

## POINTS TO REMEMBER

Henry's law	$P = K_H X$ , where, $P$ = partial pressure of a gas over solution, $K_H$ = Henry's constant, $X$ = mole fraction of the gas in solution
Raoult's law	$P = X_A P_A^0 + X_B P_B^0$ , where, $P$ = total pressure of the solution, $X_A$ and $X_B$ = mole fraction of substituents A and B. $p_A^0$ and $P_B^0$ = partial pressure of A and B, respectively
Relationship between Dalton's law and Raoult's law	$Y_A = \frac{X_A P_A^0}{P} = \frac{P_A}{P}$ , $Y_B = \frac{X_B P_B^0}{P} = \frac{P_B}{P}$ , where, $Y_A$ and $Y_B$ denotes mole fraction of components A and B in vapor phase
Lowering of vapor pressure	$\frac{P_A^0 - P}{P_A^0} = x_B$ , relative lowering of vapor pressure = mole fraction of solute
Elevation in boiling point	$\Delta T_B = \frac{K_B W_B}{M_B \times W_A} \times 1000$
Depression in freezing point	$\Delta T_f = \frac{RT_f \times w_{\text{solute}}}{M_{\text{solute}} \times W_{\text{solvent}}} \times 1000$
Osmotic pressure	Osmotic pressure, $\pi = CRT$
van't Hoff factor, $i$	$i = \frac{\text{Normal molecular wt. (calculated value)}}{\text{Observed molecular wt. (experimental value)}}$
van't Hoff factor in case of association	For association, $\alpha = \frac{i-1}{n-1}$
van't Hoff factor in case of dissociation	For dissociation, $\alpha = \frac{i-1}{\frac{1}{n} - 1}$

## Solved Examples

## JEE Main/Boards

**Example 1:** One litre of sea water weighs 1030 g and contain about  $6 \times 10^{-3}$  g of dissolved  $O_2$ . Calculate the concentration of dissolved oxygen in ppm.

**Sol:** Mass of  $O_2$  in mg =  $6 \times 10^{-3}$  g  $\times 10^3$  mg/g = 6 mg

ppm of  $O_2$  in 1030 g sea water

$$= \frac{\text{Mass of } O_2 \text{ in mg}}{\text{Mass of sea water in mg}} \times 10^6$$

$$= \frac{6}{(1030 \times 1000) \text{mg}} \times 10^6 = 5.8 \text{ ppm}$$

**Example 2:** The osmotic pressure of a solution of an organic substance containing 18 g in one litre of solution at 293 K is  $2.414 \times 10^5 \text{ Nm}^{-2}$ . Find the molecular mass of the substance if  $S = 8.3 \text{ JK}^{-1}$  per mol.

**Sol:** Applying the equation,  $PV = \frac{w}{m} \cdot ST$  or  $m = \frac{w}{PV} \cdot ST$

Given,  $P = 2.414 \times 10^5 \text{ Nm}^{-2}$ ,

$V = 1.0 \text{ liter} = 1 \times 10^{-3} \text{ m}^3$ ,

$S = 8.3 \text{ JK}^{-1}$  per mol,

$w = 18 \text{ g}$  and  $T = 293 \text{ K}$

$$m = \frac{18}{2.414 \times 10^5 \times 1 \times 10^{-3}} \times 8.3 \times 293 = 181.33$$

**Example 3:** What is the molality of 40.0 wt% ethylene glycol solution used for automobile antifreeze? (molar mass of ethylene glycol = 62 g mol<sup>-1</sup>).

**Sol:** 100 g ethylene glycol solution has

= 40 g ethylene glycol

60 g water (solvent) has = 40 g ethylene glycol

Or 0.060 kg water has

$$= \frac{40}{62} \text{ mole ethylene glycol}$$

$$\therefore \text{Molality} = \frac{\text{mole of solute}}{\text{kg of solvent}} = \frac{40/62}{0.060} = 10.75 \text{ molal}$$

**Example 4:** To 500 cm<sup>3</sup> of water 3.0 × 10<sup>3</sup> kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K<sub>f</sub> and density of water are 1.86 K kg<sup>-1</sup> and 0.997 g cm<sup>-3</sup>, respectively.

**Sol:** Mass of solute = 3 × 10<sup>-3</sup> kg = 3 g

Mass of solvent = 500 × 0.997 = 498.5 g

$$\alpha = 23\% = 0.23,$$

$$i = 1 - \alpha + n\alpha = 1 - 0.23 + 2 \times 0.23 = 1.23$$

$$\Delta T_f = i(\text{molality} \times K_f)$$

$$\Rightarrow 1.23 \times \left( \frac{3 \times 1000}{60 \times 498.5} \right) \times 1.86 \Rightarrow \Delta T_f = 0.229$$

**Example 5:** Concentration of NaOH solution is 3.0 molal and its density is 1.110 g/mL. What is the molarity of the solution?

$$\text{Sol: Molarity} = \frac{w}{M} \times \frac{1000}{V}$$

[V = volume of the solution]

3 mol. of NaOH = 120 g of NaOH

Weight of the solution = [120 + 1000] g

$$= 1120 \text{ g}$$

1.110 g solution has the volume = 1 c.c.

$$\therefore 1120 \text{ g solution has the volume} = \frac{1}{1.110} \times 1120$$

$$\text{Hence, molarity} = \left[ \frac{w}{M} \right] \times \frac{1000}{V}$$

$$= 3 \times \frac{1000}{1120} \times 1.110 = 2.9732 \text{ M}$$

**Example 6:** Why does the use of the pressure cooker reduces cooking time?

**Sol:** At higher pressure over the liquid (due to weight of the pressure cooker lid) the liquid boils at higher temperature and cooking occurs faster.

**Example 7:** One liter of a sample of hard water contains 1 mg of CaCl<sub>2</sub> and 1 mg of MgCl<sub>2</sub>. Find the total hardness in terms of parts of CaCO<sub>3</sub> per 10<sup>6</sup> parts of water by mass.

**Sol:** CaCl<sub>2</sub> → CaCO<sub>3</sub>

$$111 \text{ g} \quad 100 \text{ g}$$

$$\therefore 1 \text{ mg of CaCl}_2 \text{ is equivalent to } \left( \frac{100}{111} \times 1 \right) \text{ mg CaCO}_3$$

MgCl<sub>2</sub> → CaCO<sub>3</sub>

$$95 \quad 100$$

$$\therefore 1 \text{ mg of MgCl}_2 \text{ is equivalent to } = \left( 2 \times \frac{1}{3} \right) = 0.82 \text{ mg}$$

$$\text{Total mass of CaCO}_3 = \left( \frac{100}{111} + \frac{100}{95} \right) \text{ mg}$$

$$= 1.9535 \text{ mg}$$

Given volume = 1 liter, mass

$$= 1000 \text{ g} = 10^6 \text{ mg}$$

Thus, 1.9535 mg of CaCO<sub>3</sub> is present in 10<sup>6</sup> mg of H<sub>2</sub>O.

Hardness = 1.9535 ppm

**Example 8:** Vapor pressure of mixtures of C<sub>6</sub>H<sub>6</sub> and C<sub>7</sub>H<sub>8</sub> at 50°C are given by P<sub>M</sub> = 179 X<sub>B</sub> + 92, respectively where X<sub>B</sub> is the mole fraction of C<sub>6</sub>H<sub>6</sub>. Calculate

(a) Vapor pressure of pure liquids.

(b) Vapor pressure of liquid mixture obtained by mixing 936g C<sub>6</sub>H<sub>6</sub> and 736 g toluene.

(c) If the vapors are removed and condensed into liquid and again brought to the temperature of 50°C, what would be the mole fraction of C<sub>6</sub>H<sub>6</sub> in vapor state?

**Sol:** Given, P<sub>M</sub> = 179X<sub>B</sub> + 92

For pure C<sub>6</sub>H<sub>6</sub>,

X<sub>B</sub>, i.e., mole fraction of benzene = 1

$$\therefore P_B^0 = 179 + 92 = 271 \text{ mm}$$

(a) For pure C<sub>7</sub>H<sub>8</sub>; X<sub>B</sub> = 0

$$\therefore P_T^0 = 179 \times 0 + 92 = 92 \text{ mm}$$

$$(b) X_B = \frac{\frac{936}{78}}{\frac{936}{78} + \frac{736}{92}} = \frac{12}{12+8} = 0.60$$

$$X_T = \frac{\frac{736}{92}}{\frac{936}{78} + \frac{736}{92}} = \frac{8}{12+8} = 0.40$$

$$P_M = 179 \times 0.6 + 92 = 107.4 + 92 = 199.4 \text{ mm}$$

(c) Mole fraction of  $C_6H_6$  in vapor phase of initial mixture  
 $X'_B = P'_B / P_M$

$$\therefore X'_B = [271 \times 0.6] / 199.4 = 0.815$$

$$\text{Similarly, } X'_T = [92 \times 0.4] / 199.4 = 0.185$$

These fractions of vapors are taken out and condensed into liquid. The liquid is again brought to  $50^\circ\text{C}$  to get again vapour-liquid equilibrium.

$\therefore$  Mole fraction of components in vapor phase of initial mixture = Mole fraction of components in liquid phase of II mixture.

$$\begin{aligned} \therefore P_M &= P_B^0 \cdot X'_B + P_T^0 \cdot X'_T \\ &= 271 \times 0.815 + 92 \times 0.185 \text{ mm} \\ &= 220.865 + 17.02 = 237.885 \text{ mm} \end{aligned}$$

**Example 9:** The solution of a non-volatile solute in water freezes at  $-0.30^\circ\text{C}$ . The vapor pressure of pure water at 298 K is 23.51 mm Hg and  $K_f$  of water is 1.86 degree/molal. Calculate the vapor pressure of this solution at 298 K.

**Sol:**  $\Delta T_f = \text{molality} \times K_f$ ;  $0.30 = \text{molality} \times 1.86$

$$\text{molality} = \frac{0.30}{1.86} = \frac{10}{62} = \frac{5}{31} \Rightarrow \frac{n \times 1000}{W(\text{gm})}$$

$n$  = moles of solute,  $W$  = wt. of solvent

$M$  = mol. wt. solvent,  $N$  = mole of solvent

$$\frac{n}{N \times 18} = \frac{5}{31 \times 1000}$$

$$\Rightarrow \frac{n}{N} = \frac{5 \times 18}{31 \times 1000} = \frac{9}{3100}$$

$$\therefore P_s = \frac{N}{n+N} P^0 \Rightarrow \frac{\frac{N}{1 + \frac{N}{n}}}{1 + \frac{N}{n}} P^0$$

$$\Rightarrow P_s = \frac{\frac{3100}{9}}{1 + \frac{3100}{9}} \times 23.51 = 23.442 \text{ mm}$$

**Example 10:**  $x$  g of non-electrolytic compound (molar mass = 200) is dissolved in 1.0 liter of 0.05 M NaCl solution. The osmotic pressure of this solution is found to be 4.92 atm at  $27^\circ\text{C}$ . Calculate the value of ' $x$ '. Assume complete dissociation of NaCl and ideal behavior of this solution.

**Sol:** (i) For NaCl;  $\pi_1 = i(\text{CRT})$

$$\pi_1 = 2 \times 0.05 \times 0.0821 \times 300 ; \Rightarrow \pi_1 = 2.463 \text{ atm}$$

For unknown compound

$$\pi_2 = \text{CRT} \Rightarrow \pi_2 = \frac{x}{200 \times 1} \times 0.821 \times 300 ;$$

$$\Rightarrow \pi_2 = 0.1231 \times \text{atm}$$

Total osmotic pressure  $\pi = \pi_1 + \pi_2$

$$4.92 = 2.463 + 0.1231x ; \quad x = 19.959 \text{ g}$$

## JEE Advanced/Boards

**Example 1:** Two liquids A and B form ideal solution. At 300 K, the vapor pressure of a solution containing 1 mole of A and 3 moles of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapor pressure of the solution increases by 10 mm of Hg. Determine the vapor pressure of A and B in their pure state.

**Sol:** Let the VP of pure A and B are  $P_A^0$  and  $P_B^0$ , respectively.

Total VP of solution (1 mole A + 3 moles B)

$$P_M = X_A P_A^0 + X_B P_B^0 \Rightarrow 550 = \frac{1}{4} P_A^0 + \frac{3}{4} P_B^0$$

$$\text{or } P_A^0 + 3P_B^0 = 2200 \quad \dots (i)$$

Total VP of solution (1 mole A + 4 moles B)

$$P_M = \frac{1}{5} P_A^0 + \frac{4}{5} P_B^0 \Rightarrow 560 = \frac{1}{5} P_A^0 + \frac{4}{5} P_B^0$$

$$\text{or } P_A^0 + 4P_B^0 = 2800 \quad \dots (ii)$$

Solving (i) and (ii)

$$P_A^0 = 400 \text{ mm of Hg} \quad P_B^0 = 600 \text{ mm of Hg}$$

**Example 2:** Two liquids A and B form an ideal solution at temperature  $T$ . When the total vapor pressure above the solution is 400 torr, the mole fraction of A in the vapor phase is 0.40 and in the liquid phase 0.75. What are the vapor pressure of pure A and pure B at temperature  $T$ ?

**Sol:** Mole fraction of A in vapor phase  $Y_A = 0.4$  and in liquid phase  $X_A = 0.75$

$$P_{\text{Total}} = 400 \text{ torr}$$

Let VP of pure A and B are  $P_A^0$  and  $P_B^0$

$$X_A P_A^0 = Y_A P_{\text{Total}}$$

$$P_A^0 = \frac{Y_A P_{\text{Total}}}{X_A} = \frac{0.4 \times 400}{0.75} = \frac{160}{0.75}$$

$$P_A^0 = 213.33 \text{ torr.}$$

$$P_{\text{Total}} = X_A P_A^0 + (1 - X_A) P_B^0$$

$$400 = 0.75 \left( \frac{160}{0.75} \right) P_B^0 + (1 - 0.75),$$

$$P_B^0 = 960 \text{ torr}$$

**Example 3:** Calculate the freezing point of an aqueous solution of nonelectrolyte having an osmotic pressure of 0.2 atmosphere at 300 K.

( $K_f = 1.86 \text{ K kg mol}^{-1}$ ,  $R = 0.821 \text{ liter-atm K}^{-1} \text{ mol}^{-1}$ ) (assume molarity = molality)

$$\text{Sol: } \pi = CRT, C = \frac{\pi}{RT} = \frac{2}{0.821 \times 300} \text{ mol lit}^{-1}$$

In dilute solution, the density of water can be taken as  $1.90 \text{ gm cm}^{-3}$ .

Hence, molality  $\approx$  molarity

$$\Delta T_f = (\text{molality} \times K_f) = \frac{2}{0.821 \times 300} \times 1.86; \Rightarrow \Delta T_f = 0.151 \text{ K}$$

$$\therefore (T_f)_{\text{solution}} = (T_f)_{\text{solvent}} - \Delta T_f = (273 - 0.151)$$

$$(T_f)_{\text{solution}} = 272.749 \text{ K or } -0.151^\circ\text{C}$$

**Example 4:** Vapor pressure of water at 293 K is 17.51 mm. Lowering of vapor pressure of a sugar solution is 0.0614 mm. Calculate (i) relative lowering of vapor pressure, (ii) vapor pressure of the solution and (iii) mole fraction of water.

**Sol:** Here, we are given that

vapor pressure of water; ( $P^0$ ) = 17.51 mm

Lowering of vapor pressure

$$(P^0 - P_s) = 0.0614 \text{ mm}$$

(i) Relative lowering of vapor pressure

$$= \frac{P^0 - P_s}{P^0} = \frac{0.0614 \text{ mm}}{17.51 \text{ mm}} = 0.00351$$

(ii) Vapor pressure of the solution ( $P_s$ )

$$P^0 - P_s = 0.0614 \text{ mm; } P^0 = 17.51 \text{ mm}$$

$$\therefore 17.51 \text{ mm} - P_s = 0.0614 \text{ mm}$$

$$\text{or } P_s = 17.51 \text{ mm} - 0.0614 \text{ mm} = 17.4468 \text{ mm}$$

(iii) To calculate mole fraction of water

$$\text{By Raoult's law, } \frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A + n_B} = x_B,$$

mole fraction of solute, i.e.,

$$x_B = \frac{P^0 - P_s}{P^0} = 0.00351$$

$\therefore$  Mole fraction of solvent (water),

$$X_A = 1 - x_B = 1 - 0.00351 = 0.99649$$

**Example 5:** Ethylene dibromide ( $\text{C}_2\text{H}_4\text{Br}_2$ ) and 1,2-dibromo propane form a series of ideal solutions over the whole range of composition. At  $85^\circ\text{C}$ , the vapor pressure of these two liquids are 173 and 127 torr, respectively. What would be the mole fraction of ethylene dibromide in a solution at  $85^\circ\text{C}$  equilibrated with 1:1 molar mixture in the vapor?

**Sol:** Suppose the mole fraction of ethylene dibromide in the liquid phase =  $x$ . Then, mole fraction of 1,2-dibromo propane will be =  $1 - x$ .

Vapor pressure of ethylene dibromide

$$= x \times P^0 = x \times 173 \text{ torr} = 173x \text{ torr}$$

Vapor pressure of 1,2-dibromo propane

$$= (1 - x) \times 127 \text{ torr}$$

As they have 1:1 molar ratio in the vapor phase,

$$173x = (1 - x) \times 127 \text{ or } 173x = 127 - 127x$$

$$\text{or } 300x = 127 \text{ or } x = \frac{127}{300} = 0.423$$

**Example 6:** Vapor pressure of solution containing 6 g of a non-volatile solute in 180 g water is 20.0 torr. If 1 mol water is further added vapor pressure increases by 0.02 torr. Calculate vapor pressure of water and molecular weight of non-volatile solute with temperature remaining constant.

**Sol:** Let molecular wt. of solute =  $m$  and VP of water (solvent) =  $P^0$

$$P_{\text{solution}} = 20 \text{ torr}$$

$$\text{moles of solute, } n = \frac{6}{m}$$

$$\text{moles of solvent, } N = \frac{180}{18} = 10$$

$$\therefore P_s = \left( \frac{N}{n + N} \right) P^0$$

$$\Rightarrow 20 = \left( \frac{10}{\frac{6}{m} + 10} \right) P^0 = \left( \frac{10m}{6 + 10m} \right) P^0 \quad \dots (i)$$

If 1 mol water is further added, then moles of solvent  $N = 10 + 1 = 11$  mol and VP of solution becomes

$$P_s = 20 + 0.02 = 20.02 \text{ torr}$$

$$\Rightarrow P_s = \frac{N}{n+N} P^0$$

$$20.02 = \left( \frac{11}{\frac{6}{m} + 11} \right) = \left( \frac{11m}{6 + 11m} \right) P^0 \quad \dots \text{(ii)}$$

Now, divide (2) by (1)

$$\frac{20.02}{20} = \frac{11(6 + 10m)}{10(6 + 11m)}$$

$$\Rightarrow m = 54 \text{ g}$$

Put this value of  $m$  in (i) or (ii)

$$P^0 = 22.22 \text{ torr}$$

**Example 7:** The density of a solution containing 13% by mass of sulfuric acid is 1.09 g/mL. Calculate the molarity and normality of the solution.

**Sol:** Volume of 100 g of the solution

$$= \frac{100}{d} = \frac{100}{1.09} \text{ mL} = \frac{100}{1.09 \times 1000} \text{ liter} = \frac{1}{1.09 \times 10} \text{ liter}$$

Number of moles of  $\text{H}_2\text{SO}_4$  in 100 g of the solution

$$= \frac{13}{98}$$

$$\text{Molarity} = \frac{\text{No. of moles } \text{H}_2\text{SO}_4}{\text{Volume of soln. in litre}}$$

$$= \frac{13}{98} \times \frac{1.09 \times 10}{1} = 1.445 \text{ M}$$

[Note: In solving such numericals, the following formula can be applied:]

$$\text{Molarity} = \frac{\% \text{strength of soln.} \times \text{density of soln.} \times 10}{\text{Mol. mass}}$$

Similarly, normality

$$= \frac{\% \text{strength of soln.} \times \text{density of soln.} \times 10}{\text{Eq. mass}}$$

We know that,

$$\begin{aligned} \text{Normality} &= \text{Molarity} \times n \\ &= 1.445 \times 2 \end{aligned}$$

$$\left[ n = \frac{\text{Mol. mass}}{\text{Eq. mass}} = \frac{98}{49} = 2 \right] = 2.89 \text{ N}$$

**Example 8:** Calculate the molarity, molality and mole fraction of ethyl alcohol in a solution of total volume 95 mL prepared by adding 50 mL of ethyl alcohol (density =  $0.789 \text{ mL}^{-1}$ ) to 50 mL water (density =  $1.00 \text{ g mL}^{-1}$ ).

**Sol:** No. of moles of ethyl alcohol

$$= \frac{\text{Vol.} \times \text{density}}{\text{Mol. mass}} = \frac{50 \times 0.789}{49} = 0.8576$$

No. of moles of water

$$= \frac{\text{Vol.} \times \text{density}}{\text{Mol. mass}} = \frac{50 \times 1}{18} = 2.7777$$

$$\text{Molarity} = \frac{\text{No. of moles}}{\text{Vol. of sol. in mL}} \times 1000$$

$$= \frac{0.8576}{95} \times 1000 = 9.027 \text{ M}$$

$$\text{Molality} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent in grams}} \times 1000$$

$$= \frac{0.8576}{50} \times 1000 = 17.152 \text{ m}$$

$$\text{Mole fraction} = \frac{0.8576}{0.8576 + 2.7777} = \frac{0.8576}{3.6353} = 0.236$$

**Example 9:** A current of dry air was bubbled through a bulb containing 26.66 g of an organic compound in 200 g of water and then through a bulb at the same temperature, containing water and finally through a tube containing anhydrous calcium chloride. The loss of mass in bulb containing water was 0.087 g and gain in mass of the calcium chloride tube was 2.036 g. Calculate the molecular mass of the organic substance.

$$\text{Sol: } \frac{P_0 - P_s}{P_0} = \frac{\text{Loss in mass solvent bulb}}{\text{Gain in mass of } \text{CaCl}_2 \text{ tube}} = \frac{0.087}{2.036}$$

Let the molecular mass of the organic substance be  $m$ . According to Raoult's law,

$$\frac{P_0 - P_s}{P_0} = \frac{w/m}{\frac{w}{m} + \frac{W}{M}}$$

$$\frac{0.087}{2.036} = \frac{\frac{26.66}{m}}{\frac{26.66}{m} + \frac{200}{18}} = \frac{26.66}{26.66 + \frac{200}{18}m}; m = 53.75$$

**Example 10:** 2.0 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 ( $K_f$ ) of benzene is  $4.9 \text{ K kg mol}^{-1}$ . What is the percentage association of the acid if it forms dimer in the solution?

**Sol:** Mass of solute (benzoic acid),  $w_2 = 2.0$  g

Mass of solvent (benzene),  $w_1 = 25.0$  g

Observed  $\Delta T_f = 1.62$  K

$K_f = 4.9$  K kg mol<sup>-1</sup>

∴ Observed molar mass of benzoic acid

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

$$= \frac{1000 \text{ g kg}^{-1} \times 4.9 \text{ K kg mol}^{-1} \times 2.0 \text{ g}}{1.62 \text{ K} \times 25.0 \text{ g}} = 242 \text{ g mol}^{-1}$$

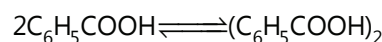
Calculated molar mass of benzoic acid

(C<sub>6</sub>H<sub>5</sub>COOH) = 72 + 5 + 12 + 32 + 1 = 122 g mol<sup>-1</sup>

van't Hoff factor,  $i = \frac{\text{Calculated mol. mass}}{\text{Observed mol. mass}}$

$$= \frac{122}{242} = 0.504$$

If  $\alpha$  is the degree of association of benzoic acid, then we have



Initial moles            1            0

After association       1 -  $\alpha$         $\alpha/2$

∴ The total number of moles after association

$$= 1 - \alpha + \frac{\alpha}{2} = 0.504$$

$$\alpha = (1 - 0.504) \times 2 = 0.496 \times 2 = 0.992$$

Or percentage association = 99.2%

## JEE Main/Boards

### Exercise 1

**Q.1** How many grams of H<sub>2</sub>SO<sub>4</sub> are required to prepare 250 mL of 0.2 molar solution?

**Q.2** A solution contains 23g of ethanol and 72g of water. Calculate the mole fraction of ethanol and water.

**Q.3** 2.82 g glucose (mo. mass = 180) are dissolved in 30g of H<sub>2</sub>O. Calculate the (i) Molality of the solution (ii) Mole fraction of glucose and water.

**Q.4** Prove that the relative lowering of vapour pressure is equal to the mole fraction of non-volatile solute in the solution.

**Q.5** What is the relation between elevation of boiling point and osmosis pressure?

**Q.6** One litre aqueous solution of sucrose (molar mass = 342 g mol<sup>-1</sup>) weighing 1015 g is found to record an osmotic pressure of 4.85 atm at 293 K. What is the molality of the sucrose solution?

**Q.7** A solution containing 12.5 g of a non-electrolyte substance in 175 g of water gave a boiling point elevation of 0.70 K. Calculate the molar mass of the substance. (Elevation constant for water is  $K_b = 0.52$  K kg mol<sup>-1</sup>)

**Q.8** A solution of a non-volatile solute in water freezes at -30.0. The vapour pressure of pure water at 298 K is 23.51 mm Hg and  $K_f$  for water is 1.86 degree/mol. Calculate the vapour pressure of this solution at 298 K.

**Q.9** The vapour pressure of pure benzene at 25°C is 639.7 mm Hg and the vapour pressure of a solution of non-volatile solute in benzene at the same temperature is 631.9 mm Hg.

Calculate the mole fraction of the solute and the molality of the solution. (C = 12, H = 1)

**Q.10** (i) What is osmotic pressure and how is it reached to the molecular mass of a non-volatile substance?

(ii) What advantage the osmotic pressure method has over the elevation of boiling point method for determining molecular masses?

**Q.11** State Raoult's law for solutions of nonvolatile solute in volatile solvents. Derive a mathematical expression for this law?

**Q.12** What is the molarity of a 13% solution (by weight) of sulphuric acid? Its density is 1.020 g cm<sup>-3</sup> (Atomic masses : H = 1, O = 16, S = 32 amu)

**Q.13** What is the molar concentration of solute particles in the human blood if the osmotic pressure is 72 atm at the body temperature of 37°C? (R = 0.0821 L atm K<sup>-1</sup> mol<sup>-1</sup>)

**Q.14** Calculate the molar concentration of urea solution if it exerts an osmotic pressure of 2.45 atm at 300K. ( $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$ )

**Q.15** To 500 cm<sup>3</sup> of water,  $3.0 \times 10^{-5}$  kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point?  $K_f$  and density of water are  $1.86 \text{ K kg}^{-1}/\text{mol}$  and  $0.997 \text{ g cm}^{-3}$  respectively.

**Q.16** How many mL of 0.1M HCl are required to react completely with 1g mixture of  $\text{Na}_2\text{CO}_3$  and  $\text{NaHCO}_3$  containing equimolar amount of two?

**Q.17** The boiling point of benzene is 353.23K. When 1.80g of a non-volatile solute was dissolved in 90g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute.  $K_b$  for benzene is  $2.53 \text{ K kg mol}^{-1}$ .

**Q.18** 1.0 g of a non-electrolyte solute dissolved in 50g of benzene lowered the freezing point of benzene by 0.40K. The freezing point depression constant of benzene is  $5.12 \text{ K kg mol}^{-1}$ . Find the molecular mass of the solute.

**Q.19** Calculate the mass of a non-volatile solute (mol mass = 40) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

**Q.20** What is the relation between elevation in boiling point and molar heat of vapourisation?

**Q.21 (a)** The outer shells of two eggs are removed. One of the egg is placed in pure water and other is placed in saturated solution of sodium chloride. What will be observed and why?

**(b)** A decimolar solution of potassium ferrocyanide.  $\text{K}_4[\text{Fe}(\text{CN})_6]$  is 50% dissociated at 300K. Calculate osmotic pressure of the solution. [ $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ]

**Q.22** Why do calculations based on lowering in freezing points of a solutions sometime give abnormal molar mass value for solutes? How may the equation for the related colligative property be modified for substance exhibiting abnormal molar mass value? A solute contains 7.45g KCl per litre of solution. It has an osmotic pressure of 4.68 atm at 300K. Calculate the degree of dissociation for KCl in this solution.

**Q.23** 0.6 mL of acetic acid ( $\text{CH}_3\text{COOH}$ ) having density  $1.06 \text{ g mL}^{-1}$ , in dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was  $0.0205^\circ\text{C}$ . Calculate van't Hoff factor and dissociation constant of acid.

**Q.24** Two elements A and B form compound having formula  $\text{AB}_2$  and  $\text{AB}_4$ . When dissolved in 20g of benzene ( $\text{C}_6\text{H}_6$ ) 1g of  $\text{AB}_2$  lowers the freezing point by 2.3 K whereas 1.0 g of  $\text{AB}_4$  lowers by 1.3K. The molar depression constant for benzene is  $5.1 \text{ K kg mol}^{-1}$ . Calculate atomic masses of A and B.

**Q.25** 19.5 g of  $\text{CH}_2\text{FCOOH}$  is dissolved in 500g water. The depression in freezing point of water observed is  $1.0^\circ\text{C}$ . Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

**Q.26** Vapour pressure of pure acetone and chloroform at 328K are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition plot  $P_{\text{total}}$ ,  $P_{\text{chloroform}}$  and  $p_{\text{acetone}}$  as a function of  $x_{\text{acetone}}$ . The experimental data observed for different composition of mixture as:

$100 \times x_{\text{acetone}}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
$P_{\text{acetone}}$	0	549	110.1	202.4	322.7	405.9	454.1	521.1
$P_{\text{chloroform}}$	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7

Plot this data also on the same graph paper. Indicate whether it has positive deviation or negative deviation from the ideal solution.

**Q.27 (a)** Derive the relationship between relative lowering of vapour pressure and mole fraction of the volatile liquid.

**(b) (i)** Benzoic acid completely dissolves in benzene. What will be the vapour pressure of a solution containing 61g of benzoic acid per 500g benzene when the vapour pressure of the pure benzene of the temperature of experiment is 66.6 torr?

**(ii)** What would have been the vapour pressure in the absence of dissolution?

**(iii)** Derive a relationship between mole-fraction and vapour pressure of a component of an ideal solution in phase and vapour phase.

**Q.28 (a)** Which solution has higher concentration: 1 molar or 1 molal solution of the same solute. Give reasons.

**(b)** 0.5 g KCl was dissolved in 100g of water and the solution originally at  $20^\circ\text{C}$ , froze at  $-0.24^\circ\text{C}$ . Calculate the percentage ionization of salt. KCl per 1000g water = 1.86.

**Q.29** How will you explain Henry's law in terms of Le Chatelier's principle and Kinetic theory of gases? or

State Henry's law for the solubility of gases in liquid. Explain it in terms of Le Chatelier's theorem.

## Exercise 2

### Single Correct Choice Type

**Q.1** Mole fraction of A vapours above the solution in mixture of A and B ( $X_A = 0.4$ ) will be [Given:  $P_A^0 = 100$  mm Hg and  $P_B^0 = 200$  mm Hg]

- (A) 0.4 (B) 0.8  
(C) 0.25 (D) None of these

**Q.2** The exact mathematical expression of Raoult's law is

- (A)  $\frac{P^0 - P_s}{P^0}$  (B)  $\frac{P^0 - P_s}{P^0} = \frac{N}{n}$   
(C)  $\frac{P^0 - P_s}{P_s} = \frac{n}{N}$  (D)  $\frac{P^0 - P_s}{P^0} = n \times N$

**Q.3** A mixture contains 1 mole of volatile liquid A ( $P_A^0 = 100$  mm Hg) and 3 moles of volatile liquid B ( $P_B^0 = 80$  mm Hg). If solution behaves ideally, the total pressure of the distillate is

- (A) 85 mm Hg (B) 85.88 mm H  
(C) 90 mm Hg (D) 92 mm Hg

**Q.4** Assuming each salt to be 90% dissociated, which of the following will have highest boiling point?

- (A) Decimolar  $Al_2(SO_4)_3$   
(B) Decimolar  $BaCl_2$   
(C) Decimolar  $Na_2SO_4$   
(D) A solution obtained by mixing equal volumes of (B) and (C)

**Q.5** The vapour pressure of a solvent decreased by 10 mm of Hg when a non-volatile solute was added to the solvent. The mole fraction of solute in solution is 0.2, what would be mole fraction of the solvent if decrease in vapour pressure is 20 mm of Hg.

- (A) 0.2 (B) 0.4 (C) 0.6 (D) 0.8

**Q.6** Elevation of boiling point of 1 molar aqueous glucose solution (density = 1.2 g/mL) is

- (A)  $K_b$  (B)  $1.20 K_b$  (C)  $1.02 K_b$  (D)  $0.98 K_b$

**Q.7** What will be the molecular weight of  $CaCl_2$  determined in its aq. solution experimentally from depression of freezing point?

- (A) 111 (B) <111 (C) >111 (D) Data insufficient

**Q.8** 1.0 molal aqueous solution of an electrolyte  $A_2B_3$  is 60% ionized. The boiling point of the solution at 1 atm is  $K_{b(H_2O)} = 0.52$  K kg mol<sup>-1</sup>

- (A) 274.76 K (B) 377 K (C) 376.4 K (D) 374.76 K

**Q.9** The van't Hoff factor for a dilute aqueous solution of glucose is

- (A) Zero (B) 1.0 (C) 1.5 (D) 2.0

**Q.10** The correct relationship between the boiling points of very dilute solution of  $AlCl_3$  ( $T_1K$ ) and  $CaCl_2$  ( $T_2K$ ) having the same molar concentration is

- (A)  $T_1 = T_2$  (B)  $T_1 > T_2$  (C)  $T_2 < T_1$  (D)  $T_2 \leq T_1$

**Q.11** A 0.001 molal solution of a complex  $[MA_3]$  in water has the freezing point of  $-0.0054^\circ C$ . Assuming 100% ionization of the complex salt and  $K_f$  for  $H_2O = 1.86$  km<sup>-1</sup>, what the correct representation for the complex

- (A)  $[MA_6]$  (B)  $[MA_7]A$  (C)  $[MA_6]A_2$  (D)  $[MA_5]A_3$

**Q.12** The vapour pressure of a solution of a non-volatile electrolyte B in a solvent A is 95% of the vapour pressure of the solvent at the same temperature. If the molecular weight of the solvent is 0.3 times the molecular weight of solute, the weight ratio of the solvent and solute are

- (A) 0.15 (B) 5.7 (C) 0.2 (D) 4.0

**Q.13** The vapour pressure of a saturated solution of sparingly soluble salt ( $XCl_3$ ) was 17.20 mm Hg at  $27^\circ C$ . If the vapour pressure of pure  $H_2O$  is 17.25 mm Hg at 300K, what is the solubility of sparingly soluble salt  $XCl_3$  in mole/litre

- (A)  $4.04 \times 10^{-2}$  (B)  $8.08 \times 10^{-2}$   
(C)  $2.02 \times 10^{-2}$  (D)  $4.04 \times 10^{-3}$

**Q.14** At 300K, the vapour pressure of an ideal solution containing 3 mole of A and 2 mole of B is 600 torr. At the same temperature, if 1.5 mole of A and 0.5 mole of C (non-volatile) are added to this solution the vapour pressure of solution increases by 30 torr. What is the value of  $P_B^0$ ?

- (A) 940 (B) 405 (C) 90 (D) None of these

**Q.15** The freezing point depression of a 0.1 M aq. solution of weak acid (HX) is  $-0.20^\circ C$ . What is the value of equilibrium constant for the reaction?

$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$  [Given:  $K_f$  for water = 1.8 kg mol<sup>-1</sup> K and Molality = Molarity]

- (A)  $1.45 \times 10^{-4}$  (B)  $1.35 \times 10^{-3}$   
(C)  $1.21 \times 10^{-2}$  (D)  $1.35 \times 10^{-4}$



**Q.16** What is the following plots represents an ideal binary mixture?

(A) Plot of  $P_{\text{total}}$  v/s  $1/X_B$  is linear ( $X_B$  = mole fraction of 'B' in liquid phase)

(B) Plot of  $P_{\text{total}}$  v/s  $Y_A$  is linear ( $Y_B$  = mole fraction of 'A' in vapour phase)

(C) Plot of  $\frac{1}{P_{\text{total}}}$  v/s  $Y_A$  is linear

(D) Plot of  $\frac{1}{P_{\text{total}}}$  v/s  $Y_B$  is non-linear

**Q.17** Two liquids A and B form an ideal solution. What is the vapour pressure of solution containing 2 moles of A and 3 moles of at 300K? Vapour pressure of pure liquid A ( $P_A^0$ ) = 100 torr, Vapour pressure of pure liquid B ( $P_B^0$ ) = 300 torr/

- (A) 200 torr                      (B) 140 torr  
(C) 180 torr                      (D) None of these

**Q.18** The van't Hoff factor for 1.0 M  $\text{Ba}(\text{NO}_3)_2$  solution is 2.74. The degree of dissociation is

- (A) 91.3%      (B) 87%      (C) 100%      (D) 74%

## Previous Years' Questions

**Q.1** The Henry's law constant for the solubility of  $\text{N}_2$  gas in water at 298 K in  $1.0 \times 10^5$  atm. The mole fraction of  $\text{N}_2$  in air is 0.8. The number of moles of  $\text{N}_2$  from air dissolved in 10 moles of water at 298 K and 5 atm pressure is **(2009)**

- (A)  $4.0 \times 10^{-4}$                       (B)  $4.0 \times 10^{-5}$   
(C)  $5.0 \times 10^{-4}$                       (D)  $4.0 \times 10^{-6}$

**Q.2** The normality of 0.3 M phosphorus acid ( $\text{H}_3\text{PO}_3$ ) is **(1999)**

- (A) 0.1      (B) 0.9      (C) 0.3      (D) 0.6

**Q.3** With increase of temperature, which of these changes? **(2002)**

- (A) Molality  
(B) Weight fraction of solute  
(C) Fraction of solute present in water  
(D) Mole fraction

**Q.4** 25 mL of a solution of barium hydroxide on titration with a 0.1 molar solution of hydrochloric acid gave litre value of 35 mL. The molality of barium hydroxide solution was **(2003)**

- (A) 0.07      (B) 0.14      (C) 0.28      (D) 0.35

**Q.5** Which of the following moles of expressing concentration is independent of temperature? **(1988)**

- (A) Molarity                      (B) Molality  
(C) Formality                      (D) Normality

**Q.6** Two solutions of a substance (non-electrolyte) are mixed in the following manner 480 mL of 1.5M first solution + 520 mL of 1.2 M second solution. What is the molarity of the final mixture **(2005)**

- (A) 1.20 M                      (B) 1.50 M  
(C) 1.344 M                      (D) 2.70 M

**Q.7** Increasing the temperature of an aqueous solution will cause **(1993)**

- (A) Decrease in molality  
(B) Decrease in molarity  
(C) Decrease in mole fraction  
(D) Decrease in %w/w

**Q.8**  $6.02 \times 10^{20}$  molecules of urea are present in 100 mL of its solution. The concentration of urea solution is **(2004)**

- (A) 0.02 M      (B) 0.01 M      (C) 0.001 M      (D) 0.1 M

[Avogadro constant,  $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$ ]

**Q.9** To neutralize completely 20 mL of 0.1 M aqueous solution of phosphorus acid ( $\text{H}_3\text{PO}_3$ ), the volume of 0.1M aqueous KOH solution required is **(2004)**

- (A) 40 mL      (B) 20 mL      (C) 10 mL      (D) 60 mL

**Q.10** A 5.2 molal aqueous solution of methyl alcohol,  $\text{CH}_3\text{OH}$ , is supplied. What is the mole fraction of methyl alcohol in the solution? **(2011)**

- (A) 0.100      (B) 0.190      (C) 0.086      (D) 0.050

**Q.11** The density of solution prepared by dissolving 120 g of urea (mol mass = 60 u) in 1000g water is 1.15 g/mL. The molarity of this solution is **(2012)**

- (A) 0.50 M      (B) 1.78 M      (C) 1.02 M      (D) 2.05 M

**Q.12** Equimolar solutions in the same solvent have  
(2005)

- (A) Same boiling point but different freezing point  
(B) Same freezing point but different boiling point  
(C) Same boiling and same freezing point  
(D) Different boiling and different freezing point

**Q.13** Two liquids X and Y form an ideal solution. At 300K, vapour pressure of the solution containing 1 mol of X and 3 moles of Y is 550 mm Hg. At the same temperature, if 1 mol of Y is further added to this solution, vapour pressure of the solution increases by 10 mm Hg. Vapour pressure (in mm Hg) of X and Y in their pure states will be respectively (2009)

- (A) 200 and 300      (B) 300 and 400  
(C) 400 and 600      (D) 500 and 600

**Q.14** The vapour pressure of water at 20°C is 17.5 mm Hg. If 18g of glucose ( $C_6H_{12}O_6$ ) is added to 178.2 g of water at 20°C the vapour pressure of the resulting solution will be (2005)

- (A) 15.750 mm Hg      (B) 16.500 mm Hg  
(C) 17.325 mm Hg      (D) 17.675 mm Hg

**Q.15** A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be (2007)

- (A) 350      (B) 300      (C) 700      (D) 360

**Q.16** Which of the following liquid pair shows a positive deviation from Raoult's law (2004)

- (A) Water–nitric acid  
(B) Benzene–methanol  
(C) Water–hydrochloric acid  
(D) Acetone–chloroform

**Q.17** A 5.25% solution of a substance is isotonic with 1.5% solution of urea (molar mass =  $60\text{g mol}^{-1}$ ) in the same solvent. If the densities of both the solutions are assumed to be equal to  $1.0\text{ g cm}^{-3}$ , molar mass of the substance will be (2007)

- (A)  $90.0\text{ g mol}^{-1}$       (B)  $115.0\text{ g mol}^{-1}$   
(C)  $105.0\text{ g mol}^{-1}$       (D)  $210.0\text{ g mol}^{-1}$

**Q.18** Value of gas constant R is (2002)

- (A) 0.082 litre atm      (B)  $0.987\text{ cal mol}^{-1}\text{K}^{-1}$   
(C)  $8.3\text{ J mol}^{-1}\text{K}^{-1}$       (D)  $83\text{ erg mol}^{-1}\text{K}^{-1}$

**Q.19** During depression of freezing point in a solution the following are in equilibrium (2003)

- (A) Liquid solvent, solid solvent  
(B) Liquid solvent, solid solute  
(C) Liquid solute, solid solute  
(D) Liquid solute, solid solvent

**Q.20** The degree of dissociation ( $\alpha$ ) of a weak electrolyte,  $A_xB_y$  is related to van't Hoff factor ( $i$ ) by the expression (2011)

- (A)  $\alpha = \frac{i-1}{(x+y-1)}$       (B)  $\alpha = \frac{i-1}{x+y+1}$   
(C)  $\alpha = \frac{x+y-1}{i-1}$       (D)  $\alpha = \frac{x+y+1}{i-1}$

**Q.21** At 80°C, the vapour pressure of pure liquid 'A' is 520 mm Hg and that of pure liquid 'B' is 1000 mm Hg. If a mixture solution of 'A' and 'B' boils at 80°C and 1 atm pressure, the amount of 'A' in the mixture is (1 atm = 760 mm Hg) (2008)

- (A) 52 mol percent      (B) 34 mol percent  
(C) 48 mol percent      (D) 50 mol percent

**Q.22** If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water ( $\Delta T_f$ ), when 0.01 mol of sodium sulphate is dissolved in 1 kg of water, is ( $K_f = 1.86\text{ K kg mol}^{-1}$ ) (2010)

- (A) 0.0372 K      (B) 0.0558 K  
(C) 0.0744 K      (D) 0.0186 K

**Q.23** Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at  $-6^\circ\text{C}$  will be: [ $K_f$  for water =  $1.86\text{ K kg mol}^{-1}$ , and molar mass of ethylene glycol =  $62\text{g mol}^{-1}$ ]

- (A) 204.30g      (B) 400.00 g  
(C) 304.60 g      (D) 804.32g

**Q.24**  $K_f$  for water is  $1.86 \text{ K kg mol}^{-1}$ . If your automobile radiator holds  $1.0 \text{ kg}$  of water, how many grams of ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) must you add to get the freezing point of the solution lowered to  $-2.8^\circ\text{C}$ ? **(2012)**

- (A) 72g (B) 93g (C) 39g (D) 27g

**Q.25** Consider separate solutions of  $0.500 \text{ M C}_2\text{H}_5\text{OH}_{(\text{aq})}$ ,  $0.100 \text{ M Mg}_3(\text{PO}_4)_2_{(\text{aq})}$ ,  $0.250 \text{ M KBr}_{(\text{aq})}$  and  $0.125 \text{ M Na}_3\text{PO}_4_{(\text{aq})}$  at  $25^\circ\text{C}$ . Which statement is true about these solutions, assuming all salts to be strong electrolytes? **(2014)**

- (A) They all have the same osmotic pressure.  
 (B)  $0.100 \text{ M Mg}_3(\text{PO}_4)_2_{(\text{aq})}$  has the highest osmotic pressure.

(C)  $0.125 \text{ M Na}_3\text{PO}_4_{(\text{aq})}$  has the highest osmotic pressure.

(D)  $0.500 \text{ M C}_2\text{H}_5\text{OH}_{(\text{aq})}$  has the highest osmotic pressure.

**Q.26** The vapour pressure of acetone at  $20^\circ\text{C}$  is  $185 \text{ torr}$ . When  $1.2 \text{ g}$  of a non-volatile substance was dissolved in  $100 \text{ g}$  of acetone at  $20^\circ\text{C}$ , its vapour pressure was  $183 \text{ torr}$ . The molar mass ( $\text{g mol}^{-1}$ ) of the substance is: **(2014)**

- (A) 32 (B) 64 (C) 128 (D) 488

**Q.27**  $18 \text{ g}$  glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) is added to  $178.2 \text{ g}$  water. The vapor pressure of water (in torr) for this aqueous solution is. **(2016)**

- (A) 76.0 (B) 752.4 (C) 759.0 (D) 7.6

## JEE Advanced/Boards

### Exercise 1

**Q.1** At  $25^\circ\text{C}$ , the vapour pressure of methyl alcohol is  $96.0 \text{ torr}$ . What is the mole fraction of  $\text{CH}_3\text{OH}$  in a solution in which the (partial) vapour pressure of  $\text{CH}_3\text{OH}$  is  $23.0 \text{ torr}$  at  $25^\circ\text{C}$ ?

**Q.2** The vapour pressure of pure liquid solvent A is  $0.80 \text{ atm}$ . When a non-volatile substance B is added to the solvent its vapour pressure drops to  $0.60 \text{ atm}$ . What is the mole fraction of components B in the solution?

**Q.3** The vapour pressure of pure water at  $26^\circ\text{C}$  is  $25.21 \text{ torr}$ . What is the vapour pressure of a solution which contains  $20.0 \text{ g}$  glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ , in  $70 \text{ g}$  water?

**Q.4** The vapour pressure of pure water at  $25^\circ\text{C}$  is  $23.76 \text{ torr}$ . The vapour pressure of a solution containing  $5.40 \text{ g}$  of a non-volatile substance in  $90.0 \text{ g}$  water is  $23.32 \text{ torr}$ . Compute the molecular weight of the solute.

**Q.5** What weight of the non-volatile solute, urea needs to be dissolved in  $100 \text{ g}$  of water, in order to decrease the vapour pressure of water by  $25\%$ ? What will be the molality of the solution?

**Q.6** When  $10.6 \text{ g}$  of a non-volatile substance is dissolved in  $740 \text{ g}$  of ether, its boiling point is raised  $0.284^\circ\text{C}$ . What is the molecular weight of the substance? Molal boiling point constant for ether is  $2.11^\circ\text{C kg/mol}$ .

**Q.7** A solution containing  $3.24 \text{ g}$  of a nonvolatile nonelectrolyte and  $200 \text{ g}$  of water boils at  $100.130^\circ\text{C}$  at  $1 \text{ atm}$ . What is the molecular weight of the solute? ( $K_b$  for water  $0.513^\circ\text{C/m}$ ).

**Q.8** The molecular weight of an organic compound is  $58.0 \text{ g/mol}$ . Compute the boiling point of a solution containing  $24.0 \text{ g}$  of the solute and  $600 \text{ g}$  of water, when the barometric pressure is such that pure water boils at  $99.725^\circ\text{C}$ .

**Q.9** An aqueous solution of a non-volatile solute boils at  $100.17^\circ\text{C}$ . At what temperature will this solution freeze? [ $K_f$  for water  $1.86^\circ\text{C/m}$ ]

**Q.10** Find the freezing point of a glucose solution whose osmotic pressure at  $25^\circ\text{C}$  is found to be  $30 \text{ atm}$ .  $K_f(\text{water}) = 1.86 \text{ kg/mol K}$ .

**Q.11** The vapour pressure of an aqueous solution of glucose is  $750 \text{ mm Hg}$  at  $373 \text{ K}$ . Calculate molality and mole fraction of solute.

**Q.12** The vapour pressure of pure benzene at  $25^\circ\text{C}$  is  $639.7 \text{ mm of Hg}$  and the vapour pressure of a solution of a solute in  $\text{C}_6\text{H}_6$  at the same temperature is  $631.7 \text{ mm of Hg}$ . Calculate molality of solution.

**Q.13** The vapour pressure of pure benzene at a certain temperature is  $640 \text{ mm of Hg}$ . A nonvolatile non-

electrolyte 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.14** 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.15** Benzene and toluene form two ideal solutions A and B at 313K. Solution A (total pressure  $P_A$ ) contains equal moles of toluene and benzene. Solution B contain equal masses of both (total pressure  $P_B$ ). The vapour pressure of benzene and toluene are 160 and 60 mm Hg respectively at 313K. Calculate the value of  $P_A/P_B$ .

**Q.16** Sea water is found to contain 5.85% NaCl and 9.50% MgCl by weight of solution. Calculate its normal boiling point assuming 80% ionization for NaCl and 50% ionization of MgCl<sub>2</sub> [ $K_f(\text{H}_2\text{O}) = 0.51 \text{ kg mol}^{-1} \text{ K}$ ].

**Q.17** The latent heat of fusion of ice is 80 calories per gram at 0°C. What is the freezing point of a solution of KCl in water containing 7.45 grams of solute in 500 grams of water, assuming that the salt is dissociated to the external of 95%?

**Q.18** A complex is represented as  $\text{CoCl}_3 \cdot x\text{NH}_3$ . Its 0.1 molal solution in aq. solution shows  $\Delta T_f = 0.558^\circ\text{C}$ .  $K_f$  for  $\text{H}_2\text{O}$  is  $1.86 \text{ K mol}^{-1} \text{ kg}$ . Assuming 100% ionization of complex and coordination no. of Co is six, calculate formula of complex.

**Q.19** The molar volume of liquid benzene (density =  $0.877 \text{ g mL}^{-1}$ ) increases by a factor of 2750 as it vaporizes at 20°C and that of liquid toluene (density =  $0.867 \text{ mL}^{-1}$ ) increases by a factor of 7720 at 20°C. Solution of benzene and toluene has a vapour pressure of 46.0 torr. Find the mole fraction of benzene in vapour above the solution.

**Q.20** At 100°C, benzene and toluene have vapour pressure of 1375 and 558 torr respectively. Assuming these two form an ideal binary solution, calculate the composition of the solution that boils at 1 atm and 100°C. What is the composition of vapour issuing at these conditions?

**Q.21** At 300K, the solution of glucose in water of concentration 0.01 M and 0.001M are separated by semipermeable membrane. Pressure needs to be applied on which solution, to prevent osmosis? Calculate the magnitude of this applied pressure.

**Q.22** At 10°C, the osmotic pressure of urea solution is 500mm. The solution is diluted and the temperature is

raised to 25°C, when the osmotic pressure is found to be 105.3 mm. Determine extent of dilution.

**Q.23** The freezing point of a solution containing 0.2g of acetic acid in 20.0 g of benzene is lowered by  $0.45^\circ\text{C}$ . Calculate the degree of association of acetic acid in benzene.

**Q.24** 0.85% aqueous solution of  $\text{NaNO}_3$  is apparently 90% dissociated at 27°C. Calculate its osmotic pressure. ( $R = 0.082 \text{ l atm K}^{-1} \text{ mol}^{-1}$ ).

**Q.25** 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.

**Q.26** Calculate the boiling point of a solution containing 0.61g of benzoic acid in 50g of carbon disulphide assuming 84% dimerization of the acid. The boiling point and  $K_b$  of  $\text{CS}_2$  are  $46.2^\circ\text{C}$  and  $2.3 \text{ K kg mol}^{-1}$ , respectively.

**Q.27** At 25°C, 1 mol of A having a vapour pressure of 100 torr and 1 mol of B having a vapour pressure of 300 torr were mixed. The vapour at equilibrium is removed, condensed and the condensate is heated back to 25°C. The vapours now formed are again removed, recondensed and analysed. What is the mole fraction of A in this condensate?

**Q.28** Phenol associates in benzene to a certain extent to form a dimer. A solution containing  $20 \times 10^{-3} \text{ kg}$  phenol in 1kg of benzene has its freezing point depressed by 0.69K. Calculate the fraction of phenol that has dimerised  $K$  for benzene =  $5.12 \text{ kg mol}^{-1} \text{ K}$ .

**Q.29** 30 mL of  $\text{CH}_3\text{OH}$  ( $d = 0.7980 \text{ gm cm}^{-3}$ ) and 70 mL of  $\text{H}_2\text{O}$  ( $d = 0.9984 \text{ gm cm}^{-3}$ ) are mixed at 25°C to form a solution of density  $0.9575 \text{ gm cm}^{-3}$ . Calculate the freezing point of the solution.  $K_f$  ( $\text{H}_2\text{O}$ ) is  $1.86 \text{ kg mol}^{-1} \text{ K}$ . Also calculate its molarity.

## Exercise 2

### Single Correct Choice Type

**Q.1** For an ideal binary liquid solution with  $P_A^0 > P_B^0$ , which relation between  $X_A$  (mole fraction of A in liquid phase) and  $Y_A$  (mole fraction of A in vapour phase) is correct?

- (A)  $Y_A < Y_B$                       (B)  $X_A > X_B$   
 (C)  $\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$                       (D)  $\frac{Y_A}{Y_B} < \frac{X_A}{X_B}$

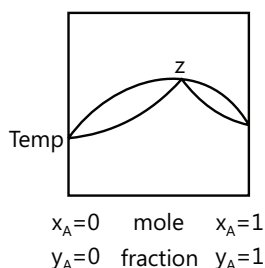
**Q.2** Which of the following aqueous solution will show maximum vapour pressure at 300K?

- (A) 1 M NaCl                      (B) 1 M CaCl<sub>2</sub>  
(C) 1 M AlCl<sub>3</sub>                      (D) 1 M C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>

**Q.3** At a given temperature, total vapour pressure in Torr of a mixture of volatile components A and B is given by  $P_{\text{Total}} = 120 - 75X_B$  hence, vapour pressure of pure A and B respectively (in Torr) are

- (A) 120, 75                      (B) 120, 95  
(C) 120, 45                      (D) 75, 45

**Q.4** A liquid mixture having composition corresponding to point z in the figure shown in subjected to distillation at constant pressure. Which of the following statement is correct about the process



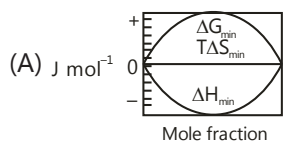
- (A) The composition of distillate differs from the mixture  
(B) The boiling point goes on changing  
(C) The mixture has highest vapour pressure than for any other composition  
(D) Composition of an azeotrope alters on changing the external pressure

**Q.5** The following graph represents variation of boiling point with composition of liquid and vapour of binary liquid mixture. The graph is plotted at constant pressure. Which of the following statement(s) is incorrect. Here X and Y stands for mole fraction in liquid and vapour phase respectively

$$\Rightarrow t = \sqrt{\frac{2L}{\omega^2 R}}$$

- (A)  $X_{\text{benzene}} = 0.5$  and  $Y_{\text{toluene}} = 0.2$   
(B)  $X_{\text{toluene}} = 0.3$  and  $Y_{\text{benzene}} = 0.6$   
(C)  $X_{\text{benzene}} = 0.3$  and  $Y_{\text{toluene}} = 0.4$   
(D)  $X_{\text{benzene}} = 0.7$  and  $Y_{\text{toluene}} < 0.3$

**Q.6** Which of the following represent correctly the changes in thermodynamic properties during the formation of 1 mol of an ideal binary solution

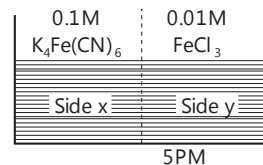


(B)  $\tan \theta = \frac{v^2}{Rg} = \frac{(10)^2}{(10)(10)} = 1$

(C)  $\theta = \tan^{-1}(1) = 45^\circ$

(D)  $\frac{dv}{dt} = a$

**Q.7** FeCl<sub>3</sub> on reaction with K<sub>4</sub>[Fe(CN)<sub>6</sub>] in aqueous solution given blue colour. These are separated by a semipermeable membrane AB as shown. Due to osmosis there is



- (A) Blue colour formation in side X  
(B) Blue colour formation in side Y  
(C) Blue colour formation in both of the sides X and Y  
(D) No blue colour formation

### Multiple Correct Choice Type

**Q.8** Acetone and carbon disulphide form binary liquid solution showing positive deviation from Raoult's law. The normal boiling point ( $T_b$ ) of pure acetone is less than that of pure CS<sub>2</sub>. Pick out the incorrect statement among the following

- (A) Boiling temperature of mixture is always less than boiling temperature of acetone  
(B) Boiling temperature of Azeotropic mixture is always less than boiling temperature of acetone  
(C) When a small amount of CS<sub>2</sub> (less volatile component) is added to excess of acetone boiling point of resulting mixture increases  
(D) A mixture of CS<sub>2</sub> and CH<sub>3</sub>COCH<sub>3</sub> can be completely separated by simple fractional distillation.

**Q.9** Which of the following would be equal to zero when the liquid pairs form an ideal solution

- (A)  $\Delta H$                       (B)  $\Delta S$                       (C)  $\Delta G$                       (D)  $\Delta V$

**Q.10** For a non-volatile solute

- (A) The vapour pressure of solute is zero  
(B) Vapour pressure of solution = Vapour pressure of pure solvent  
(C) Vapour pressure of solution = Vapour pressure of solvent in solution  
(D) All of the above

**Q.11** A difference between diffusion and osmosis is

- (A) A semipermeable membrane is required for osmosis while diffusion requires no semipermeable membrane  
 (B) In osmosis movement of molecules is only in one direction whereas in diffusion movement is on both sides  
 (C) In osmosis only the solvent moves while in diffusion both solute and solvent move  
 (D) None of the above

**Q.12** Which of the following statement is/are correct?

- (A) The freezing point of water is depressed by the addition of glucose  
 (B) The degree of dissociation of a weak electrolyte decrease as its concentration decreases  
 (C) Energy is released when a substance dissolves in water provided that the hydration energy of the substance is more than its lattice energy  
 (D) If two liquids that form an ideal solution are mixed, the change in entropy is positive

**Q.13** Which of the following gases are highly soluble in water

- (A) HCl (B) SO<sub>2</sub> (C) NH<sub>3</sub> (D) H<sub>2</sub>

**Q.14** Which of the following would be equal to zero when the liquid pairs form an ideal solution.

- (A)  $\Delta H$  (B)  $\Delta S$  (C)  $\Delta G$  (D)  $\Delta V$

**Q.15** Two miscible liquids A and B having vapour pressure in pure state  $P_A^0$  and  $P_B^0$  are mixed in mole fraction  $X_A$  and  $X_B$  to get a mixture having total vapour pressure of mixture  $P_M$ . Which of the following relation are correct?

- (A)  $X_A = \frac{P_M - P_B^0}{P_A^0 - P_B^0}$  (B)  $\frac{X_{A(l)}}{X'_{A(V)}} = \frac{P_M}{P_A^0}$   
 (C)  $\frac{X_{A(l)}}{X'_{A(V)}} = \frac{P_M}{P_B^0}$  (D) All of these

**Q.16** Which relations are not correct for aqueous dilute solution of K<sub>3</sub>PO<sub>4</sub> if its degree of dissociation is  $\alpha$ ?

- (A)  $\frac{\Delta P}{P^0} = \frac{\text{Molality} \times 18 \times (1 + 3\alpha)}{1000}$   
 (B)  $\frac{\Delta P}{P^0} = \frac{\pi_{\text{obs}} \times 18 \times (1 + 3\alpha)}{RT \times 1000}$   
 (C)  $\frac{\Delta P}{P^0} = \frac{\Delta T_{\text{f obs}} \times 18}{K_f \times 1000}$   
 (D)  $M_w \text{ of } K_2PO_4 = M_w_{\text{obs}} \times (1 + 3\alpha)$

**Q.17** Which of the following is/are true?

- (A) For the same solution, elevation in boiling point = depression in freezing point  
 (B) The Van't Hoff factor for a dilute solution of BaCl<sub>2</sub>.  
 (C) The elevation in boiling point is due to increase in vapour pressure.  
 (D) The depression in freezing point is due to decrease in vapour pressure.

**Q.18** Which pairs of liquids on mixing is/are expected to show no net volume change and no heat effect?

- (A) Acetone and ethanol  
 (B) Chloro benzene and bromo benzene  
 (C) Chloroform and benzene  
 (D) n-Butyl chloride and n-butyl bromide

### Assertion Reasoning Type

**Q.19 Statement-I:** Addition of ethylene glycol (non-volatile) to water lowers the freezing point of water hence used as antifreezing

**Statement-II:** Heat must be removed from the water to make it freeze.

- (A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I  
 (B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I  
 (C) Statement-I is true, statement-II is false.  
 (D) Statement-I is false, statement-II is true

**Q.20 Statement-I:** The freezing of water is an endothermic process.

**Statement-II:** Heat must be removed from the water to make it freeze.

- (A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I.  
 (B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I.  
 (C) Statement-I is true, statement-II is false.  
 (D) Statement-I is false, statement-II is true

**Comprehension Type**

The various relations between colligative properties and molecular mass are applicable only to solutions of non-electrolytes and in dilute solutions. Out of various colligative properties osmotic pressure measurement is especially suitable for the determination of molecular masses of proteins whereas freezing point depression and other colligative properties are too small. Certain solutes which dissociate or associate in solution affect the colligative property and hence molecular mass determination also. In case of association observed molecular mass is more than normal the correction factor  $i < 1$ . For dissociation of solute  $i > 1$  and observed molecular mass is less than the normal molecular mass

**Q.21** Which of the following 0.1 m aqueous solution will have the lowest freezing point?

- (A)  $\text{Al}_2(\text{SO}_4)_3$                       (B)  $\text{C}_6\text{H}_{12}\text{O}_6$   
(C) KI                                      (D)  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

**Q.22** Correction factor for 0.1M ideal solution is

- (A) 0.1                      (B) 1                      (C) 0.01                      (D)  $2 > 1$

**Q.23** The Van't Hoff factor for 0.1M  $\text{Ba}(\text{NO}_3)_2$  solution is 2.74. The degree of dissociation is

- (A) 91.3%                      (B) 87%                      (C) 100%                      (D) 74%

**Q.24** Which one of the following statements gives below concerning properties of a solution describe a colligative effect?

- (A) Boiling point of pure water increase by addition of EtOH  
(B) Vapour pressure of pure water decrease by addition of  $\text{HNO}_3$   
(C) Vapour pressure of pure benzene decrease by addition of naphthalene  
(D) Boiling point of pure benzene increase by addition of toluene

**Q.25** After adding a solute, freezing point of water decreases to  $-0.186^\circ\text{C}$ . What is the value of  $\Delta T$ ? ( $k_b = 0.521$ ;  $k_f = 1.86$ )

- (A) 0.521                      (B) 0.0521  
(C) 1.86                      (D) 0.0186

**Match the Columns**

**Q.26**  $P_A$  = partial pressure of components A in liquid mixture.  $P_A^0$  = vapour pressure of A,  $\chi_A$  = mole fraction of A in liquid

Column I	Column II
(A) $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$	(p) Azeotropic mixture
(B) $\text{C}_2\text{H}_2\text{Br} + \text{C}_2\text{H}_5\text{I}$	(q) Obeys Raoult's law
(C) $P_A = \chi_A P_A^0$	(r) Non-ideal solution with positive deviation
(D) $\text{H}_2\text{O} + \text{H}_2\text{SO}_4$	(s) Non-ideal solution with negative deviation
	(t) Ideal solution

**Q.27** Match the following

Column I	Column II
(A) Urea, glucose, fructose	(p) 1 : 0.8 : 1
(B) NaCl, $\text{MgCl}_2$ , $\text{K}_2\text{SO}_4$	(q) 1 : 2 : 1
(C) $\text{Al}_2(\text{SO}_4)_3$ , $\text{Na}_3\text{PO}_4$ , $\text{K}_3\text{r}[\text{Fe}(\text{CN})_6]$	(r) 1 : 1 : 1
(D) Glucose, NaCl, $\text{CaCl}_2$	(s) 2 : 3 : 3

**Q.28**

Column I	Column II
(A) ppm	(p) Van't Hoff factor
(B) $\Delta T_b$	(q) Molal depression
(C) $K_f$	(r) Elevation in boiling point
(D) $i$	(s) $\frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$

**Previous Years' Questions**

**Q.1** An azeotropic solution of two liquids has boiling point lower than either of them when it **(1981)**

- (A) Shows negative deviation from Raoult's law  
(B) Shows no deviation from Raoult's law  
(C) Shows positive deviation from Raoult's law  
(D) Is saturated

**Q.2** Which of the following 0.1M aqueous solution will have the lowest freezing point? **(1989)**

- (A) Potassium sulphate (B) Sodium chloride  
(C) Urea (D) Glucose

**Q.3** During depression of freezing point in a solution the following are in equilibrium **(2003)**

- (A) Liquid solvent, solid solvent  
(B) Liquid solvent, solid solute  
(C) Liquid solute, solid solute  
(D) Liquid solute, solid solvent

**Q.4** The freezing point (in °C) of solution containing 0.1 g of  $K_3[Fe(CN_6)]$  (mol. wt. 329) in 100 g of water ( $K_f = 1.86 \text{ K kg mol}^{-1}$ ) is **(2011)**

- (A)  $-2.3 \times 10^{-2}$  (B)  $-5.7 \times 10^{-2}$   
(C)  $-5.7 \times 10^{-3}$  (D)  $-1.2 \times 10^{-2}$

### Paragraph 3

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9.

Given, freezing point depression constant of water ( $k_f^{\text{water}} = 1.86 \text{ K kg mol}^{-1}$ )

freezing point depression constant of ethanol ( $k_f^{\text{ethanol}} = 2.0 \text{ K kg mol}^{-1}$ )

Boiling point elevation constant of water ( $k_b^{\text{water}} = 0.52 \text{ K kg mol}^{-1}$ )

Boiling point elevation constant of ethanol ( $k_b^{\text{ethanol}} = 1.2 \text{ K kg mol}^{-1}$ )

Standard freezing point of water = 273 K

Standard freezing point of ethanol = 155.7 K

Standard boiling point of water = 373 K

Standard boiling point of ethanol = 351.5 K

Vapour pressure of pure water = 32.8 mm Hg

Vapour pressure of pure ethanol = 40 mm Hg

Molecular weight of water = 18 g mol<sup>-1</sup>

Molecular weight of ethanol = 46 g mol<sup>-1</sup>

In answering the following questions, consider the solution to be ideal dilute solution and solute to be non-volatile and non-dissociative. **(2008)**

**Q.5** The freezing point of the solution M is

- (A) 268.7 K (B) 268.5 K  
(C) 234.2 K (D) 150.9 K

**Q.6** The vapour pressure of the solution M is

- (A) 39.3 mm Hg (B) 36.0 mm Hg  
(C) 29.6 mm Hg (D) 28.8 mm Hg

**Q.7** Water is added to the solution M such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is

- (A) 380.4 K (B) 376.2 K  
(C) 375.5 K (D) 354.7 K

**Q.8** Following statement is true only under some specific conditions. Write the condition, for it "Two volatile and miscible liquids can be separated by fractional distillation into pure components".

**Q.9** An organic compound ( $C_xH_{2y}O_y$ ) was burnt with twice the amount of oxygen needed for complete combustion to  $CO_2$  and  $H_2O$ . The hot gases when cooled to 0°C and 1 atm pressure, measured 2.24 L. The water collected during cooling weigh 0.9g. The vapour pressure of pure water at 20°C is 17.5 mm Hg and is lowered by 0.104 mm when 50g of the organic compound are dissolved in 1000g of water. Give the molecular formula of the organic compound. **(1983)**

**Q.10** The vapour pressure of ethanol and methanol are 44.5 and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by the mixing 60g of ethanol with 40g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour. **(1986)**

**Q.11** The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile, non-electrolyte solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of solution is 600 mm Hg. What is the molecular weight of the solid substance? **(1990)**



**Q.12** The degree of dissociation of  $\text{Ca}(\text{NO}_3)_2$  in a dilute aqueous solution, containing 7.0g of the salt per 100g of water at  $100^\circ\text{C}$  is 70%. If the vapour-pressure of water at  $100^\circ\text{C}$  is 760 mm, calculate the vapour pressure of the solution. **(1991)**

**Q.13** Nitrobenzene is formed as the major product along with a minor product in the reaction of benzene with a hot mixture of nitric acid and sulphuric acid. The minor product consists of carbon : 42.86%, hydrogen : 2.40%, nitrogen : 16.67% and oxygen : 38.07%,

(i) Calculate the empirical formula of the minor product.

(ii) When 5.5g of the minor product is dissolved in 45g of benzene, the boiling point of the solution is  $1.84^\circ\text{C}$  higher than that of pure benzene. Calculate the molar mass of the minor product then determine its molecular and structural formula. (Molal boiling point elevation constant of benzene is  $2.53 \text{ K kg mol}^{-1}$ ). **(1999)**

**Q.14** The vapour pressure of two miscible liquids (A) and (B) are 300 and 500 mm of Hg respectively. In a flask 10 moles of (A) is mixed with 12 moles of (B). However, as soon as (B) is added, (A) starts polymerizing into a completely insoluble solid. The polymerization follows first order kinetic. After 100min, 0.525 mole of a solute is dissolved which arrests the polymerization completely. The final vapour pressure of the solution is 400 mm of Hg. Estimate the rate constant of the polymerization and ideal behavior for the final solution. **(2001)**

**Q.15** Consider the three solvents of identical molar masses. Match their boiling point with their  $k_b$  values **(2003)**

Solvents	Boiling point	$k_b$ values
X	$100^\circ\text{C}$	0.92
Y	$27^\circ\text{C}$	0.63
Z	$283^\circ\text{C}$	0.53

**Q.16** When 20 g of naphthoic acid ( $\text{C}_{11}\text{H}_8\text{O}_2$ ) is dissolved in 50 g of benzene ( $K_f = 1.72 \text{ K kg mol}^{-1}$ ), a freezing point depression of 2 K is observed. The van't Hoff factor (i) is **(2007)**

- (A) 0.5      (B) 1      (C) 2      (D) 3

#### Paragraph for Question Nos. 17 to 19

Properties such as boiling point, freezing point and vapor pressure of a pure solvent change when solute molecules are added to get homogeneous solution.

These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles.

A solution M is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9.

Given: Freezing point depression constant of water ( $K_f^{\text{water}}$ ) =  $1.86 \text{ K kg mol}^{-1}$  Freezing point depression constant of ethanol ( $K_f^{\text{ethanol}}$ ) =  $2.0 \text{ K kg mol}^{-1}$  Boiling point elevation constant of water ( $K_b^{\text{water}}$ ) =  $0.52 \text{ K kg mol}^{-1}$

Boiling point elevation constant of ethanol ( $K_b^{\text{ethanol}}$ ) =  $1.2 \text{ K kg mol}^{-1}$

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative. **(2008)**

**Q.17** The freezing point of the solution M is

- (A) 268.7 K      (B) 268.5 K  
(C) 234.2 K      (D) 150.9 K

**Q.18** The vapour pressure of the solution M

- (A) 39.3 mm Hg      (B) 36.0 mm Hg  
(C) 29.5 mm Hg      (D) 28.8 mm Hg

**Q.19** Water is added to the solution M such that the fraction of water in the solution becomes 0.9. The boiling point of this solution is

- (A) 380.4 K      (B) 376.2 K  
(C) 375.5 K      (D) 354.7 K

**Q.20** The Henry's law constant for the solubility of  $\text{N}_2$  gas in water at 298 K is  $1.0 \times 10^5 \text{ atm}$ . The mole fraction of  $\text{N}_2$  in air is 0.8. The number of moles of  $\text{N}_2$  from air dissolved in 10 moles of water at 298 K and 5 atm pressure is **(2009)**

- (A)  $4.0 \times 10^{-4}$       (B)  $4.0 \times 10^{-5}$   
(C)  $5.0 \times 10^{-4}$       (D)  $4.0 \times 10^{-6}$

**Q.21** The freezing point (in  $^\circ\text{C}$ ) of a solution containing 0.1 g of  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (Mol. Wt. 329) in 100 g of water ( $K_f = 1.86 \text{ K kg mol}^{-1}$ ) is **(2011)**

- (A)  $-2.3 \times 10^{-2}$       (B)  $-5.7 \times 10^{-2}$   
(C)  $-5.7 \times 10^{-3}$       (D)  $-1.2 \times 10^{-2}$

**Q.22** For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is  $2^\circ\text{C}$ . Assuming concentration of solute is much lower than the concentration of solvent, the vapor pressure (mm of Hg) of the solution is (take  $K_b = 0.76 \text{ K kg mol}^{-1}$ )  
(2012)

- (A) 724      (B) 740      (C) 736      (D) 718

**Q.23** If the freezing point of a 0.01 molal aqueous solution of a cobalt (III) chloride-ammonia complex (which behaves as a strong electrolyte) is  $-0.05580^\circ\text{C}$ , the number of chloride(s) in the coordination sphere of the complex is [ $K_f$  of water =  $1.86 \text{ K kg mol}^{-1}$ ]

**Q.24** The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is  $2.0 \text{ g cm}^{-3}$ . The ratio of the molecular weights of the solute and solvent  $\left(\frac{MW_{\text{solute}}}{MW_{\text{solvent}}}\right)$ , is  
(2016)

**Q.25** Mixture(s) showing positive deviation from Raoult's law at  $35^\circ\text{C}$  is (are)  
(2016)

- (A) Carbon tetrachloride + methanol  
(B) Carbon disulphide + acetone  
(C) Benzene + toluene  
(D) Phenol + aniline

## MASTERJEE Essential Questions

### JEE Main/Boards

#### Exercise 1

- Q.2      Q.4      Q.9  
Q.14      Q.29

#### Exercise 2

- Q.2      Q.4      Q.14  
Q.17

#### Previous Years' Questions

- Q.6      Q.9      Q.11  
Q.16      Q.17

### JEE Advanced/Boards

#### Exercise 1

- Q.6      Q.10      Q.16  
Q.20      Q.21      Q.25

#### Exercise 2

- Q.6      Q.7      Q.12  
Q.15      Q.17      Q.25  
Q.28

#### Previous Years' Questions

- Q.1      Q.13

## Answer Key

### JEE Main/Boards

#### Exercise 1

<b>Q.1</b> 4.9 gm	<b>Q.2</b> 0.89	<b>Q.3</b> (i) 0.52m, (ii) 0.99
<b>Q.6</b> 0.2121 m	<b>Q.7</b> 53.06g mol <sup>-1</sup>	<b>Q.8</b> 23.44 mm Hg
<b>Q.9</b> 0.988; 0.156 m	<b>Q.12</b> 1.35 mol/litre; 1.52 mol/kg	<b>Q.13</b> 0.283 mol/L
<b>Q.14</b> 0.099 mol L <sup>-1</sup>	<b>Q.15</b> 0.23 K	
<b>Q.16</b> 158.9 mL of 0.1 M HCl	<b>Q.17</b> 57.5 g mol <sup>-1</sup>	<b>Q.18</b> 256 g mol <sup>-1</sup>
<b>Q.19</b> 10 g	<b>Q.21</b> (b) 7.389 atm	
<b>Q.22</b> Degree of dissociation = 90%	<b>Q.23</b> 18.6 × 10 <sup>-4</sup>	
<b>Q.24</b> Atomic mass of A = 25.59; B = 42.64	<b>Q.25</b> 1.0753; 30.68 × 10 <sup>-4</sup>	<b>Q.28</b> (b) 92%

#### Exercise 2

##### Single Correct Choice Type

<b>Q.1</b> C	<b>Q.2</b> C	<b>Q.3</b> A	<b>Q.4</b> A	<b>Q.5</b> C	<b>Q.6</b> D
<b>Q.7</b> B	<b>Q.8</b> D	<b>Q.9</b> B	<b>Q.10</b> B	<b>Q.11</b> C	<b>Q.12</b> B
<b>Q.13</b> A	<b>Q.14</b> C	<b>Q.15</b> B	<b>Q.16</b> C	<b>Q.17</b> D	<b>Q.18</b> B

##### Previous Years' Questions

<b>Q.1</b> A	<b>Q.2</b> D	<b>Q.3</b> C	<b>Q.4</b> A	<b>Q.5</b> B	<b>Q.6</b> C
<b>Q.7</b> B	<b>Q.8</b> B	<b>Q.9</b> A	<b>Q.10</b> C	<b>Q.11</b> D	<b>Q.12</b> C
<b>Q.13</b> C	<b>Q.14</b> C	<b>Q.15</b> A	<b>Q.16</b> B	<b>Q.17</b> D	<b>Q.18</b> C
<b>Q.19</b> A	<b>Q.20</b> A	<b>Q.21</b> D	<b>Q.22</b> B	<b>Q.23</b> D	<b>Q.24</b> B
<b>Q.25</b> A	<b>Q.26</b> B	<b>Q.27</b> B			

### JEE Advanced/Boards

#### Exercise 1

<b>Q.1</b> 0.24	<b>Q.2</b> 0.25	<b>Q.3</b> 24.5 torr
<b>Q.4</b> 57.24 g/mol	<b>Q.5</b> 111.1 g, 18.52 molal	<b>Q.6</b> 106 g/molal
<b>Q.7</b> 64.0 g/mol	<b>Q.8</b> 100.079°C	<b>Q.9</b> -0.62°C
<b>Q.10</b> T = -2.28°C	<b>Q.11</b> 0.741m, 0.013	<b>Q.12</b> 0.162 m
<b>Q.13</b> 65.25	<b>Q.14</b> 17.38	<b>Q.15</b> 0.964
<b>Q.16</b> T <sub>b</sub> = 101.9°C	<b>Q.17</b> T <sub>f</sub> = -0.73°C	<b>Q.18</b> [Co(NH <sub>3</sub> )Cl]Cl <sub>2</sub>
<b>Q.19</b> 0.73	<b>Q.20</b> x <sub>B</sub> = 0.2472, y <sub>B</sub> = 0.4473	

**Q.21**  $P = 0.2217 \text{ atm}$  should be applied**Q.23** 94.5%**Q.26**  $46.33^\circ\text{C}$ **Q.29**  $-19.91^\circ\text{C}$ , 7.63M**Q.24** 4.64 atm**Q.27**  $x = 0.1$ **Q.22** ( $V_{\text{total}} = 5 \cdot V_{\text{original}}$ )**Q.25** 0.95; 1.95**Q.28**  $a = 0.7333$ 

## Exercise 2

### Single Correct Choice Type

**Q.1** C**Q.2** D**Q.3** C**Q.4** D**Q.5** B**Q.6** C**Q.7** D

### Multiple Correct Choice Type

**Q.8** A, C, D**Q.9** A, D**Q.10** A, C**Q.11** A, B, C**Q.12** A, C, D**Q.13** A, B, C**Q.14** A, D**Q.15** A, B**Q.16** A, C, D**Q.17** B, D**Q.18** B, D

### Assertion Reasoning Type

**Q.19** C**Q.20** D

### Comprehension Type

**Q.21** A**Q.22** B**Q.23** B**Q.24** C**Q.25** B

### Match the Columns

**Q.26**  $A \rightarrow p, r; B \rightarrow q, t; C \rightarrow q, t; D \rightarrow p, s$ **Q.27**  $A \rightarrow r; B \rightarrow s; C \rightarrow p; D \rightarrow q$ **Q.28**  $A \rightarrow s; B \rightarrow r; C \rightarrow q; D \rightarrow p$ 

## Previous Years' Questions

**Q.1** C**Q.2** A**Q.3** A**Q.4** A**Q.5** D**Q.6** A**Q.7** B**Q.8** Condition**Q.9**  $\text{C}_5\text{H}_{10}\text{O}_{11}$ **Q.10** 0.657**Q.11** 65.25**Q.12** 746.32**Q.13** 168**Q.14**  $1.005 \times 10^{-4} \text{ min}^{-1}$ **Q.15** Subjective**Q.16** A**Q.17** D**Q.18** B**Q.19** B**Q.20** A**Q.21** A**Q.22** A**Q.23** 3**Q.24** 9**Q.25** A,B

## Solutions

### JEE Main/Boards

#### Exercise 1

**Sol 1:** We have

Molecular mass of  $\text{H}_2\text{SO}_4 = 98\text{g}$

Let weight be  $w$

Then moles  $n = \frac{w}{98}$

Now  $\frac{n}{V} = 0.2$

$$\frac{w \times 1000}{98 \times 250} = 0.2$$

$w = 4.9\text{ g}$

**Sol 2:** Molecular wt of ethanol = 46 gm

Moles of ethanol  $n_1 = \frac{23}{46} = 0.5$

Molecular mass of water = 18 gm

Moles of water,  $n_2 = \frac{72}{18} = 4$

$$X_e = \frac{n_1}{n_1 + n_2} = \frac{0.5}{4 + 0.5} = 0.11$$

$$X_w = \frac{n_2}{n_1 + n_2} = \frac{4}{4 + 0.5} = 0.89$$

**Sol 3:** Moles of glucose,  $n_1 = \frac{2.82}{180} = 0.0152$

$$(i) \text{ Molality} = \frac{n_1 \times 1000}{30} = \frac{0.0152}{30} \times 1000 = 0.52$$

(ii) moles of water,  $n_2 = \frac{30}{18} = 1.66$

$$X_g = \frac{0.0152}{0.0152 + 1.66} \approx 0.01$$

$$X_w = 1 - X_g = 0.99$$

**Sol 5:**  $\Delta T_b = k_b m$

$\pi = CRT$

$$\therefore \frac{\pi}{\Delta T_b} = \frac{CRT}{k_b m} = \frac{n}{V k_b n} RT \cdot w_s = \frac{RT}{k_b} \cdot \delta_s$$

Where  $\delta_s = \text{density of solute} = \frac{W_s}{V}$

$$\therefore \pi = \frac{RT \delta_s}{k_b} \Delta T_b$$

**Sol 6:** We have,

$\pi = CRT$

$$\Rightarrow C = \frac{\pi}{RT} = \frac{4.85}{0.0821 \times 293} = 0.201\text{ m}$$

Weight of solvent of solute =  $0.201 \times 1 = 0.201$

Weight of solvent =  $1015 - 68.95\text{g} = 946.04\text{g}$

$$\therefore \text{Molality} = \frac{0.201}{946.04} \times 1000$$

Molality = 0.2121m

**Sol 7:** We have

$$\Delta T_b = k_b m \Rightarrow m = \frac{\Delta T_b}{k_b} = \frac{0.7}{0.52}; m = 1.346\text{m}$$

$$m = \frac{n}{w_s}$$

$$n = 1.346 \times 75 \times 1000; n = 0.235$$

$$n = \frac{w}{m} \Rightarrow M = \frac{w}{n} = \frac{12.5}{0.235}$$

$M = 53.6\text{ g mol}^{-1}$

**Sol 8:** We have,

$$\Delta T_f = 0.3^\circ\text{C} = k_f m$$

$$m = \frac{0.3}{1.86} = 0.161\text{m}$$

Now we have,

$$\frac{P_0 - P}{P_0} = X_a$$

$$m = \frac{n}{w_s} \Rightarrow w_s = \frac{n}{m}$$

$$n_s = \frac{w_s}{M_s} = \frac{n}{M_s}$$

$$X_a = \frac{n}{n_s + n} = \frac{n}{\frac{n}{mM_s} + n} = \frac{1}{1 + \frac{1}{mM_s}} = \frac{1}{1 + \frac{1}{18 \times 0.161}} = \frac{1}{1000}$$

$$X_a = 2.88 \times 10^{-3}$$

$$\text{Now, } P_0 = 23.51 \text{ mmHg}$$

$$\frac{23.51 - P}{23.51} = 2.88 \times 10^{-3}$$

$$\Rightarrow P = 23.44 \text{ mmHg}$$

$$\text{Sol 9: } X_a = \frac{P_0 - P}{P_0}$$

$$\frac{639.7 - 631.9}{639.7} = 1.22 \times 10^{-2}$$

Also, from previous question.

$$X_a = \frac{1}{1 + \frac{1}{mM_s}}, M_s = 78 \text{ g}$$

$$1 + \frac{1}{mM_s} = \frac{1}{X_a}$$

$$\frac{1}{mM_s} = \frac{1}{X_a} - 1 = \frac{1 - X_a}{X_a}$$

$$mM_s = \frac{X_a}{1 - X_a}$$

$$m = \frac{X_a}{(1 - X_a) \cdot M_s}$$

By substituting the values,

$$\text{We get } m = 0.156 \text{ m}$$

**Sol 10:** (i) Osmotic pressure is the excess pressure which must be applied to a given solution in order to increase its vapour pressure until it becomes equal to that of the solution.

$$M_0 = \frac{wRT}{\pi V}; w = \text{weight of solute}$$

$\pi$  = osmotic pressure

(ii) Osmotic pressure has a relatively large magnitude and is easy to measure compared to  $\Delta T_b$ .

**Sol 12:** For every 1 kg of solution,

$$\text{wt. of } H_2SO_4 = \frac{13}{100} \times 1000 = 130 \text{ g}$$

$$\text{moles, } n = \frac{130}{98} = 1.326$$

$$\text{Wt. of solvent} = 870 \text{ g}$$

$$\text{Volume of sol}^n = \frac{1}{s} = \frac{1000}{1.020} = 980.39 \text{ cm}^3 = 980.39 \text{ ml}$$

$$\text{Molarity} = \frac{1326}{980.39} \times 1000 = 1.35 \text{ M}$$

$$\text{Molality} = \frac{n}{W_s} = \frac{1.326 \times 1000}{870} = 1.52 \text{ m}$$

**Sol 13:** We have,

$$\pi = CRT$$

$$\therefore C = \frac{\pi}{RT} = \frac{7.2}{0.0821 \times 310}$$

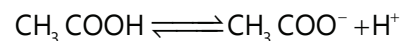
$$(T = 37^\circ C = 310 \text{ K})$$

$$C = 0.283 \text{ M}$$

**Sol 14:**  $\pi = CRT$

$$C = \frac{\pi}{RT} = \frac{2.45}{0.0821 \times 300} \Rightarrow C = 0.099 \text{ M}$$

**Sol 15:** We have,



$$n = 2, \alpha = 0.23$$

$$i = 1 + (n - 1)\alpha = 1 + 0.23 = 1.23$$

$$\text{Now, } n = \frac{3 \times 10^{-3}}{60 \times 10^{-3}} = 0.05$$

Mass of water =  $V_s$

$$= 500 \times 0.997$$

$$= 498.5 \text{ gm}$$

$$\therefore m = \frac{0.05 \times 1000}{498.5}$$

$$m = 0.1$$

$$\therefore \Delta T_f = i m k_f = 1.23 \times 0.1 \times 1.86$$

$$\Delta T_f = 0.23 \text{ K}$$

**Sol 16:** Let moles of  $Na_2CO_3$  and  $NaHCO_3$  be  $n$  each and wt. of  $NaHCO_3$  be  $x$  then,

$$\frac{x}{84} = \frac{1 - x}{104} \Rightarrow x = 0.446 \text{ g}$$

$$\text{Then, } n = \frac{x}{84} = 5.32 \times 10^{-3}$$

Now, moles of HCl = moles of



$$\Rightarrow \frac{V \times 0.1}{1000} = 5.32 \times 10^{-3} (1 + 2) = V = 158.9 \text{ ml}$$

**Sol 17:** we have,

$$M = \frac{k_B w_B}{\Delta T_b \times w_A} \times 1000$$

$$= \frac{2.53 \times 180 \times 1000}{(354.11 - 353.23) \times 90} = M = 57.5 \text{ g mol}^{-1}$$

**Sol 18:**  $M = \frac{k_f \times w_B}{\Delta T_f \times w_A} \times 1000 = \frac{5.12 \times 1}{0.4 \times 50} \times 1000$

$$M = 256 \text{ g mol}^{-1}$$

**Sol 19:** We have,  $P = 0.8P_0$

$$\therefore X_A = \frac{P_0 - P}{P_0} = 0.2$$

$$0.2 = \frac{M}{40}$$

$$\frac{M}{40} + \frac{114}{40 + 114}$$

$$\Rightarrow \frac{M}{200} + 0.2 = \frac{M}{40}$$

$$\Rightarrow M = 10 \text{ g}$$

**Sol 20:**  $\Delta T_b = k_b m$

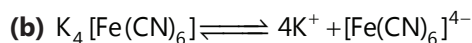
$$\text{But, } k_b = \frac{R T_b^2}{1000 \times \Delta H_v}$$

$$\therefore T_b = \frac{R T_b^2}{1000 \times \Delta H_v} \cdot m$$

$$\text{or } \Delta T_b \propto \frac{1}{\Delta H_v}$$

**Sol 21: (a)** For egg shell placed in pure water, endosmosis will take place and shell will swell.

For Egg shell placed in saturated NaCl solution, exosmosis will occur and shell will shrink.



$$n = 5$$

$$\alpha = 0.5$$

$$\Rightarrow i = 1 + (n - 1)\alpha$$

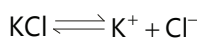
$$\Rightarrow 1 + 4\alpha$$

$$\Rightarrow 3$$

$$\pi = iCRT$$

$$= 3 \times 0.1 \times 0.0821 \times 300 = 7.389 \text{ atm}$$

**Sol 22:** For reasons and equations, refer text



$$n = 2$$

$$i = 1 + (n - 1)\alpha = 1 + \alpha$$

$$\therefore \pi = iCRT$$

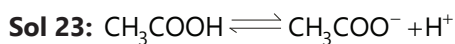
$$i = \frac{\pi}{CRT}$$

$$1 + \alpha = \frac{4.68 \times 74.5}{7.45 \times 0.0821 \times 300}$$

$$1 + \alpha = 1.9$$

$$\alpha = 0.9$$

Degree of dissociation = 90%



$$1 - \alpha \qquad \qquad \alpha \qquad \qquad \alpha$$

$$k_a = \frac{\alpha^2}{1 - \alpha}$$

$$n = 2$$

$$i = 1 + \alpha$$

$$\Delta T_f = i k_f m$$

Weight of acetic acid =  $1.06 \times 0.6 = 0.636 \text{ g}$

$$m = \frac{0.636}{\frac{60}{1}} = 0.0106$$

$$i = \frac{0.0205}{1.86 \times 0.0106} = 1.04$$

$$\alpha = 0.04$$

$$k_a = \frac{C\alpha^2}{1 - \alpha} = \frac{1.06 \times 0.6}{60} \times \frac{(0.04)^2}{(1 - 0.04)}$$

$$k_a = 18.6 \times 10^{-6}$$

**Sol 24:** We have,

$$M = \frac{k_f \times w_a}{\Delta T_f \times w_s} \times 1000$$

Let atomic mass of A and B be a and b respectively.

$$\therefore a + 2b = \frac{5.1 \times 1}{2.3 \times 20} \times 1000 = 110.87$$

$$a + 4b = \frac{5.1 \times 1}{1.3 \times 20} \times 1000 = 196.15$$

$$\therefore 2b = 85.28$$

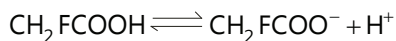
$$b = 42.64$$

$$a = 25.60$$

**Sol 25:**  $k_f = 1.86$

$$[\text{CH}_2\text{FCOOH}]_C = \frac{19.5 \times 1000}{78 \times 500} = 0.5\text{M}$$

$$m = \frac{19.5}{\frac{78}{\frac{500}{1000}}} = 0.5\text{m}$$



$$n = 2$$

$$i = 1 + \alpha$$

$$\Delta T_f = i k_f m$$

$$i = \frac{1}{1.86 \times 0.5} = 1.075$$

$$\alpha = 0.075$$

$$k_a = \frac{C\alpha^2}{1 - \alpha} = 3.06 \times 10^{-3}$$

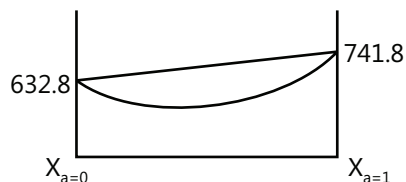
**Sol 26:**  $P_T = P_a = P_c = 741.8X_a + 632.8X_c$   
 $= 741.8X_a + 632.8(1 - X_a)$

$$P_T = 632.8 + 109X_a$$

$$P_C = 632.8 - 632.8X_a$$

$$P_a = 632.8X_a$$

Plotting this and given that a



It will show negative deviation

**Sol 27:**

(a) Refer text

(b) (i)  $= 1 - \left(1 - \frac{1}{n}\right)\alpha$

$$1 - \left(1 - \frac{1}{2}\right) = \frac{1}{2}$$

$$\frac{P_0 - P}{P_0} = iX = \frac{1}{2} \cdot \frac{61}{\frac{122}{\frac{61}{122} + \frac{500}{78}}}$$

$$\frac{66.6 - P}{66.6} = 0.036$$

$$P = 64.20 \text{ torr}$$

(ii)  $\frac{P_0 - P}{P_0} = 0.072$ ;  $P = 61.78 \text{ torr}$

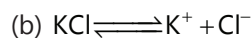
(iii) Refer Text

**Sol 28:** (a) For 1 molal

$$i = \frac{n}{w_s} \approx \frac{n}{qV}$$

$$\text{For 1 molar} = 1 = \frac{n}{V}$$

For density,  $p > 1$ : 1 molal will have more concentration.



$$n = 2$$

$$i = 1 + \alpha$$

$$m = \frac{0.5}{\frac{74.5}{\frac{100}{1000}}} = 0.067$$

$$\Delta T_f = i k_f m$$

$$i = \frac{0.24}{1.86 \times 0.067} = 1.92$$

$$\Rightarrow \alpha = 0.92$$

92% ionisation

**Sol 29:** As, we increase the pressure over a gas, the number of gaseous particles per unit volume increase and also the rate at which the gases are striking the surface of solution to enter it. According to Le-Chatelier's principle, the gas will try to return to its previous state and its solubility will increase, until a new equilibrium is reached resulting in an increase in the pressure of the gas above the solution and hence its solubility increase.



## Exercise 2

### Single Correct Choice Type

**Sol 1: (C)** We have,

$$P = P_A + P_B = X_A P_A^0 + X_B P_B^0$$

$$= 0.4 \times 100 + 0.6 \times 200$$

$$= 40 + 120 = 160 \text{ mm Hg}$$

$$P_A = 40 \text{ mmHg}$$

$$P_A = P \cdot Y_A$$

$$Y_A = \frac{40}{160} = 0.25$$

**Sol 2: (C)** Raoult's Law =  $\frac{P_0 - P}{P_0} = \frac{n}{n+N}$

$$\frac{n+N}{n} = \frac{P_0}{P_0 - P}$$

$$1 + \frac{N}{n} = \frac{P_0}{P_0 - P}$$

$$\frac{N}{n} = \frac{P_0 - P_0 + P}{P_0 - P} \Rightarrow \frac{P_0 - P}{P} = \frac{N}{n}$$

**Sol 3: (A)**  $P = X_A P_A^0 + X_B P_B^0$

$$= \frac{1}{1+3} \cdot 100 + \frac{3}{1+3} \cdot 80 = 25 + 60 = 85 \text{ mm Hg}$$

**Sol 4: (A)**  $\Delta T_b = i k_b m$

$T_b$  will be highest for solute for which  $\Delta T_b$  is highest or  $i$  is highest.

For same degree of dissociation,  $i \propto n$ ,  $n$  is largest for  $Al_2(SO_4)_3$  ( $n = 5$ )

**Sol 5: (C)**  $\frac{P_0 - P}{P_0} = X_a$

$$\frac{\Delta P}{P_0} = X_a$$

$$\frac{\Delta P_1}{\Delta P_2} = \frac{X_{a1}}{X_{a2}}$$

$$\frac{10}{20} = \frac{0.2}{X_{a2}} \Rightarrow X_{a2} = 0.4$$

$$\therefore X_s = 1 - 0.4 = 0.6$$

**Sol 6: (D)** For every 1L solution, moles of glucose = 1, weight of sol<sup>n</sup> =  $1.2 \times 1000 = 1.2 \text{ kg}$

Weight of glucose = 180 g

Weight of solvent =  $1200 - 180 = 1020 \text{g}$

$$\therefore \text{molality} = \frac{1}{1.02} = 0.98 \text{m}$$

$$\therefore \Delta T_b = K_b m = 0.98 K_b$$

**Sol 7: (B)**  $i = \frac{\text{Normal molecular wt}}{\text{Observed molecular wt}} > 1$

$\Rightarrow$  Observed molecular wt < normal molecular wt.

**Sol 8: (D)**  $A_2 B_3 \rightleftharpoons 2A^+ + 3B^-$

$$\alpha = 0.6$$

$$n = 5$$

$$i = 1 + (n-1)\alpha = 3.4$$

$$\Delta T_b = i K_b m$$

$$= 3.4 \times 0.52 \times 1$$

$$= 1.768 \text{K}$$

$$T_b = 373 + 1.768 = 374.768 \text{ K}$$

**Sol 9: (B)** Since, glucose does not dissociate,  $n = 0 \Rightarrow i = 1$

**Sol 10: (B)**  $\Delta T_b = i K_b m$

For v equimolar solution are equimolar also very dilute.

$$\therefore \Delta T_b \propto i$$

$$i_{AlCl_3} > i_{CaCl_2}$$

(as  $i \propto n$ ,  $n_{AlCl_3} = 4$ ,  $n_{CaCl_2} = 2$ )

$$\Delta T_b AlCl_3 > \Delta T_b CaCl_2$$

$$T_1 > T_2$$

**Sol 11: (C)**  $\Delta T_f = i K_f m$

$$i = \frac{\Delta T_f}{K_f m} = \frac{0.0054}{1.86 \times 0.001} = 2.903$$

$$\alpha = 1$$

$$\therefore 1 + (n-1)\alpha = 2.9 \approx 3$$

$$n - 1 = 2$$

$$n = 3$$

$\therefore$  Out of the given options, only (C) is possible

**Sol 12: (B)** We have

$$P = 0.95 P_0$$

$$\frac{P_0 - P}{P_0} = X_a = 0.05$$

$$\frac{w_a}{M_a} = 0.05$$

$$\frac{w_a + w_b}{M_a + M_b}$$

$$\frac{w_a}{M_a} = \frac{1}{20} \frac{w_a}{M_a} + \frac{1}{20} \frac{w_b}{M_b}$$

$$\frac{19}{20} \frac{w_a}{M_a} = \frac{1}{20} \frac{w_b}{M_b}$$

$$\frac{w_b}{w_a} = 19 \cdot \frac{M_b}{M_a}$$

$$19 \times 0.3 = 5.7$$

**Sol 13: (A)**  $XCl_3 \rightarrow X + 3Cl$ 

$$n = 4$$

$$\alpha = 1$$

$$i = 1 + 3 = 5$$

$$X_A = \frac{P_0 - P}{P_0}$$

$$X_A = \frac{17.25 - 17.2}{17.25 \times 4}$$

$$X_A = 7.24 \times 10^{-4} = \frac{n}{n+N}$$

$$\text{For } n+N=1, n = 7.24 \times 10^{-4}$$

$$N = 0.999$$

$$m_w = \frac{N \cdot 18}{1000}$$

$$V_w = \frac{N \cdot 18}{1000} L$$

$$\therefore [A] = \frac{n}{V_w}$$

$$\frac{X_A \cdot 1000}{(1 - X_A) \cdot 18}$$

$$[A] = 4.04 \times 10^{-2} \text{ mole/L}$$

**Sol 14: (C)** Initially

$$P = P_A + P_B = P_A^0 \cdot X_A + P_B^0 \cdot X_B$$

$$600 = \frac{3}{5} P_A^0 + \frac{2}{5} P_B^0$$

$$3P_A^0 + 2P_B^0 = 3000$$

$$9P_A^0 + 6P_B^0 = 9000$$

... (i)

After adding C,

$$P = P_A + P_B$$

$$630 = \frac{3+1.5}{3+2+1.5+0.5} P_A^0 + \frac{2}{3+2+1.5+0.5} P_B^0$$

$$630 = \frac{9}{14} P_A^0 + \frac{4}{14} P_B^0$$

$$9P_A^0 + 4P_B^0 = 8820$$

... (ii)

$$(i) - (ii) \rightarrow 2P_B^0 = 180$$

$$P_B^0 = 90 \text{ torr}$$

**Sol 15: (B)**  $HX \rightleftharpoons H^+ + X^-$ 

$$n = 2$$

$$i = 1 + (n-1)\alpha = 1 + \alpha$$

$$m = M = 0.1$$

$$\Delta T_f = i k_f m$$

$$i = \frac{\Delta T_f}{k_f m} = \frac{0.2}{1.8 \times 0.1} = 1.11$$

$$\alpha = 0.11$$

$$\therefore k_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.1 \times (0.11)^2}{(1-0.11)} = 1.35 \times 10^{-3}$$

**Sol 16: (C)**  $P_T$  vs  $X_B$  is linear

$$P_T = P_A^0 \cdot X_A + P_B^0 \cdot X_B$$

$$P_B = Y_B P_T$$

$$P_B^0 X_B = Y_B (P_A^0 X_A^0 + P_B^0 X_B^0)$$

$$\Rightarrow \frac{1}{P_T} = \frac{1}{P_B} \cdot Y_B \text{ Linear} = \frac{1}{P_A} \cdot Y_A$$

**Sol 17: (D)**  $P = P_A^0 X_A + P_B^0 X_B$ 

$$= \frac{100.2}{5} + 300 \frac{3}{5} = 40 + 90 = 130 \text{ torr}$$

**Sol 18: (B)**  $Ba(NO_3)_2 \rightarrow Ba^{2+} + 2NO_3^-$ 

$$n = 3$$

$$i = 1 + (n-1)\alpha$$

$$i = 1 + 2\alpha$$

$$2.74 = 1 + 2\alpha$$

$$\alpha = \frac{1.74}{2} = 0.87 = 87\%$$

## Previous Years' Questions

**Sol 1: (A)**  $P_{N_2} = K_H \times X_{N_2}$

$$X_{N_2} = \frac{1}{10^5} \times 0.8 \times 5 = 4 \times 10^{-5}$$

in 10 mole, solubility is  $4.0 \times 10^{-4}$

**Sol 2: (D)** Basicity of  $H_3PO_3$  is 2.

Hence 0.3 M  $H_3PO_3 = 0.6 N$ .

**Sol 3: (C)** With increase of temperature, fraction of solute present in water changes.

**Sol 4: (A)** For HCl  $M = N = 0.1$

$$N_1 V_1 = N_2 V_2; 25 \times N_1 = 0.1 \times 35$$

$$N_1 = \frac{0.1 \times 35}{25};$$

$$\therefore M = \frac{0.1 \times 35}{25 \times 2} = 0.07$$

**Sol 5: (B)** Mobility do not depends on temp. as it do not depends on volume.

**Sol 6: (C)**  $M_1 V_1 + M_2 V_2 = M_3 V_3;$

$$1.5 \times 480 + 1.2 \times 520 = M \times 1000$$

$$M = \frac{720 + 624}{1000} = 1.344 M$$

**Sol 7: (B)** An increase in temperature increases the volume of the solution and thus decreases its molarity.

**Sol 8: (B)** Mole urea =  $\frac{0.02 \times 10}{6.02 \times 10^{23}} = 10^{-3}$  moles

Conc. of solution (in molarity) =  $\frac{10^{-3}}{100} \times 1000 = 0.01 M$

**Sol 9: (A)**  $H_3PO_3$  is a dibasic acid

$$N_1 V_1(\text{acid}) = N_2 V_2(\text{base})$$

$$0.1 \times 2 \times 20 = 0.1 \times 1 \times V_2$$

$$\therefore V_2 = \frac{0.1 \times 2 \times 20}{0.1 \times 1} = 40 \text{ mL}$$

**Sol 10: (C)**  $X_{\text{methyl alcohol}} = \frac{5.2}{5.2 + \frac{1000}{18}} = 0.086$

**Sol 11: (D)** Molarity =  $\frac{\text{moles of sulphur}}{\text{volume of sol. (l)}}$

$$= \frac{120 \times 1.15}{60 \times 1120} \times 1000 = 2.05 M$$

**Sol 12: (C)** Equimolar solutions in the same solvent have same boiling and same freezing point.

**Sol 13: (C)** As  $P_T = P_x^0 \cdot X_x + P_y^0 \cdot X_y$

$$550 = P_x^0 \cdot \frac{1}{4} + P_y^0 \cdot \frac{3}{4}$$

$$P_x^0 + 3P_y^0 = 2200 \quad \dots (i)$$

On adding 1 mole of Y (P) be comes 560 so

$$560 = P_x^0 \cdot \frac{1}{5} + P_y^0 \cdot \frac{4}{5}$$

$$P_x^0 + 4P_y^0 = 2800 \quad \dots (ii)$$

From eq. (i) and (ii)

$$P_x^0 = 400 \text{ mm Hg}$$

$$P_y^0 = 600 \text{ mm Hg}$$

**Sol 14: (C)**  $\frac{P^0 - P_s}{P^0} = \frac{n}{n+N}$

$$n = \frac{18}{180} = 0.1N = \frac{178.2}{18} = 9.9 = 0.1 N$$

$$\frac{175 - P_0}{17.5} = \frac{0.1}{0.1 + 9.9}; \frac{175 - P_0}{17.5} = \frac{1}{100}$$

$$1750 - 100P_s = 17.5; 1732.5 = 100P_s$$

$$P_s = 17.325 \text{ mm Hg}$$

**Sol 15: (A)** Let the vapour pressure of pure ethyl alcohol be  $P$ ,

According to Raoult's law

$$290 = 200 \times 0.4 + P \times 0.6$$

$$P = \frac{290 - 80}{0.6} = 350 \text{ mm Hg}$$

**Sol 16: (B)** In solution showing positive type of deviation, the partial pressure of each component of solution is greater than the vapour pressure as expected according to Raoult's law.

In solution of methanol and benzene, methanol molecules are held together due to hydrogen bonding as shown below,

On adding benzene, the benzene molecules get in between the molecule of methanol thus breaking the hydrogen bonds. As the resulting solution has weak intermolecular attraction, the escaping tendency of alcohol and benzene molecule from the solution increases. Consequently, the vapour pressure of the solution is greater than the vapour pressure as expected from Raoult's law.

**Sol 17: (D)** Solution with the same osmotic pressure are isotonic.

Let the molar mass of the substance be M

$$\pi_1 = C_1 RT = C_2 RT = \pi_2$$

$$\text{So, } C_1 = C_2$$

As density of the solutions are same

$$\text{So, } \frac{5.25}{M} = \frac{15}{60}; \quad M = \frac{5.25 \times 60}{1.5} = 210 \text{ g mol}^{-1}$$

**Sol 18: (C)** Value of R =  $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

**Sol 19 (A)** During depression of freezing point in a solution liquid solvent, solid solvent are in equilibrium.

**Sol 20: (A)**  $A_x B_y \rightarrow xA^{y+} + yB^{x-}$

$$1 - \alpha \quad \alpha \quad y\alpha$$

$$i = 1 - \alpha + x\alpha + y\alpha$$

$$i = 1 + \alpha(x + y - 1)$$

$$\alpha = \frac{i - 1}{(x + y - 1)}$$

**Sol 21: (D)**  $P_T = P_A^\circ X_A + P_B^\circ X_B$

$$760 = 520X_A + P_B^\circ (1 - X_A) \Rightarrow X_A = 0.5$$

Thus, mole % of A = 50 %

**Sol 22: (B)** Vant Hoff's factor (i) for  $\text{Na}_2\text{SO}_4 = 3$

$$\therefore \Delta T_f = (i) k_f m_k = 3 \times 1.80 \times \frac{0.01}{1} = 0.0558 \text{ K}$$

$$\text{Sol 23: (D)} \quad \Delta T_f = K_f \times m = K_f \times \frac{w_2 \times 1000}{w_1 \times m_2}$$

$w_1$  and  $w_2$  = wt of solvent and solute respecting

$m_2$  = mw of solute

$$\Delta T_f = 0^\circ - (-6^\circ) = 6 = 1.86 \times \frac{w_2 \times 1000}{w_1 \times m_2}$$

Therefore  $w_2 = 800 \text{ g}$

**Sol 24: (B)**  $\Delta T_f = K_f \cdot m$

$$2.8 = 1.86 \times \frac{\text{wt}}{62} \times \frac{1000}{1000}$$

Wt = 93 g

**Sol 25: (A)**  $\pi = i CRT$

$$\pi_{\text{C}_2\text{H}_5\text{OH}} = 1 \times 0.500 \times R \times T = 0.5 RT$$

$$\pi_{\text{Mg}_3(\text{PO}_4)_2} = 5 \times 0.100 \times R \times T = 0.5 RT$$

$$\pi_{\text{KBr}} = 2 \times 0.250 \times R \times T = 0.5 RT$$

$$\pi_{\text{Na}_3\text{PO}_4} = 4 \times 0.125 \times RT = 0.5 RT$$

$$\text{Sol 26: (B)} \quad \frac{P_0 - P_s}{P_s} = \frac{n}{N}$$

$$\frac{185 - 183}{183} = \frac{1.2 / M}{100 / 58}$$

$M \approx 64 \text{ g/mol}$

**Sol 27: (B)** Moles of glucose =  $\frac{18}{180} = 0.1$

$$\text{Moles of water} = \frac{178.2}{18} = 9.9$$

$$\Rightarrow n_{\text{Total}} = 10$$

$$\Rightarrow \frac{\Delta P}{P^\circ} = \frac{0.1}{10}$$

$$\Rightarrow \Delta P = 0.01 P^\circ$$

$$= 0.01 \times 760 = 7.6 \text{ torr}$$

$$P_s = 760 - 7.6 = 752.4 \text{ torr}$$

## JEE Advanced/Boards

### Exercise 1

**Sol 1:**  $P_{\text{CH}_3\text{OH}} = P_A^0 \cdot X_A = 23$

$$X_A = \frac{23}{96} = 0.24$$

**Sol 2:**  $\frac{P_0 - P}{P_0} = X_B$

$$\frac{0.8 - 0.6}{0.8} = X_B$$

$$X_B = 0.25$$

**Sol 3:**  $X_g = \frac{20}{\frac{20}{180} + \frac{70}{18}} = 0.027$

$$\frac{P_0 - P}{P_0} = X_g$$

$$\frac{25.21 - P}{P_0} = 0.027$$

$$P = 24.51 \text{ torr}$$

**Sol 4:**  $\frac{P_0 - P}{P_0} = X_a$

$$\frac{23.76 - 23.32}{23.76} = \frac{5.4}{\frac{5.4}{M} + \frac{90}{18}}$$

$$\Rightarrow \frac{5.4}{M} = 0.018$$

$$\frac{5.4}{M} + 5$$

$$\Rightarrow \frac{5.4}{M} = 0.09 + \frac{0.0972}{M}$$

$$\Rightarrow M = 57.24 \text{ gm}$$

**Sol 5:**  $P = 0.75P_0$

$$\frac{P_0 - P}{P_0} = \frac{n_u}{n_u + n_w}$$

$$\frac{P_0 - P}{P_0} = \frac{n_u}{n_w}$$

$$\frac{P_0 - 0.75P_0}{0.75P_0} = \frac{w \times 18}{60 \times 100}$$

$$w = \frac{60 \times 100}{3 \times 18}$$

$$w = 111.11 \text{ gm}$$

$$m = \frac{111.11}{\frac{60}{1000}}$$

$$m = 18.52 \text{ mol}$$

**Sol 6:**  $\Delta T_b = K_b m$

$$0.284 = \frac{2.11 \times 10.6 \times 1000}{M \times 740}$$

$$m = \frac{2.11 \times 10.6 \times 1000}{740 \times 0.284}$$

$$m = 106.42 \text{ g}$$

**Sol 7:**  $\Delta T_b = K_b M$

$$0.130 = \frac{0.513 \times 3.24 \times 1000}{M \times 200}$$

$$l_c = \frac{0.513 \times 3.24 \times 1000}{0.13 \times 200}$$

$$l_c = 64 \text{ gm}$$

**Sol 8:**  $\Delta T_b = K_b M$

$$0.513 \times \frac{24}{\frac{58}{600/1000}}$$

$$\Delta T_b = 0.353^\circ \text{C}$$

$$T_b = 99.725 + 0.353$$

$$\Delta T_b = 100.078^\circ \text{C}$$

**Sol 9:**  $\Delta T_b = K_b M$

$$\Delta T_f = K_f M$$

$$\Delta T_f = \frac{K_f}{K_b} \cdot \Delta T_b = \frac{0.86}{0.513} \times 0.17 = 0.62^\circ \text{C}$$

$$\therefore T_f = -0.62^\circ \text{C}$$

**Sol 10:**  $\pi = CRT$

$$C = \frac{30}{0.0821 \times 298}$$

$$C = 1.226 \text{ mole/L}$$

$$M \approx C$$

$$\Delta T_f = K_f M = K_f C = 1.86 \times 1.226$$

$$\Delta T_f = 2.28^\circ \text{C}$$

$$\therefore T_f = -2.28^\circ \text{C}$$

**Sol 11:**  $P_0 = 760 \text{ mm}$

$$\frac{P_0 - P}{P_0} = \frac{760 - 750}{760}$$

$$\frac{1}{76} = X_a$$

$$X_a = 0.013$$

$$\text{For, } n_A + n_S = 1 \Rightarrow n_A = X_a = 0.013$$

$$n_S = 1 - n_A = 0.987$$

$$M_S = 17.766 \text{ g}$$

$$\therefore m = \frac{n_a}{M_s} = \frac{0.013 \times 1000}{17.766}$$

$$m = 0.741 \text{ Molal}$$

**Sol 12:** Refer to solution 9, Exercise 1

$$\text{Sol 13: We have, } \frac{P_0 - P}{P_0} = X_a = \frac{P_0 - P}{P_0} = \frac{n_A}{n_S}$$

$$\frac{640 - 600}{600} = \frac{2.175 \times 78}{M.39}$$

$$M = 65.25 \text{ gm}$$

$$\text{Sol 14: } m = 0.5 = \frac{n_a}{w_s}$$

$$\text{For 1 kg water, } n_a = 0.5$$

$$n_w = \frac{1000}{18}$$

$$\therefore X_a = \frac{n_a}{n_a + n_w} = \frac{0.5}{0.5 + \frac{1000}{18}}$$

$$X_a = 8.92 \times 10^{-3}$$

$$\frac{P_0 - P}{P_0} = X_a$$

$$P = P_0(1 - X_a) = 17.54 \times 0.99$$

$$P = 17.38 \text{ mmHg}$$

**Sol 15:** For A,

$$X_b = X_a = \frac{1}{2}$$

$$P_A = X_b P_b^0 + X_a P_a^0 = \frac{160 + 60}{2}$$

$$P_A = 110 \text{ mmHg}$$

For B, Let's mass of each be m.

$$n_b = \frac{m}{78}, n_a = \frac{m}{92}$$

$$\therefore X_b = \frac{\frac{m}{78}}{\frac{m}{78} + \frac{m}{92}} = 0.541$$

$$P_B = X_b P_b^0 + (1 - X_b) P_a^0$$

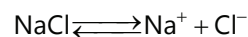
$$P_B = 114.11 \text{ atm}$$

$$\frac{P_A}{P_B} = \frac{110}{114.11}$$

$$\frac{P_A}{P_B} = 0.964$$

**Sol 16:**  $\Delta T_b = K_b (i_1 m_1 + i_2 m_2)$

For NaCl



$$n = 2, \alpha = 0.8$$

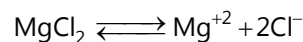
$$i = 1 + (n - 1)\alpha$$

$$i = 1 + 0.8$$

$$i = 1.8$$

$$m = \frac{5.84}{\frac{58.5}{\frac{100}{1000}}} = 1$$

For  $\text{MgCl}_2$



$$n = 3, \alpha = 0.5$$

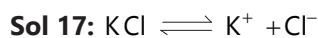
$$i = 1 + 2 \times 0.5 = 2$$

$$m = \frac{9.5}{\frac{95}{\frac{100}{1000}}} = 1$$

$$\Delta T_b = 0.51(1.8 \times 1 + 2 \times 1)$$

$$\Delta T_b = 1.938^\circ \text{C}$$

$$T_b = 101.938^\circ \text{C}$$



$$n = 2, \alpha = 0.95$$

$$i = 1 + (n-1)\alpha$$

$$i = 1 + 0.95$$

$$i = 1.95\alpha$$

$$K_f = \frac{RT_f^2}{1000 \times \Delta H_f}$$

$$\Delta H_f = 80 \text{ cal/gm} = 334.72 \text{ J/gm}$$

$$K_f = \frac{8.314 \times (273)^2}{1000 \times 334.72} = 1.851$$

$$M = \frac{7.45}{\frac{74.5}{\frac{500}{1000}}} = 0.2$$

$$\Delta T_f = iK_f m = 1.95 \times 1.851 \times 0.2 = 0.73^\circ\text{C}$$

$$T_f = -0.73^\circ\text{C}$$

**Sol 18:** Let  $n$  particles be formed after dissociation

Taking  $\alpha = 1$

$$i = 1 + (n-1) = n$$

$$\Delta T_f = iK_f \cdot m$$

$$n = i = \frac{0.558}{1.86 \times 0.1} = 3$$

Formula  $[\text{Co}(\text{NH}_3)_5\text{Cl}] - \text{Cl}_2$

**Sol 19:** Refer Exercise II, Comprehension I

**Sol 20:** At  $P_t = 1$

$$P_t = P_B^0 X_B + P_T^0 X_T$$

$$760 = 1375 X_B + 558(1 - X_B)$$

$$760 = 1375 X_B + 558 - 558 X_B$$

$$202 = 817 X_B$$

$$X_B = 0.247$$

$$X_T = 0.753$$

For Vapour

$$P_B = Y_B \cdot P_t$$

$$Y_B = \frac{P_B \times B}{P_t} = \frac{1375}{760} = 0.447$$

**Sol 21:** Pressure must be applied on 0.01 M glucose solution to prevent osmosis.

$$\text{Excess pressure} = \pi_1 - \pi_2$$

$$(C_1 - C_2)RT$$

$$(0.01 - 0.001) \times 0.0821 \times 300 = 0.2217 \text{ atm}$$

**Sol 22:**

$$\pi_b = CRT$$

$$\frac{\pi_1}{\pi_2} = \frac{C_1 T_1}{C_2 T_2}$$

$$C_2 = \frac{\pi_2 C_1 T_1}{\pi_1 T_2} \quad (T_1 = 10^\circ\text{C} = 283\text{k})$$

$$\frac{C_2}{C_1} = \frac{105.3 \times 283}{500 \times 298} \quad (T_2 = 25^\circ\text{C} = 298\text{k})$$

$$\frac{C_2}{C_1} = 0.2$$

$$C_2 = 0.2 C_1$$

$$V_2 = 5 V_1$$

**Sol 23:**  $\Delta T_f = i K_f m$

$$0.45 = i \times 5.12 \times \frac{0.2}{\frac{60}{\frac{20}{1000}}}$$

$$i = 0.527 = 1 - \left(1 - \frac{1}{n}\right)\alpha$$

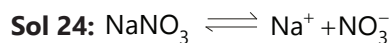
$$n = 2$$

$$i = 1 - \frac{1}{2}\alpha$$

$$\alpha = 2(1 - i)$$

$$\alpha = 0.945$$

$\therefore$  94.51 association



$$n = 2, \alpha = 0.9$$

$$i = 1 + (n-1)\alpha = 1.9$$

$$\pi = i CRT = 1.9 \times \frac{0.85}{85} \times 10 \times 0.082 \times 300$$

$$(T = 27^\circ\text{C} = 300\text{k})$$

$$\pi = 4.64 \text{ atm}$$

**Sol 25:**  $\pi_1 = \pi_2$  $iC_1RT = C_2RT$  (for glucose) $\alpha = 0 \Rightarrow i = 1$ )For NaCl,  $i = 1 + (n-1)\alpha = 1 + \alpha$ 

$$(1 + \alpha) \frac{1.2 \times 10}{58.5} = \frac{7.2}{180} \times 10$$

$$1 + \alpha = 1.95$$

$$\alpha = 0.95$$

$$i = 1.95$$

**Sol 26:**  $2C_6H_5 \rightleftharpoons (C_6H_5COOH)_2$ 

$$n = 2, \alpha = 0.84$$

$$i = 1 - \left(1 - \frac{1}{n}\right)\alpha = i = \frac{\alpha}{2} = 0.58$$

$$\Delta T_b = i K_b M$$

$$0.58 \times 2.3 \times \frac{0.61}{\frac{122}{50}} = \frac{\Delta T_b}{1000}$$

$$\Delta T_b = 0.1334^\circ C$$

$$T_b = 46.2^\circ + 0.1334^\circ C$$

$$T_b = 46.3334^\circ C$$

**Sol 27:** For first distillate

$$X_A = X_B = 0.5$$

$$P_T = \frac{P_A^0 + P_B^0}{2} = \frac{100 + 300}{2}$$

$$P_T = 200 \text{ Torr}$$

$$P_A = X_A P_A^0 = 50 \text{ torr}$$

$$P_A = Y_A P_T$$

$$Y_A = \frac{P_A}{P_T} = \frac{50}{200} = 0.25$$

$$Y_B = 0.75$$

For second distillate

$$X_A = Y_A = 0.25, X_B = Y_B = 0.75$$

$$P_T^0 = 100 \times 0.25 + 300 \times 0.75$$

$$P_T = 250 \text{ Torr}$$

$$\text{Now, } P_A = Y_A P_T$$

$$Y_A = \frac{P_A}{P_T} = \frac{100 \times 0.25}{250}$$

$$Y_A = 0.1$$

$$Y_B = 0.9$$

Mole fraction of A in final condensate = 0.1

**Sol 28:** For phenol,  $n = 2$ 

$$i = 1 - \left(1 - \frac{1}{n}\right)\alpha = 1 - \frac{\alpha}{2}$$

Now,

$$\Delta T_f = i R_f m$$

$$0.69 = \left(1 - \frac{\alpha}{2}\right) 5.12 \times \frac{20}{94} \Rightarrow 1 - \frac{\alpha}{2} = 0.63$$

$$\frac{\alpha}{2} = 0.366$$

$$\alpha = 0.7333$$

**Sol 29:**

$$\text{Mass of } CH_3OH = V \times \rho = 30 \times 0.7980 \text{ gm} = 23.94 \text{ gm}$$

$$\text{Moles of } CH_3OH, n = 0.748$$

$$\text{mass of water} = 70 \times 0.9984$$

$$m = \frac{n}{m_s^0} = \frac{0.748}{69.888} \times 1000$$

$$m = 10.70$$

$$\Delta T_f = k_f m = 10.7 \times 1.86$$

$$\Delta T_f = 19.91^\circ C$$

$$T_f = -19.91^\circ C$$

$$\text{Mass of final solution} = 23.94 \times 69.888 = 93.828 \text{ gm}$$

$$\text{Volume} = \frac{\text{Mass}}{\text{Density}} = \frac{93.828}{0.9575} = 98 \text{ ml}$$

$$\text{There for Molarity} = \frac{n}{V} = \frac{0.748}{98} \times 1000 = 7.63 \text{ M}$$

$$\text{Molarity} = 7.63 \text{ M}$$

## Exercise 2

### Single Correct Choice Type

**Sol 1: (C)**  $\because P_A^0 > P_B^0$  $Y_A$  will be more than  $X_A$ 

$$\text{i.e. } \frac{(n_A)L}{(n_B)L} < \frac{(n_A)V}{(n_B)V}$$



$$\frac{X_A}{X_B} < \frac{Y_A}{Y_B} \Rightarrow \frac{Y_A}{X_A} > \frac{Y_B}{X_B}$$

$$\frac{Y_A}{Y_B} > \frac{X_A}{X_B}$$

**Sol 2: (D)** Relative lowering will be least in  $C_{12}H_{22}O_{11}$  which will not dissociate;  $i = 1$

For rest,  $i > 1$  and show greater decrease.

**Sol 3: (C)**  $P = P_A + P_B$

$$X_A P_A + X_B P_B^0$$

$$P_A^0 (1 - X_B) + X_B P_B^0$$

$$P = P_A^0 - X_B (P_A^0 - P_B^0)$$

$$P_A^0 = 120$$

$$P_A^0 - P_B^0 = 75$$

$$P_B^0 = 45$$

**Sol 4: (D)** A liquid mixture having composition corresponding to point z in the figure shown in subjected to distillation at constant pressure, composition of an azeotrope alters on changing the external pressure

**Sol 5: (B)** From the graph

$$\text{When } X_{\text{Benzene}} = 0.5, Y_{\text{Toluene}} = 0.8$$

$$\text{When } Y_{\text{Toluene}} = 0.3, Y_{\text{Benzene}} = 0.6$$

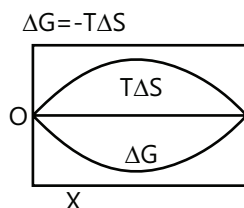
$$X_{\text{Benzene}} = 0.3, Y_{\text{Toluene}} = 0.9$$

$$X_{\text{Benzene}} = 0.7, Y_{\text{Toluene}} > 0.3$$

**Sol 6: (C)**  $\Delta H_{\text{mix}} = 0$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -T\Delta S$$



**Sol 7: (D)** Through a semipermeable membrane, only solvent can flow and not the solute.

### Multiple Correct Choice Type

**Sol 8: (A, C, D)** Only (B) is wrong.

**Sol 9: (A, D)** For ideal solution.

$$\Delta H = 0, \Delta V = 0$$

**Sol 10: (A, C)** Both are correct facts.

**Sol 11: (A, B, C)** All are correct.

**Sol 12: (A, C, D)** Degree of dissociation increases as  $c$  decrease

$$\left( \alpha = \sqrt{\frac{R_a}{c}} \right)$$

For ideal soln.,  $\Delta G = \Delta H - T\Delta S$

$$\Delta G = -T\Delta S \quad (H = 0)$$

$$\Delta S = \frac{-\Delta G}{T} > 0 \quad (\because \Delta G < 0)$$

**Sol 13: (A, B, C)** Due to polarity and H-bonding.

**Sol 14: (A, D)** For ideal solution.

$$\Delta H = 0, \Delta V = 0$$

**Sol 15: (A, B)**  $P_M = X_A P_A^0 + X_B P_B^0$

$$P_M = X_A P_A^0 + P_B^0 - X_A P_B^0$$

$$\frac{P_M - P_B^0}{P_A^0 - P_B^0} = X_A$$

$$P_A = P_T X_{A(V)}$$

$$X'_{A(V)} = \frac{P_A}{P_T} = \frac{X_{A(l)} P_A^0}{P_T}$$

$$\frac{X_{A(l)}}{X'_{A(V)}} = \frac{P_T}{P_A^0}$$

**Sol 16: (A, C, D)**  $K_3PO_4 \rightarrow 3K^+ + PO_4^{3-}$

$$n = 4$$

$$i = 1 + (n-1)\alpha = 1 + 3\alpha$$

$$\frac{\Delta P}{P^0} = iX_A$$

$$m = \frac{n}{w_s}$$

$$\text{For 1 kg solved, } N = \frac{1000}{18}$$

$$m = \frac{18n}{1000}$$

$$n = \frac{1000m}{18}$$

$$X = \frac{n}{n+N} = \frac{1000m}{18 \left( \frac{1000m}{18} + \frac{1000}{18} \right)}$$

$$X = \frac{m}{m+1}$$

$$\frac{\Delta P}{P^0} = \frac{i n}{N+n} \approx \frac{i n}{N}$$

$$\frac{\Delta P}{P^0} = \frac{(1+3\alpha)m \cdot 18}{1000}$$

$$\frac{\Delta P}{P^0} = \frac{\Delta T_f}{K_f} \cdot \frac{18}{1000}$$

$$1+3\alpha = \frac{M_w}{M_{w\text{obs}}}$$

**Sol 17: (B, D)** Vant-hoff factor for a dil. sol. of  $\text{BaCl}_2$  is  $1+3-1=3$  (D) is correct

$\Delta T_b$  is also due to lowering in vapour pressure.

**Sol 18: (B, D)** Acetone and ethanol will show negative deviation due to H-bonding between them.

Chloroform and benzene will show positive deviation because of intramolecular H-bonding in chloroform.

### Assertion Reasoning Type

**Sol 19: (C)** The added substance once must be non-volatile.

**Sol 20: (D)** As heat must be removed from the water to make it freeze, it is exothermic process.

### Comprehension Type

**Sol 21: (A)**  $\Delta T_f = i k_f m$

$$\Delta T_f \propto i$$

And  $i \propto n$

$n$  is maximum for  $\text{Al}_2(\text{SO}_4)_3$

**Sol 22: (B)** Correction factor is 1

**Sol 23: (B)**  $\text{Ba}(\text{NO}_3)_2 \rightleftharpoons \text{Ba}^{2+} + 2\text{NO}_3^-$

$$n = 3$$

$$i = 1 + (n-1)\alpha$$

$$\alpha = \frac{i-1}{n-1} = \frac{2.74-1}{3-1}$$

$$\alpha = 0.87$$

8.7% dissociation

**Sol 24: (C)** Colligative effects involve properties whose magnitude depends upon number of particles.

**Sol 25: (B)**  $\frac{\Delta T_b}{\Delta T_f} = \frac{k_b}{k_f}$

$$\Delta T_f = \frac{0.186 \times 0.521}{1.86} = 0.0521$$

**Sol 26: A**  $\rightarrow$  p, r

This mixture will be show positive deviation due to H-bonding between  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{H}_2\text{O}$

B  $\rightarrow$  q, t

They will form ideal solution as

$$F_{A-A} = F_{A-B} = F_{B-B}$$

No strong interactions

C  $\rightarrow$  q, t

This is Raoult's law for ideal solution

D  $\rightarrow$  p, s

Very strong intramolecular H-bonding in  $\text{H}_2\text{SO}_4$  leads to negative deviation.

**Sol 27: A**  $\rightarrow$  r

No dissociation in any of these

$$\therefore i = 1 \text{ for all.}$$

B  $\rightarrow$  s

Strong electrolytes,  $\alpha = 1$

$$1 + (2-1) : 1 + (3-1) : 1 + (3-1) = 2 : 3 : 3$$

C → p

$$1 + (5-1) : 1 + (4-1) : 1 + (5-1) = 5 : 4 : 5 = 1 : 0.8 : 1$$

D → q

$$1 : 1 + (2-1) : 1 + (3-1)$$

1:2:3

**Sol 28:** A → s

Definition of ppm

B → r

C → q

D → p

## Previous Years' Questions

**Sol 1: (C)** In case of positive deviation from Raoult's law, the observed vapour pressure is greater than the ideal vapour pressure and boiling of azeotrope becomes lower than either of pure liquid.

**Sol 2: (A)**  $K_2SO_4$ :  $i = 3$ ; NaCl:  $i = 2$ Urea  $i = 1$ ; Glucose:  $i = 1$ 

Greater the value of 'i', greater the lowering in freezing point, lower will be the freezing temperature, if molarity, in all cases are same. Therefore,  $K_2SO_4$  solution has the lowest freezing point.

**Sol 3: (A)** During freezing, liquid solvent solidify and solid solvent remains in equilibrium with liquid solvent.

**Sol 4: (A)** Van't Hoff factor ( $i$ ) = 4  $\{3K^+ + [Fe(CN)_6]^{3-}\}$ 

$$\text{Molality} = \frac{0.1}{329} \times \frac{1000}{100} = \frac{1}{329} \Rightarrow -\Delta T_f = iK_f m$$

$$= 4 \times 1.86 \times \frac{1}{329} = 2.3 \times 10^{-2}$$

$$\Rightarrow T_f = -2.3 \times 10^{-2} \text{ } ^\circ\text{C}$$

(As % freezing point of water is  $0^\circ\text{C}$ )**Sol 5: (D)** In the given solution 'M',  $H_2O$  is soluteTherefore, molality of  $H_2O$ 

$$= \frac{0.1}{0.9 \times 46} \times 1000 = 2.4$$

$$\Rightarrow -\Delta T_f = k_f^{\text{ethanol}} \times 2.4 = 2 \times 2.4 = 4.8$$

$$\Rightarrow T_f = 155.7 - 4.8 = 150.9 \text{ K}$$

**Sol 6: (A)** Vapour pressure =  $p(H_2O) + p(\text{ethanol})$ 

$$= 32.8 \times 0.1 + 40 \times 0.9$$

$$= 3.28 + 36 = 39.28 \text{ mm}$$

**Sol 7: (B)** New ethanol is solute.

$$\text{Molality of solute} = \frac{0.1}{0.9 \times 18} \times 1000 = 6.17$$

$$\Rightarrow \Delta T_b = 6.17 \times 0.52 = 3.20$$

$$\Rightarrow T_b = 373 + 3.2 = 376.2 \text{ K}$$

$$\text{Sol 8: } \lim_{m \rightarrow 0} \left( \frac{\Delta T_f}{m} \right) = k_f (\text{Cryoscopic constant})$$

**Sol 9:** From lowering of vapour pressure information:

$$\frac{0.104}{17.5} = x_2 = \frac{n_2}{n_1 + n_2}$$

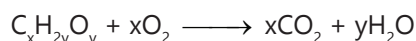
$$\Rightarrow \frac{n_1}{n_2} + 1 = 168.27$$

$$\Rightarrow \frac{n_1}{n_2} = 167.27$$

$$\Rightarrow \frac{1000}{18} \times \frac{M}{50} = 167.27$$

$$\Rightarrow M = 150 \text{ g/mol}$$

Also, the combustion reaction is:

 $\therefore$  18y g of  $H_2O$  is produced from 1.0 mole of compound.

$$\therefore 0.9 \text{ g of } H_2O \text{ will be produced from } \frac{0.9}{18y} = \frac{1}{20y} \text{ mol}$$

$$\Rightarrow \text{At the end, moles of } O_2 \text{ left} = \frac{x}{20y}$$

$$\text{Moles of } CO_2 \text{ formed} = \frac{x}{20y}$$

$$\Rightarrow \text{Total moles of gases at STP} = \frac{2x}{20y} = \frac{2.24}{22.4}$$

$$\Rightarrow x = y$$

$$\Rightarrow \text{Molar mass; } 150 = 12x + 2x + 16x = 30x$$

$$\Rightarrow x = \frac{150}{30} = 5$$

$$\Rightarrow \text{Formula} = C_5 H_{10} O_5$$

$$\text{Sol 10: Moles of ethanol} = \frac{60}{46} = 1.3$$

$$\text{Moles of methanol} = \frac{40}{32} = 1.25$$

$$\text{Mole fraction of ethanol} = \frac{1.3}{1.3 + 1.25} = 0.51$$

$$\text{Vapour pressure of solution} = p_{\text{ethanol}} + p_{\text{methanol}}$$

$$= 0.51 \times 44.5 + 0.49 \times 88.7 = 66.16 \text{ mm}$$

Mole fraction of methanol in vapour phase

$$= \frac{p_{\text{methanol}}}{\text{Total vapour pressure}} = \frac{43.463}{66.16} = 0.657$$

**Sol 11:** According to Raoult's law:

$$p = p_0 x_1$$

$$\Rightarrow 600 = 640 \left( \frac{n_1}{n_1 + n_2} \right)$$

$$\Rightarrow \frac{n_2}{n_1} = \frac{64}{60} - 1 = \frac{1}{15}$$

$$\Rightarrow n_2 = \frac{39}{78} \times \frac{1}{15} = 0.033$$

$$\Rightarrow \frac{2.175}{M} = 0.033 \Rightarrow M = 65.25$$

**Sol 12:**  $\text{Ca}(\text{NO}_3)_2 \longrightarrow \text{Ca}^{2+} + 2\text{NO}_3^-$

$$1 - \alpha \quad \alpha \quad 2\alpha$$

$$i = 1 + 2\alpha, \text{ where, } \alpha = 0.7$$

$$\Rightarrow i = 1 + 2 \times 0.7 = 2.4$$

$$\Rightarrow \text{Mole fraction of solvent} = \frac{n_1}{n_1 + in_2}$$

$$= \frac{\left( \frac{100}{18} \right)}{\left( \frac{100}{18} \right) + 2.4 \times \frac{7}{164}} = 0.982$$

$$\Rightarrow p = p_0 x_1$$

$$= 760 \times 0.982 \text{ (VP of H}_2\text{O at 100}^\circ\text{C} = 760 \text{ mm of Hg)}$$

$$= 746.32 \text{ mm}$$

**Sol 13:** (i) Empirical formula determination

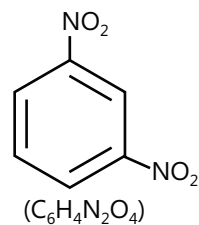
Element	C	H	N	O
Weight %	42.86	2.40	16.67	38.07
Moles	3.57	2.40	1.19	2.38
Simplest ratio	3	2	1	2

$$\Rightarrow \text{Empirical formula} = \text{C}_3\text{H}_2\text{NO}_2$$

$$(ii) \Delta T_b = 1.84 = 2.53 \times \frac{5.5}{M} \times \frac{1000}{45}$$

$$\Rightarrow M = 168$$

Empirical formula weight (84) is half of molar mass, molecular formula is  $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$  – a dinitro benzene.



**Sol 14:** Let after 100 min, x moles of A are remaining  
unpolymerized moles of B = 12.

Mole of non-volatile solute = 0.525

$$\text{Mole fraction of A} = \frac{x}{x + 12 + 0.525}$$

$$\text{Mole fraction of B} = \frac{12}{x + 12 + 0.525}$$

$$400 = \left( \frac{x}{x + 12 + 0.525} \right) \times 300 + \left( \frac{12}{x + 12 + 0.525} \right) \times 500$$

$$x = 9.9$$

$$\text{Moles of A polymerized in 100 min} = 10 - 9.9 = 0.10$$

$$k = \frac{1}{t} \ln \frac{10}{9.9} = \frac{1}{100} \ln \frac{10}{9.9} \text{ min}^{-1} = 1.005 \times 10^{-4} \text{ min}^{-1}$$

**Sol 15:** Higher the value of  $k_b$  of a solvent suggest that there is larger polarity of solvent molecules, which in turn implies higher boiling point due to dipole-dipole interaction.

Therefore, the correct order of  $k_b$  values of the three given solvents is:

Solvents	Boiling point	$k_b$
X	100°C	0.63
Y	27°C	0.53
Z	283°C	0.92

**Sol 16: (A)**

$$\Delta T_f = K_f \times \text{molality} \times i$$

$$2 = 1.72 \times \frac{20}{172} \times \frac{1000}{50} \times i$$

$$i = 0.5$$

Hence (A) is correct.

**Sol 17: (D)**  $\Delta T_f = K_f \times m$

$$2 \times \frac{0.1}{0.9 \times 46} \times 1000 = 4.83\text{K}$$

Freezing point of solution M = 155.7 – 4.83 = 150.87 K  
 $\approx 150.9$  K

**Sol 18: (B)**  $P = 0.9 \times 40 = 36$  mm Hg

**Sol 19: (B)**  $\Delta T_b = K_b \times m = 0.52 \times \frac{0.1}{0.9 \times 18} \times 1000 = 3.2$  K

$T_b = 373 + 3.2 = 376.2$  K

**Sol 20: (A)**  $P = K_H X_{N_2}$

$$0.8 \times 5 = 1 \times 10^5 \times X_{N_2}$$

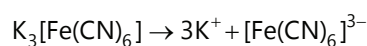
$X_{N_2} = 4 \times 10^{-5}$  (in 10 moles of water)

$$\Rightarrow 4 \times 10^{-5} = \frac{n_{N_2}}{n_{N_2} + 10}$$

$$n_{N_2} \times 5 \times 10^{-5} + 4 \times 10^{-4} = n_{N_2}$$

$$\Rightarrow n_{N_2} = 4 \times 10^{-4}$$

**Sol 21: (A)**



$i = 4$

$$\Delta T_f = K_f \times i \times \frac{m}{M} \times \frac{1000}{W} = 1.86 \times 4 \times \frac{0.1}{329} \times \frac{1000}{100} = 2.3 \times 10^{-2}$$

$$T_f = -2.3 \times 10^{-2}$$

**Sol 22: (A)**

$$\Delta T_b = 2^\circ C; \quad m_a = 2.5g$$

$$m_{\text{solvent}} = 100g \quad K_b = 0.76 K kg mol^{-1}$$

$P_{\text{solution}} = ?$

$$\Delta T_b = K_b \times m$$

$$2 = 0.76 \times m \quad \therefore m = \frac{2}{0.76}$$

$$\frac{P^0 - P}{P} = m \times MM \times 10^{-3} \quad \therefore \frac{760 - P}{P} = \frac{2}{0.76} \times 18 \times 10^{-3}$$

$$760 - P = \frac{36}{760} P \quad \therefore 760 = \frac{796}{760} P$$

$$\therefore P = 760 \left( \frac{796}{760} \right) \text{ torr} = 725.6 \text{ torr} \approx 724 \text{ torr}$$

**Sol 23:**

$$\Delta T_f = i \times K_f \times m$$

$$0.0558 = i \times 1.86 \times 0.01$$

$$i = 3$$

$\therefore$  Complex is  $[Co(NH_3)_5Cl]Cl_2$

$$\text{Sol 24: } \frac{X_{\text{solute}}}{X_{\text{solvent}}} = \frac{0.1}{0.9} = \frac{1}{9}$$

$$\frac{W_{\text{solute}}}{W_{\text{solvent}}} = \frac{M_{\text{solvent}}}{M_{\text{solute}}} = \frac{1}{9} \quad \dots (i)$$

$$W_{\text{solute}} + W_{\text{solvent}} = W_{\text{solution}} = \text{density} \times \text{volume}$$

$$W_{\text{solute}} + W_{\text{solvent}} = 2 \times V \quad \dots (ii)$$

Molarity = molality

$$\frac{n_{\text{solute}}}{V_{\text{solvent}}} = \frac{n_{\text{solute}}}{W_{\text{solvent}}}$$

$$W_{\text{solvent}} = V_{\text{solution}} = \frac{W_{\text{solute}} + W_{\text{solvent}}}{2}$$

$$\Rightarrow 2W_{\text{solvent}} = W_{\text{solute}} + W_{\text{solvent}}$$

$$\Rightarrow W_{\text{solute}} = W_{\text{solvent}} \quad \dots (iii)$$

Using eq. (i) and (iii), we get

$$\frac{M_{\text{solute}}}{M_{\text{solvent}}} = 9$$

**Sol 25: (A, B)** Conceptual fact