Fill Ups & Integer type Questions of Solutions

Fill in the Blanks

1. Given that ΔT_f is the depression in freezing point of the solvent in a solution of a non-volatile solute of molality, m, the quantity $\underset{m\to 0}{Lt}\ (\Delta T_f / m)$ is equal to ……….. (1994 - 1 Mark)

Ans: K_f

Solutions : K_f; Depression in freezing point, $\Delta T_f = K_f \cdot m$, where K_f is the molar depression constant or cryoscopy constant and m is the molality of the solution given by moles of solute per 1000 g of the solvent.

Integer Value Correct Type

1. 29.2% (w/w) HCl stock solution has a density of 1.25 g mL^{-1}. The molecular weight of HCl is 36.5 g mol^{-1}. The volume (mL) of stock solution required to prepare a 200 mL
Solution of 0.4 M HCl is : (2012)

Ans : 8

Solution: Molarity of stock solution of HCl

$$= \frac{29.2 \times 1000 \times 1.25}{100 \times 36.5}$$

Let the volume of stock solution required = V mL

Thus $$V \times \frac{29.2 \times 1000 \times 1.25}{100 \times 36.5} = 200 \times 0.4 = 8 \text{ mL}$$

2. MX_2 dissociates into M^{2+} and X^- ions in an aqueous solution, with a degree of dissociation (a) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is (JEE Adv. 2014)

Ans: 2

Solutions:

$$\begin{array}{cccc} MX_2 & \rightleftharpoons M^{2+} & + & 2X^- \\ 1-\alpha & \alpha & & 2\alpha \end{array}$$

$$i = \frac{\text{obser. depression in f.pt of aq. solution}}{\text{depression of f.p.t. in absence of ionic dissociation}}$$

$$= \frac{1-\alpha+\alpha+2\alpha}{1} = 1+2\alpha = 1+2\times0.5=2$$

3. A compound H_2X with molar weight of 80g is dissolved in a solvent having density of 0.4 g ml^{-1}. Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is (JEE Adv. 2014)

Ans : 8

Solutions : $\text{Molality} = \frac{\text{wt. of solute in 1 L of solution} \times 1000}{\text{wt. of solvent in 1 L of solution} \times \text{mol. wt. of solute}}$

Calculation of wt. of solvent

1 mL of solvent = 0.4 g

1000 mL of solvent = 400 g

Calculation of wt. of solute

1000 mL of solution contain = 3.2 × 80 g solute = 256 g

$$\therefore \quad \text{Molality} = \frac{256\times1000}{400\times80} = 8$$

4. If the freezing point of a 0.01 molar aqueous solution of a cobalt(III) chloride-ammonia complex (which behaves as a strong electrolyte) is –0.0558°C, the number of chloride(s) in the coordination sphere of the complex is [K_f of water = 1.86 K kg mol^{-1}] (JEE Adv. 2015)

Ans : 1

Solution :

Given $\Delta T_f = 0.0558°C$

as we know, $\Delta T_f = i \times K_f \times m$

$\Rightarrow 0.0558 = i \times 1.86 \times 0.01$

$i = 3$

Therefore the complex will be $[Co(NH_3)_5Cl]\ Cl2$

Hence number of chloride in co-ordination sphere is 1.

5. 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 g cm^{-3} .

The ratio of the molecular weights of the solute and solvent, $\left(\frac{MW_{solute}}{MW_{solvent}}\right)$ **, is**

Ans: 9

solution: 1 mole solution has 0.1 mole solute and 0.9 mole solvent.

Let M_1 = Molar mass solute

M_2 = Molar mass solvent

Molality, m = $\frac{0.1}{0.9M_2}\times 1000$ .....(1)

Molarity, M = $\frac{0.1}{0.1M_1 + 0.9M_2}\times 2\times 1000$ ....(2)

$\because m = M$

$$\Rightarrow \frac{0.1\times 1000}{0.9M_2} = \frac{200}{0.1M_1 + 0.9M_2}$$

$$\Rightarrow \frac{M_1}{M_2} = 9$$

Subjective Questions of Solutions, Past year Questions (Part - 1)

1. What is the molarity and molality of a 13% solution (by weight) of sulphuric acid with a density of 1.02 g/ml? To what volume should 100 ml of this acid be diluted in order to prepare a 1.5 N solution? (1978)

Ans : 1.38 M, 1.57 m, 184 ml

Solution :

TIPS/Formulae : (i) $\text{Molarity} = \dfrac{\text{Moles of solute}}{\text{Volume of solution in L}}$

(ii) $N_1V_1 = N_2V_2$

A 13% solution (by weight) contains 13g of solute (i.e. H_2SO_4) per 100 gm of solution

$$\text{Moles of solute} = \frac{\text{Mass of } H_2SO_4}{\text{M. wt. of } H_2SO_4} = \frac{13}{98} = 0.1326$$

Volume of solution in L

$$= \frac{\text{Mass of solution}}{\text{density of solution} \times 1000} = \frac{100}{1.02 \times 1000} = 0.0980 \text{ Litre}$$

$$\therefore \quad \text{Molarity of solution} = \frac{0.1326}{0.0980} = \mathbf{1.35\ M}$$

$$\text{Again, Molality} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

Mass of solute in 100 ml of solution = 13 g [13 % solution]

Mass of solvent = Mass of solution – Mass of solvent

= 100 – 13 = 87 g

$$\therefore \text{Molality} = \frac{13/98}{87/1000} = \mathbf{1.57\ m}$$

$$\text{Normality} = \text{Molarity} \times \frac{\text{Mol. wt.}}{\text{Eq. wt.}} \text{ or } 1.35 \times \frac{98}{49} = 2.70\,\text{N}$$

$$\left[\begin{array}{l} \because \text{Eq. wt} = \dfrac{98}{2} \\ 2H_2SO_4 = 49 \end{array}\right]$$

$N_1 = 2.70$, $V_1 = 100$ ml, $N_2 = 1.5$, $V_2 =?$

$N_1V_1 = N_2V_2$; $2.70 \times 100 = 1.5 \times V_2$

$$\text{or } V_2 = \frac{2.70 \times 100}{1.5} = 180\,\text{ml.}$$

∴ 100 ml of this acid should be diluted to 180 ml to prepare 1.5 N solution

2. A bottle of commercial sulphuric acid (density 1.787 g/ml) is labelled as 86 percent by weight. What is the molarity of the acid. What volume of the acid has to be used to make 1 litre of 0.2 M H_2SO_4? (1979)

Ans: 15.81M; 12.65

Solution:

$$M = \frac{86/98}{100/1.787} \times 1000 = \frac{0.8775}{55.5} \times 1000 = \mathbf{15.81\,M}$$

$M_1V_1 = M_2V_2$

$M_1 = 15.81$, $V_1 =?$

$M_2 = 0.2$, $V_2 = 1$ L $= 1000$ ml

∴ $15.81 \times V_1 = 0.2 \times 1000$

$$\text{or } V_1 = \frac{0.2 \times 1000}{15.81} = 12.65\,\text{ml}$$

∴ Amount of acid to be used to make 1 L of 0.2 M H_2SO_4 = 12.65.

3. 0.5 gm of fuming H_2SO_4 (Oleum) is diluted with water. This solution is completely neutralized by 26.7 ml of 0.4 N NaOH. Find the percentage of free SO_3 in the sample of oleum. (1980)

Ans: 3.84%

Solution:

$$N_1 = 1,\ V_1 = ?,\ N_2 = 26.7,\ V_2 = 0.4$$
$$N_1 V_1 = N_2 V_2;\ 1 \times V_1 = 26.7 \times 0.4$$
$$V_1 = \frac{26.7 \times 0.4}{1} = 10.68$$

49g (Q eq wt of H_2SO_4 = 49) of H_2SO_4 will be neutralised by = 1N 1000 ml NaOH

∴ 0.5g of H2SO4 will be neutralised by

$$= \frac{1000}{49} \times 0.5 = 10.20\,\text{ml 1N NaOH}$$

Volume of 1 N NaOH used by dissolved

SO_3 = 10.68 – 10.20 = 0.48 ml

$SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$

$$\therefore \text{Eq wt of } SO_3 = \frac{\text{Mol wt}}{2} = \frac{80}{2} = 40$$

Wt of SO_3 in 0.48 ml of 1 M solution

$$= \frac{40}{1000} \times 0.48 = 0.0192\ \text{g}$$

$$\%\ \text{of}\ SO_3 = \frac{0.0192}{0.5} \times 100 = \mathbf{3.84\%}$$

4. The vapour pressure of pure benzene is 639.7 mm of mercury and the vapour of a solution of a solute in benzene at the same temperature is 631.9 mm of mercury. Calculate the molality of the solution. (1981 - 3 Marks)

Ans : 0.156 m/kg

Solution :

TIPS/Formulae : $\frac{P^o - P}{P^o} = \frac{n}{N}$ [Roults Equation]

Now the solution contains ‘m’ moles of solute per 1000 gm of benzene

Vapour pressure of benzene, $P^o = 639.7$ mm

Vapour pressure of solution, $P = 631.9$ mm

Moles of benzene (Mol. wt. 78), $N = 1000/78$

Moles of solute, $n = ?$

Substitute these values in the Raoult’s equation

$$\frac{P^o - P}{P^o} = \frac{n}{N} \text{ or } \frac{639.7 - 631.9}{639.7} = \frac{n \times 78}{1000}$$

$$\text{or } \frac{7.8}{639.7} = \frac{78\,n}{1000} \quad \therefore\ n = \frac{1000 \times 7.8}{78 \times 639.7} = \mathbf{0.156}$$

Hence, molality of solution = 0.156 m

5. An organic compound CxH2yOy was burnt with twice the amount of oxygen needed for complete combustion to CO_2 and H2O. The hot gases when cooled to 0°C and 1 atm. pressure, measured 2.24 liters. The water collected during cooling weighed 0.9 g. The vapour pressure of pure water at 20°C is 17.5 mm Hg and is lowered by 0.104 mm when 50 g of the organic compound are dissolved in 1000 g of water. Give the molecular formula of the organic compound. (1983 - 5 Marks)

Ans: $(CH_2O)_5$ or $C_5H_{10}O_5$

Solution: The chemical equation for the combustion of organic compound $C_xH_{2y}O_y$ can be represented as:

$C_xH_{2y}O_y + 2xO_2 = x\ CO_2 + y\ H_2O + x\ O_2$

The gases obtained after cooling = x + x = 2x

∴ 2x = 2.24 litres [∵ H_2O is in liquid state]

$$\text{or } x = \frac{2.24}{2} = 1.12 \text{ litres}$$

Number of moles of CO_2 =

$$\frac{1.12 \text{ litres}}{22.4 \text{ litres mole}}$$

$$[\because 22.4 \text{ L at NTP} = 1 \text{mole}]$$

=1/20 mole = 0.05 mole

The empirical formula of the organic compound is $C(H_2O)$ ...(1)

The mole fraction of the solute (A)

= relative decrease in vapour pressure of the solvent (B)

$$\frac{p^\circ - p}{p^\circ} = \frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

$$\text{or } \frac{0.104}{17.5} = \frac{\frac{50}{M_A}}{\frac{50}{M_A} + \frac{1000}{18}} \qquad [M_A = \text{mol.wt.g A}]$$

$$\text{or } \frac{0.104}{17.5} = \frac{50}{M_A\left(\frac{50 \times 18 + 1000M_A}{18M_A}\right)}$$

$$\text{or } \frac{104}{17500} = \frac{50 \times 18}{900 + 1000M_A} \text{ or } M_A = 150.6$$

Molecular wt. of the organic compound

$(CH_2O)n = 150$

Molecular wt. of $CH_2O = 12 + 2 + 16 = 30$

$\therefore 30 \times n = 150$ $\quad$ [$\because$ $(CH_2O)\ n$ = mol. formula]

or $n = 150/30 = 5$

$\therefore$ Molecular formula of the given organic compound is

$(CH_2O)_5$ or $C_5H_{10}O_5$.

6. 'Two volatile and miscible liquids can be separated by fractional distillation into pure component', is true under what conditions? (1984 - 1 Mark)

Solution: If they form an ideal solution which obeys' Raoult's Law and for which $\Delta H_{mixing} = 0$ and $\Delta V_{mixing} = 0$

Thus we can separate two volatile and miscible liquids by fractional distillation if, they should not form a zeotropic solutions.

Subjective Questions of Solutions, Past year Questions (Part - 2)

7. The vapour pressure of ethanol and methanol are 44.5 mm and 88.7 Hg respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour. (1986 - 4 Marks)

Ans : 66.17 mm, 0.65

Solution :

TIPS/Formulae :

$P_{total} = p_A + p_B$

Molecular weight of CH_3OH = 12 + 3 + 16 + 1 = 32

Molecular weight of C_2H_5OH= 24 + 5 + 16 + 1 = 46

According to Raoult's law

$P_{total} = p_1 + p_2$

where P_{total} = Total vapour pressure of the solution

p_1 = Partial vapour pressure of one component

p_2 = Partial vapour pressure of other component

Again, p_1 = Vapour pressure (p°_1) × mole fraction

Similarly, p_2 = Vapour pressure (p°_2) x mole fraction

Mole fraction of CH_3OH = $\dfrac{\frac{40}{32}}{\frac{40}{32}+\frac{60}{46}} = 0.49$

Mole fraction of ethanol = $\dfrac{\frac{60}{46}}{\frac{60}{46}+\frac{40}{32}} = 0.51$

NOTE THIS STEP: Thus now let us first calculate the partial vapour pressures, i.e., p_1 and p_2 of the two component.

Partial vapour pressure of CH_3OH (p_1) = 88.7 × 0.49 = 43.48 mm

Partial vapour pressure of C_2H_5OH (p_2) = 44.5 × 0.51 = 22.69 mm

∴ Total vapour pressure of the solution = 43.48 + 22.69 mm = 66.17 mm

Mole fraction of CH3OH in vapour = $\dfrac{43.48}{66.17} = \mathbf{0.65}$

8. The vapour pressure of a dilute aqueous solution of glucose ($C_6H_{12}O_6$) is 750 mm of mercury at 373 K. Calculate (i) molality and (ii) mole fraction of the solution. (1989 - 3 Marks)

Ans: 0.7503 mol/kg, 0.9868

Solution:

TIPS/Formulae:

Molality, $M = \dfrac{\text{moles of solute}}{\text{kg of solvent}}$

Mole fraction, $x_A = \dfrac{n_A}{n_A + n_B}, \quad x_B = \dfrac{n_B}{n_A + n_B}$

$$p_1 = x_1 p_1^\circ$$

$$\therefore x_1 = \frac{p_1}{p_1^\circ} = \frac{750}{760} = 0.9868$$

x_2 (solute) = 1 – 0.9868 = 0.0132

$$\text{Molality, } m = \frac{x_2}{x_1 M_1} \times 1000 = \frac{0.0132 \times 1000}{0.9868 \times 18}$$

= 0.7503 mol kg^{-1}

9. 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 the solution is 600 mm Hg. What is the molecular weight of the solid substance? (1990 - 3 Marks)

Ans: 65.25

Solution:

TIPS/Formulae:

According to Raoult's law,

$$\frac{p^\circ - p}{p^\circ} = \frac{w/m}{w/m + W/M}$$

Here, p° = 640 mm

p = 600 mm

w= 2.175 g

= 39.0

m =?

M = 78

Substituting the various values in the above equation for Roult's law:

$$\frac{640 - 600}{640} = \frac{2.175/m}{2.175/m + 39/78}$$

$$\frac{1}{16} = \frac{2.175}{2.175 + 0.5\,m} \Rightarrow m = \mathbf{65.25}$$

10. The degree of dissociation of calcium nitrate in a dilute aqueous solution, containing 7.0 g. of the salt per 100 gm of water at 100ºC is 70%. If the vapour pressure of water at 100ºC is 760 mm, calculate the vapour pressure of the solution. (1991 - 4 Marks)

Ans : 746.3 mm Hg

Solution :

TIPS/Formulae : First find moles of Ca(NO3)2 and water.

Then use the expression $\frac{p^\circ - p}{p^\circ} = \frac{n}{n+N}$ to find vapour pressure of solution.
Let initially 1 mole of $Ca(NO_3)_2$ is taken

Degree of dissociation of $Ca(NO_3)_2$ = 70/100 = 0.7

Ionisation of $Ca(NO_3)_2$ can be represented as

	$Ca(NO_3)_2$	$\rightleftharpoons$	Ca^{2+}	$+$	$2NO_3^-$
At start	1		0		0
At equilibrium	1 – 0.7		0.7		2 × 0.7

∴ Total number of moles in the solution at equilibrium = (1 – 0.7) + 0.7 + 2 × 0.7 = 2.4

No. of moles when the solution contains 1 gm of calcium nitrate instead of 1 mole of the salt

$$n = \frac{2.4}{164} \times 7 = 0.102$$

$$\frac{\text{Wt. of water}}{\text{Mol. wt. of water}} = \frac{100}{18} = 5.55$$

$$\text{Applying Raoult's law, } \frac{p^0 - p}{p^0} = \frac{n}{n+N}$$

$$\frac{760 - p}{760} = \frac{0.102}{0.102 + 5.55} \Rightarrow \frac{760 - p}{760} = 0.0180$$

$$\Rightarrow p = 760 - (760 \times 0.0180) = \mathbf{746.3\ mm\ Hg}$$

11. Addition of 0.643 g of a compound to 50 ml. of benzene (density : 0.879 g/ml.) lowers the freezing point from 5.51ºC to 5.03ºC. If Kf for benzene is 5.12 K kg mol–1, calculate the molecular weight of the compound. (1992 - 2 Marks)

Ans : 156.056

Solution :

TIPS/Formulae :

Given Wt. of benzene (solvent),

W = Volume × density = 50 × 0.879 = 43.95 g

Wt. of compound (solute), w = 0.643 g

Mol. wt. of benzene, M = 78; Mol. wt. of solute, m = ?

Depression in freezing point, DTf = 5.51 – 5.03 = 0.48

Moral freezing constant, $K_f = 5.12$

Now we know that,

$$m = \frac{1000 \times K_f \times w}{W \times \Delta T_f} = \frac{1000 \times 5.12 \times 0.643}{43.95 \times 0.48} = \mathbf{156.056}$$

12. What weight of the non-volatile solute, urea ($NH_2 - CO - NH_2$) needs to be dissolved in 100g of water, in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution? (1993 - 3 Marks)

Ans : 18.52 m

Solution :

TIPS/Formulae :

$$\frac{p^{\circ}-p}{p^{\circ}} = \frac{\frac{w}{m}}{\frac{w}{m}+\frac{W}{M}}$$

Here, w and m are wt. and molecular wt. of solute, W and M are wt. and molecular weight of solvent

p = Pressure of solution; p° = Normal vapour pressure

Let the initial (normal) pressure (p°) = p

∴ Pressure of solution = $\frac{75}{100}\times p=\frac{3}{4}p$

m = 60, M = 18, W = 100 gm

$$\therefore \frac{p-\frac{3}{4}p}{p} = \frac{w/60}{\frac{w}{60}+\frac{100}{18}} \Rightarrow \frac{1}{4} = \frac{w/60}{(w/60)+5.55}$$

$$\frac{4w}{60} = \frac{w}{60}+5.55 \Rightarrow \frac{3w}{60} = \frac{w}{20} = 5.55 \text{ or } w = \mathbf{111\ g}$$

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

$$= \frac{111\times 1000}{60\times 100} = \mathbf{18.52\ m}$$

13. The molar volume of liquid benzene (density=0.877 g mL^{-1}) increases by a factor of 2750 as it vaporises at 20°C and that of liquid toluene (density=0.867 g mL^{-1}) increases by a factor of 7720 at 20°C. A solution of benzene and toluene at 20°C has a vapour pressure of 46.0 Torr. Find the mole fraction of benzene in the vapour above the solution. (1996 - 3 Marks)

Ans : 0.73

Solution :

TIPS/Formulae :

$$\text{(i)} \quad \text{Volume} = \frac{\text{No. of moles} \times \text{molar mass}}{\text{density}}$$

$$\text{(ii)} \quad PV = nRT \text{ or } P = \frac{nRT}{V}$$

Volume of 1 mole of liq. benzene =78/0.877

Volume of 1 mole of toluene = 92/0.867

In vapour phase,

At 20°C, for 1 mole of benzene,

$$\text{Volume} = \frac{1 \times 78 \times 2750}{0.877} = 244583.80 \text{ mL} = 244.58 \text{ L}$$

Similarly for 1mole of toluene,

$$\text{volume} = \frac{1 \times 92}{0.867} \times 7720 = 819192.61 \text{ mL} = 819.19 \text{ L}$$

As we know that, PV = nRT

$$\text{For benzene, } P_B^o = \frac{nRT}{V} = \frac{1 \times 0.0821 \times 293}{244.58} \text{atm} = 0.098 \text{ atm}$$

$$\text{For toluene, } P_T^o = \frac{nRT}{V} = \frac{1 \times 0.0825 \times 293}{819.19} \text{atm} = 0.029 \text{ atm}$$

$$P = P_B^o . X_B + P_T^o . X_T$$

$$\because \quad X_B + X_T = 1 \quad \therefore \quad X_T = 1 - X_B$$

$$P = P_B^o . X_B + P_T^o (1 - X_B)$$

Total vapour-pressure = 46 torr = 46/760 = 0.060 atm

Thus, $0.060 = 0.098\ X_B + 0.029\ (1 - X_B)$

$\Rightarrow 0.060 = 0.098\ X_B + 0.029 - 0.029\ X_B$

$\Rightarrow 0.031 = 0.069\ X_B$

$$\therefore\ X_B = \frac{0.031}{0.069} = 0.45\ \text{(in liquid phase)}$$

$X_B + X_T = 1$

$X_T = 1 - 0.45 = 0.55$ (in liquid phase)

Also, $P_B' = P_B^o X_B = P X_B'$

So, $0.098 \times 0.045 = 0.060 \times X_B'$

$$X_B' = \frac{0.098 \times 0.45}{0.060} = \mathbf{0.735\ (in\ gas\ phase)}$$

Subjective Questions of Solutions, Past year Questions (Part - 3)

14. A solution of a nonvolatile solute in water freezes at – 0.30°C. The vapour pressure of pure water at 298 K is 23.51 mm Hg and Kf for water is 1.86 K kg mol^{-1}. Calculate the vapour pressure of this solution at 298 K. (1998 - 4 Marks)

Ans: 23.44 mm Hg

Solution:

TIPS/Formulae:

$$\Delta T_t = K_f .m$$

$$\frac{P^o - p}{p^o} = \frac{\text{moles of solute}}{\text{moles of solvent}}$$

Depression in freezing point, $\Delta T_f = 0 - (-0.30) = 0.30$

Now we know that $\Delta T_f = K_f m$

$$\therefore \; m = \frac{\Delta T_f}{K_f} = \frac{0.30}{1.86} = 0.161$$

According to Raoult’s law

$$\frac{p^\circ - p}{p^\circ} = \frac{\text{No. of moles of solute}}{\text{No. of moles of solvent}}$$

$$\frac{23.51 - p}{23.51} = \frac{0.161}{1000/18} = \frac{0.161 \times 18}{1000}$$

($\because$ No. of moles of $H_2O = 1000/18$)

On usual calculations

$$\frac{23.51 - p}{23.51} = .0020898$$

p = 23.51– 23.51´0.0020898 = 23.51 – .068

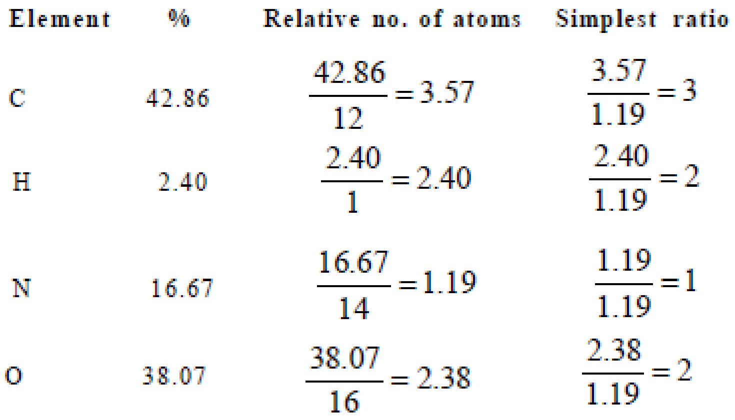
p = 23.44 mm Hg

15. 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 5.5 g of the minor product is dissolved in 45 g of benzene, the boiling point of the solution is 1.84 °C higher than that of pure benzene. Calculate the molar mass of the minor product and determine its molecular and structural formula. (Moral boiling point elevation constant of benzene is 2.53 K kg mol–1.) (1999 - 10 Marks)

Ans : 168 g, $C_6H_4(NO_2)_2$, m-dinitrobenzene

Solution :

TIPS/Formulae : ΔT_b = kb ´ m



Element	%	Relative no. of atoms	Simplest ratio
C	42.86	$\frac{42.86}{12} = 3.57$	$\frac{3.57}{1.19} = 3$
H	2.40	$\frac{2.40}{1} = 2.40$	$\frac{2.40}{1.19} = 2$
N	16.67	$\frac{16.67}{14} = 1.19$	$\frac{1.19}{1.19} = 1$
O	38.07	$\frac{38.07}{16} = 2.38$	$\frac{2.38}{1.19} = 2$

∴Empirical formula of the minor product is $C_3H_2NO_2$ Molar empirical formula mass of the minor prodouct = 3 × 12 + 2 × 1 + 1 × 14 + 2 × 16 = 84 g mol^{-2}

Let M be the molar mass of the minor product. For 5.5 g of the minor product dissolved in 45 g benzene, the molality

(m) of the solution = $\frac{5.5 g/M}{0.045 kg}$

Substituting this in the expression of elevation of boiling point,

$$\Delta T_b = K_b m \Rightarrow 1.84K = (2.53\ \text{Kmol}^{-1})\left(\frac{5.5\text{g}/M}{0.045\text{kg}}\right)$$

or $M = 168\ \text{g mol}^{-1}$

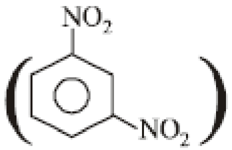
No. of unit of empirical formula in molecular formula

$$= \frac{168\,\text{g mol}^{-1}}{84\,g\,\text{F}} = 2$$

Hence the molecular formula of the minor product is

$2\ (C_3H_2NO_2)$, i.e., $C_6H_4(NO_2)_2$

The product is m - dinitrobenzene .



16. To 500 cm^3 of water, 3.0 × 10^{-3} kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? Kf and density of water are 1.86 K kg^{-1} mol^{-1} and 0.997 g cm^{-3}, respectively. (2000 - 3 Marks)

Ans : 0.228 K

Solution :

TIPS/Formulae :

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

Weight of water = 500 × 0.997 = 498.5 g

(weight = volume × density)

No. of moles of acetic acid

$$= \frac{\text{Wt. of } CH_3COOH \text{ in g}}{\text{Mol. wt. of } CH_3COOH} = \frac{3\times10^{-3}\times10^{3}}{60} = 0.05$$

Since 498.5 g of water has 0.05 moles of CH_3COOH

$$1000 \text{ g of water has} = \frac{0.05 \times 1000}{498.5} = 0.1$$

Therefore molality of the solution = 0.1

Determination of van’t Hoff factor, i

	$CH_3COOH \longrightarrow$	$CH_3COO^- +$	H^+
No. of moles at start	1	0	0
No. of moles at equb.	1 − 0.23	0.23	0.23

Therefore vant Hoff factor

$$= \frac{\text{No. of particles before dissociation}}{\text{No. of particles after dissociation}}$$

$$= \frac{1 - 0.23 + 0.23 + 0.23}{1} = 1.23$$

Now we know that

$\Delta T_f = ixK_f\ xm = 1.23 \text{ x } 1.86 \text{ x } 0.1 = 0.228K$

17. 1.22g of benzoic acid is dissolved in 100 g of acetone and 100 g of benzene separately. Boiling point of the solution in acetone increases by 0.17° C, while that in the benzene increases by 0.13° C; Kb for acetone and benzene is 1.7 K kg mol^{-1} and 2.6 K kg mol^{-1}. Find molecular weight of benzoic acid in two cases and justify your answer. (2004 - 2 Marks)

Ans : 122, 224

Solution :

TIPS/Formulae :

$\Delta T_b = K_b \times M$

In first case,

$$\Delta T_b = K_b \times m = K_b \times \frac{Wt.\text{ of solute}}{\text{Mol. wt. of solute}}$$

$$\text{or } 0.17 = 1.7 \times \frac{1.22}{M \times 100 \times 10^{-3}} \text{ or } \mathbf{M = 122}$$

Thus the benzoic acid exists as a monomer in acetone

(ii) In second case,

$$\Delta T_b = K_b \times \frac{\text{Wt. of solute}}{\text{Mol. wt. of solute}}$$

$$\text{or } \quad 0.13 = 2.6 \times \frac{1.22}{M' \times 100 \times 10^{-3}} \Rightarrow \boldsymbol{M' = 224}$$

NOTE : Double the expected molecular weight of benzoic acid (244) in acetone solution indicates that benzoic acid exists as a dimer in acetone.

18. 75.2 g of C_6H_5OH (phenol) is dissolved in a solvent of K_f = 14. If the depression in freezing point is 7 K then find the % of phenol that dimerises. (2006 - 6M)

Ans : 75%

Solution :

	$2C_6H_5OH \rightleftharpoons$	$(C_6H_5OH)_2$
Initial no. of moles	1	0
No. of moles at equilibrium	$1-\alpha$	$\alpha / 2$

Total number of moles at equilibrium = $1-\alpha+\frac{\alpha}{2} = 1-\frac{\alpha}{2}$

ΔT_f =iK_f ×(molality)

$$\Rightarrow 7 = 14 \times \frac{75.2}{94} \times \left(1-\frac{\alpha}{2}\right) \begin{bmatrix} \text{weight of phenol} = 75.2\text{g} \\ \text{mol.wt of phenol} = 94 \end{bmatrix}$$

∴ a = 0.75So the percentage of phenol that dimerises = 75%.