mol}^{-1}$. What is the percentage association of the acid?
Q. 42 A decimolar solution of potassium ferrocyanide is $50 \%$ dissociated at 300 K . Calculate the osmotic pressure of the solution. $\quad\left(\mathrm{R}=8.314 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}\right)$
Q. 43 The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g of benzene is lowered by $0.45^{\circ} \mathrm{C}$. Calculate the degree of association of acetic acid in benzene. $\left(\mathrm{K}_{\mathrm{f}}\right.$ for benzene $=5.12 \mathrm{~K}$ $\mathrm{mol}^{-1} \mathrm{~kg}$ )
Q. $44 \quad 0.85 \%$ aqueous solution of $\mathrm{NaNO}_{3}$ is apparently $90 \%$ dissociated at $27^{\circ} \mathrm{C}$. Calculate its osmotic pressure. $\left(\mathrm{R}=0.082 \mathrm{l} \mathrm{atm} \mathrm{K} \mathrm{K}^{-1} \mathrm{~mol}^{-1}\right)$
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 .

## ANSWER

## EXERCISE I

| Q. 1 | 0.24 | Q. 2 | 0.25 | Q. 3 | 24.5 torr | Q. 4 | $57.24 \mathrm{~g} / \mathrm{mol}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Q. 5 | 66.13 mm Hg | Q. 6 | 0.237 | Q. 7 | 0.682, $0.318 ; 0.829,0.171$ |  |  |
| Q. 8 | $92 \mathrm{~mol} \%$ toluene; $96.8 \mathrm{~mol} \%$ toluene |  |  |  | Q. $9 \quad \mathrm{P}_{\mathrm{A}}^{\circ}=213.33$ torr, $\mathrm{P}_{\mathrm{B}}^{\circ}=960.0$ torr |  |  |
| Q. 10 | 0.04 | Q. 11 | $111.1 \mathrm{~g}, 18.52$ molal |  |  | Q. 12 | $0.741 \mathrm{~m}, 0.013$ |
| Q. 13 | 0.162 m | Q. 14 | 65.25 | Q. 15 | 17.38 | Q. 16 | 0.964 |
| Q. 17 | $106 \mathrm{~g} / \mathrm{mol}$ | Q. 18 | $64.0 \mathrm{~g} / \mathrm{mol}$ | Q. 19 | $100.079^{\circ} \mathrm{C}$ | Q. 20 | $-0.62{ }^{\circ} \mathrm{C}$ |
| Q. 21 | $5.08^{\circ} \mathrm{C} / \mathrm{m}$ | Q. 22 | $50.8 \mathrm{~g} / \mathrm{mol}$ | Q. 23 | $2050 \mathrm{~g} / \mathrm{mol}$ | Q. 24 | $x=25.6, y=42.6$ |

Q. $25 \mathrm{~K}_{\mathrm{b}}=0.512 \mathrm{~kg} \mathrm{~mol} \mathrm{~K}^{-1}, \mathrm{~T}_{\mathrm{b}}=373.20 \mathrm{~K}$
Q. $26 \quad 38.71 \mathrm{~g}$
Q. $27 \quad 156.06$
Q. $28 \quad \mathrm{C}_{6} \mathrm{H}_{6}$
Q. $29 \mathrm{~T}_{\mathrm{f}}=-2.28^{\circ} \mathrm{C}$
Q. 30
$\mathrm{P}=0.2217 \mathrm{~atm}$ should be applied
Q. $31 \quad\left(\mathrm{~V}_{\text {final }}=5 . \mathrm{V}_{\text {original }}\right)$
Q. $32 \quad 54.2 \mathrm{~g}$
Q. $33 \quad 0.81 \mathrm{~atm}$
Q. $34 \quad 13.8 \mathrm{~atm}$
Q. $35 \quad 5.4 \times 10^{5} \mathrm{~g} / \mathrm{mol}$
Q. $36 \quad 2.4 \times 10^{5} \mathrm{~g} / \mathrm{mol}$
Q. $37 \quad 59.99$
Q. $38 \quad M_{A} / M_{B}=0.33$
Q. $39 \quad \mathrm{i}=2.5$
Q. 403 ions
Q. $41 \quad \alpha=99.2 \%$
Q. 42
$7.482 \times 10^{5} \mathrm{Nm}^{-2}$
Q. $43 \quad 94.5 \%$
Q. 44 4.64 atm
Q. 45 0.95; 1.95

