06

Solutions

TOPIC 1

Expression of Concentration

01 If 80 g of copper sulphate $CuSO_4 \cdot 5H_2O$. is dissolved in deionised water to make 5 L of solution. The concentration of the copper sulphate solution is $x \times 10^{-3}$ mol L^{-1}. The value of x is ....

[Atomic masses $Cu = 63.54$ u, $S = 32$ u, $O = 16$ u, $H = 1$ u]

[2021, 1 Sep Shift-II]

Ans. ***(64)***

Given, mass of $CuSO_4.5H_2O = 80$ g

The concentration of copper sulphate solution is $x \times 10^{-3}$ mol/L.

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (L)}} \quad \text{...(i)}$$

Molar mass of

$$CuSO_4 \cdot 5H_2O = 63.54 + 32 + 16 \times 4$$
$$= 5 \times 18 = 249.54 \text{ g / mol}$$

Number of moles of solute

$$= \frac{\text{Weight of solute}}{\text{Molecular mass of solute}}$$
$$= \frac{80 \text{ g}}{249.54 \text{ g / mol}} = 0.32 \text{ mol}$$

Volume of solution = 5 L

From Eq. (i),

$$\text{Molarity} = \frac{0.3205}{5} = 64.11 \times 10^{-3} \text{ mol / L}$$

$\therefore \quad x = 64.11$

or $\quad x \approx 64$

Hence, answer is 64.

02 The molarity of the solution prepared by dissolving 6.3 g of oxalic acid $(H_2C_2O_4 \cdot 2H_2O)$ in 250 mL of water in mol L^{-1} is $x \times 10^{-2}$. The value of x is .... (Nearest integer)

[Atomic mass $H = 1.0$, $C = 12.0$, $O = 16.0$]

[2021, 31 Aug Shift-I]

Ans. ***(20)***

$$\text{Molarity} = \frac{\text{number of moles of solute}}{\text{volume of solution (in litre)}}$$
$$= \frac{\text{weight of solute/molecular mass of solute}}{\text{volume of solution (in litre)}}$$

Molecular mass of solute

$$[H_2C_2O_4 \cdot 2H_2O] = 126 \text{ g}$$
$$x \times 10^{-2} = \frac{6.3 \text{ g} / 126 \text{ g}}{250 \text{ mL}} \times 1000$$
$$x \times 10^{-2} = 0.2$$
$$x \times 10^{-2} = 20 \times 10^{-2}$$

$\therefore \quad x = 20$

03 The density of NaOH solution is 1.2 g cm^{-3}. The molality of this solution is .... m.

(Round off to the nearest integer)

[Use : Atomic masses : $Na = 23.0$ u, $O = 16.0$ u, $H = 1.0$ u, density of H_2O : 1.0 g cm^{-3}]

[2021, 27 July Shift-I]

Ans. ***(5)***

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Weight of solution (kg)}}$$

Consider 1 litre solution, (1 litre = 1000 g)

Density of water is 1 g/mL

Mass of solution = Density × Volume

$$= 1.2 \times 1000 \text{ g}$$
$$= 1200 \text{ g}$$

Neglecting volume of NaOH.

Mass of water = 1000 g

Mass of NaOH = (1200 − 1000) g

$$= 200 \text{ g}$$
$$\text{Moles of NaOH} = \frac{200}{40} = 5 \text{ mol}$$
$$\text{Molarity} = \frac{5 \text{ mol}}{1 \text{kg}} = 5 \text{ mol /kg}$$

04 100 mL of Na_3PO_4 solution contains 3.45 g of sodium. The molarity of the solution is ...... $\times 10^{-2}$ mol L^{-1}. (Nearest integer)

[Atomic masses - $Na = 23.0$ u, $O = 16.0$ u, $P = 31.0$ u]

[2021, 26 Aug Shift-II]

Ans. ***(50)***

Number of mole of Na^+ ions

$$= \frac{\text{mass of sodium}}{\text{molar mass of sodium}}$$
$$= \frac{3.45}{23}$$

So, number of mole of Na_3PO_4

$$= \frac{\text{moles of sodium}}{3}$$

{as 1 molecule of Na_3PO_4 contains 3 atoms of Na}

$$= \frac{3.45}{3 \times 23} = 0.05$$
$$\text{Molarity} = \frac{\text{Moles of } Na_3PO_4}{\text{Volume of solution (in L)}}$$
$$= \frac{0.05}{100} \times 1000$$
$$= 0.50$$
$$= 50 \times 10^{-2}$$

$\therefore$ Answer is 50.

05 The exact volumes of 1 M NaOH solution required to neutralise 50 mL of 1 M H_3PO_3 solution and 100 mL of 2 M H_3PO_2 solution, respectively, are

[2021, 16 March Shift-II]

(a) 100 mL and 100 mL
(b) 100 mL and 50 mL
(c) 100 mL and 200 mL
(d) 50 mL and 50 mL

Ans. ***(c)***

$$\underset{\substack{50 \text{ mL} \\ 1\text{M}}}{H_3PO_3} + \underset{\substack{1 \text{ M} \\ V = ?}}{2NaOH} \longrightarrow Na_2HPO_3 + 2H_2O$$

Millimoles of $H_3PO_3 = M \times V = 1 \times 50 = 50$

For 1 millimole of H_3PO_3, we require 2 millimoles of NaOH.

For 50 millimole of H_3PO_3, we require $(2 \times 50) = 100$ millimoles of NaOH.

Millimoles of NaOH $= M \times V = 100$

$$1 \times V = 100$$
$$V = 100 \text{ mL}$$

$$\underset{\substack{100\text{ mL}\\ 2\text{ M}}}{H_3PO_2} + \underset{\substack{1\text{ M}\\ V=?}}{NaOH} \rightarrow NaH_2PO_2 + H_2O$$

Millimoles of $H_3PO_2 = M \times V = 2 \times 100 = 200$

For 1 millimole of H_3PO_2, we require 1 millimoles of NaOH.

For 200 millimole of H_3PO_2, we require 200 millimoles of NaOH.

So, volume of NaOH $= 200$ mL

06 A 6.50 molal solution of KOH (*aq*) has a denisity of 1.89 g cm^{-3}. The molarity of the solution is ...... mol dm^{-3} (Round off to the nearest integer).

[Atomic masses: K : 39.0 u, O : 16.0u, H : 1.0 u]

[2021, 16 March Shift-I]

Ans. ***(9)***

$$\text{Molality}(m) = \frac{M \times 1000}{\{(1000d) - M \times M_{\text{solute}}\}}$$

where, M = molarity

d = density of solution

M_{solute} = molar mass of solute

Putting the values,

$$6.50 = \frac{M \times 1000}{(1000 \times 1.89) - (M \times 56)}$$

On solving, $M = \dfrac{12285}{1364}$

$$M = 9 \text{ molar}$$

07 4.5 g of compound A (MW = 90) was used to make 250 mL of its aqueous solution. The molarity of the solution in M is $x \times 10^{-1}$. The value of x is .... (Rounded off to the nearest integer).

[2021, 24 Feb Shift-I]

Ans. ***(2)***

Given, weight of compound $A = 4.5$ g

Molecular weight of compound $A = 90$ g/mol

Volume of solution (in mL) $= 250$ mL

Now, molarity is defined as number of moles of solute or compound A divided by volume of solution (in L).

$$M = \frac{\text{Number of moles of solute }(n)}{\text{Volume of solution}}$$

$$= \frac{\frac{4.5}{90}}{\frac{250}{1000}} = 0.2 \text{ or } = 2 \times 10^{-1} \text{ M}$$

$$\therefore \quad n = \frac{\text{Weight of solute (compound } A)}{\text{Molecular weight of solute (compound } A)}$$

Hence, $x \times 10^{-1}\ \mu$

$$x = 2$$

08 A solution of two components containing n_1 moles of the 1st component and n_2 moles of the 2nd component is prepared. M_1 and M_2 are the molecular weights of component 1 and 2 respectively. If d is the density of the solution in g mL^{-1}, C_2 is the molarity and χ_2 is the mole-fraction of the 2nd component, then C_2 can be expressed as **[2020, 6 Sep Shift-I]**

(a) $C_2 = \dfrac{1000\,\chi_2}{M_1 + \chi_2\,(M_2 - M_1)}$

(b) $C_2 = \dfrac{d\chi_2}{M_2 + \chi_2\,(M_2 - M_1)}$

(c) $C_2 = \dfrac{1000\,d\chi_2}{M_1 + \chi_2\,(M_2 - M_1)}]$

(d) $C_2 = \dfrac{d\chi_1}{M_2 + \chi_2\,(M_2 - M_1)}$

Ans. ***(c)***

In first component,

Mass = number of moles × molecular weight $= n_1 M_1$

In second component,

$$\text{Mass} = n_2 M_2$$

Mass of solution $= n_1 M_1 + n_2 M_2$ ...(i)

$$\text{Mole-fraction}\ (\chi_2) = \frac{n_2}{n_1 + n_2}$$

$$\therefore \quad n_1 = \frac{n_2(1 - \chi_2)}{\chi_2} \quad \text{...(ii)}$$

Place the value of n_1 in eq. (i)

$$\therefore \quad \frac{n_2(1 - \chi_2)M_1}{\chi_2} + n_2 M_2$$

$$\Rightarrow \quad \frac{n_2}{\chi_2}(M_2\chi_2 - M_1\chi_2 + M_1)$$

Volume of solution,

$$= \frac{n_2(M_2\chi_2 - M_1\chi_2 + M_1)}{1000 \times d \times \chi_2} \text{ L}$$

$$C_2 = \frac{1000 \times n_2 \times d\chi_2}{n_2(M_2\chi_2 - M_1\chi_2 + M_1)}$$

$$\therefore \quad C_2 = \frac{1000d\,\chi_2}{M_1 + \chi_2(M_2 - M_1)}$$

Hence, the correct option is (c).

09 The hardness of a water sample containing 10^{-3} M $MgSO_4$ expressed as $CaCO_3$ equivalents (in ppm) is......

(molar mass of $MgSO_4$ is 120.37 g/mol) **[2020, 9 Jan Shift-II]**

Ans. ***(100)***

Hardness in ppm

$$= \frac{\text{Mass of } CaCO_3 \text{ equivalent to the total number of moles of hardness causing substances} \times 10^6}{\text{Mass of water sample}}$$

Here, $[Mg^{2+}] = 10^{-3}$ M

$n_{Mg^{2+}} = 10^{-3}$ per 1 L water ≅ 1000 g

Mass of 10^{-3} moles of $CaCO_3 = 10^{-3} \times 100$ g $= 0.1$ g

$$\therefore \quad \text{ppm} = \frac{0.1 \times 10^6}{1000} = 100 \text{ ppm}$$

10 10.30 mg of O_2 is dissolved into a litre of sea water of density 1.03 g/mL. The concentration of O_2 in ppm is **[2020, 9 Jan Shift-II]**

Ans. ***(10.00)***

Mass of $O_2 = 10.30$ mg (Given)

Mass of sea water solution

$= $ volume × density

$= 1\text{ L} \times 1.03$ g/mL

$= 1000\text{ mL} \times 1.03 \text{ g mL}^{-1} = 1030$ g

$$\text{ppm} = \frac{\text{mass of } O_2}{\text{mass of solution}} \times 10^6$$

$$= \frac{10.30 \times 10^{-3} \text{ g} \times 10^6}{1030 \text{ g}}$$

$$= 10 \text{ ppm}$$

11 What would be the molality of 20% (mass/mass) aqueous solution of KI?

Molar mass of KI = 166 g mol^{-1}) **[2019, 9 April Shift-II]**

(a) 1.48 (b) 1.51 (c) 1.35 (d) 1.08

Ans. ***(b)***

Key Idea Molality is defined as number of moles of solute per kg of solvent.

$$m = \frac{w_2}{Mw_2} \times \frac{1000}{w_1}$$

w_2 = mass of solute

Mw_2 = molecular mass of solute
w_1 = mass of solvent.

The molality of 20% (mass/mass) aqueous solution of KI can be calculated by following formula.

$$m = \frac{w_2 \times 1000}{Mw_2 \times w_1}$$

20% aqueous solution of KI means that 20 gm of KI is present in 80 gm solvent.

$$m = \frac{20}{166} \times \frac{1000}{80} = 1.506 \approx 1.51 \text{ mol/kg}$$

12 The mole fraction of a solvent in aqueous solution of a solute is 0.8. The molality (in mol kg^{-1}) of the aqueous solution is **[2019, 12 April Shift-I]**

(a) 13.88×10^{-2} (b) 13.88×10^{-1}
(c) 13.88 (d) 13.88×10^{-3}

Ans. ***(c)***

Key Idea

$$\text{Molality}(m) = \frac{\text{Mass of solute}(w_2) \times 1000}{\text{Molar mass of solute}(M_2) \times \text{mass of solvent}(w_1)}$$

$$m = \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

and also, $m = n_2 \times \frac{1000}{n_1 \times M_1}$

$X_{\text{solvent}} = 0.8$ (Given)

It means that $n_{\text{solvent}}(n_1) = 0.8$

and $n_{\text{solute}}(n_2) = 0.2$

Using formula $m = n_2 \times \frac{1000}{n_1 \times M_1}$

$$= 0.2 \times \frac{1000}{0.8 \times 18} = 13.88 \text{ mol kg}^{-1}$$

13 A solution of sodium sulphate contains 92 g of Na^+ ions per kilogram of water. The molality of Na^+ ions in that solution in mol kg^{-1} is **[2019, 9 Jan Shift-I]**

(a) 16 (b) 4
(c) 132 (d) 8

Ans. ***(b)***

$$\text{Molality}(m) = \frac{\text{Number of moles of solute}}{\text{Mass of solvent (in g)}} \times 1000$$

$$= \frac{\text{Mass of solute (in g)} \times 1000}{\left[\begin{array}{l}\text{Molecular weight of solute} \\ \quad \times \text{mass of solvent (in g)}\end{array}\right]}$$

$$= \frac{w_{Na^+} \times 1000}{M_{Na^+} \times w_{H_2O}} = \frac{92 \times 1000}{23 \times 1000} = 4 \text{ mol kg}^{-1}$$

14 The amount of sugar ($C_{12}H_{22}O_{11}$) required to prepare 2 L of its 0.1 M aqueous solution is

(a) 17.1 g (b) 68.4 g
(c) 136.8 g (d) 34.2 g

[2019, 10 Jan Shift-II]

Ans. ***(b)***

$$\text{Molarity} = \frac{\text{Number of moles of solute}(n)}{\text{Volume of solution (in L)}}$$

Also, $n = \frac{w_B \text{ (g)}}{M_B \text{ (g mol}^{-1})}$

$\therefore$ $\text{Molarity} = \frac{w_B / M_B}{V}$

Given, w_B = mass of solute (B) in g

M_B = Gram molar mass of B ($C_{12}H_{22}O_{11}$) $= 342 \text{ g mol}^{-1}$

Molarity = 0.1 M, Volume (V) = 2 L

$\Rightarrow$ $0.1 = \frac{w_B / 342}{2}$

$\Rightarrow$ $w_B = 0.1 \times 342 \times 2 \text{ g} = 68.4 \text{ g}$

15 8 g of NaOH is dissolved in 18 g of H_2O. Mole fraction of NaOH in solution and molality (in mol kg^{-1}) of the solution respectively are

(a) 0.2, 11.11 (b) 0.167, 22.20
(c) 0.2, 22.20 (d) 0.167, 11.11

[2019, 12 Jan Shift-II]

Ans. ***(d)***

Mole fraction of solute

$$= \frac{\text{number of moles of solute} + \text{number of moles solvent}}{\text{number of moles of solute}}$$

$$\chi_{\text{Solute}} = \frac{n_{\text{Solute}}}{n_{\text{Solute}} + n_{\text{Solvent}}}$$

$$= \frac{\frac{w_{\text{Solute}}}{Mw_{\text{Solute}}}}{\frac{w_{\text{Solute}}}{Mw_{\text{Solute}}} + \frac{w_{\text{Solvent}}}{Mw_{\text{Solvent}}}}$$

Given, $w_{\text{Solute}} = w_{\text{NaOH}} = 8 \text{ g}$

$Mw_{\text{Solute}} = Mw_{\text{NaOH}} = 40 \text{ g mol}^{-1}$

$w_{\text{Solvent}} = w_{H_2O} = 18 \text{ g}$

$Mw_{\text{Solvent}} = 18 \text{ g mol}^{-1}$

$$\therefore \chi_{\text{Solute}} = \chi_{\text{NaOH}} = \frac{\frac{8}{40}}{\frac{8}{40} + \frac{18}{18}}$$

$$= \frac{0.2}{0.2 + 1} = \frac{0.2}{1.2} = 0.167$$

Now, molality

$$(m) = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

$$= \frac{\frac{w_{\text{Solute}}}{Mw_{\text{Solute}}}}{w_{\text{Solvent}} \text{(in g)}} \times 1000$$

$$= \frac{\frac{8}{40}}{18} \times 1000 = \frac{0.2}{18} \times 1000 = 11.11 \text{ mol kg}^{-1}$$

Thus, mole fraction of NaOH in solution and molality of the solution respectively are 0.167 and 11.11 mol kg^{-1}

16 A 5.2 molal aqueous solution of methyl alcohol, CH_3OH, is supplied. What is the mole fraction of methyl alcohol in the solution ? **[AIEEE 2011]**

(a) 0.100 (b) 0.190
(c) 0.086 (d) 0.050

Ans. ***(c)***

5.2 molal aqueous solution of CH_3OH suggests that 5.2 moles of CH_3OH are dissolved in 1000 g of water.

$n_1(CH_3OH) = 5.2$

$n_2(H_2O) = \frac{1000}{18} = 55.56$

$\therefore$ $n_1 + n_2 = 5.20 + 55.56 = 60.76$ mol

$\therefore$ X_{CH_3OH} = Mole fraction of CH_3OH

$$= \frac{n_1}{n_1 + n_2} = \frac{5.2}{60.76} = 0.086$$

17 The molality of a urea solution in which 0.0100 g of urea, $[(NH_2)_2CO]$ is added to 0.3000 dm^3 of water at STP is **[AIEEE 2011]**

(a) 0.555 m (b) 5.55×10^{-4} m
(c) 33.3 m (d) 3.33×10^{-2} m

Ans. ***(b)***

$$\text{Molality} = \frac{\text{moles of solute}}{\text{kg of water}}$$

$$\text{Moles of urea} = \frac{0.010}{60} \text{ mol}$$

Water at STP ($d = 1 \text{ g/cm}^3 = 1 \text{ kg/dm}^3$)

$= 0.3 \text{ dm}^3 = 0.3 \text{ kg}$

$$\therefore \quad \text{Molality} = \frac{0.010}{60 \times 0.3} = 5.55 \times 10^{-4} \text{ m}$$

18 The density (in g mL^{-1}) of a 3.60 M sulphuric acid solution that is 29% H_2SO_4 (molar mass = 98 g mol^{-1}) by mass will be **[AIEEE 2007]**

(a) 1.64 (b) 1.88 (c) 1.22 (d) 1.45

Ans. ***(c)***

Molarity

$$= \frac{10 \times \text{density} \times \text{\% by wt. of solute}}{\text{mol wt. of the solute}}$$

$$\text{Density} = \frac{3.60 \times 98}{10 \times 29}$$
$$= 1.216\ \text{gmL}^{-1} = 1.22\ \text{gmL}^{-1}$$

19 Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is **[AIEEE 2007]**

(a) $\frac{2}{3}$ (b) $\frac{1}{3} \times \frac{273}{298}$

(c) $\frac{1}{3}$ (d) $\frac{1}{2}$

Ans. ***(c)***

Suppose the equal mass of methane and oxygen $= w = 1\text{g}$

$$\text{Mole fraction of oxygen} = \frac{w/32}{w/32 + w/16}$$
$$= \frac{1/32}{3/32} = \frac{1}{3}$$

Let the total pressure $= p$

Pressure exerted by oxygen (partial pressure)

$$= X_{O_2} \times p_{\text{total}} = p \times \frac{1}{3}$$

Thus, the fraction of the total pressure exerted by oxygen is 1/3.

20 Density of a 2.05 M solution of acetic acid in water is 1.02 g / mL. The molality of the solution is **[AIEEE 2006]**

(a) 1.14 mol kg^{-1} (b) 3.28 mol kg^{-1}

(c) 2.28 mol kg^{-1} (d) 0.44 mol kg^{-1}

Ans. ***(c)***

$$\text{Molality}\,(m) = \frac{M}{1000\,d - MM_1} \times 100$$

M = Molarity; M_1 = Molecular mass

d = density

$$= \frac{2.05}{(1000 \times 1.02) - (2.05 \times 60)} \times 1000$$
$$= 2.28\ \text{mol kg}^{-1}$$

21 Two solutions of a substance (non-electrolyte) are mixed in the following manner. 480 mL of 1.5 M first solution + 520 mL of 1.2 M second solution.

What is the molarity of the final mixture ? **[AIEEE 2005]**

(a) 2.70 M (b) 1.34 M

(c) 1.50 M (d) 1.20 M

Ans. ***(b)***

The molarity of the resulting solution is given by

$$\text{Total molarity} = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$
$$= \frac{1.5 \times 480 + 1.2 \times 520}{480 + 520} = 1.34\ \text{M}$$

22 6.02×10^{20} molecules of urea are present in 100 mL of its solution. The concentration of urea solution is (Avogadro constant, $N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$) **[AIEEE 2004]**

(a) 0.001 M (b) 0.01 M

(c) 0.02 M (d) 0.1 M

Ans. ***(b)***

Avogadro's number, N_A

$= 6.02 \times 10^{23}$ molecules = 1 mol

$\therefore 6.02 \times 10^{20}$ molecules = 0.001 mol in 100 mL or (0.1 L) solution

$$\therefore \text{Molar concentration} = \frac{\text{mol}}{\text{volume in litre}}$$
$$= \frac{0.001}{0.1} = 0.01\ \text{M}$$

23 To neutralise completely 20 mL of 0.1 M aqueous solution of phosphorous acid (H_3PO_3), the volume of 0.1 M aqueous KOH solution required is **[AIEEE 2004]**

(a) 10 mL (b) 20 mL

(c) 40 mL (d) 60 mL

Ans. ***(c)***

H_3PO_3 is a dibasic acid (*i.e.*, contains two ionisable protons attached directly to O).

$$H_3PO_3 \rightleftharpoons 2H^+ + HPO_4^{2-}$$

$\therefore$ 0.1 M H_3PO_3 = 0.2 N H_3PO_3

and 0.1 M KOH = 0.1 N KOH

$$\underset{(\text{KOH})}{N_1V_1} = \underset{(H_3PO_3)}{N_2V_2}$$
$$0.1\,V_1 = 0.2 \times 20;\quad V_1 = 40\ \text{mL}$$

24 25 mL of a solution of barium hydroxide on titration with 0.1 molar solution of hydrochloric acid gave a titre value of 35 mL. The molarity of barium hydroxide solution was **[AIEEE 2003]**

(a) 0.07 (b) 0.14

(c) 0.28 (d) 0.35

Ans. ***(a)***

Let molarity of $Ba(OH)_2 = M_1$

$\therefore$ Normality $= 2\,M_1$

Molarity of HCl = 0.1 M = 0.1 N_2

$$N_1V_1 = N_2V_2$$
$$2M_1 \times 25 = 0.1 \times 35$$
$$M_1 = 0.07\ \text{M}$$

25 Which of the following concentration factor is affected by change in temperature? **[AIEEE 2002]**

(a) Molarity (b) Molality

(c) Mole fraction (d) Weight fraction

Ans. ***(a)***

Molarity gets affected as it is the number of moles per unit volume (volume increases with increase in temperature).

TOPIC 2
Henry's Law and Raoult's Law

26 CO_2 gas is bubbled through water during a soft drink manufacturing process at 298 K. If CO_2 exerts a partial pressure of 0.835 bar then x m mol of CO_2 would dissolve in 0.9 L of water. The value of x is .... (Nearest integer)

(Henry's law constant for CO_2 at 298 K is 1.67×10^3 bar)

[2021, 25 July Shift-I]

Ans. ***(25)***

According to Henry's law,

$$p_{CO_2} = K_H\,X_{CO_2}$$

p_{CO_2}, K_H and X_{CO_2} are pressure of CO gas. Henry's constant and mole fraction of CO respectively.

$$\Rightarrow \quad X_{CO_2} = \frac{p_{CO_2}}{K_H} \quad \text{...(i)}$$

Given, $K_H = 0.835 \times 2 \times 10^3$ bar

$= 1.67 \times 10^3$ bar

$p_{CO_2} = 0.835$ bar

Put all values in equation (i), we get

$$X_{CO_2} = \frac{0.835}{0.835 \times 10^3 \times 2}$$
$$X_{CO_2} = 0.5 \times 10^{-3}$$

Volume of water = 0.9 L = 900 mL

Density of water = 1 g/mL

Mass of water = density × volume = 900 g

So, number of mole of water

$$= \frac{900}{18} = 50\ \text{moles}$$

$$\text{So,} \quad \frac{n_{CO_2}}{n_{CO_2} + n_{H_2O}} = 0.5 \times 10^{-3}$$

$n_{CO_2} << H_2O = 50$ moles

So, ${}^{n}CO_2 + n_{H_2O} = {}^{n}H_2O$

$n_{CO_2} = 0.5 \times 10^{-3} \times 50$

$= 25 \times 10^{-3}$ mol

Millimoles of $CO_2 = 0.025 \times 1000 = 25$

27 The vapour pressures of A and B at 25°C are 90 mm Hg and 15 mm Hg respectively. If A and B are mixed such that the mole-fraction of A in the mixture is 0.6, then the mole fraction of B in the vapour phase is $x \times 10^{-1}$. The value of x is .... (Nearest integer)

[2021, 20 July Shift-II]

Ans. ***(1)***

Partial pressure of A, $p_A^\circ = 90$ mm of Hg

Partial pressure of B, $p_B^\circ = 15$ mm of Hg

Mole fraction of A, $\chi_A = 0.6$

Mole fraction of B, $\chi_B = 0.4$

Total pressure,

$$p_T = \chi_A p_A^\circ + \chi_B p_B^\circ = (0.6 \times 90) + (0.4 \times 15)$$

$$= 54 + 6 = 60 \text{ mm}$$

Now, mole fraction of B in vapour phase,

i.e. $$Y_B = \frac{p_B}{p_T} = \frac{\chi_B p_B^\circ}{60} = 0.1 = 1 \times 10^{-1}$$

$$x = 1$$

28 At 20°C, the vapour pressure of benzene is 70 torr and that of methyl benzene is 20 torr. The mole fraction of benzene in the vapour phase at 20°C above an equimolar mixture of benzene and methyl benzene is...... $\times 10^{-2}$. (Nearest integer)

[2021, 20 July Shift-I]

Ans. ***(78)***

Vapour pressure of pure benzene, $p_A^\circ = 70$ Torr

Vapour pressure of pure methyl benzene, $p_B^\circ = 20$ Torr

This mixture is equimolar, so, number of moles of benzene, n_A = number of moles of methyl benzene, n_B

Mole fraction of benzene in vapour phase,

$$y_A = \frac{p_A}{p_T} \quad \text{...(i)}$$

where p_A is pressure of benzene in mixture.

$$p_A = \underset{\text{Mole fraction}}{p_A^\circ \chi_A}$$

$$= p_A^\circ \times \frac{n_A}{n_A + n_B} = p_A^\circ \times \frac{\frac{n}{A}}{2\frac{n}{A}} = \frac{p_A^\circ}{2}$$

p_T is total pressure,

$$p_T = p_A^\circ \chi_A + p_B^\circ \chi_B = p_A + p_B$$

(pressure of methyl benzene)

$$p_T = \frac{p_A^\circ}{2} + \frac{p_B^\circ}{2} = \frac{p_A^\circ + p_B^\circ}{2}$$

Putting in above equation (i),

$$y_A = \frac{\frac{70}{2}}{\frac{(70+20)}{2}} = \frac{70}{90}$$

$$y_A = 0.78 = 78 \times 10^{-2}$$

29 At 300 K, the vapour pressure of a solution containing 1 mole of *n*-hexane and 3 moles of *n*-heptane is 550 mm of Hg. At the same temperature, if one more mole of *n*-heptane is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. What is the vapour pressure in mm Hg of *n*-heptane in its pure state .... ?

[2020, 4 Sep Shift-I]

Ans. ***(600)***

Given,

Vapour pressure of solution = 550 mmHg

Mole of hexane $(n_{\text{hex}}) = 1$ mol

Mole of heptane $(n_{\text{hep}}) = 3$ mol

From Raoult's law,

Vapour pressure in solution = vapour pressure of pure solvent × mole fraction

$$p = p^\circ \chi$$

Here, vapour pressure of solution $= p$, vapour pressure of pure solvent $= p^\circ$ and mole fraction $= \chi$

Total vapour pressure of solution,

$$p_{\text{total}} = p^\circ_{\text{hex}} \chi_{\text{hex}} + p^\circ_{\text{hep}} \chi_{\text{hep}}$$

Case I Mole fraction of hexane,

$$\chi_{\text{hex}} = \frac{1}{1+3} = 0.25$$

Mole fraction of heptane,

$$\chi_{\text{hep}} = \frac{3}{1+3} = 0.75$$

$$p = p^\circ_{\text{hex}} 0.25 + p^\circ_{\text{hep}} \times 0.75$$

$$550 = p^\circ_{\text{hex}} 0.25 + p^\circ_{\text{hep}} \times 0.75 \quad \text{...(i)}$$

Case II According to question, when 1 mole of heptane added and vapour pressure increased by 10 mm of Hg.

Mole fraction of hexane,

$$\chi_{\text{hex}} = \frac{1}{1+4} = 0.20$$

Mole fraction of heptane,

$$\chi_{\text{hep}} = \frac{4}{1+4} = 0.80$$

$$p = p^\circ_{\text{hex}} \chi_{\text{hex}} + p^\circ_{\text{hep}} \chi_{\text{hep}}$$

Vapour pressure increased by 10 mm of Hg then $p = 560$

$$\Rightarrow \quad 560 = p^\circ_{\text{hex}} 0.20 + p^\circ_{\text{hep}} 0.80 \quad \text{...(ii)}$$

Eq. (i) multiplied by 0.20

$$\Rightarrow 550 \times 0.20 = (0.25 \times 0.20) p^\circ_{\text{hex}} + (0.75 \times 0.20) p^\circ_{\text{hep}}$$

$$\Rightarrow \quad 110 = 0.05 p^\circ_{\text{hex}} + 0.15 p^\circ_{\text{hep}} \quad \text{...(iii)}$$

Eq. (ii) multiplied by 0.25,

$$\Rightarrow \quad 560 \times 0.25 = (0.20 \times 0.25) p^\circ_{\text{hex}} + (0.8 \times 0.25) p^\circ_{\text{hep}}$$

$$140 = 0.05 p^\circ_{\text{hex}} + 0.20 p^\circ_{\text{hep}} \quad \text{...(iv)}$$

Now, Eq. (iii) and Eq. (iv)

$$\Rightarrow 0.05 p^\circ_{\text{hex}} + 0.15 p^\circ_{\text{hep}} - 0.05 p^\circ_{\text{hex}} - 0.20 p^\circ_{\text{hep}} = 110 - 140$$

$$\Rightarrow 0.15 p^\circ_{\text{hep}} - 0.20 p^\circ_{\text{hep}} = -30$$

$$\Rightarrow -0.05 p^\circ_{\text{hep}} = -30$$

$$\Rightarrow \quad p^\circ_{\text{hep}} = \frac{30}{0.05} = 600 \text{ mm of Hg}$$

Thus, vapour pressure of pure *n*-heptane (p°_{hep}) is 600 mm of Hg.

30 Henry's constant (in kbar) for four gases α, β, γ and δ in water at 298 K is given below :

	α	β	γ	δ
K_H	50	2	2×10^{-5}	0.5

(density of water $= 10^3$ kg m^{-3} at 298 K). This table implies that

[2020, 3 Sep Shift-I]

(a) α has the highest solubility in water at a given pressure

(b) solubility of γ at 308 K is lower than at 298 K

(c) The pressure of a 55.5 molal solution of γ is 1 bar

(d) The pressure of a 55.5 molal solution of δ is 250 bar

Ans. ***(d)***

Henry's equation for solubility (S) of a gas (β) in a liquid is expressed in terms of mole- fraction of the gas (χ_B) at a given temperature,

$$p = K_H \times \chi_B = K_H \times S$$

So, solubility of gas, $S \propto \frac{1}{K_H}$ at T(K) and given pressure.

Order of solubility of the gases (high the value of K_H, lower is the solubility) :

$$\gamma > \delta > \beta > \alpha$$

So, option (a) is not correct.

Again, $K_H \propto$ temperature, i.e. solubility of the gas will decrease with increase in temperature also.

But this conclusion cannot be drawn from table.

So, option (b) is not correct.

We know, mole-fraction of a solute (B) in a binary aqueous solution,

$$\chi_B = \frac{18\,\text{m}}{1000 + 18\,\text{m}}$$

$$[\because m = \text{molality}]$$

For γ at $m = 55.5$ molal

$$p = K_{\text{H}}^{\gamma} \times m = (2 \times 10^{-5}) \times \left(\frac{18 \times 55.5}{1000 + 18 \times 55.5}\right)$$

$$= 1.81 \times 10^{-5}\ \text{K bar} = 1.8 \times 10^{-2}\ \text{bar}$$

So, option (c) is not correct.

For δ at $m = 55.5$ molal

$$p = K_{\text{H}}^{\delta} = (0.5) \times \left(\frac{18 \times 55.5}{1000 + 18 \times 55.5}\right)$$

$$= 0.2498\ \text{k bar} \simeq 250\ \text{bar}$$

So, option (d) is correct.

31 At 35°C, the vapour pressure of CS_2 is 512 mm Hg and that of acetone is 344 mm Hg. A solution of CS_2 in acetone has a total vapour pressure of 600 mm Hg. The false statement amongst the following is **[2020, 7 Jan Shift-I]**

(a) Raoult's law is not obeyed by this system

(b) CS_2 and acetone are less attracted to each other than to themselves

(c) a mixture of 100 mL CS_2 and 100 mL acetone has a volume < 200 mL

(d) heat must be absorbed in order to produce the solution at 35°C

Ans. ***(c)***

The incorrect statement among the given statements is (c) and the explanation of all the statements is as follows :

According to Raoult's law, vapour pressure of the solution p_{id} (ideal vapour pressure) $= p_A{}^\circ + (p_B{}^\circ - p_A{}^\circ)x_B$

$(A = \text{solvent : acetone}, B = \text{solute} : CS_2)$

Given; $p_A{}^\circ = 344$ mm Hg.

$p_B{}^\circ = 512$ mm Hg.

$\therefore \quad p_{\text{id}} = 3.44 + (512 - 344)x_B$

or $\quad p_{\text{id}} = 344 + 168\,x_B$

and so, $0 < x_B < 1$.

Also, total vapour pressure (p)

$= 600$ mmHg

$\therefore$ For any value of x_B, $p > p_{\text{id}}$.

Since $p \neq p_{\text{id}}$, so, option (a) is correct.

Option (b) is also correct. Since $p > p_{\text{id}}$, (i.e. positive deviation) therefore attractive force between CS_2 and acetone is weaker than $CS_2 - CS_2$ or acetone-acetone attraction.

Option (c) is incorrect as for positive deviation, $\Delta V > 0$ because final volume of solution must be greater than the sum of volumes of components taken.

Option (d) is correct. Since, in such solution, $\Delta_{\text{mix}}H$ is positive because energy is required to break A—A and B—B bonds.

32 Two open beakers one containing a solvent and the other containing a mixture of that solvent with a non-volatile solute are together sealed in a container. Over time **[2020, 7 Jan Shift-II]**

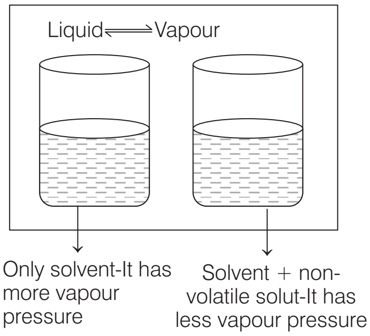
(a) the volume of the solution decreases and the volume of the solvent increases

(b) the volume of the solution does not change and the volume of the solvent decreases

(c) the volume of the solution increases and the volume of the solvent decreases

(d) the volume of the solution and the solvent does not change

Ans. ***(c)***



If a non-volatile solute is added to a solvent to form a solution, the vapour pressure gets decreased.

$\therefore$According to Raoult's law, if vapour pressure of pure solvent is p°, vapour pressure of solvent in solution (p) is $= p^\circ \cdot x_A$.

$\therefore \qquad p < p^\circ$

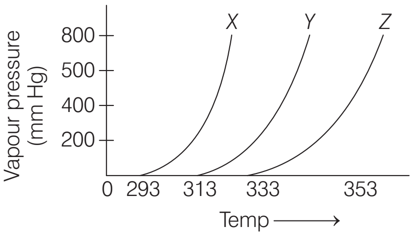
Since, vapour pressure of solution is less, there will be net backward reaction [i.e. vapour $\longrightarrow$ liquid] in that beaker.

Thus, its volume increases.

In another beaker containing only net reaction is forward,

Thus, volume decreases.

33 A graph of vapour pressure and temperature for three different liquids X, Y, and Z is shown below : **[2020, 8 Jan Shift-I]**



The following inference are made :

A. X has higher intermolecular interactions compared to Y.

B. X has lower intermolecular interactions compared to Y.

C. Z has lower intermolecular interactions compared to Y.

The correct inference(s) is/are :

(a) (C)	(b) (B)
(c) (A)	(d) (A) and (C)

Ans. ***(b)***

From given graph it can be seen that, X has higher vapour pressure as compared to Y at lower temperature (or to attain same vapour pressure, Y need higher temperature than X). It means that intermolecular interactions must be weaker in X as compared to Y, which further must be weaker than Z by the same reason also. Hence, option (b) is correct.

34 The vapour pressures of pure liquids A and B are 400 and 600 mmHg, respectively at 298 K. On mixing the two liquids, the sum of their initial volumes is equal to the volume of the final mixture. The mole fraction of liquid B is 0.5 in the mixture. The vapour pressure of the final solution, the mole fractions of components A and B in vapour phase, respectively are **[2019, 8 April Shift-I]**

(a) 450 mmHg, 0.4, 0.6

(b) 500 mmHg, 0.5, 0.5

(c) 450 mmHg, 0.5,0.5

(d) 500 mmHg, 0.4,0.6

Ans. ***(d)***

According to Dalton's law of partial pressure $p_{\text{total}} = p_A + p_B$

$$= \overset{\circ}{p}_A\chi_A + \overset{\circ}{p}_B\,\chi_B \qquad \text{...(i)}$$

Given, $\overset{\circ}{p}_A = 400$ mm Hg, $\overset{\circ}{p}_B = 600$ mm Hg

$\chi_B = 0.5, \chi_A + \chi_B = 1$

$\therefore \qquad \chi_A = 0.5$

On substituting the given values in Eq. (i). We get,

$p_{\text{total}} = 400 \times 0.5 + 600 \times 0.5 = 500$ mm Hg

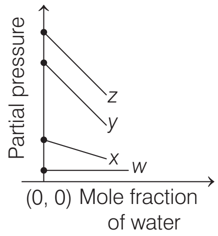
Mole fraction of A in vapour phase,

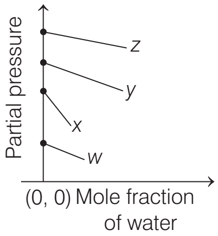
$$Y_A = \frac{p_A}{p_{\text{total}}} = \frac{p_A^{\circ}\chi_A}{p_{\text{total}}} = \frac{0.5\times400}{500} = 0.4$$

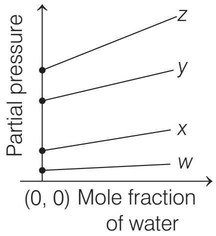
Mole of B in vapour phase,

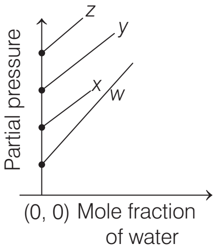
$$Y_A + Y_B = 1$$
$$Y_B = 1 - 0.4 = 0.6$$

35 For the solution of the gases w, x, y and z in water at 298 K, the Henry's law constants (K_H) are 0.5, 2, 35 and 40 K bar, respectively. The correct plot for the given data is **[2019, 8 April Shift-II]**

(a) 

(b) 

(c) 

(d) 

Ans. ***(a)***

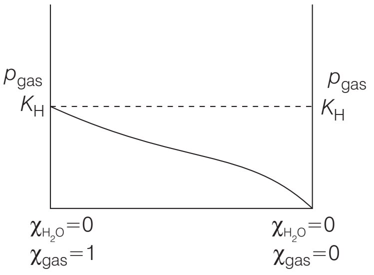
According to Henry's law (at constant temperature)

$$p_{\text{gas}} = K_H \times \chi_{\text{gas (solute)}}$$
$$= K_H \times [1 - \chi_{H_2O\,(\text{solvent})}]$$
$$p_{\text{gas}} = K_H - K_H\,\chi_{H_2O}$$

p_{gas} = partial pressure of the gas above its solution with a liquid (solvent) say water.

χ_{gas} = mole fraction of the gas (solute) in the solution.

χ_{H_2O} = mole fraction of water (solvent).



[i.e. $p_{\text{gas}} = K_H$] Higher the value of K_H, higher

will be the partial pressure of the gas (p_{gas}), at a given temperature. The plot of p_{gas} vs χ_{H_2O} gives a (–ve) slope.

$$p_{\text{gas}} = K_H - K_H \times \chi_{H_2O}$$

Comparing the above equation with the equation of straight line $y = mx + c$

Slope $= -K_H$, intercept $= K_H$

So, (i) Higher the value of K_H, more (–ve) will be the slope and it is for z (K_H = 40 K bar)

(ii) Higher the value of K_H, higher with the value of intercept, i.e. partial pressure and it is also for z.

36 Liquid M and liquid N form an ideal solution. The vapour pressures of pure liquids M and N are 450 and 700 mmHg, respectively, at the same temperature. Then correct statement is **[2019, 9 April Shift-I]**

x_M = mole fraction of M in solution;

x_N = mole fraction of N in solution;

y_M = mole fraction of M in vapour phase;

y_N = mole fraction of N in vapour phase

(a) $\frac{x_M}{x_N} > \frac{y_M}{y_N}$

(b) $\frac{x_M}{x_N} = \frac{y_M}{y_N}$

(c) $\frac{x_M}{x_N} < \frac{y_M}{y_N}$

(d) $(x_M - y_M) < (x_N - y_N)$

Ans. ***(a)***

Key Idea For a solution of volatile liquids the partial vapour pressure of each component of the solution is directly proportional to its mole fraction present in solution. This is known as Raoult's law.

Liquid M and N form an ideal solution. Vapour pressures of pure liquids M and N are 450 and 700 mm Hg respectively.

$\therefore \quad p^{\circ}_N > p^{\circ}_M$

So, by using Raoult's law

$$y_N > x_N \quad \text{...(i)}$$

and $$x_M > y_M \quad \text{...(ii)}$$

Multiplying (i) and (ii) we get

$$y_N\,x_M > y_M\,x_N$$

$$\therefore \quad \frac{x_M}{x_N} > \frac{y_M}{y_N}$$

Thus, correct relation is (a).

37 Which one of the following statements regarding Henry's law is not correct?

(a) Different gases have different K_H (Henry's law constant) values at the same temperature

(b) Higher the value of K_H at a given pressure, higher is the solubility of the gas in the liquids

(c) The value of K_H increases with increase of temperature and K_H is function of the nature of the gas

(d) The partial pressure of the gas in vapour phase is proportional to the mole fraction of the gas in the solution **[2019, 9 Jan Shift-I]**

Ans. ***(b)***

At constant temperature, solubility of a gas (S) varies inversely with Henry's law constant (K_H)

$$K_H = \frac{\text{Pressure}}{\text{Solubility of a gas in a liquid}} = \frac{P}{S}$$

Thus, higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.

38 Liquids A and B form an ideal solution in the entire composition range. At 350 K, the vapour pressures of pure A and pure B are 7×10^3 Pa and 12×10^3 Pa, respectively. The composition of the vapour in equilibrium with a solution containing 40 mole percent of A at this temperature is

(a) $x_A = 0.76$; $x_B = 0.24$

(b) $x_A = 0.28$; $x_B = 0.72$

(c) $x_A = 0.4$; $x_B = 0.6$

(d) $x_A = 0.37$; $x_B = 0.63$ **[2019, 10 Jan Shift-I]**

Ans. ***(b)***

For ideal solution,

$$p = x'_A\,p^{\circ}_A + x'_B\,p^{\circ}_B$$

$\because \quad x'_A = 0.4, x'_B = 0.6$

$$p^\circ_A = 7\times 10^3\ \text{Pa},\ p^\circ_B = 12\times 10^3\ \text{Pa}$$

On substituting the given values in Eq. (i), we get

$$p = 0.4\times 7\times 10^3 + 0.6\times 12\times 10^3$$
$$= 10\times 10^3\ \text{Pa} = 1\times 10^4\ \text{Pa}$$

In vapour phase,

$$x_A = \frac{p_A}{p} = \frac{x'_A\, p^\circ_A}{p} = \frac{0.4\times 7\times 10^3}{1\times 10^4} = 0.28$$

$$\therefore \quad x_B = 1 - 0.28 = 0.72 \qquad [\because x_A + x_B = 1]$$

39 On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa, respectively. Vapour pressure of the solution obtained by mixing 25 g of heptane and 35 g of octane will be (molar mass of heptane $= 100\ \text{g mol}^{-1}$ and of octane $= 114\ \text{g mol}^{-1}$). **[AIEEE 2010]**

(a) 72.0 kPa
(b) 36.1 kPa
(c) 96.2 kPa
(d) 144.5 kPa

Ans. ***(a)***

$$p_T = X_H\cdot p^\circ_H + X_0\cdot p^\circ_0$$
$$X_H = \frac{25/100}{25/100 + 35/114} = 0.45$$
$$\therefore \quad X_0 = 0.55$$
$$p_T = 0.45\times 105 + 0.55\times 45$$
$$= 72.0\ \text{kPa}$$

40 Two liquids *X* and *Y* form an ideal solution at 300 K, vapour pressure of the solution containing 1 mol of *X* and 3 mol of *Y* is 550 mmHg. 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 mmHg) of *X* and *Y* in their pure states will be, respectively **[AIEEE 2009]**

(a) 200 and 300
(b) 300 and 400
(c) 400 and 600
(d) 500 and 600

Ans. ***(c)***

$$p_T = p_A{}^\circ X_A + p_B{}^\circ X_B$$
$$550 = p_A{}^\circ \times \frac{1}{4} + p_B{}^\circ \times \frac{3}{4}$$

Thus, $\quad p_A{}^\circ + 3p_B{}^\circ = 2200 \qquad$ ...(i)

When 1 mole of *Y* is further added to the solution, vapour pressure of a solution becomes 560 mm Hg.

Thus, $\quad 560 = p_A{}^\circ \times \frac{1}{5} + p_B{}^\circ \times \frac{4}{5}$

Thus, $\quad p_A{}^\circ + 4p_B{}^\circ = 2800 \qquad$ ...(ii)

On subtracting Eq. (ii) by Eq. (i), we get

$$p_B{}^\circ = 2800 - 2200$$
$$\Rightarrow \quad p_B{}^\circ = 600$$

Putting the value of $p_B{}^\circ$ in Eq. (i)

$$p_A{}^\circ + 3\times 600 = 2200$$
$$p_A{}^\circ = 2200 - 1800 = 400$$

41 A binary liquid solution is prepared by mixing *n*-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution? **[AIEEE 2009]**

(a) The solution formed is an ideal solution
(b) The solution is non-ideal, showing positive deviation from Raoult's law
(c) The solution is non-ideal, showing negative deviation from Raoult's law
(d) *n*-heptane shows positive deviation while ethanol show negative deviation from Raoult's law

Ans. ***(b)***

n-heptane and ethanol forms non-ideal solution. As a result, *n*-heptane-ethanol molecular interaction is very poor in comparison to ethanol-ethanol or *n*-heptane so the resulting gives positive deviation from Raoult's law.

42 A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. 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 **[AIEEE 2007]**

(a) 350
(b) 300
(c) 700
(d) 360

Ans. ***(a)***

According to Raoult's law,

$$p = p^\circ{}_A X_A + p^\circ{}_B X_B$$
$$290 = 200\times 0.4 + p^\circ{}_B \times 0.6$$
$$p^\circ{}_B = 350\ \text{mm}$$

43 Benzene and toluene form nearly ideal solutions. At 20°C, the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapour pressure of benzene at 20°C for a solution containing 78 g of benzene and 46 g of toluene in torr is **[AIEEE 2005]**

(a) 53.5
(b) 37.5
(c) 25
(d) 50

Ans. ***(d)***

Mixture contains 78 g benzene = 1 mol benzene and 46 g toluene = 0.5 mol toluene

Total moles of benzene and toluene = 1.5 mol

Mole fraction of benzene in mixture

$$= \frac{1}{1.5} = \frac{2}{3}$$

Vapour pressure of benzene

$$p^\circ_b = 75\ \text{torr}$$

∴Partial vapour pressure of benzene

$$= p^\circ{}_b X_b$$
$$= 75\times \frac{2}{3} = 50\ \text{torr}$$

44 Which of the following liquid pairs shows a positive deviation from Raoult's law? **[AIEEE 2004]**

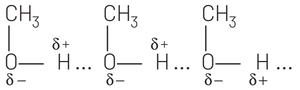
(a) Water — hydrochloric acid
(b) Benzene — methanol
(c) Water — nitric acid
(d) Acetone — chloroform

Ans. ***(b)***

Water and hydrochloric acid; and water and nitric acid form miscible solutions. They show negative deviation.

In case of CH_3COCH_3 and $CHCl_3$, there is interaction between them, thus force of attraction between $CH_3COCH_3....CHCl_3$ is larger than between $CHCl_3....CHCl_3$ or $CH_3COCH_3....CH_3COCH_3$ and thus, vapour pressure is less than expected—a negative deviation.

In case of CH_3OH, there is association by intermolecular H-bonding. When benzene is added to CH_3OH, H-bonding breaks and thus, force of attraction between CH_3OH and benzene molecule is smaller than between CH_3OH or benzene molecules (in pure state). Vapour pressure of mixture is greater than expected—a positive deviation.



$$\underset{\delta-}{\overset{\overset{CH_3}{|}}{O}}-\overset{\delta+}{H}\cdots\underset{\delta-}{\overset{\overset{CH_3}{|}}{O}}-\overset{\delta+}{H}\cdots\underset{\delta-}{\overset{\overset{CH_3}{|}}{O}}-\underset{\delta+}{H}\cdots$$

45 If liquid *A* and *B* form an ideal solution, the **[AIEEE 2003]**

(a) enthalpy of mixing is zero
(b) entropy of mixing is zero
(c) free energy of mixing is zero
(d) free energy as well as the entropy of mixing are each zero

Ans. ***(a)***

For ideal solution, $\Delta H = 0$, $\Delta V = 0$;

$$F_{A-A} = F_{B-B} = F_{A-B}$$

46 In a mixture of A and B, components show negative deviation when **[AIEEE 2002]**

(a) A—B interaction is stronger than A—A and B—B interaction

(b) A—B interaction is weaker than A—A and B—B interaction

(c) $\Delta V_{mix} > 0, \Delta S_{mix} > 0$

(d) $\Delta V_{mix} = 0, \Delta S_{mix} > 0$

Ans. ***(a)***

Negative deviation means lower vapour pressure. It suggests high boiling point, thus resultant intermolecular force should be stronger than individual one.

TOPIC 3
Colligative Properties

47 40 g of glucose (Molar mass = 180) is mixed with 200 mL of water. The freezing point of solution is .... K. (Nearest integer)

$[\text{Given, } K_f = 1.86 \text{ K kg mol}^{-1}$, density of water $= 1.00 \text{ g cm}^{-3}$, freezing point of water $= 273.15 \text{ K}]$ **[2021, 27 Aug Shift-II]**

Ans. ***(271)***

40 g of glucose mixed with 200 mL of water

180 g of glucose $=$1 moles of glucose

40 g of glucose mol $= 0.22$ mol

1 mL of water $=$ 1 g of water

$$[d = 1 \text{ g / cm}^2, 1 \text{ mL} = 1 \text{ cm}^3]$$

200 mL of water $= 200$ g of water

$$\Delta T_f = K_f m$$

where, $\Delta T_f =$ depression in freezing point,

$K_f =$ molal elevation constant

$= 1.86 \text{ K kg mol}^{-1}$ and

$m =$ molality of solution

$$\Delta T_f = \frac{1.86 \times 0.22}{200} \times 1000 \quad (\because 1000 \text{ g} = 1 \text{ kg})$$

$$\Delta T_f = 2 \text{ K}$$

$$\therefore \quad (T_f - T_f') = 2$$

$$\begin{bmatrix} T_f = \text{freezing point of water (273 K)} \\ T_f' = \text{freezing point of solution} \end{bmatrix}$$

$$273 \text{ K} - T_f' = 2 \text{K}$$

$$T_f' = (273 - 2) \text{K}$$

$$= 271 \text{K}$$

48 1 kg of 0.75 molal aqueous solution of sucrose can be cooled up to $-4°\text{C}$ before freezing. The amount of ice (in g) that will be separated out is .... (Nearest integer)

$[\text{Given, } K_f(\text{H}_2\text{O}) = 1.86 \text{ K kg mol}^{-1}]$ **[2021, 27 Aug Shift-I]**

Ans. ***(518)***

Let mass of water (initially present) $= x$ g

Mass of sucrose $= (1000 - x)$ g

Moles of sucrose $= \dfrac{1000 - x}{342}$

$$\text{Molality} = \frac{\text{moles of sucrose}}{\text{mass of water (initially)}}$$

$$0.75 = \frac{\left(\frac{1000 - x}{342}\right)}{\left(\frac{x}{1000}\right)}$$

$$\frac{x}{1000} = \frac{1000 - x}{342 \times 0.75}$$

$$256.5x = 10^6 - 1000x$$

$$\Rightarrow \quad x = 795.86 \text{ g}$$

Moles of sucrose $= 0.5969$

New mass of $\text{H}_2\text{O} = a$ kg

Depression in freezing point

$$\Delta T_f = K_f \times m$$

$$4 = \frac{0.5969}{a} \times 1.86$$

$$\Rightarrow \quad a = 0.2775 \text{ kg}$$

Ice separated $= 795.86 - 277.5$

$= 518.3 \text{ g} \approx 518 \text{ g}.$

49 1.46 g of a biopolymer dissolved in a 100 mL water at 300 K exerted an osmotic pressure of 2.42×10^{-3} bar. The molar mass of the biopolymer is .... $\times 10^4 \text{ g mol}^{-1}$. (Round off to the nearest integer)

$[\text{Use} : R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}]$ **[2021, 27 July Shift-I]**

Ans. ***(15)***

Using formula; $\pi = CRT$

$\pi =$ osmotic pressure,

$C =$ molarity (concentration)

$T =$ temperature of solution

$$\text{Molarity, } C = \frac{\text{Number of moles of solute}}{\text{Volume of solution (L)}}$$

$$\text{Moles} = \frac{\text{Given mass}}{\text{Molecular mass}} = \frac{1.46}{M}$$

$$\text{Molarity} = \frac{1.46 \times 1000}{M \times 100 (\text{mL})} = \frac{1460}{100 \times M}$$

$$\therefore \quad \pi = \frac{1460}{100 \times \text{M}} \times 0.083 \times 300$$

Given, $\quad \pi = 2.42 \times 10^{-3}$ bar

Therefore, $M = 15.02 \times 10^4$ g /mol

50 When 3.00 g of a substance 'X' is dissolved in 100 g of CCl_4, it raises the boiling point by 0.60 K. The molar mass of the substance 'X' is .... g mol^{-1}. (Nearest integer)

$[\text{Given, } K_b \text{ for } \text{CCl}_4 \text{ is } 5.0 \text{ K kg mol}^{-1}]$ **[2021, 25 July Shift-II]**

Ans. ***(250)***

Weight of substance 'X' $= 3.00$ g

Elevation in boiling point, $\Delta T_b = 0.60$

K_b (boiling constant) of CCl_4

$= 5 \text{ K kg mol}^{-1}$

$$\text{Molality } (m) = \frac{\dfrac{\text{Weight of compound}}{\text{Molar mass of compound}}}{\text{Volume of solution (in L)}}$$

$$= \frac{\frac{3}{M}}{\frac{100}{1000}} \quad \text{...(i)}$$

Formula, $\Delta T_b = K_b \times$ molality

Put value of (i) we get,

$$0.60 = 5 \times \frac{\frac{3}{M}}{\frac{100}{1000}} \Rightarrow 0.60 = 5 \times \frac{3 \times 1000}{M \times 100}$$

$$0.60 M = 5 \times 30 \Rightarrow M = \frac{150}{0.60} = 250$$

$\therefore$ Molar mass of substance 'X' is 250 g mol^{-1}.

51 Which one of the following 0.06 M aqueous solutions has lowest freezing point? **[2021, 22 July Shift-II]**

(a) $\text{Al}_2(\text{SO}_4)_3$ (b) $\text{C}_6\text{H}_{12}\text{O}_6$

(c) KI (d) K_2SO_4

Ans. ***(a)***

van't Hoff factor of $\text{Al}_2(\text{SO}_4)_3$ is 5 (maximum), so this will have lowest freezing point.

Depression in freezing point, $\Delta T_f = iK_f m$

where, $i =$ van't Hoff factor

$K_f =$ molal depression constant

$m =$ molality

For freezing point to be lowest,

ΔT_f should be highest and the i values are follows

Solute	i
$\text{C}_6\text{H}_{12}\text{O}_6$	1
$\text{Al}_2(\text{SO}_4)_3$	$5 \rightarrow i$ highest, ΔT_f maximum, T_f minimum
KI	2
K_2SO_4	3

Hence, for $\text{Al}_3(\text{SO}_4)_3$ freezing point is lowest.

52 A solute a dimerises in water. The boiling point of a 2 molar solution of A is 100.52°C.

The percentage association of A is ……… . (Round off to the nearest integer)

[Use : K_b for water $= 0.52 \text{ K kg mol}^{-1}$, boiling point of water = 100°C]

[2021, 18 March Shift-II]

Ans. ***(100)***

Given : $T_b = 100.52°\text{C}$

$T_b^\circ = 100°\text{C}$

$\Rightarrow \quad K_b = 0.52 \text{ K kg mol}^{-1}$

Elevation in boiling point,

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

$$\Delta T_b = 100.52 - 100$$

$$\Delta T_b = 0.52° \text{C}$$

For dimerisation (van't Hoff factor)

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

$\because \quad \Delta T_b = i \times K_b \times m$

$$0.52 = \left(1 - \frac{\alpha}{2}\right) \times 0.52 \times 2$$

$$\alpha = 1$$

So, percentage association = 100%

53 2 molal solution of a weak acid HA has a freezing point of 3.885°C. The degree of dissociation of this acid is ……… $\times 10^{-3}$. (Round off to the nearest integer).

[Given : Molal depression constant of water = $1.85 \text{ K kg mol}^{-1}$, freezing point of pure water = 0°C]

[2021, 18 March Shift-I]

Ans. ***(50)***

Given,

Depression in freezing point,

$$K_f = 1.85 \text{ K kg mol}^{-1}$$

$$T_f^\circ = 0°\text{C}$$

$$T_f = 3.885°\text{C}$$

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

$$= 3.885 - \text{C} = 3.885°\text{C}$$

$$\Delta T_f = 3.885°\text{C}$$

$$\Delta T_f = i \times K_f \times m$$

$$3.885 = i \times 1.85 \times 2$$

but, $\quad i = (1 + \alpha)$

$$3.885 = (1 + \alpha) \times 1.85 \times 2$$

$\Rightarrow \quad \alpha = \dfrac{0.185}{3.7}$

$\Rightarrow \quad \alpha = 0.05$

$$\alpha = 50 \times 10^{-3}$$

54 A 1 molal $K_4Fe(CN)_6$ solution has a degree of dissociation of 0.4. Its boiling point is equal to that of another solution which contains 18.1 weight per cent of a non-electrolytic solute A. The molar mass of A is ……. u. (Round off to the nearest integer).

[Density of water = 1.0 g cm^{-3}]

[2021, 17 March Shift-II]

Ans. ***(85)***

$$K_4Fe(CN)_6 \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$$

Initial conc. $\quad 1 \text{ m} \quad 0 \quad 0$

Final conc. $\quad (1 - 0.4) \text{ m} \quad 4 \times 0.4 \quad 0.4 \text{ m}$

$\quad = 0.6 \text{ m} \quad = 1.6 \text{ m}$

Effective molality = 0.6 + 1.6 + 0.4 = 2.6 m

As elevation in boiling point is a colligative property which depends on the amount of solute. So, to have same boiling point, the molality of two solutions should be same.

Molality of non-electrolyte solution = molality of $K_4[Fe(CN)_6]$ = 2.6 m

Now, 18.1 weight per cent solution means 18.1 g solute is present in 100 g solution and hence, (100 – 18.1 =) 81.9 g water.

Molality

$$= \frac{(\text{Mass of solute/Molar mass of solute})}{\text{Mass of solvent (g)}} \times 1000$$

Now, $2.6 = \dfrac{18.1/M}{81.9/1000}$

where, M is the molar mass of non-electrolyte solute

Molar mass of solute, $M = 85$

55 C_6H_6 freezes at 5.5°C. The temperature at which a solution 10 g of C_4H_{10} in 200 g of C_6H_6 freeze is ………°C. (The molal freezing point depression constant of C_6H_6 is 5.12°C/m.) **[2021, 24 Feb Shift-II]**

Ans. ***(1)***

Pure solvent : $C_6H_6(l)$

Given, $\quad T_f^\circ = 5.5°\text{C}$

$\quad K_f = 5.12°$

C/m $\Rightarrow \quad m = 200 \text{ g}$

$\quad m_{\text{solute}} = 10 \text{ g}$

Molar mass of solute

$$C_4H_{10} = 12 \times 4 + 10 = 58$$

Solute (C_4H_{10}) is non-dissociative;

$\therefore \quad i = 1$

$\therefore \quad \Delta T_f = iK_f \, m$

$\Rightarrow \quad (T_f^\circ - T_f^1) = 1 \times 5.12 \times \dfrac{(10/58)}{(200/1000)}$

$$5.5 - T_f^1 = \frac{5.12 \times 5 \times 10}{58}$$

$\Rightarrow \quad T_f^1 = 1.086°\text{C}$

or $\quad T_f^1 \approx 1°\text{C}$

56 The size of a raw mango shrinks to a much smaller size when kept in a concentrated salt solution. Which one of the following processes can explain this? **[2020, 2 Sep Shift-II]**

(a) Osmosis
(b) Dialysis
(c) Diffusion
(d) Reverse osmosis

Ans. ***(a)***

When a raw mango is kept in a concentrated salt solution, the mango will shrink because of exo-osmosis. Mango cell membrane acts as semi-permeable membrane and its cell cytoplasm is considered as a solution of concentration, C_1M(say). Let, the concentration of salt solution is C_2M, where $C_1 < C_2$ (mentioned).

So, osmotic pressure developed at salt solution, π_2 will be greater than that at cell cytoplasm, π_1 at a given temperature.

$$\pi_1 = C_1RT$$

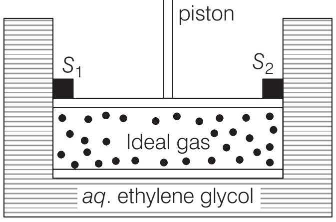
and $\quad \pi_2 = C_2RT$

So, solvent molecules (water) will flow out from mango cells to salt solution resulting shrinking of mango. This state is also known as plasmolysis.

57 A cylinder containing an ideal gas (0.1 mol of 1.0 dm^3) is in thermal equilibrium with a large volume of 0.5 molal aqueous solution of ethylene glycol at its freezing point. If the stoppers S_1 and S_2 (as shown in the figure) are suddenly withdrawn, the volume of the gas in litres after equilibrium is achieved will be ………

(Given, K_f (water) = $2.0 \text{ K kg mol}^{-1}$, $R = 0.08 \text{ dm}^3 \text{ atm K}^{-1}\text{mol}^{-1}$)

[2020, 9 Jan Shift-II]



Ans. ***(2.18)***

$K_f = 2.0$ (Given) $m = 0.5$ m (Given)
$\Delta T_f = K_f \times m = 2 \times 0.5 = 1$
$\therefore T_f =$ Actual freezing point of water is -1.
$= 273 - 1 = 272$ K.

Pressure of gas after the stoppers are withdrawn = 1 atm (atmospheric pressure)

$$\therefore \quad V = \frac{nRT}{p} = \frac{0.1 \times 0.08 \times 272}{1 \text{ atm}}$$
$$= 2.176 \text{ L} \approx 2.18 \text{ L}$$

58 The osmotic pressure of a solution of NaCl is 0.10 atm and that of a glucose solution is 0.20 atm. The osmotic pressure of a solution formed by mixing 1 L of the sodium chloride solution with 2 L of the glucose solution is $x \times 10^{-3}$ atm. x is .... (nearest integer).

[2020, 4 Sep Shift-II]

Ans. ***(167)***

Osmotic pressure, $\pi = i \times C \times RT$
Here, i = van't Hoff factor,
T = temperature
C = concentration and
R = gas constant.
For NaCl, $i = 2$

So, $\pi_{\text{NaCl}} = i \times C_{\text{NaCl}} \times RT$
$0.1 = 2 \times C_{\text{NaCl}} \times RT$
$$C_{\text{NaCl}} = \frac{0.05}{RT}$$

For glucose, $i = 1$ because it cannot ionise

So, $\pi_{\text{glucose}} = i \times C_{\text{glucose}} \times RT$
$0.2 = 1 \times C_{\text{glucose}} \times RT$
$$C_{\text{glucose}} = \frac{0.2}{RT}$$

($\because n_{\text{NaCl}}$ = numbers of moles NaCl)

n_{NaCl} in 1 L $= C_{\text{NaCl}} \times V_{\text{litre}}$
$= \frac{0.05}{RT}$ (n_{glucose} = number of moles of glucose)

$$n_{\text{glucose}} \text{ in } 2\text{ L} = C_{\text{glucose}} \times V_{\text{litre}} = \frac{0.4}{RT}$$
$$V_{\text{total}} = 1 + 2 = 3\text{ L}$$

So, final conc. NaCl $= \frac{0.05}{3RT}$

Final conc. glucose $= \frac{0.4}{3RT}$

$$\pi_{\text{total}} = \pi_{\text{NaCl}} + \pi_{\text{glucose}}$$
$$= [i \times C_{\text{NaCl}} + C_{\text{glucose}}]\, RT$$
$$= \left(\frac{2 \times 0.05}{3RT} + \frac{0.4}{3RT}\right) \times RT = \frac{0.5}{3} \text{ atm}$$
$$= 0.1666 \text{ atm} = 166.6 \times 10^{-3} \text{ atm}$$
$$= 167.00 \times 10^{-3} \text{ atm}$$

So, $x = 167.00$

59 A set of solutions is prepared using 180 g of water as a solvent and 10 g of different non-volatile solutes A, B and C. The relative lowering of vapour pressure in the presence of these solutes are in the order

[Given, molar mass of $A = 100$ g mol^{-1}; $B = 200$ g mol^{-1}; $C = 10{,}000$ g mol^{-1}]

[2020, 6 Sep Shift-II]

(a) $B > C > A$ (b) $C > B > A$
(c) $A > B > C$ (d) $A > C > B$

Ans. ***(c)***

Relative lowering in vapour pressure

$$(\text{RLVP}) = \frac{p^\circ - p_S}{p^\circ} = \chi_{\text{solute}} \quad \text{or RLVP}$$
$$= \frac{\Delta p}{p^\circ} = \chi_{\text{solute}}$$

$n \rightarrow$ moles of solute $= \frac{w}{M}$;

$N \rightarrow$ moles of solvent $= \frac{W}{M}$

Given, weight of solvent (water) = 180 g

Weight of different non-volatile solute w_A, w_B and $w_C = 10$

Molar mass of $M_A = 100$ g mol^{-1}
$M_B = 200$ g mol^{-1}
$\Rightarrow \quad M_C = 10{,}000$ g mol^{-1}

RLVP for A,

$$\left(\frac{\Delta p}{p^\circ}\right)_A = \frac{\frac{10}{100}}{\frac{10}{100} + \frac{180}{18}}$$
$$= \frac{0.1}{1.1} = 0.091$$

RLVP for B,

$$\left(\frac{\Delta p}{p^\circ}\right)_B = \frac{\frac{10}{200}}{\frac{10}{200} + \frac{180}{18}} = \frac{0.05}{10.05} = 0.0049$$

RLVP for C,

$$\left(\frac{\Delta p}{p^\circ}\right)_C = \frac{\frac{10}{10{,}000}}{\frac{10}{10{,}000} + \frac{180}{18}}$$
$$= \frac{0.001}{0.001 + 10} = \frac{0.001}{10.001}$$
$$= 0.000099$$

From the above value the relative lowering of vapour pressure in the presence of there solute are in the following order :

$$\left(\frac{\Delta p}{p^\circ}\right)_A > \left(\frac{\Delta p}{p^\circ}\right)_B > \left(\frac{\Delta p}{p^\circ}\right)_C$$

Hence, option (c) is correct.

60 1 g of a non-volatile, non-electrolyte solute is dissolved in 100 g of two different solvents A and B, whose ebullisocopic constants are in the ratio of 1 : 5. The ratio of the elevation in their boiling points, $\frac{\Delta T_b(A)}{\Delta T_b(B)}$, is

[2019, 10 April Shift-II]

(a) 5 : 1 (b) 10 : 1 (c) 1 : 5 (d) 1 : 0.2

Ans. ***(c)***

The expression of elevation of boiling point,

$$\Delta T_b = K_b \times m \times i = k_b \times \frac{w_2 \times 1000}{M_2 \times w_1} \times i$$

where, m = molality
i = van't Hoff factor = 1 (for non-electrolyte/non-associable)
w_2 = mass of solute in g = 1 g (present in both of the solutions)
M_2 = molar mass of solute in g mol^{-1} (same solute in both of the solutions)
w_1 = mass of solvent in g = 100 g (for both of the solvents A and B)
K_b = ebullioscopic constant

So, the expression becomes,

$$\Delta T_b \propto K_b$$
$$\Rightarrow \quad \frac{\Delta T_b(A)}{\Delta T_b(B)} = \frac{K_b(A)}{K_b(B)} = \frac{1}{5}$$
$$\left[\text{Given } \frac{K_b(A)}{K_b(B)} = \frac{1}{5}\right]$$

61 At room temperature, a dilute solution of urea is prepared by dissolving 0.60 g of urea in 360 g of water. If the vapour pressure of pure water at this temperature is 35 mm Hg, lowering of vapour pressure will be (Molar mass of urea = 60 g mol^{-1})

[2019, 10 April Shift-I]

(a) 0.027 mmHg (b) 0.031 mmHg
(c) 0.017 mmHg (d) 0.028 mmHg

Ans. ***(c)***

Key Idea For dilute solution, lowering of vapour pressure $(\Delta p) = p^\circ - p$ and relative lowering of vapour pressure $= \frac{\Delta p}{p^\circ}$ which is a colligative property of solutions.

$$\frac{\Delta p}{p^\circ} = \chi_B \times i \Rightarrow \Delta p = \chi_B \times i \times p^\circ$$

where, p° = vapour pressure of pure solvent
i = van't Hoff factor
χ_B = mole fraction of solute

Given,

p° = vapour pressure of pure water of 25°C

$= 35$ mm Hg

χ_B = mole fraction of solute (urea)

$$= \frac{n_B}{n_A + n_B} = \frac{\frac{0.60}{60}}{\frac{360}{18} + \frac{0.60}{60}} = \frac{0.01}{20 + 0.01}$$

$$= \frac{0.01}{20.01} = 0.0005$$

i = van't Hoff factor = 1 (for urea)

Now, according to Raoult's law,

$$\Delta p = \chi_B \times i \times p^\circ$$

On substituting the above given values, we get

$$\Delta p = 0.0005 \times 1 \times 35 = 0.0175 \text{ mm Hg}$$

62 A solution is prepared by dissolving 0.6 g of urea (molar mass = 60 g mol^{-1}) and 1.8 g of glucose (molar mass = 180 g mol^{-1}) in 100 mL of water at 27°C. The osmotic pressure of the solution is ($R = 0.08206$ L atm K^{-1} mol^{-1})

[2019, 12 April Shift-II]

(a) 8.2 atm (b) 2.46 atm

(c) 4.92 atm (d) 1.64 atm

Ans. ***(c)***

Key Idea Osmotic pressure is proportional to the molarity (C) of the solution at a given temperature (T).

Thus, $\pi \propto C$, $\pi = CRT$ (for dilute solution)

$$\pi = \frac{n}{V} RT$$

For the relation, $\pi = CRT = \frac{n}{V} RT$

Given, mass of urea = 0.6 g

Molar mass of urea = 60 g mol^{-1}

Mass of glucose = 1.8 g

Molar mass of glucose = 180 g mol^{-1}

$$\pi = \frac{[n_2\,(\text{urea}) + n_2\,(\text{glucose})]}{V} RT$$

$$= \frac{\left(\frac{0.6}{60} + \frac{1.8}{180}\right)}{100} \times 1000 \times 0.0821 \times 300$$

$$= (0.01 + 0.01) \times 10 \times 0.0821 \times 300$$

$$\pi = 4.92 \text{ atm}$$

63 Elevation in the boiling point for 1 molal solution of glucose is 2 K. The depression in the freezing point for 2 molal solution of glucose in the same solvent is 2 K. The relation between K_b and K_f is

(a) $K_b = 1.5\,K_f$ (b) $K_b = 0.5\,K_f$

(c) $K_b = K_f$ (d) $K_b = 2K_f$

[2019, 10 Jan Shift-II]

Ans. ***(d)***

Elevation in boiling point

$(\Delta T_b) = K_b \times m \times i$

Depression is freezing point

$(\Delta T_f) = K_f \times m \times i$

where, m = molality

For the glucose solution (van't Hoff factor, $i = 1$),

$$\Delta T_b^{1m} = \Delta T_f^{2m} = 2K$$

So, $K_b \times 1 \times 1 = K_f \times 2 \times 1$

$\Rightarrow$ $K_b = 2K_f$

64 Freezing point of a 4% aqueous solution of X is equal to freezing point of 12% aqueous solution of Y. If molecular weight of X is A, then molecular weight of Y is

(a) 4A (b) 2A

(c) 3A (d) A

[2019, 12 Jan Shift-I]

Ans. ***(c)***

Given, Freezing point of 4% aqueous solution of X.

= Freezing point of 12% aqueous solution of Y

or $(\Delta T_f)_X = (\Delta T_f)_Y$ $[\because \Delta T_f = T_f^\circ - T_f]$

$K_f \times m_X = K_f m_Y$

where, m_X and m_Y are molality of X and Y, respectively.

or $m_X = m_Y$

Now,

$$\text{molality} = \frac{\text{Number of moles of solute}\,(n)}{\text{Mass of solvent (in kg)}}$$

$$n = \frac{\text{Weight}}{\text{Molecular mass}}$$

$$\frac{w_X}{M_X \times (w_{\text{solvent}})_1} = \frac{w_Y}{M_Y \times (w_{\text{solvent}})_2}$$

Given, $w_X = 4$ and $w_{\text{solvent})_1} = 96$

$w_Y = 12$ and $w_{(\text{solvent})_2} = 88$

$M_X = A$

$$\therefore \quad \frac{4 \times 1000}{M_X \times 96} = \frac{12 \times 1000}{M_Y \times 88}$$

Thus, $$M_Y = \frac{12 \times 1000 \times M_X \times 96}{4 \times 1000 \times 88}$$

$$= \frac{96 \times 12}{4 \times 88} \times A$$

$$= 3.27A \approx 3\,A$$

65 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is **[JEE Main 2016]**

(a) 76.0 (b) 752.4

(c) 759.0 (d) 7.6

Ans. ***(b)***

Vapour pressure of water (p°) = 760 torr

Number of moles of glucose

$$= \frac{\text{Mass (g)}}{\text{Molecular mass (g mol}^{-1})}$$

$$= \frac{18 \text{ g}}{180 \text{ gmol}^{-1}} = 0.1 \text{ mol}$$

Molar mass of water = 18 g/mol

Mass of water (given) = 178.2g

Number of moles of water

$$= \frac{\text{Mass of water}}{\text{Molar mass of water}}$$

$$= \frac{178.2\text{g}}{18 \text{ g/mol}} = 9.9 \text{ mol}$$

Total number of moles = (0.1 + 9.9) moles = 10 moles

Now, mole fraction of glucose in solution = Change in pressure with respect to initial pressure

i.e. $\frac{\Delta p}{p^\circ} = \frac{0.1}{10}$

or $\Delta p = 0.01p^\circ = 0.01 \times 760 = 7.6$ torr

$\therefore$ Vapour pressure of solution

$= (760 - 7.6)$ torr

$= 752.4$ torr

66 The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass (g mol^{-1}) of the substance is

[JEE Main 2015]

(a) 32 (b) 64

(c) 128 (d) 488

Ans. ***(b)***

Given, $p_o = 185$ torr at 20° C

$p_s = 183$ torr at 20° C

Mass of non-volatile substance, $m = 1.2$ g

Mass of acetone taken = 100 g

$M = ?$

As, we have

$$\frac{p_o - p_s}{p_s} = \frac{n}{N}$$

Putting the values, we get,

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

$$\Rightarrow \quad \frac{2}{183} = \frac{1.2 \times 58}{100 \times M}$$

$$\therefore \quad M = \frac{183 \times 1.2 \times 58}{2 \times 100}$$

$$M = 63.684 \approx 64 \text{ g/mol}$$

67 K_f for water is 1.86 K kg mol^{-1}. If your automobile radiator holds 1.0 kg of water, then how many grams of ethylene glycol ($C_2H_6O_2$) must you add to get the freezing point of the solution lowered to –2.8°C? **[AIEEE 2012]**

(a) 72 g (b) 93 g
(c) 39 g (d) 27 g

Ans. ***(b)***

Coolant is glycol ($C_2H_6O_2$) and it is non-electrolyte.

$$\Delta T_f = 2.8°\text{ C} \Rightarrow \Delta T_f = \frac{1000 K_f w_1}{m_1 w_2}$$

$$2.8 = \frac{1000 \times 1.86 \times w_1}{62 \times 1000}$$

$$\Rightarrow \quad w_1 = 93.33 \text{ g}$$

68 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 $-6°$ C will be (K_f for water $= 1.86$ K kg mol^{-1} and molar mass of ethylene glycol $= 62$ g mol^{-1}) **[AIEEE 2011]**

(a) 804.32 g (b) 204.30 g
(c) 400.00 g (d) 304.60 g

Ans. ***(a)***

ΔT_f = Freezing point of H_2O – freezing point of ethylene glycol solution

$= 0 - (-6°) = 6°$

$K_f = 1.86°$ K kg mol^{-1}

$w_1 =$ Mass of ethylene glycol in grams

$w_2 =$ Mass of solvent (H_2O) in grams $= 4000$ g

$m_1 =$ Molar mass of ethylene glycol $= 62$ g mol^{-1}

$$\Delta T_f = \frac{1000\, K_f\, w_1}{m_1\, w_2} \Rightarrow 6 = \frac{1000 \times 1.86 \times w_1}{62 \times 4000}$$

$$w_1 = 804.32 \text{ g}$$

69 The vapour pressure of water at 20°C is 17.5 mmHg. If 18 g 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 **[AIEEE 2008]**

(a) 17.675 mmHg (b) 15.750 mmHg
(c) 16.500 mmHg (d) 17.325 mmHg

Ans. ***(d)***

This problem is related to the relative lowering of vapour pressure as glucose is a non-volatile solute. Thus, according to Raoult's law,

$$\frac{p^0 - p_{\text{solute}}}{p^0} = X_{\text{solute}}$$

$$\text{Moles of glucose} = \frac{18}{180} = 0.1$$

$$\text{Moles of } H_2O = \frac{178.2}{18} = 9.9$$

$$X_{\text{glucose}} = \frac{0.1}{9.9 + 0.1} = \frac{0.1}{10}$$

$$\text{Thus,} \quad \frac{17.5 - p_s}{17.5} = \frac{0.1}{10}$$

$$\text{So,} \quad p_s = 17.325 \text{ mm Hg}$$

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

(a) 90.0 g mol^{-1} (b) 115.0 g mol^{-1}
(c) 105.0 g mol^{-1} (d) 210.0 g mol^{-1}

Ans. ***(d)***

Osmotic pressure of isotonic solutions are equal.

Therefore, $\pi_1 = \pi_2$

$\Rightarrow \quad C_1RT = C_2RT \Rightarrow C_1 = C_2$

If densities of both the solutions are equal, then 5.25 g of a substance and 1.5 g of urea are dissolved in the same volume of the solvent, thus,

$$C_1 = \frac{5.25/M}{V}$$

[$\because M =$ molecular weight of unknown substance]

$$C_2 = \frac{5.25/60}{V}$$

$$\therefore \quad \frac{5.25/M}{V} = \frac{1.5/60}{V} \Rightarrow M = 210.0 \text{ g mol}^{-1}$$

71 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water. The vapour pressure of water for this aqueous solution at 100°C is **[AIEEE 2006]**

(a) 759.00 torr (b) 7.60 torr
(c) 76.00 torr (d) 752.40 torr

Ans. ***(d)***

According to Raoult's law, relative lowering of vapour pressure,

$$\frac{p° - p_s}{p°} = \frac{n}{N}$$

$$\frac{760 - p_s}{760} = \frac{18/180}{18/180 + 178.2/18}$$

$$\frac{760 - p_s}{760} = \frac{0.1}{10}$$

$$\Rightarrow \quad p_s = 760 - 7.6 = 752.40 \text{ torr}$$

72 Equimolar solutions in the same solvent have **[AIEEE 2005]**

(a) different boiling point and different freezing point
(b) same boiling point and same freezing point
(c) same freezing point but different boiling point
(d) same boiling point but different freezing point

Ans. ***(b)***

Boiling point and freezing point depend on K_b (molal elevation constant) and K_f (molal depression constant) of the solvent. Thus, equimolar solution (of the non-electrolyte), will have same boiling point and also same freezing point.

$\Delta T_f = K_f \times \text{molality};$

$\Delta T_b = K_b \times \text{molality}$

Note In this question, nature of solute has not been mentioned. Hence, we have assumed that solute is non-electrolyte.

73 A pressure cooker reduces cooking time for food because **[AIEEE 2003]**

(a) heat is more evenly distributed in the cooking space
(b) boiling point of water involved in cooking is increased
(c) the higher pressure inside the cooker crushes the food material
(d) cooking involves chemical changes helped by a rise in temperature

Ans. ***(b)***

Higher pressure inside the cooker increases boiling point, thus heat consistently given is used up by food material instead in boiling and constant boiling evaporation.

74 For an aqueous solution, freezing point is – 0.186°C. Elevation of the boiling point of the same solution is ($K_f = 1.86°$ mol^{-1} kg and $K_b = 0.512°$ mol^{-1} kg) **[AIEEE 2002]**

(a) 0.186° (b) 0.0512°
(c) 1.86° (d) 5.12°

Ans. ***(b)***

We know that, $\Delta T_b = mK_b$, $\Delta T_f = mK_f$

$$\frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f} = \frac{0.512}{1.86}$$

$$\Delta T_b = \frac{0.512}{1.86} \times 0.186 = 0.0512°$$

TOPIC 4

Abnormal Molecular Masses and Distribution Law

75 1.22 g of an organic acid is separately dissolved in 100 g of benzene (K_b = 2.6 K kg mol^{-1}) and 100 g of acetone (K_b = 1.7 K kg mol^{-1}). The acid is known to dimerise in benzene but remain as a monomer in acetone. The boiling point of the solution in acetone increases by 0.17°C. The increase in boiling point of solution in benzene in °C is $x \times 10^{-2}$. The value of x is .... (Nearest integer)

[Atomic mass : C = 12.0, H = 1.0, O= 16.0] **[2021, 31 Aug Shift-II]**

Ans. ***(13)***

With benzene as solvent, RCOOH dimerises.

$$2RCOOH \rightleftharpoons (RCOOH)_2$$

$$\therefore \quad i = \frac{1}{2}$$

$$\Delta T_b = i \times K_b \times m$$

where, ΔT_b = boiling point elevation,

K_b = ebulliscopic constant

m = molality

i = van't Hoff factor

$$\Delta T_b = \frac{1}{2} \times 2.6 \times \frac{1.22/M_w}{100/1000} \quad \text{...(i)}$$

With acetone as solvent, no dimerisation.

$$\therefore \quad i = 1$$

$$\Delta T_b = i \times K_b \times m$$

$$0.17 = 1 \times 1.7 \times \frac{1.22/M_w}{100/1000} \quad \text{...(ii)}$$

Eq. (i) divide by Eq. (ii),

$$\frac{\Delta T_b}{0.17} = \frac{\frac{1}{2} \times 2.6 \times \frac{1.22/M_w}{100/1000}}{1 \times 1.7 \times \frac{1.22/M_w}{100/1000}}$$

$$\Rightarrow \quad \Delta T_b = \frac{0.26}{2} = 13 \times 10^{-2}$$

$$x = 13$$

76 Which one of the following 0.10 M aqueous solutions will exhibit the largest freezing point depression ? **[2021, 31 Aug Shift-I]**

(a) Hydrazine (b) Glucose

(c) Glycine (d) $KHSO_4$

Ans. ***(d)***

The van't Hoff factor (i) is highest for $KHSO_4$ as it dissociate into its ions. van't Hoff factor is the ratio of total number of ions produced after complete dissociation to before dissociation. Hydrazine, glucose and glycine will not dissociate to produce ions.

Whereas, $KHSO_4$ dissociates into ions.

$$KHSO_4 \longrightarrow K^+ + HSO_4^-$$

Hence, i will highest for $KHSO_4$

$\therefore$ Colligative property i.e. freezing point depression will be highest for $KHSO_4$ as $\Delta T_f \propto i$ [$\because m$ is constant i.e. 0.1]

Hence, correct option is (d).

77 In a solvent 50% of an acid HA dimerises and the rest dissociates. The van't Hoff factor of the acid is .... $\times 10^{-2}$.

(Round off to the nearest integer) **[2021, 27 July Shift-II]**

Ans. ***(125)***

1 mole of acid HA.

Dimerisation	$2HA \rightleftharpoons$	H_2A_2
Initial	0.5	0
Final	0	0.25

Dissociation

	$HA \rightleftharpoons$	$H^+ +$	A^-
Initial	0.5	0	0
Final	0	0.5	0.5

$$\text{van't Hoff factor } (i) = \frac{\text{Final moles}}{\text{Initial moles}}$$

$$= \frac{0.25 + 0.5 + 0.5}{1}$$

$$= 1.25 = 125 \times 10^{-2}$$

78 83 g of ethylene glycol dissolved in 625 g of water. The freezing point of the solution is ....K. (Nearest integer)

[Use, molal freezing point depression constant of water = 1.86 K kg mol^{-1},

Freezing point of water = 273 K and Atomic masses : C = 12.0 u, O = 16.0 u, H = 1.0 u] **[2021, 26 Aug Shift-II]**

Ans. ***(269)***

$$\Delta T_f = iK_f \times m$$

For ethylene glycol, $i = 1$

$$\text{Molality } (m) = \frac{\text{Number of moles of solute}}{\text{Weight of solvent (kg)}}$$

$$\Delta T_f = 1 \times 1.86 \times \frac{83 \times 1000}{62 \times 625} \simeq 3.98$$

Freezing point of solution = Freezing point − ΔT_f of water

$$= 273 - 3.98 \simeq 269.$$

79 Of the following four aqueous solutions, total number of those solutions whose freezing point is lower than that of 0.10 M C_2H_5OH is .... (Integer answer)

(i) 0.10 M $Ba_3(PO_4)_2$

(ii) 0.10 M Na_2SO_4

(iii) 0.10 M KCl

(iv) 0.10 M Li_3PO_4

[2021, 26 Aug Shift-I]

Ans. ***(4)***

As 0.10 M C_2H_5OH is non-dissociative in nature and all salts [0.10 M $Ba_3(PO_4)_2$, 0.10 M Na_2SO_4, 0.10 M KCl, 0.10 M Li_3PO_4] are electrolyte and dissociative in nature.

$$\Delta T_f = iK_f m$$

Where i is van't Hoff factor.

i = 1 for C_2H_5OH(no dissociation)

$i > 1$ for all other electrolytes where dissociation takes place.

So, for all these electrolytes effective molarity is more than 0.10. So, all the elecrolytes given will have low freezing point.

80 The water having more dissolved O_2 is **[2021, 22 July Shift-II]**

(a) boiling water (b) water at 80°C

(c) polluted water (d) water at 4° C

Ans. ***(d)***

At 4°C, the water have more dissolved O_2. Since, dissolution of O_2 gas in water is an exothermic process, and solubility of oxygen in water is high, at lower temperature. On increasing temperature, solubility of gas decreases and water pollution also decrease the solubility. First, the solubility of oxygen increases as temperature decreases i.e. warmer surface water requires less dissolved oxygen to reach 100% air saturation than cooler water.

81 When 12.2 g of benzoic acid is dissolved in 100 g of water, the freezing point of solution was found to be – 0.93°C ($K_f(H_2O)$ = 1.86 K kg mol^{-1}). The number (n) of benzoic acid molecules associated (assuming 100% association) is .... **[2021, 26 Feb Shift-II]**

Ans. ***(2)***

$$\underset{\text{Benzoic acid}}{n\,\text{PhCOOH}} \xrightarrow{\text{Association}} (\text{PhCOOH})_n$$

Assuming 100% association $(\alpha = 1)$,

$$\Rightarrow \qquad i = 1-\alpha\left(1-\frac{1}{n}\right)=\frac{1}{n} \qquad [\because \alpha \;\; +1]$$

Now, $\Delta T_f = K_f \times m \times i$

$$0-(0.93) = 1.86 \times \frac{w_B \times 1000}{w_A \times M_B} \times \frac{1}{n}$$

$[\because w_B =$ mass of PhCOOH $= 12.2$ g

$w_A =$ mass of $H_2O = 100$ g

$M_B =$ molar mass of PhCOOH]

$= 122\text{g mol}^{-1}$

$$= 1.86 \times \frac{12.2 \times 1000}{100 \times 122} \times \frac{1}{n}$$

$$\Rightarrow \quad n = \frac{1.86 \times 12.2 \times 1000}{0.93 \times 100 \times 122} = 2$$

∴ Number of benzoic acid molecules associated, $n = 2$

82 If a compound AB dissociates to the extent of 75% in an aqueous solution, the molality of the solution which shows a 2.5 K rise in the boiling point of the solution is .... molal. (Rounded off to the nearest integer)

$[K_b = 0.52 \text{ K kg mol}^{-1}]$

[2021, 25 Feb Shift-II]

Ans. ***(3)***

As AB is a binary electrolyte,

$$\therefore \quad AB \rightleftharpoons A^+ + B^-, n = 2$$

$$i = 1 + \alpha(n-1) = 1 + \frac{75}{100}(2-1) = 1.75$$

Given, $\Delta T_b = 2.5$ K

$K_b = 0.52 \text{ K kg mol}^{-1}$

$$\therefore \quad \Delta T_b = K_b \times m \times i$$

$$\Rightarrow \quad m = \frac{\Delta T_b}{K_b \times i} = \frac{2.5}{0.52 \times 1.75}$$

$$= 2.74 \simeq 3 \text{ mol/kg}$$

83 1 molal aqueous solution of an electrolyte A_2B_3 is 60% ionised. The boiling point of the solution at 1 atm is .... K (Rounded off to the nearest integer). [Given, K_b for $(H_2O) = 0.52 \text{ K kg mol}^{-1}$]

[2021, 25 Feb Shift-I]

Ans. ***(375)***

Given, $K_b(H_2O) = 0.52 \text{ K kg mol}^{-1}$

$$A_2B_3 \longrightarrow 2A^{+3} + 3B^{-2}$$

No. of ions, $n = 5$, concentration, $m = 1$ molal (Given)

$$\alpha = \frac{60}{100} = 0.6$$

$$\Delta T_b = i \cdot K_f \cdot m$$

$$= [(1 + (n-1)\alpha] \times K_f \times m$$

$$\Delta T_b = [(1 + (5-1)0.6] \times 0.52 \times 1$$

$$= (1 + 2.4) \times 0.52$$

$$\Delta T_b = 1.768$$

$$T_b = 1.768 + 373.15$$

$$= 374.91 = 375 \text{ K}$$

84 The elevation of boiling point of 0.10 m aqueous $CrCl_3 \cdot xNH_3$ solution is two times that of 0.05 m aqueous $CaCl_2$ solution. The value of x is ....

[Assume 100% ionisation of the complex and $CaCl_2$, coordination number of Cr as 6, and that all NH_3 molecules are present inside the coordination sphere]

[2020, 6 Sep Shift-I]

Ans. ***(5.00)***

$$\Delta T_b = i \times m \times K_b$$

For $CaCl_2$, $i = 3$, $m_{(CaCl_2)} = 0.05$ m

$$\therefore \quad \Delta T_b = 3 \times 0.05 \times K_b = 0.15 K_b$$

Molality of $CrCl_3 \cdot xNH_3 = 0.1$ m

$$\therefore \quad \Delta T_b' = i \times m \times K_b = 0.1 i K_b$$

Given that : $0.1 i K_b = 2 \times 0.15 \times K_b$

$\therefore i = 3$ and coordination number is 6.

Thus, complex will be $[Cr(NH_3)_5Cl]Cl_2$

$$\therefore \qquad x = 5$$

Hence, the correct answer is 5.

85 How much amount of NaCl should be added to 600 g of water $(\rho = 1.00 \text{ g/mL})$ to decrease the freezing point of water to -0.2°C? ...... (The freezing point depression constant for water $= 2 \text{ K kg mol}^{-1}$)

[2020, 9 Jan Shift-I]

Ans. ***(1.76)***

$$\Delta T_f = i \times m \times K_f = \frac{i \times K_f \times w_{\text{NaCl}} \times 1000}{\underset{(=58.5)}{M_{\text{NaCl}}} \times w_{H_2O}}$$

$$(m = \text{molality}) = \frac{w_B \times 1000}{M_B \times w_A}$$

$\Delta T_f = 0.2$ because freezing point $= -0.2$°C

K_f of water 2 K kg mol^{-1} (Given)

$i =$ van't Hoff factor, for NaCl $= 2$

$$\therefore w_{\text{NaCl}} = \frac{\Delta T_f \times M_{\text{NaCl}} \times w_{H_2O}}{i \times K_f \times 1000}$$

$$= \frac{0.2 \times 58.5 \times 600}{2 \times 2 \times 1000} = 1.755 \text{ g} \approx 1.76 \text{ g}$$

86 The osmotic pressure of a dilute solution of an ionic compound XY in water is four times that of a solution of 0.01 M $BaCl_2$ in water. Assuming complete dissociation of the given ionic compounds in water, the concentration of XY (in mol L^{-1}) in solution is

[2019, 9 April Shift-I]

(a) 4×10^{-2} (b) 16×10^{-4}
(c) 4×10^{-4} (d) 6×10^{-2}

Ans. ***(d)***

Key Idea Osmotic pressure is proportional to the molarity (C) of the solution at a given temperature, $\pi = CRT$

Concentration of $BaCl_2 = 0.01$ M (Given)

$\pi_{XY} = 4\pi_{BaCl_2}$ (Given)

$i \times CRT = 4 \times i \times CRT$ ...(i)

For the calculation of i,

$XY \longrightarrow X^+ + Y^-$ (Here, $i = 2$)

$BaCl_2 \longrightarrow Ba^{2+} + 2Cl^-$ (Here, $i = 3$)

Putting the values of i in (i)

$$2 \times [XY] = 4 \times 3 \times [BaCl_2]$$

$$2 \times [XY] = 12 \times 0.01$$

$$[XY] = \frac{12 \times 0.01}{2}$$

So, the concentration of XY

$= 0.06 \text{ mol L}^{-1}$

$= 6 \times 10^{-2} \text{ mol L}^{-1}$

87 Molal depression constant for a solvent is $4.0 \text{ K kg mol}^{-1}$. The depression in the freezing point of the solvent for 0.03 mol kg^{-1} solution of K_2SO_4 is (Assume complete dissociation of the electrolyte) **[2019, 9 April Shift-II]**

(a) 0.18 K (b) 0.36 K
(c) 0.12 K (d) 0.24 K

Ans. ***(b)***

Key Idea Depression in freezing point (ΔT_f) is given by $\Delta T_f = iK_f m$

$i =$ vant Hoff factor

$K_f =$ molal depression constant

$m =$ molality

$K_f = 4.0 \text{ K kg mol}^{-1}$ (Given)

$m = 0.03 \text{ mol kg}^{-1}$ (Given)

$\Delta T_f = ?$

For K_2SO_4, $i = 3$

It can be verified by the following equation :

$$K_2SO_4 \rightleftharpoons 2K^+ + SO_4^{2-}$$

Using formula

$$\Delta T_f = iK_f \times m$$

$$= 3 \times 4 \times 0.03 = 0.36 \text{ K}$$

88 A solution contain 62 g of ethylene glycol in 250 g of water is cooled upto −10°C. If K_f for water is 1.86 K kg mol^{-1}, then amount of water (in g) separated as ice is **[2019, 9 Jan Shift-II]**

(a) 32 (b) 48 (c) 64 (d) 16

Ans. ***(c)***

Considering the expression of the depression in freezing point of a solution,

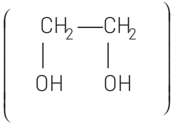
$$\Delta T_f = K_f \times m \times i$$

$$T_f^{\circ} - T_f = K_f \times \frac{w_B \times 1000}{M_B \times w_A(\text{in g})} \times i \qquad \text{...(i)}$$

Here, $T_f^{\circ} = 0°\text{C}$, $T_f = -10°\text{C}$

w_B = mass of ethylene glycol = 62 g

M_B = molar mass of ethylene glycol



$$\left(\begin{array}{cc} CH_2 — & CH_2 \\ | & | \\ OH & OH \end{array}\right)$$

$= 62\text{ g mol}^{-1}$

w_A = mass of water in g as liquid solvent,

i = van't-Hoff factor = 1

(for ethylene glycol in water)

$K_f = 1.86\text{ K kg mol}^{-1}$

On substituting in Eq. (i), we get

$$0 - (-10) = 1.86 \times \frac{62 \times 1000}{62 \times w_A} \times 1$$

$$\Rightarrow \qquad w_A = \frac{1.86 \times 62 \times 1000}{10 \times 62}$$

$$= 186\text{ g}$$

So, amount of water separated as ice (solid solvent)

$$= 250 - w_A = (250 - 186)\text{ g} = 64\text{ g}$$

89 The freezing point of a diluted milk sample is found to be −0.2° C, while it should have been −0.5°C for pure milk. How much water has been added to pure milk to make the diluted sample?

(a) 2 cups of water to 3 cups of pure milk
(b) 1 cup of water to 3 cups of pure milk
(c) 3 cups of water to 2 cups of pure milk
(d) 1 cup of water to 2 cups of pure milk

[2019, 11 Jan Shift-I]

Ans. ***(c)***

We know that,

Depression in freezing points (ΔT_f)

$$T°_f - T_f = K_f \times m \times i$$

where, K_f = molal depression constant

$$m = \text{molality} = \frac{w_{\text{solute}} \times 1000}{M_{\text{solute}} \times w_{\text{solvent (in g)}}}$$

i = van't Hoff factor

For diluted milk

$$\Delta T_{f_1} = K_f \times m_1 \times i$$

$$\Rightarrow 0 - (0.2) \Rightarrow 0.2$$

$$= K_f \times \frac{w_{\text{milk}} \times 1000}{M_{\text{milk}} \times w_1(H_2O)} \times 1$$

For pure milk

$$\Delta T_{f_2} = K_f \times m_2 \times i$$

$$\Rightarrow 0 - (-0.5) = 0.5 = K_f \times \frac{w_{\text{milk}} \times 1000}{M_{\text{milk}} \times w_2(H_2O)} \times 1$$

$$\text{So,} \quad \frac{0.2}{0.5} = \frac{K_f}{K_f} \times \frac{w_{\text{milk}} \times 1000}{M_{\text{milk}} \times w_1(H_2O)} \times \frac{M_{\text{milk}} \times w_2(H_2O)}{w_{\text{milk}} \times 1000}$$

$$= \frac{w_2(H_2O)}{w_1(H_2O)}$$

$$\Rightarrow \quad \frac{w_2\,(H_2O)(\text{in pure milk})}{w_1\,(H_2O)(\text{in diluted milk})} = \frac{2}{5}$$

i.e. 3 cups of water has to be added to 2 cups of pure milk.

90 K_2HgI_4 is 40% ionised in aqueous solution. The value of its van't Hoff factor (i) is **[2019, 11 Jan Shift-II]**

(a) 1.6 (b) 1.8
(c) 2.2 (d) 2.0

Ans. ***(b)***

The ionisation of K_2HgI_4 in aqueous solution is as follows:

$$K_2[HgI_4] \rightleftharpoons 2K^+ + [HgI_4]^{2-}$$

van't Hoff factor (i) for ionisation reaction is given as, $i = 1 + \alpha(n - 1)$

where, n = number of ions,

α = degree of ionisation or dissociation

From above equation, it is clear that $n = 3$

$$i = 1 + 0.4\,(3 - 1)$$

$$[\text{Given, } \%\,\alpha = 40\% \text{ or } \alpha = 0.4] = 1.8$$

91 Molecules of benzoic acid (C_6H_5COOH) dimerise in benzene. 'w' g of the acid dissolved in 30 g of benzene shows a depression in freezing point equal to 2 K. If the percentage association of the acid to form dimer in the solution is 80, then w is (Given that $K_f = 5\text{ K kg mol}^{-1}$, molar mass of benzoic acid $= 122\text{ g mol}^{-1}$) **[2019, 12 Jan Shift-II]**

(a) 1.8 g (b) 1.0 g (c) 2.4 g (d) 1.5 g

Ans. ***(c)***

Molecules of benzoic acid dimerise in benzene as:

$$2(C_6H_5COOH) \rightleftharpoons (C_6H_5COOH)_2$$

Now, we know that depression in freezing point (ΔT_f) is given by following equation:

$$\Delta T_f = i \times K_f \times m$$

$$= \frac{i \times K_f \times w_{\text{solute}} \times 1000}{Mw_{\text{solute}} \times w_{\text{solvent}}} \qquad \text{...(i)}$$

Given, w_{solute} (benzoic acid) = w g

w_{solvent} (benzene) = 30 g

Mw_{solute} (benzoic acid) = 122 g mol^{-1},

$\Delta T_f = 2\text{ K}$

$K_f = 5\text{ Kkg mol}^{-1}$, $\%\alpha = 80$ or $\alpha = 0.8$

	$2(C_6H_5COOH)$	$\rightleftharpoons$	$(C_6H_5COOH)_2$
Initial	1		0
Final	$1-\alpha$		$\alpha/2$
	$= 1 - 0.8 = 0.2$		$0.8/2 = 0.4$

Total number of moles at equilibrium

$$= 0.2 + 0.4 = 0.6$$

$$i = \frac{\text{Number of moles at equilibrium}}{\text{Number of moles present initially}}$$

$$i = \frac{0.6}{1} = 0.6$$

On substituting all the given values in Eq. (i), we get

$$2 = \frac{0.6 \times 5 \times w \times 1000}{122 \times 30}, \quad w = 2.44\text{ g}$$

Thus, weight of acid (w) is 2.4 g.Molecules of benzoic acid dimerise in benzene as:

$$2(C_6H_5COOH) \rightleftharpoons (C_6H_5COOH)_2$$

92 For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point? **[JEE Main 2018]**

(a) $[Co(H_2O)_6]Cl_3$
(b) $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$
(c) $[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$
(d) $[Co(H_2O)_3Cl_3] \cdot 3H_2O$

Ans. ***(a)***

Key Idea "Addition of solute particles to a pure solvent results to depression in its freezing point."
All the compounds given in question are ionic in nature so, consider their van't Hoff factor (i) to reach at final conclusion.

The solution with maximum freezing point must have minimum number of solute particles. This generalisation can be done with the help of van't Hoff factor (i) i.e.

Number of solute particles ∝ van't Hoff factor (i)

Thus, we can say directly

Solution with maximum freezing point will be the one in which soluste with minimum van't Hoff factor is present

Now, for

$$\text{Co(H}_2\text{O)}_6\text{]Cl}_3 \rightleftharpoons [\text{Co(H}_2\text{O)}_6]^{3+} + 3\text{Cl}^-$$

van't Hoff factor (i) is 4. Similarly for,

$$[\text{Co(H}_2\text{O)}_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O} \rightleftharpoons [\text{Co(H}_2\text{O)}_5\text{Cl}]^{2+} + 2\text{Cl}^- \quad \text{'}i\text{' is 3}$$

$$[\text{Co(H}_2\text{O)}_4\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O} \rightleftharpoons [\text{Co(H}_2\text{O)}_4\text{Cl}_2]^+ + \text{Cl}^- \quad \text{'}i\text{' is 2}$$

and for $[\text{Co(H}_2\text{O)}_3\text{Cl}_3]\cdot 3\text{H}_2\text{O}$, '$i$' is 1 as it does not show ionisation.

Hence, $[\text{Co(H}_2\text{O)}_3\text{Cl}_3]\cdot 3\text{H}_2\text{O}$ have minimum number of particles in the solution.

So, freezing point of its solution will be maximum.

93 The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be (K_f for benzene = 5.12 K kg mol^{-1}) **[JEE Main 2017]**

(a) 64.6 % (b) 80.4 %
(c) 74.6 % (d) 94.6 %

Ans. ***(d)***

Let the degree of association of acetic acid (CH_3COOH) in benzene is α, then

	$2\text{CH}_3\text{COOH}$	$\rightleftharpoons$	$(\text{CH}_3\text{COOH})_2$
Initial moles	1		0
Moles at equilibrium	$1-\alpha$		$\frac{\alpha}{2}$

$$\therefore \text{ Total moles} = 1-\alpha+\frac{\alpha}{2} = 1-\frac{\alpha}{2}$$

or $$i = 1-\frac{\alpha}{2}$$

Now, depression in freezing point (ΔT_f) is given as

$$\Delta T_f = i\,K_f m \qquad \ldots\text{(i)}$$

where, K_f = molal depression constant or cryoscopic constant.

m = molality

$$\text{Molality} = \frac{\text{number of moles of solute}}{\text{weight of solvent (in kg)}} = \frac{0.2}{60}\times\frac{1000}{20}$$

Putting the values in Eq. (i)

$$\therefore\ 0.45 = \left[1-\frac{\alpha}{2}\right](5.12)\left[\frac{0.2}{60}\times\frac{1000}{20}\right]$$

$$1-\frac{\alpha}{2} = \frac{0.45\times 60\times 20}{5.12\times 0.2\times 1000}$$

$$\Rightarrow\ 1-\frac{\alpha}{2} = 0.527$$

$$\Rightarrow\ \frac{\alpha}{2} = 1-0.527$$

$$\therefore\ \alpha = 0.946$$

Thus, percentage of association = 94.6%

94 Consider the separate solution of 0.500 M $\text{C}_2\text{H}_5\text{OH}\,(aq)$, 0.100 M $\text{Mg}_3(\text{PO}_4)_2\,(aq)$, 0.250 M KBr (aq) and 0.125 M $\text{Na}_3\text{PO}_4\,(aq)$ at 25°C. Which statement is true about these solutions, assuming all salts to be strong electrolytes? **[JEE Main 2014]**

(a) They all have same osmotic pressure
(b) 0.100 M $\text{Mg}_3(\text{PO}_4)_2\,(aq)$ has the highest osmotic pressure
(c) 0.125 M $\text{Na}_3\text{PO}_4\,(aq)$ has the highest osmotic pressure
(d) 0.5000 M $\text{C}_2\text{H}_5\text{OH}\,(aq)$ has the highest osmotic pressure

Ans. ***(a)***

Osmotic pressure, $\pi = i\times MRT$

Where, i = van't Hoff factor, M = Molarity
R = Gas constant,
T = Temperature

For 0.500 M $\text{C}_2\text{H}_5\text{OH}\,(aq)$, $i = 1$, thus,

$$\pi_{\text{C}_2\text{H}_5\text{OH}}(aq) = 0.5\,RT$$

For 0.100 M $\text{Mg}_3(\text{PO}_4)_2\,(aq)$, $i = 5$

$$[\because \text{Mg}_3(\text{PO}_4)_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{PO}_4^{3-}]$$

Thus, $\pi_{\text{Mg}_3(\text{PO}_4)_2}(aq) = 5\times 0.1\times RT = 0.5\,RT$

For 0.250 M KBr (aq),

$$i = 2 \quad [\because \text{KBr} \rightleftharpoons \text{K}^+ + \text{Br}^-]$$

Thus, $\pi_{\text{KBr}}(aq) = 2\times 0.250\times RT = 0.5\,RT$

For 0.125 M $\text{Na}_3\text{PO}_4\,(aq)$, $i = 4$

$$[\because \text{Na}_3\text{PO}_4 \rightleftharpoons 3\text{Na}^+ + \text{PO}_4^{3-}]$$

Thus, $\pi_{\text{Na}_3\text{PO}_4}(aq) = 4\times 0.125\times RT = 0.5\,RT$

Hence, all solutions have same osmotic pressure.

95 The degree of dissociation (α) of a weak electrolyte, A_xB_y is related to van't Hoff factor (i) by the expression **[AIEEE 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) $\alpha = \frac{x+y+1}{i-1}$

Ans. ***(a)***

van't Hoff factor (i) is related to degree of dissociation (α) as

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

Here, n are the moles of an electrolyte $(A-B)$ dissolved in a solvent.

For $A_x\,B_y$, $\quad A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$

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

96 If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f), when 0.01 mole of sodium sulphate is dissolved in 1 kg of water, is (K_f = 1.86 K kg mol^{-1}) **[AIEEE 2010]**

(a) 0.0372 K (b) 0.0558 K
(c) 0.0744 K (d) 0.0186 K

Ans. ***(b)***

$$\text{Na}_2\text{SO}_4 \longrightarrow 2\text{Na}^+ + \text{SO}_4^{2-}$$

van't Hoff factor (i) for $\text{Na}_2\text{SO}_4 = 3$

$$\Delta T_f = i\times K_f\times m = 3\times 1.86\times 0.01$$

$$\left[\because m = \frac{0.01\text{ mol}}{1\text{ kg}} = 0.01\text{ mol kg}^{-1}\right]$$

$$= 0.0558\text{ K}$$

97 If α is the degree of dissociation of Na_2SO_4, the van't Hoff factor (i) used for calculating the molecular mass is **[AIEEE 2005]**

(a) $1-2\alpha$ (b) $1+2\alpha$
(c) $1-\alpha$ (d) $1+\alpha$

Ans. ***(b)***

$$\text{Na}_2\text{SO}_4 \rightleftharpoons 2\text{Na}^+ + \text{SO}_4^{2-}$$

van't Hoff factor, $i = [1+(y-1)\alpha]$

where y is the number of ions from one mole solute, (in this case = 3), α is the degree of dissociation, $i = (1+2\alpha)$

98 Which one of the following aqueous solutions will exhibit highest boiling point? **[AIEEE 2004]**

(a) 0.01 M Na_2SO_4 (b) 0.01 M KNO_3
(c) 0.015 M urea (d) 0.015 M glucose

Ans. ***(a)***

The colligative property will be given as

$$\Delta T_b = i\times k_b\times m$$

Where, ΔT_b = Elevation in boiling point
i = van't Hoff factor
K_b = molal elevation constant
m = molality of the solution

From the above equation, it is clear that,

$$\Delta T_b\,\alpha\,i$$

This suggests that higher the value of i, larger is the boiling point of the solution.

For 100% dissociation, i = number of ions produced by one mole of solute

Thus, for

(a) Na_2SO_4

$Na_2SO_4 \rightleftharpoons 2Na^+ + SO_4^{2-}$

[3 ions]

$\therefore\ i = 3$

(b) KNO_3

$KNO_3 \rightleftharpoons K^+ + NO_3^-$

[2 ions]

$\therefore\ i = 2$

(c) Urea [(NH_2CONH_2) and (d) glucose are poor electrolytes, therefore i for these two solutes are equal to zero.

Hence, 0.01 M Na_2SO_4 possess highest boiling point.

99 Which one of the following statements is false? **[AIEEE 2004]**

(a) Raoult's law states that the vapour pressure of a component over a solution is proportional to its mole fraction

(b) The osmotic pressure (π) of a solution is given by the equation $\pi = MRT$, where M is the molarity of the solution

(c) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is $BaCl_2 > KCl > CH_3COOH >$ sucrose

(d) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression

Ans. ***(d)***

(a) $p_A = X_A p_A^\circ$ true

(b) $\pi = iMRT = MRT$ true

[If van't Hoff factor, $i = 1$]

(c) $\pi \propto i$

Greater the value of i, larger is the value of π.

i, for $BaCl_2$ (strong electrolyte) is 3.

$[BaCl_2 \rightleftharpoons Ba^{2+} + Cl^-$ (2 ions)]

i for KCl is 2. $[KCl \rightleftharpoons K^+ + Cl^-]$

i for CH_3COOH is

2 $[CH_3COOH \rightleftharpoons CH_3COO^- + H^+]$

But CH_3COOH is weak electrolyte than KCl.

i for sucrose is 1 as it is a non-electrolyte.

Thus,

i (for $BaCl_2$) > KCl > CH_3COOH > sucrose

Thus, (c) is also true.

(d) $\Delta T_f = K_f m$.

K_f is dependent on solvent.

Thus, freezing points

$= [T\ (\text{solvent}) - \Delta T_f]$ are different.

Thus, (d) is false.

100 In a 0.2 molal aqueous solution of a weak acid HX, the degree of ionisation is 0.3. Taking K_f for water as 1.85, the freezing point of the solution will be nearest to **[AIEEE 2003]**

(a) −0.480°C (b) −0.360°C

(c) −0.260°C (d) +0.480°C

Ans. ***(a)***

$HX \rightleftharpoons H^+ + X^{-1}$

$\alpha = 0.3$

$i = 1 + \alpha = 1.3$

ΔT_f = molality $\times K_f \times i$

$= 0.2 \times 1.85 \times 1.3 = 0.481^\circ$

$\therefore$ Freezing point $= -0.481^\circ$ C