# CH2 – SOLUTIONS

2.1. Calculate the mass percentage of benzene ($C_6H_6$) and carbon tetrachloride ($CCl_4$) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.

Ans: Mass of solution = Mass of $C_6H_6$ + Mass of $CCl_4$
= 22 g+122 g= 144 g
Mass % of benzene = 22/144 x 100 =15.28 %
Mass % of $CCl_4$ = 122/144 x 100 = 84.72 %

2.2. Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.

Ans: 30% by mass of $C_6H_6$ in $CCl_4$ => 30 g $C_6H_6$ in 100 g solution
∴ no. of moles of $C_6H_6$,$({}^{n}C_6h_6)$ = 30/78 = 0.385

(molar mass of $C_6H_6$ = 78g)

no. of moles of

$$CCl_4\ (n_{CCl_4}) = \frac{70}{154} = 0.455$$

$$x_{C_6H_6} = \frac{n_{C_6H_6}}{n_{C_6H_6} + n_{CCl_4}}$$

$$= \frac{0.385}{0.385 + 0.455} = \frac{0.385}{0.84} = 0.458$$

$$x_{CCl_4} = 1 - 0.458 = 0.542$$

2.3. Calculate the molarity of each of the following solutions
(a) 30 g of $Co(NO_3)26H_2O$ in 4·3 L of solution
(b) 30 mL of 0-5 M $H_2SO_4$ diluted to 500 mL.
Ans:

*(a)* $$\text{Molarity of solution} = \frac{\text{Mass of solute / Molar mass of solute}}{\text{Volume of solution in litres}}$$

Mass of solute, $Co(NO_3)_2.6\ H_2O$ = 30 g.
Molar mass of solute, $Co(NO_3)_2.6H_2O = 59 + 2 \times 14 + 6 \times 16 + 6 \times 18 = 291\ g\ mol^{-1}$.
Volume of solution = 4·3 L

$$\text{Molarity (M)} = \frac{(30g) / (291g\ mol^{-1})}{(4{\cdot}3L)} = 0{\cdot}024\ mol\ L^{-1} = \mathbf{0{\cdot}024\ M}$$

*(b)* Volume of undiluted $H_2SO_4$ solution ($V_1$) = 30 mL
Molarity of undiluted $H_2SO_4$ solution ($M_1$) = 0·5 M
Volume of diluted $H_2SO_4$ solution ($V_2$) = 500 mL
Molarity of diluted $H_2SO_4$ ($M_2$) can be calculated as :

$$M_1V_1 = M_2V_2$$

or $$M_2 = \frac{M_1V_1}{V_2} = \frac{(30mL) \times (0{\cdot}5M)}{(500mL)} = \mathbf{0{\cdot}03\ M}$$

2.4. Calculate the mass of urea ($NH_2CONH_2$) required in making 2.5 kg of 0.25 molal aqueous solution.

Ans: 0.25 Molal aqueous solution to urea means that
moles of urea = 0.25 mole
mass of solvent ($NH_2CONH_2$) = 60 g $mol^{-1}$
∴ 0.25 mole of urea = 0.25 x 60=15g
Mass of solution = 1000+15 = 1015g = 1.015 kg
1.015 kg of urea solution contains 15g of urea
∴ 2.5 kg of solution contains urea =15/1.015 x 2.5 = 37 g

2.5. Calculate
(a) molality
(b) molarity and
(c) mole fraction of KI if the density of 20% (mass/mass) aqueous KI solution is 1·202 g $mL^{-1}$.

Ans:

Step I. Calculation of molality of solution
Weight of KI in 100 g of the solution = 20 g
Weight of water in the solution = 100 – 20 = 80 g = 0-08 kg
Molar mass of KI = 39 + 127 = 166 g $mol^{-1}$.

$$\text{Molality of solution } (m) = \frac{\text{No of gram moles of KI}}{\text{Mass of water in kg}} = \frac{(20\text{g})/(166\text{g mol}^{-1})}{(0{\cdot}08\text{kg})}$$
$$= 1{\cdot}506 \text{ mol kg}^{-1} = \mathbf{1{\cdot}506\ m.}$$

Step II. Calculation of molarity of solution

Weight of solution = 100 g ; Density of solution = 1·202 g $mL^{-1}$.

$$\text{Volume of solution} = \frac{\text{Weight of solution}}{\text{Density}} = \frac{(100\text{g})}{(1{\cdot}202\text{g mL}^{-1})} = 83{\cdot}19 \text{ mL}$$

$$\text{Molarity of solution (M)} = \frac{\text{No. of gram moles of KI}}{\text{Volume of solution in litres}} = \frac{(20\text{g})/(166\text{g mol}^{-1})}{(0{\cdot}083\text{L})}$$
$$= 1{\cdot}45 \text{ mol L}^{-1} = \mathbf{1{\cdot}45\ M}$$

Step III. Calculation of mole fraction of Kl

$$n_{KI} = \frac{\text{Mass of KI}}{\text{Molar mass of KI}} = \frac{(20\text{g})}{(166\text{g mol}^{-1})} = 0{\cdot}12 \text{ mol}$$

$$n_{H_2O} = \frac{\text{Mass of water}}{\text{Molar mass of water}} = \frac{(80\text{g})}{(18\text{g mol}^{-1})} = 4{\cdot}44 \text{ mol.}$$

$$x_{KI} = \frac{n_{KI}}{n_{KI} + n_{H_2O}} = \frac{(0{\cdot}12\text{mol})}{(0{\cdot}12 + 4{\cdot}44)\text{mol}} = \frac{0{\cdot}12}{4{\cdot}56} = \mathbf{0{\cdot}0263.}$$

2.6. $H_2 S$, a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of $H_2S$ in water at STP is 0.195 m, calculate Henry's law constant.

Ans: Solubility of $H_2S$ gas = 0.195 m

= 0.195 mole in 1 kg of solvent
1 kg of solvent = 1000g

$$= \frac{1000}{18} = 55.55 \text{ moles}$$

$$\therefore \; x_{H_2S} = \frac{0.195}{0.195 + 55.55}$$

$$= \frac{0.195}{55.745} = 0.0035$$

– Pressure at STP = 0.987 bar

Applying Henry's law,

$$P_{H_2S} = K_H \times x_{H_2S}$$

$$\Rightarrow \quad K_H = \frac{P_{H_2S}}{x_{H_2S}} = \frac{0.987}{0.0035} = 282 \text{bar}$$

2.7. Henry's law constant for $CO_2$ in water is 1.67 x $10^8$ Pa at 298 K. Calculate the quantity of $CO_2$ in 500 mL of soda water when packed under 2.5 atm $CO_2$ pressure at 298 K.

Ans.:

$$K_H = 1.67 \times 10^8 \text{ Pa}$$

$$P_{CO_2} = 2.5 \text{ atm} = 2.5 \times 101325 \text{ Pa}$$

$$\therefore \; x_{CO_2} = \frac{P_{CO_2}}{K_H} = \frac{2.5 \times 101325}{1.67 \times 10^8} = 1.517 \times 10^{-3}$$

For 500 mL of soda water, water present $\simeq$ 500 mL

$$= 500\text{g} = \frac{500}{18} = 27.78 \text{ moles}$$

$$\therefore \quad n_{H_2O} = 27.78 \text{ moles}$$

$$\therefore \quad \frac{n_{CO_2}}{27.78} = 1.517 \times 10^{-3}$$

$$n_{CO_2} = 42.14 \times 10^{-3} \text{ mole}$$
$$= 42.14 \text{ mmol}$$
$$= 42.14 \times 10^{-3} \times 44 \text{ g}$$
$$= 1.854 \text{ g}$$

2.8 The vapour pressures of pure liquids A and B are 450 mm and 700 mm of Hg respectively at 350 K. Calculate the composition of the liquid mixture if total vapour pressure is 600 mm of Hg. Also find the composition in the vapour phase.

Ans:

Vapour pressure of pure liquid A ($P^\circ A$) = 450 mm

Vapour pressure of pure liquid B (P∘B) = 700 mm
Total vapour pressure of the solution (P) = 600 mm

$$\begin{aligned}
\text{According to Raoult's Law, P} &= P_A^\circ x_A + P_B^\circ x_B = P_A^\circ x_A + P_B^\circ(1 - x_A) \\
(600\text{ mm}) &= 450\text{ mm} \times x_A + 700\text{ mm}\,(1 - x_A) \\
&= 700\text{ mm} + x_A\,(450 - 700)\text{ mm} \\
&= 700 - x_A(250\text{ mm}) \\
\text{or}\qquad x_A &= \frac{(600 - 700)\text{ mm}}{-(250\text{ mm})} = 0{\cdot}40 \\
\text{Mole fraction of A } (x_A) &= 0{\cdot}40 \\
\text{Mole fraction of B } (x_B) &= 1 - 0{\cdot}40 = 0{\cdot}60 \\
P_A &= P_A^\circ x_A = (450\text{ mm}) \times 0{\cdot}40 = 180\text{ mm} \\
P_B &= P_B^\circ x_B = (700\text{ mm}) \times 0{\cdot}60 = 420\text{ mm} \\
\text{Mole fraction of A in the vapour phase} &= \frac{P_A}{P_A + P_B} = \frac{(180\text{ mm})}{(180 + 420)\text{ mm}} = \mathbf{0{\cdot}30} \\
\text{Mole fraction of B in the vapour phase} &= \frac{P_B}{P_A + P_B} = \frac{(420\text{ mm})}{(180 + 420)\text{ mm}} = \mathbf{0{\cdot}70}
\end{aligned}$$

2.9. Vapour pressure of pure water at 298 K is 23.8 m m Hg. 50 g of urea ($NH_2CONH_2$) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution and its relative lowering.

Ans:

$P^o = 23.8$ mm
$w_2 = 50$g, $M_2$ (urea) = 60g mol$^{-1}$
$w_1 = 850$ g, $M_1$ (water)= 18g mol$^{-1}$
**To find:** $P_s$ and $(P^o - P_s)/P^o$
**Solution:** Applying Raoult's law,

$$\frac{P^o - P_s}{P^o} = \frac{n_2}{n_1 + n_2} = \frac{w_2 / M_2}{w_1 / M_1 + w_2 / M_2}$$

$$\therefore \quad \frac{P^o - P_s}{P^o} = \frac{50/60}{850/18 + 50/60}$$

$$= \frac{0.83}{47.22 + 0.83} = 0.017$$

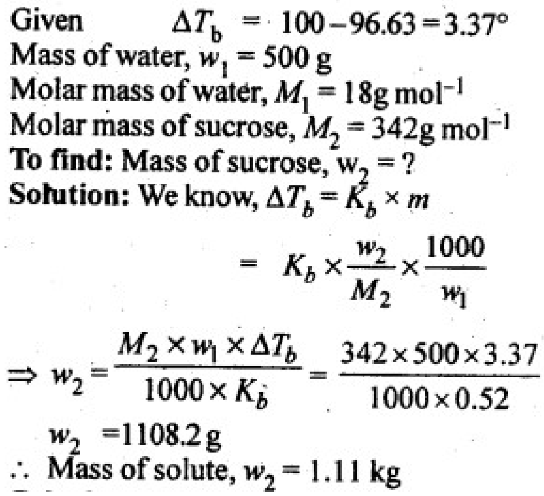
Putting $P^o = 23.8$ mm, we have

$$\frac{23.8 - P_s}{P_s} = 0.017$$

$$\begin{aligned}
\Rightarrow \quad 23.8 - P_s &= 0.017\,P_s \\
\text{or,} \quad 1.017\,P_s &= 23.8 \\
\text{or,} \quad P_s &= \mathbf{23.4\ mm}
\end{aligned}$$

2.10. Boiling point of water at 750 mm Hg is 99.63°C. How much sucrose is to be added to 500 g of water such that it boils at 100°C.

Ans:



Given $\Delta T_b = 100 - 96.63 = 3.37°$

Mass of water, $w_1 = 500$ g

Molar mass of water, $M_1 = 18 \text{g mol}^{-1}$

Molar mass of sucrose, $M_2 = 342 \text{g mol}^{-1}$

**To find:** Mass of sucrose, $w_2$ = ?

**Solution:** We know, $\Delta T_b = K_b \times m$

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

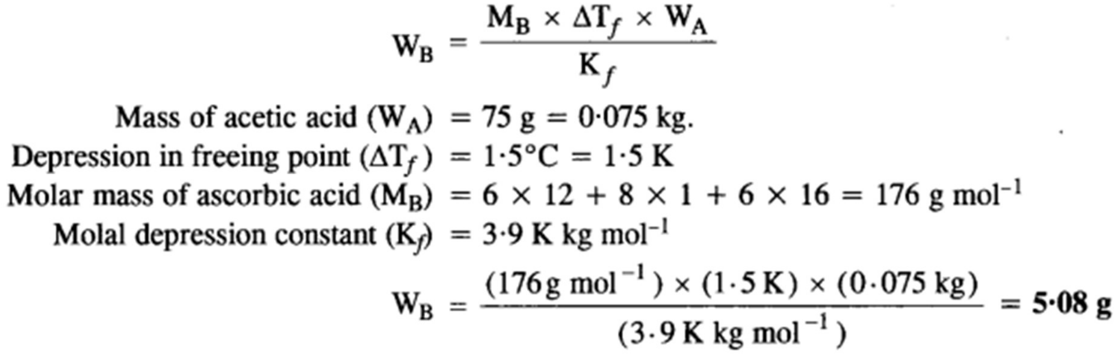
$$\Rightarrow w_2 = \frac{M_2 \times w_1 \times \Delta T_b}{1000 \times K_b} = \frac{342 \times 500 \times 3.37}{1000 \times 0.52}$$

$w_2 = 1108.2$ g

$\therefore$ Mass of solute, $w_2 = 1.11$ kg

2.11 Calculate the mass of ascorbic acid (vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1·5°C. ($K_f$ for $CH_3COOH$) = 3·9 K kg $mol^{-1}$)

Ans:



$$W_B = \frac{M_B \times \Delta T_f \times W_A}{K_f}$$

Mass of acetic acid ($W_A$) = 75 g = 0·075 kg.

Depression in freeing point ($\Delta T_f$) = 1·5°C = 1·5 K

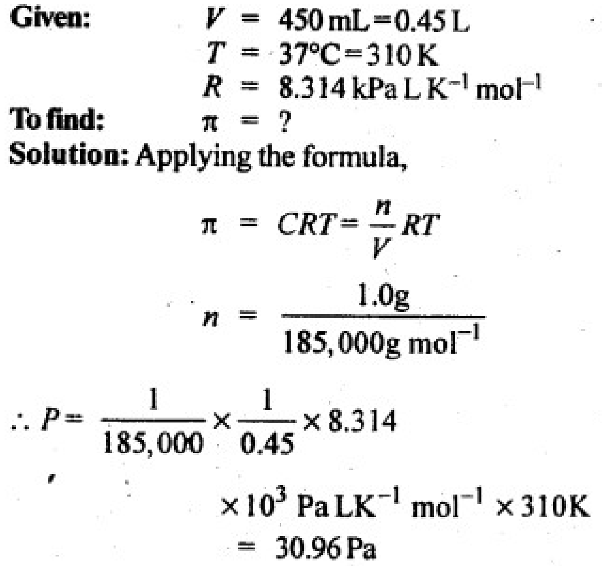
Molar mass of ascorbic acid ($M_B$) = $6 \times 12 + 8 \times 1 + 6 \times 16 = 176 \text{ g mol}^{-1}$

Molal depression constant ($K_f$) = $3 \cdot 9 \text{ K kg mol}^{-1}$

$$W_B = \frac{(176 \text{g mol}^{-1}) \times (1 \cdot 5 \text{K}) \times (0 \cdot 075 \text{ kg})}{(3 \cdot 9 \text{ K kg mol}^{-1})} = \mathbf{5 \cdot 08 \text{ g}}$$

2.12. Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C.

Ans:



**Given:** $V = 450\,\text{mL} = 0.45\,\text{L}$

$T = 37°\text{C} = 310\,\text{K}$

$R = 8.314\,\text{kPa L K}^{-1}\,\text{mol}^{-1}$

**To find:** $\pi = ?$

**Solution:** Applying the formula,

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

$$n = \frac{1.0\text{g}}{185{,}000\text{g mol}^{-1}}$$

$$\therefore P = \frac{1}{185{,}000} \times \frac{1}{0.45} \times 8.314$$

$$\times 10^3\,\text{Pa L K}^{-1}\,\text{mol}^{-1} \times 310\text{K}$$

$$= 30.96\,\text{Pa}$$

NCERT EXERCISES

2.1. Define the terra solution. How many types of solutions are formed? Write briefly about each type with an example.

Sol: A solution is a homogeneous mixture of two or more chemically non-reacting substances. Types of solutions: There are nine types of solutions.

Types of Solution Examples

Gaseous solutions

(a) Gas in gas Air, mixture of $0_2$ and $N_2$, etc.

(b) Liquid in gas Water vapour

(c) Solid in gas Camphor vapours in N2 gas, smoke etc.

Liquid solutions

(a) Gas in liquid C02 dissolved in water (aerated water), and 02 dissolved in water, etc.

(b) Liquid in liquid Ethanol dissolved in water, etc.

(c) Solid in liquid Sugar dissolved in water, saline water, etc.

Solid solutions

(a) Gas in solid Solution of hydrogen in palladium

(b) Liquid in solid Amalgams, e.g., Na-Hg

(c) Solid in solid Gold ornaments (Cu/Ag with Au)

2.2. Suppose a solid solution is formed between two substances, one whose particles are very large and the other whose particles are very small. What type of solid solution is this likely to be ?

Sol: The solution likely to be formed is interstitial solid solution.

2.3 Define the following terms:

(i) Mole fraction

(ii) Molality
(iii) Molarity
(iv) Mass percentage

Sol: (i) **Mole fraction:** It is defined as the ratio of the number of moles of the solute to the total number of moles in the solution. If A is the number of moles of solute dissolved in B moles of solvent, then Mole fraction of solute

$$(X_A) = \frac{n_A}{n_A + n_B} \quad \dots (1)$$

Mole fraction of solvent $(X_B) = \frac{n_B}{n_A + n_B}$ ... (2)

Adding the above two equations, we get

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = \frac{n_A + n_B}{n_A + n_B} = 1$$

i.e., $X_A + X_B = 1$

$\therefore X_A = 1 - X_B$ or $X_B = 1 - X_A$

(ii) **Molality:** It is defined as die number of moles of a solute present in 1000g (1kg) of a solvent.

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

NOTE: Molality is considered better way of expressing concentration of solutions, as compared to molarity because molality does not change with change in temperature since the mass of solvent does not vary with temperature,

(iii) **Molarity:** It is defined as the number of moles of solute present in one litre of solution.

Molarity (M) =

$$\frac{\text{Number of moles of solute}}{\text{Volume of Solution in litre}} = \frac{n}{V}$$

$$n = \frac{\text{Weight in grams}}{\text{Molecular weight of solute}}$$

$$\therefore\ M = \frac{\text{Weight in grams}}{\text{Volume of solution in litres}} \times \frac{1}{\text{Molecular weight of solute}}$$

Strength : This is weight (in gms) of solute per litre of solution

$$\therefore\ \text{Molarity} = \frac{\text{Strength}}{\text{Molecular weight of solute}}$$

or Strength = Molarity × Molecular weight

NOTE: Molarity is the most common way of expressing concentration of a solution in laboratory. However, it has one disadvantage. It changes with temperature because volume of a solution alters due to expansion and contraction of the liquid with temperature.

(iv) **Mass percentage:** It is the amount of solute in grams present in 100g of solution.

$$= \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

2.4. Concentrated nitric acid used in the laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of acid if the density of the solution is 1·504 g $mL^{-1}$ ?

Sol: Mass of $HNO_3$ in solution = 68 g

Molar mass of $HNO_3$ = 63 g $mol^{-1}$

Mass of solution = 100 g

Density of solution = 1·504 g $mL^{-1}$

$$\text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Density of solution}}$$

$$= \frac{(100\,g)}{(1\cdot504\ g\ mL^{-1})} = 66\cdot5\ mL = 0\cdot0665\ L$$

$$\text{Molarity of solution (M)} = \frac{\text{Mass of } HNO_3 \text{ / Molar mass of } HNO_3}{\text{Volume of solution in Litres}}$$

$$= \frac{(68g / 63 g\ mol^{-1})}{(0\cdot0665\,L)} = 16\cdot23\ mol\ L^{-1} = \mathbf{16\cdot23\ M.}$$

2.5. A solution of glucose in water is labelled as 10% w/w, what would be the molality and mole fraction of each component in the solution? If the density of solution is 1 .2 g m $L^{-1}$, then what shall be the molarity of the solution?

Sol: 10 percent w/w solution of glucose in water means 10g glucose and 90g of water.

Molar mass of glucose = 180g $mol^{-1}$ and molar mass of water = 18g $mol^{-1}$

$$\therefore\quad 10g \text{ of glucose} = \frac{10}{180} = 0\cdot0555 \text{ moles}$$

$$\text{and } 90g \text{ of } H_2O = \frac{90}{18} = 5 \text{ moles}$$

∴ Molality of solution

$$= \frac{\text{Moles of solute} \times 1000}{\text{Mass of solution in grams}}$$

$$= \frac{0\cdot0555}{90} \times 1000 = 0\cdot617\,m$$

Mole fraction of glucose

$$= X_g = \frac{\text{No. of moles of glucose}}{\text{No. of moles of glucose} + \text{No. of moles of water}}$$

$$= \frac{0{\cdot}0555}{5 + 0{\cdot}0555} = 0{\cdot}01$$

Mole fraction of water

$$= X_w = \frac{\text{No. of moles of water}}{\text{No. of moles of glucose} + \text{No. of moles of water}}$$

$$= \frac{5}{5 + 0{\cdot}0555} = 0{\cdot}99.$$

Volume of 100g of solution

$$= \frac{\text{Mass of solution}}{\text{Density}} = \frac{100}{1{\cdot}2} = 83{\cdot}33 \text{ mL}$$

$$\therefore \text{ Molarity of solution} = \frac{0{\cdot}0555}{83{\cdot}33} \times 1000$$

$$= 0{\cdot}67 \text{ M.}$$

2.6. How many mL of 0.1 M HCl are required to react completely with 1 g mixture of $Na_2CO_3$ and $NaHCO_3$ containing equimolar amounts of both?

Sol: Calculation of no. of moles of components in the mixture.

Let $x$ g of $Na_2CO_3$ is present in the mixture.
$\therefore$ $(1-x)$ g of $NaHCO_3$ is present in the mixture.
Molar mass of $Na_2CO_3$
$= 2 \times 23 + 12 + 3 \times 16 = 106 \text{ g mol}^{-1}$
and molar mass of $NaHCO_3$
$= 23 \times 1 + 1 + 12 + 3 \times 16 = 84 \text{ g mol}^{-1}$

No. of moles of $Na_2CO_3$ in $x$ g $= \frac{x}{106}$

No. of moles of $NaHCO_3$ in $(1-x)$ g $= (1-x)/84$
As given that the mixture contains equimolar amounts of $Na_2CO_3$ and $NaHCO_3$, therefore

$$\frac{x}{106} = \frac{1-x}{84}$$

$106 - 106x = 84x$
$106 = 190x$

$$\therefore \quad x = \frac{106}{190} = 0{\cdot}558\text{g}$$

$\therefore$ No. of moles of $Na_2CO_3$ present

$$= \frac{0{\cdot}558}{106} = 0{\cdot}00526$$

and no. of moles of $NaHCO_3$ present

$$= \frac{1 - 0{\cdot}558}{84} = 0{\cdot}00526$$

Calculation of no. of moles of HCl required
$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$
$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$
As can be seen, each mole of $Na_2CO_3$ needs 2 moles of HCl,
$\therefore$ 0·00526 mole of $Na_2CO_3$ needs
$= 0{\cdot}00526 \times 2 = 0{\cdot}01052$ mole
Each mole of $NaHCO_3$ needs 1 mole of HCl.
$\therefore$ 0·00526 mole of $NaHCO_3$ needs
$= 1 \times 0{\cdot}00526 = 0{\cdot}00526$ mole
Total amount of HCl needed will be
$= 0{\cdot}01052 + 0{\cdot}00526 = 0{\cdot}01578$ mole.
0·1 mole of 0.1 M HCl are present in 1000 mL of HCl
$\therefore$ 0·01578 mole of 0·1 M HCl will be present in

$$= \frac{1000}{0{\cdot}1} \times 0{\cdot}01578 = 157{\cdot}8 \text{ mL.}$$

2.7. Calculate the percentage composition in terms of mass of a solution obtained by mixing 300 g of a 25% and 400 g of a 40% solution by mass.

Sol:

$$\begin{aligned}
\text{Mass of one component in solution} &= \frac{(300\text{ g}) \times 25}{100} = 75\text{g} \\
\text{Mass of other component in solution} &= \frac{(400\text{g}) \times 40}{100} = 160\text{g} \\
\text{Total mass of solute} &= (75 + 160)\text{g} = 235\text{ g} \\
\text{Total mass of solution} &= (300 + 400)\text{g} = 700\text{ g} \\
\text{\% of solute in the final solution} &= \frac{(235\text{g})}{(700\text{g})} \times 100 = \mathbf{33{\cdot}57} \\
\text{\% of solvent in the final solution} &= 100 - 33{\cdot}57 = \mathbf{66{\cdot}43}
\end{aligned}$$

2.8. An antifreeze solution is prepared from 222.6 g of ethylene glycol, ($C_2H_6O_2$) and200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g $\text{mL}^{-1}$, then what shall be the molarity of the solution?

Sol:

Mass of solute = 222·6g

Molar mass of solute, $C_2H_4(OH)_2$

$= 12 \times 2 + 4 + 2\,(12 + 1) = 62\text{ g mol}^{-1}$

$$\therefore \quad \text{Moles of solute} = \frac{222{\cdot}6}{62} = 3{\cdot}59$$

Mass of solvent = 200 g

$$\therefore \quad \text{Molality} = \frac{3{\cdot}59}{200} \times 1000 = 17{\cdot}95\text{ mol kg}^{-1}$$

Total mass of solution = 422·6 g

$$\text{Volume of solution} = \frac{422{\cdot}6}{1{\cdot}072} = 394{\cdot}21\text{ mL.}$$

$$\therefore \quad \text{Molarity} = \frac{3{\cdot}59}{394{\cdot}2} \times 1000 = 9{\cdot}1\text{ mol L}^{-1}$$

2.9. A sample of drinking water was found to be severely contaminated with chloroform ($CHCl_3$), supposed to be a carcinogen. The level of contamination was 15 ppm (by mass).

(i) express this in percent by mass.

(ii) determine the molality of chloroform in the water sample.

**Sol:** 15 ppm means 15 parts in million ($10^6$) by mass in the solution.

$\therefore$ Percentage by mass$= \frac{15}{10^6} \times 100 = 15 \times 10^{-4}\%$

As only 15g of chloroform is present in $10^6$g of the solution, mass of the solvent = $10^6$ g

Molar mass of $CHCl_3 = 12 + 1 + 3 \times 35{\cdot}5$
$= 119{\cdot}5 \text{ g mol}^{-1}$

Moles of $CHCl_3 = \frac{15}{119{\cdot}5}$

$\therefore$ Molality$= \frac{15/119{\cdot}5 \times 1000}{10^6} = 1{\cdot}25 \times 10^{-4}$ m

**2.10. What role does the molecular interaction play in solution of alcohol in water?**

**Sol:** In case of alcohol as well as water, the molecules are interlinked by intermolecular hydrogen bonding. However, the hydrogen bonding is also present in the molecules of alcohol and water in the solution but it is comparatively less than both alcohol and water. As a result, the magnitude of attractive forces tends to decrease and the solution shows positive deviation from Raoult's Law. This will lead to increase in vapour pressure of the solution and also decrease in its boiling point.

**2.11. Why do gases always tend to be less soluble in liquids as the temperature is raised?**

**Sol:** When gases are dissolved in water, it is accompanied by a release of heat energy, i.e., process is exothermic. When the temperature is increased, according to Lechatlier's Principle, the equilibrium shifts in backward direction, and thus gases becomes less soluble in liquids.

**2.12. State Henry's law and mention some of its important applications.**

**Sol:**

**Henry's law:** The solubility of a gas in a liquid at a particular temperature is directly proportional to the pressure of the gas in equilibrium with the liquid at that temperature.

or

The partial pressure of a gas in vapour phase is proportional to the mole fraction of the gas (x) in the solution. $p = KHX$

where KH is Henry's law constant.

Applications of Henry's law :

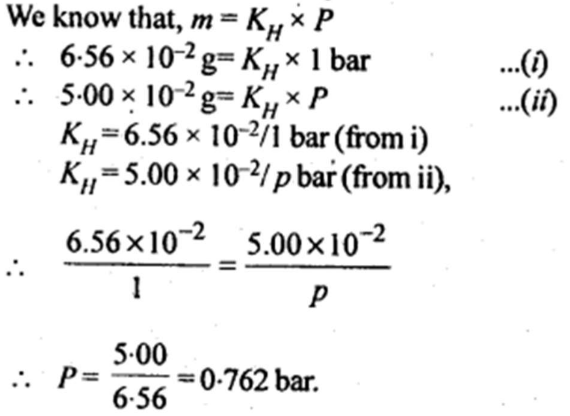
(i) In order to increase the solubility of $CO_2$ gas in soft drinks and soda water, the bottles are normally sealed under high pressure. Increase in pressure increases the solubility of a gas in a solvent according to Henry's Law. If the bottle is opened by removing the stopper or seal, the pressure on the surface of the gas will suddenly decrease. This will cause a decrease in the solubility of the gas in the liquid i.e. water. As a result, it will rush out of the bottle producing a hissing noise or with a fiz.

(ii) As pointed above, oxygen to be used by deep sea divers is generally diluted with helium inorder to reduce or minimise the painfril effects during decompression.

(iii) As the partial pressure of oxygen in air is high, in lungs it combines with haemoglobin to form oxyhaemoglobin. In tissues, the partial pressure of oxygen is comparatively low. Therefore, oxyhaemoglobin releases oxygen in order to carry out cellular activities.

**2.13. The partial pressure of ethane over a solution containing $6.56 \times 10^{-3}$ g of ethane is 1 bar. If the solution contains $5.00 \times 10^{-2}$ g of ethane, then what shall be the partial pressure of the gas?**

Sol:



We know that, $m = K_H \times P$

∴ $6{\cdot}56 \times 10^{-2}$ g $= K_H \times 1$ bar ...(i)

∴ $5{\cdot}00 \times 10^{-2}$ g $= K_H \times P$ ...(ii)

$K_H = 6.56 \times 10^{-2}/1$ bar (from i)

$K_H = 5.00 \times 10^{-2}/p$ bar (from ii),

$$\therefore \quad \frac{6.56\times10^{-2}}{1}=\frac{5.00\times10^{-2}}{p}$$

$$\therefore \quad P=\frac{5{\cdot}00}{6{\cdot}56}=0{\cdot}762 \text{ bar.}$$

**2.14. According to Raoult's law, what is meant by positive and negative deviaitions and how is the sign of $\Delta_{sol}H$ related to positive and negative deviations from Raoult's law?**

Sol: Solutions having vapour pressures more than that expected from Raoult's law are said to exhibit positive deviation. In these solutions solvent – solute interactions are weaker and $\Delta_{sol}H$ is positive because stronger A – A or B – B interactions are replaced by weaker A – B interactions. Breaking of the stronger interactions requires more energy & less energy is released on formation of weaker interactions. So overall $\Delta_{sol}$ H is positive. Similarly $\Delta_{sol}V$ is positive i.e. the volume of solution is some what more than sum of volumes of solvent and solute. So there is expansion in volume on solution formation.

Similarly in case of solutions exhibiting negative deviations, A – B interactions are stronger than A-A&B-B. So weaker interactions are replaced by stronger interactions so , there is release of energy i.e. $\Delta_{sol}$ H is negative.

2.15. An aqueous solution of 2 percent non-volatile solute exerts a pressure of 1·004 bar at the boiling point of the solvent. What is the molecular mass of the solute ?

Sol:

According to Raoult's Law,

$$\frac{P_A^\circ - P_S}{P_S} = \frac{n_B}{n_A} = \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

$P_A^\circ$ (for water) = 1·013 bar ; $P_S$ = 1·004 bar ; $W_B$ = 2g ; $W_A$ = 100 – 2 = 98 g ;
$M_A$ = 18 g mol$^{-1}$.

$$\frac{(1\cdot013 - 1\cdot004)\text{ bar}}{(1\cdot004\text{ bar})} = \frac{(2\text{ g}) \times (18\text{ g mol}^{-1})}{M_B \times (98\text{ g})}$$

$$\therefore \quad M_B = \frac{(2\text{ g}) \times (18\text{ g mol}^{-1}) \times (1\cdot004\text{ bar})}{(0\cdot009\text{ bar}) \times (98\text{ g})} = \mathbf{41\cdot0\ g\ mol^{-1}}$$

2.16 Heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35.0 g of octane?

Sol.

Molar mass of heptane ($C_7H_{16}$)
$= 7 \times 12 + 16 = 100\text{ g mol}^{-1}$
Molar mass of octane ($C_8H_{18}$)
$= 8 \times 12 + 18 = 114\text{ g mol}^{-1}$
Moles of heptane present in mixture

$$= \frac{26\cdot0}{100} = 0\cdot26\text{ mol}$$

Moles of octane present in mixture

$$= \frac{35\cdot0}{114} = 0\cdot307\text{ mol}$$

Mole fraction of heptane $x_H$

$$= \frac{0\cdot26}{0\cdot26 + 0\cdot307} = 0\cdot458$$

Mole fraction of octane, $x_O = (1 - 0\cdot458) = 0\cdot542$
Vapour pressure of heptane $= x_H \times P^\circ$
$= 0.458 \times 105.2\text{ kPa} = 48.18\text{ kPa}$
Vapour pressure of octane $= x_O \times P^\circ$
$= 0\cdot542 \times 46\cdot8\text{ kPa} = 25\cdot36\text{ kPa}$
Vapour pressure of mixture
$= 48\cdot18 + 25\cdot36 = 73\cdot54\text{ kPa}$

2.17. The vapour pressure of water is 12.3 kPa at 300 K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it

Sol: 1 molal solution of solute means 1 mole of solute in 1000g of the solvent.

Molar mass of water (solvent) = 18 g $mol^{-1}$

$$\therefore \text{Moles of water} = \frac{1000}{18} = 55{\cdot}5 \text{ moles.}$$

$$\therefore \text{Mole fraction of solute} = \frac{1}{1 + 55{\cdot}5} = 0{\cdot}0177$$

$$\text{Now, } \frac{P^\circ - P_s}{P^\circ} = x_2$$

$$\frac{12{\cdot}3 - P_s}{12{\cdot}3} = 0{\cdot}0177$$

$$\Rightarrow P_s = 12{\cdot}08 \text{ kPa}$$

2.18. Calculate the mass of a non-volatile solute (molecular mass 40 g $mol^{-1}$) that should be dissolved in 114 g of octane to reduce its pressure to 80%. (C.B.S.E. Outside Delhi 2008)

Sol: According to Raoult's Law,

$$\frac{P_A^\circ - P_S}{P_S} = \frac{n_B}{n_A} = \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

Let $P_A^\circ = 1$ atm, $P_S = 0{\cdot}8$ atm ; $P_A^\circ - P_S = 0{\cdot}2$ atm ; $M_B = 40$ g $mol^{-1}$; $W_A = 114$ g ; $M_A$ ($C_8H_{18}$) = 114 g $mol^{-1}$.

$$W_B = \frac{(P_A^\circ - P_S)}{P_S} \times \frac{M_B \times W_A}{M_A}$$

$$= \frac{(0\cdot 2 \text{ atm})}{(0\cdot 8 \text{ atm})} \times \frac{(40 \text{g mol}^{-1}) \times (114 \text{g})}{(114 \text{g mol}^{-1})} = \mathbf{10{\cdot}0 \text{ g}}.$$

2.19. A solution containing 30g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18g of water is then added to the solution and the new of vapour pressure becomes 2.9 kPa at 298 K. Calculate
(i) molar mass of the solute.
(ii) vapour pressure of water at 298 K.

**Sol:** Let the molar mass of solute = Mg mol$^{-1}$

∴ **Moles of solute present**

$$= \frac{30g}{M\,g\,mol^{-1}} = \frac{30}{M}\text{ mol}$$

**Moles of solvent present,** $(n_1) = \frac{90}{18} = 5$ **moles.**

$$\therefore \quad \frac{P^\circ - P_s}{P^\circ} = \frac{n_2}{n_1 + n_2}$$

$$\frac{P^\circ - 2{\cdot}8}{P^\circ} = \frac{30/M}{5 + 30/M}$$

$$1 - \frac{2{\cdot}8}{P^\circ} = \frac{30}{(5M + 30)}$$

$$1 - \frac{30}{5M + 30} = \frac{2{\cdot}8}{P^\circ}$$

$$1 - \frac{6}{M + 6} = \frac{2.8}{P^\circ}$$

$$\frac{M + 6 - 6}{M + 6} = \frac{2{\cdot}8}{P^\circ}$$

$$\frac{M}{M + 6} = \frac{2 \cdot 8}{P^\circ}$$

$$\frac{P^\circ}{2 \cdot 8} = 1 + \frac{6}{M} \qquad \ldots(i)$$

After adding 18 *g* of water,
Moles of water becomes

$$= \frac{90 + 18}{18} = \frac{108}{18} = 6 \text{ moles}$$

$$\therefore \quad \frac{P^\circ - P_s}{P^\circ} = \frac{30/M}{6 + 30/M}$$

$P_s$ New vapour pressure = 2·9 kPa

$$\frac{P^\circ - 2{\cdot}9}{P^\circ} = \frac{30\ M}{M\ (6M + 30)} = \frac{5}{M + 5}$$

$$1 - \frac{2{\cdot}9}{P^\circ} = \frac{5}{M + 5}$$

$$1 - \frac{5}{M + 5} = \frac{2{\cdot}9}{P^\circ}$$

$$\frac{M + 5 - 5}{M + 5} = \frac{2{\cdot}9}{P^\circ}$$

$$\frac{P^\circ}{2{\cdot}9} = \frac{M + 5}{M} \Rightarrow = 1 + \frac{5}{M}$$

$$\frac{P^\circ}{2{\cdot}9} = 1 + \frac{5}{M} \qquad ...(ii)$$

Dividing equation (*i*) by (*ii*), we get,

$$\frac{2\cdot 9}{2\cdot 8}=\frac{1+6/M}{1+5/M}$$

$$2\cdot 9\left(1+\frac{5}{M}\right)=2\cdot 8\left(1+\frac{6}{M}\right)$$

$$2\cdot 9+\frac{2\cdot 9\times 5}{M}=2\cdot 8+\frac{2\cdot 8\times 6}{M}$$

$$2\cdot 9+\frac{14\cdot 5}{M}=2\cdot 8+\frac{16\cdot 8}{M}$$

$$0\cdot 1=\frac{16\cdot 8}{M}-\frac{14\cdot 5}{M}=\frac{2\cdot 3}{M}$$

$$M=\frac{2\cdot 3}{0\cdot 1}$$

$M = 23\text{ g mol}^{-1}$

Putting M = 23, in equation (*i*), we get,

$$\frac{P^\circ}{2\cdot 8}=1+\frac{6}{23}=\frac{29}{23}$$

$$P^\circ=\frac{29}{23}\times 2\cdot 8=3\cdot 53\text{ kPa.}$$

2.20. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K. Calculate the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K.

Sol: Mass of sugar in 5% (by mass) solution means 5gin 100g of solvent (water)

Molar mass of sugar = $342\text{g mol}^{-1}$

Molality of sugar solution $=\frac{5\times 1000}{342\times 100}=0\cdot 146$

$\therefore \Delta T_f$ for sugar solution $= 273\cdot 15-271=2\cdot 15^\circ$

$\Delta T_f = K_f\times m$

$\Delta T_f = K_f\times 0.146 \Rightarrow K_f = 2\cdot 15/0\cdot 146$

Molality of glucose solution

$$=\frac{5}{180}\times\frac{1000}{100}=0.278$$

(Molar mass of glucose = $180\text{ g mol}^{-1}$)

$$\Delta T_f=K_f\times m=\frac{2\cdot 15}{0\cdot 146}\times 0\cdot 278=4\cdot 09^\circ$$

$\therefore$ Freezing point of glucose solution

$= 273\cdot 15-4\cdot 09=269\cdot 06\text{ K.}$

2.21. Two elements A and B form compounds having formula $AB_2$ and $AB_4$. When dissolved in 20g of benzene ($C_6H_6$), 1 g of $AB_2$ lowers the freezing point by 2.3 K whereas 1.0 g of $AB_4$ lowers it by 1.3 K. The molar depression constant for benzene is 5.1 K kg mol$^{-1}$. Calculate atomic masses of A and B.

Sol:

Using the relation, $M_2 = \dfrac{1000 \times k_f \times w_2}{w_1 \times \Delta T_f}$

$$\therefore \quad M_{AB_2} = \frac{1000 \times 5{\cdot}1 \times 1}{20 \times 2{\cdot}3} = 110{\cdot}87 \text{ g mol}^{-1}$$

$$M_{AB_4} = \frac{1000 \times 5{\cdot}1 \times 1}{20 \times 1{\cdot}3} = 196{\cdot}15 \text{ g mol}^{-1}$$

Let the atomic masses of *A* and *B* are 'p' and 'q' respectively.

Then molar mass of

$AB_2 = p + 2q = 110{\cdot}87 \text{ g mol}^{-1}$ ...(*i*)

And molar mass of

$AB_4 = p + 4q = 196{\cdot}15 \text{ g mol}^{-1}$ ...(*ii*)

Substracting equation (*ii*) from equation (*i*), we get $2q = 85.28 \Rightarrow q = 42.64$

Putting $q = 42.64$ in equ. (*i*), we get

$p = 110.87 - 85.28$

$p = 25.59$

Thus, atomic mass of $A = 25.59 \text{ g mol}^{-1}$ and atomic mass of $B = 42.64 \text{ g mol}^{-1}$

2.22. At 300 K, 36 g glucose present per litre in its solution has osmotic pressure of 4·98 bar. If the osmotic pressure of the solution is 1·52 bar at the same temperature, what would be its concentration?

Sol:

$$\pi = CRT = \frac{W_B \times R \times T}{M_B \times V}$$

For both the solutions, R, T and V are constants

**Ist case :** $$(4{\cdot}98 \text{ bar}) = \frac{(36 \text{ g}) \times R \times T}{(180 \text{ g mol}^{-1}) \times V}$$

**IInd case :** $$(1{\cdot}52 \text{ bar}) = \frac{W_B \times R \times T}{M_B \times V} \quad \ldots(ii)$$

Divide eqn. (*ii*) by eqn. (*i*),

$$\frac{(1{\cdot}52 \text{ bar})}{(4{\cdot}98 \text{ bar})} = \frac{W_B}{M_B} \times (5 \text{ mol})$$

or $$\frac{W_B}{M_B} = \frac{1{\cdot}52}{4{\cdot}98} \times \frac{1}{(5 \text{ mol})} = \mathbf{0{\cdot}0610 \text{ mol}^{-1}}$$

**2.23. Suggest the most important type of intermolecular attractive interaction in the following pairs:**

**(i) n-hexane and n-octane**

**(ii) $I_2$ and $CCl_4$.**

**(iii) $NaCl0_4$ and water**

**(iv) methanol and acetone**

**(v) acetonitrile ($CH_3CN$) and acetone ($C_3H_60$)**

Sol: (i) Both w-hexane and n-octane are non-polar. Thus, the intermolecular interactions will be London dispersion forces.

(ii) Both $I_2$ and $CCl_4$ are non-polar. Thus, the intermolecular interactions will be London dispersion forces.

(iii) $NaCl0_4$ is an ionic compound and gives $Na^+$ and $Cl0_4^-$ ions in the Solution. Water is a polar molecule. Thus, the intermolecular interactions will be ion-dipole interactions.

(iv) Both methanol and acetone are polar molecules. Thus, intermolecular interactions will be dipole-dipole interactions.

(v) Both $CH_3CN$ and $C_3H_6O$ are polar molecules. Thus, intermolecular interactions will be dipole-dipole interactions.

**2.24. Based on solute solvent interactions, arrange the following in order of increasing solubility in n-octane and explain. Cyclohexane, KCl, $CH_3OH$, $CH_3CN$.**

Sol: n-octane ($C_8H_{18}$) is a non-polar liquid and solubility is governed by the principle that like dissolve like. Keeping this in view, the increasing order of solubility of different solutes is:

$KCl < CH_3OH < CH_3C{=}N < C_6H_{12}$ (cyclohexane).

**2.25. Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water?**

**(i) phenol**

**(ii) toluene**

**(iii) formic acid**

**(iv) ethylene glycol**

**(v) chloroform**

**(vi) pentanol**

Sol: (i) Phenol (having polar – OH group) – Partially soluble.

(ii) Toluene (non-polar) – Insoluble.

(iii) Formic acid (form hydrogen bonds with water molecules) – Highly soluble.

(iv) Ethylene glycol (form hydrogen bonds with water molecules) Highly soluble.

(v) Chloroform (non-polar)- Insoluble.

(vi) Pentanol (having polar -OH) – Partially soluble.

2.26. If the density of lake water is 1·25 g mL-1, and it contains 92 g of $Na^+$ ions per kg of water, calculate the molality of $Na^+$ ions in the lake. (C.B.S.E. Outside Delhi 2008)

Sol:

$$\text{Molality of Na}^+ \text{ ions } (m) = \frac{\text{No. of moles of Na}^+ \text{ ions}}{\text{Mass of water in kg}}$$

$$= \frac{(92\,\text{g}) / (23\,\text{g mol}^{-1})}{1\,\text{kg}} = 4 \text{ mol kg}^{-1} = \mathbf{4\ m}$$

2.27. If the solubility product of CuS is 6 x $10^{-16}$, calculate the maximum molarity of CuS in aqueous solution.

Sol:

$CuS \rightleftharpoons Cu^{2+} + S^{2-}$, $K_{sp} = 6 \times 10^{-16}$

Maximum molarity of CuS in aqueous solution means solubility of CuS.

Let the solubility of CuS be $S$ mol $L^{-1}$

$\therefore \quad K_{sp} = [Cu^{2+}]\,[S]^{2-}$

$6 \times 10^{-16} = S \times S = S^2$

$\therefore S = \sqrt{6 \times 10^{-16}} = 2.45 \times 10^{-8}$ mol $L^{-1}$.

2.28. Calculate the mass percentage of aspirin ($C_9H_8O_4$ in acetonitrile ($CH_3CN$) when 6.5g of CHO is dissolved in 450 g of CH3CN.

Solution:

Mass of aspirin = 6.5 g

Mass of acetonitrile = 450 g

Then, total mass of the solution = (6.5 + 450) g = 456.5 g

Therefore, mass percentage of $C_9H_8O_4$ = 6.5456.5 × 100%

= 1.424%

2.29. Nalorphene ($C_{19}H_{21}NO_3$), similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the mass of 1.5 x $10^{-3}$ m aqueous solution required for the above dose.

Solution:

$1{\cdot}5 \times 10^{-3}$ m aqueous solution of nalorphene means that $1{\cdot}5 \times 10^{-3}$ mole of nalorphene is dissolved in 1 kg of water.

Molar mass of nalorphene, $C_{19}H_{21}NO_3$

$= 19 \times 12 + 21 + 14 + 3 \times 16 = 311 \text{ g mol}^{-1}$

$\therefore$ $1{\cdot}5 \times 10^{-3}$ mole of nalorphene

$= 1{\cdot}5 \times 10^{-3} \times 311 \text{g} = 0{\cdot}467 \text{ g}$

$\therefore$ Mass of solution $= 0{\cdot}467 + 1000 = 1000{\cdot}467$ g.

For 0·467g of nalorphene, mass of solution required = 1000·467g

For 1·5 mg ($1{\cdot}5 \times 10^{-3}$g) of nalorphene, mass of solution required

$$= \frac{1000{\cdot}467}{0{\cdot}467} \times 1{\cdot}5 \times 10^{-3} = 3{\cdot}21\text{g}.$$

2.30. Calculate the amount of benzoic acid ($C_5H_5COOH$) required for preparing 250 mL of 0· 15 M solution in methanol.

Solution:

$$\text{Molarity (M)} = \frac{\text{Mass of solute/molar mass}}{\text{Volume of solution in litres}}$$

$$\text{M} = 0{\cdot}15 \text{ M} = 0{\cdot}15 \text{ mol L}^{-1}\ ;$$

$$\text{Molar mass of solute} = 7 \times 12 + 6 \times 1 \times 2 \times 16 = 122 \text{ g mol}^{-1};$$

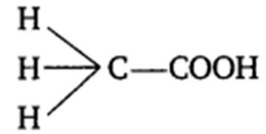
$$\text{Volume of solution} = 250 \text{ mL} = 0{\cdot}25 \text{ L}.$$

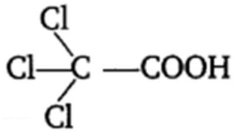
$$(0{\cdot}15 \text{ mol L}^{-1}) = \frac{\text{Mass of solute}}{(122 \text{ g mol}^{-1}) \times (0{\cdot}25\text{L})}$$

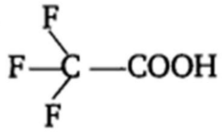
$$\text{Mass of solute} = (0{\cdot}15 \text{ mol L}^{-1}) \times (122 \text{ g mol}^{-1}) \times (0{\cdot}25 \text{ L}) = \mathbf{4{\cdot}575 \text{ g}}$$

2.31. The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.

Solution:


Acetic acid


Trichloroacetic acid


Trifluoroacetic acid

Fluorine being more electronegative than chlorine has the highest electron withdrawing inductive effect. Thus, triflouroacetic acid is the strongest trichloroacetic acid is second most and acetic acid is the weakest acid due to absence of any electron withdrawing group. Thus, $F_3CCOOH$ ionizes to the largest extent while $CH_3COOH$ ionizes to minimum extent in water. Greater the extent of ionization greater is the depression in freezing point. Hence, the order of depression in freezing point will be $CH_3COOH < Cl_3CCOOH < F_3CCOOH$.

**2.32. Calculate the depression in the freezing point of water when 10g of $CH_3CH_2CHClCOOH$ is added to 250g of water. Ka = 1.4 x 1o$^{-3}$ Kg = 1.86 K kg mol$^{-1}$.**

**Solution:**

Mass of solute ($CH_3CH_2CHClCOOH$) = 10 g

Molar mass of

$CH_3CH_2CHClC00H = 4 \times 12 + 7 \times 1 + 1 \times 35.5 + 2 \times 16 = 48 + 7 + 35.5 + 32$

$= 122.5$ g mol$^{-1}$

\frac{\text { Mass / Molar mass }}{\text { Mass of solvent (Kg) }} = Mass / Molar mass Mass of solvent (Kg) [latex/latex]=[latex]10 g(122.5 g mol−1)×(0.25Kg) = 0.326 m

Let α be the degree of dissociation of $CH_3CH_2CHClCOOH$ then

$$CH_3CH_2CHClCOOH \rightleftharpoons CH_3CH_2CHClCOO^- + H^+$$

| | | | |
|---|---|---|---|
| Initial conc. | C mol$^{-1}$ Kg | 0 | 0 |
| At equilibrium | C (1 − α) | Cα | Cα |

$$\therefore \quad K_a = \frac{C\alpha . C\alpha}{C(1-\alpha)}$$

$$= \frac{C\alpha^2}{1-\alpha} \quad [\because \text{considering } (1-\alpha) = 1 \text{ for dilute solution}]$$

$$\text{Now,} \quad K_a = \frac{C\alpha^2}{1}$$

$$\Rightarrow \quad K_a = C\alpha^2$$

$$\Rightarrow \quad \alpha = \sqrt{\frac{K_a}{C}}$$

$$= \sqrt{\frac{1.4 \times 10^{-3}}{0.326}} \qquad (\because K_a = 1.4 \times 10^{-3})$$

$$= 0.0655$$

$$CH_3CH_2CHClCOOH \rightleftharpoons CH_3CH_2CHClCOO^- + H^+$$

| | | | |
|---|---|---|---|
| Initial no. of moles | 1 | 0 | 0 |
| At equilibrium | 1 − α | α | α |

Total no. of moles after dissociation = 1 – α + α + α

= 1 + α

Van't Hoff factor

Total no. of moles after dissociation

$$(i) = \frac{\text{Total no. of moles after dissociation}}{\text{No. of moles before dissociation}}$$

$\therefore i = 1+\alpha 1$
$= 1 + \alpha$
$= 1 + 0.0655$
$= 1.0655$
Hence, the depression in the freezing point of water is given as:
$\Delta T_f = i.K_f m$
$= 1.0655 \times 1.86 \text{ kg mol}^{-1} \times 0.326 \text{ mol kg}^{-1}$
$= 0.65K$

**2.33. 19.5g of $CH_2FCOOH$ is dissolved in 500g of water. The depression in the freezing point of water observed is 1.0°C. Calculate the van's Hoff factor and dissociation constant of fluoroacetic acid.**

**Solution:**

Calculation of Van't Hoff factor (i)
Given, $w_1 = 500 \text{ g} = 0.5 \text{ kg}$, $w_2 = 19.5 \text{ g}$, $K_f = 1.86 \text{ K kg mol}^{-1}$, $\Delta T_f = 1 \text{ K}$
Molar mass of $CH_2FCOOH$ ($M_2$)
$= 2 \times 12 + 3 \times 1 + 1 \times 19 + 2 \times 16$
$= 24 + 3 + 19 + 32$
$= 78 \text{ g mol}^{-1}$
$\Delta T_f = i \, K_f \, m$

$$i = \frac{\Delta T_f}{K_f m} \qquad \text{...(i)}$$

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

$$= \frac{19.5\text{ g}}{(78\text{ g mol}^{-1}) \times (0.5\text{ kg})}$$

$$= 0.5\ \text{mol kg}^{-1} \qquad \text{...(ii)}$$

From eq. (i), we get

$$i = \frac{1}{(1.86\text{ K kg mol}^{-1}) \times (0.5\text{ mol kg}^{-1})}$$

$$= 1.0753$$

**Calculation of dissociation constant, $K_a$**

Let $\alpha$ be the degree of dissociation of $CH_2FCOOH$ then

$$CH_2FCOOH \rightleftharpoons CH_2FCOO^- + H^+$$

| | $CH_2FCOOH$ | $CH_2FCOO^-$ | $H^+$ |
|---|---|---|---|
| Initial conc. | $C$ mol $L^{-1}$ | 0 | 0 |
| At equilibrium | $C(1-\alpha)$ | $C\alpha$ | $C\alpha$ |

Total = $C(1+\alpha)$

$$\therefore \qquad i = \frac{C(1+\alpha)}{C}$$

$$\Rightarrow \qquad i = 1 + \alpha$$

$$\Rightarrow \qquad \alpha = i - 1$$

$$= 1.0753 - 1$$
$$= 0.0753$$

Now, $$K_a = \frac{[CH_2FCOO^-][H^+]}{[CH_2FCOOH]}$$
$$= \frac{C\alpha . C\alpha}{C(1-\alpha)}$$
$$= \frac{C\alpha^2}{1-\alpha}$$

Taking the volume of the solution as 500 mL, we have the concentration :

$$C = \frac{\frac{19.5}{78}}{500} \times 1000 \text{ M}$$
$$= 0.5 \text{ M}$$

Therefore, $$K_a = \frac{C\alpha^2}{1-\alpha}$$
$$= \frac{0.5 \times (0.0753)^2}{1 - 0.0753}$$
$$= \frac{0.5 \times 0.00567}{0.9247}$$
$$= 0.00307$$
$$= 3.07 \times 10^{-3}$$

2.34. Vapour pressure of water at 293 K is 17·535 mm Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water.

Solution:

According to Raoult's Law,

$$\frac{P_A^\circ - P_S}{P_S} = \frac{n_B}{n_A} \text{ or } \frac{P_A^\circ}{P_S} - 1 = \frac{n_B}{n_A}$$

$$\frac{P_A^\circ}{P_S} = 1 + \frac{n_B}{n_A} = 1 + \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

$W_B = 25$ g ; $W_A = 450$ g ; $M_B = 180$ g mol$^{-1}$ ;

$M_A = 18$ g mol$^{-1}$; $P_A^\circ = 17{\cdot}535$ mm

$$\frac{P_A^\circ}{P_S} = 1 + \frac{(25\text{g}) \times (18\text{g mol}^{-1})}{(180\text{g mol}^{-1}) \times (450\text{g})} = 1 + 0{\cdot}0055 = 1{\cdot}0055$$

$$P_S(\text{V.P of water in solution}) = \frac{(17{\cdot}535\text{mm})}{(1{\cdot}0055)} = \mathbf{17{\cdot}44\ mm}$$

**2.35. Henry's law constant for the molality of methane in benzene at 298 K is 4.27 x $10^5$ mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.**

Solution:

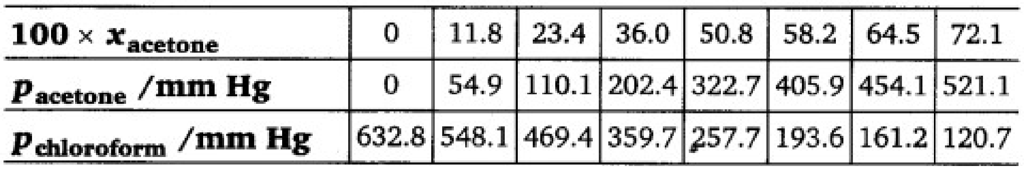
Here, p = 760 mm Hg, $K_H = 4.27 \times 10^5$ mm Hg (at 298 K)
According to Henry's law, p = $K_{H\chi}$
χ = pkH
= 760 mmHg4.27×105 mmHg
= $177.99 \times 10^{-5}$
= $178 \times 10^{-5}$
Hence, the mole fraction of methane in benzene is $178 \times 10^{-5}$.

**2.36. 100g of liquid A (molar mass 140 g $mol^{-1}$) was dissolved in 1000g of liquid B (molar mass 180g $mol^{-1}$). The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 torr.**

Solution:

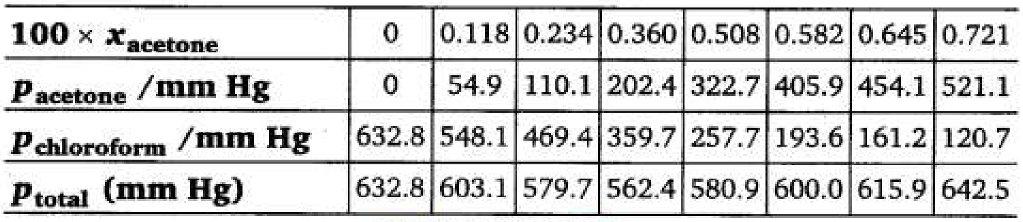
Number of moles of liquid A, $n_A$ = w1M1 = 100140 mol = 0.714 mol
Number of moles of liquid B,$n_B$ = w2M2 = 1000180 mol = 5.556 mol
Then, mole fraction of A, $\chi_A$ = nAnA+nB
= 0.714 mol(0.714+5.556)mol = 0.114
Mole fraction of B, $\chi_B$ = 1 – 0.114 = 0.886
Vapour pressure of pure liquid B, p0B = 500 torr
Therefore, vapour pressure of liquid B in the solution,
$P_B$ = p0B$\chi_B$
= 500 × 0.886
= 443 torr
Total vapour pressure of the solution, $p_{total}$ = 475 torr
∴ Vapour pressure of liquid A in the solution,
$P_A = P_{total} - P_B$
= 475 – 443 = 32 torr
Now, $P_A$ = p0A$\chi_A$
⇒ pAχA = 320.114
= 280.7 torr
Hence, the vapour pressure of pure liquid A is 280.7 torr.

**2.37. Vapour pressures of pure acetone and chloroform at 328 K are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition, plot $P_{total}$, $P_{chlroform}$ and $P_{acetone}$ as a function of $\chi_{acetone}$. The experimental data observed for different compositions of mixtures is:**

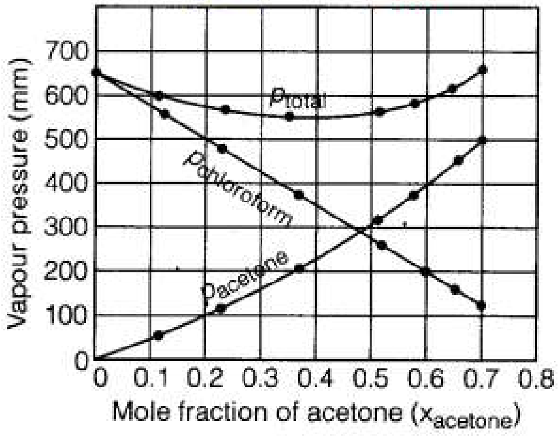


| $100 \times x_{acetone}$ | 0 | 11.8 | 23.4 | 36.0 | 50.8 | 58.2 | 64.5 | 72.1 |
|---|---|---|---|---|---|---|---|---|
| $p_{acetone}$ /mm Hg | 0 | 54.9 | 110.1 | 202.4 | 322.7 | 405.9 | 454.1 | 521.1 |
| $p_{chloroform}$ /mm Hg | 632.8 | 548.1 | 469.4 | 359.7 | 257.7 | 193.6 | 161.2 | 120.7 |

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



| $100 \times x_{acetone}$ | 0 | 0.118 | 0.234 | 0.360 | 0.508 | 0.582 | 0.645 | 0.721 |
|---|---|---|---|---|---|---|---|---|
| $p_{acetone}$ /mm Hg | 0 | 54.9 | 110.1 | 202.4 | 322.7 | 405.9 | 454.1 | 521.1 |
| $p_{chloroform}$ /mm Hg | 632.8 | 548.1 | 469.4 | 359.7 | 257.7 | 193.6 | 161.2 | 120.7 |
| $p_{total}$ (mm Hg) | 632.8 | 603.1 | 579.7 | 562.4 | 580.9 | 600.0 | 615.9 | 642.5 |



It can be observed from the graph that the plot for the ptotai of the solution curves downwards. Therefore, the solution shows negative deviation from the ideal behaviour.

2.38. Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and toluene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80g of benzene is mixed with 100g of toluene.
Solution:
Molar mass of benzene ($C_6H_6$) = 6 × 12 + 6 × 1 = 78g $mol^{-1}$
Molar mass of toluene ($C_6H_5CH_3$ ) = 7 × 12 + 8 × 1 = 92 g $mol^{-1}$
No. of moles present in 80 g of benzene = 8078 mol = 1.026 mol
No. of moles present in 100 g of toluene = 10092 mol = 1.087 mol
Mole fraction of benzene, $\chi_{C6H6}$, = 1.0261.026+1.087 = 0.486
∴ Mole fraction of toluene,$\chi_{C6H5CH3}$5013 = 1 – 0.486 = 0.514
It is given that vapour pressure of pure benzene, p0C6H6 = 50.71 mm Hg
Vapour pressure of pure toluene, p0C6H5CH3 = 32.06 mm Hg

Therefore, partial vapour pressure of benzene,
$P_{total} = \chi_{C6H6} \times$ p0C6H6
= 0.486 × 50.71
= 24.645 mm Hg
Partial vapour pressure of toluene, $P_{C6H5CH3} = \chi_{C6H5CH3} \times$ P0C6H5CH3
= 0.514 × 32.06
= 16.479 mm Hg
Total vapour pressure of solution (p) = 24.645 + 16.479
= 41.124 mm Hg
Mole fraction of benzene in vapour phase
= χC6H6×p0C6H6ptotal
= 0.486×(50.71)mm(41.124)mm
= 0.599 ≅ 0.6

**2.39. The air is a mixture of a number of gases. The major components are oxygen and nitrogen with an approximate proportion of 20% is to 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K if Henry's law constants for oxygen and nitrogen are 3.30 x $10^7$ mm and 6.51 x $10^7$ mm respectively, calculate the composition of these gases in water.**

**Solution:**

Percentage of oxygen ($O_2$) in air = 20%
Percentage of nitrogen ($N_2$) in air = 79%
Also, it is given that water is in equilibrium with air at a total pressure of 10 atm that is, (10 × 760) mm = 7600 mm
Therefore, partial pressure of oxygen,
$PO_2$ = 20100 x 7600 mm
= 1520 mm Hg
Partial pressure of nitrogen, $pN_2$ = 79100 x 7600 mm
= 6004 mm Hg
Now, according to Henry's law,
$p = K_{H.\chi}$
For oxygen:

$$p_{O_2} = K_H \cdot \chi_{O_2}$$

$$\Rightarrow \qquad \chi_{O_2} = \frac{p_{O_2}}{K_H}$$

$$= \frac{1520 \text{ mm}}{3.30 \times 10^7 \text{ mm}}$$

$$= 4.61 \times 10^{-5}$$

$$(\text{Given } K_H = 3.30 \times 10^7 \text{ mm})$$

**For nitrogen :**

$$p_{N_2} = K_H \cdot \chi_{N_2}$$

$$\Rightarrow \qquad \chi_{N_2} = \frac{p_{N_2,}}{K_H}$$

6004 mm6.51×107 mm

(Given $K_H = 6.51 \times 10^7$ mm)

$= 9.22 \times 10^{-5}$

Hence, the mole fractions of oxygen and nitrogen in water are $4.61 \times 10^{-5}$ and $9.22 \times 10^{-5}$ respectively.

**2.40. Determine the amount of $CaCl_2$ (i = 2.47) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27°C.**

Solution:

We know that,

$\pi = i\,RT$

$\Rightarrow \pi = i\,RT$

$\Rightarrow w =$

Given,

$\pi = 0.75$ atm

$V = 2.5L$

$i = 2.47$

$T = (27 + 273)K = 300K$

$R = 0.0821 \text{ L atm } K^{-1} mol^{-}$

Molar mass of $CaCl_2(M) = 1 \times 40 + 2 \times 35.5 = 111 \text{ g mol}^{-1}$

Therefore, w = 0.75×111×2.52.47×0.0821×300 = 3.42g

Hence the required amount of $CaCl_2$ is3.42g

**2.41. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of $K_2SO_4$ in 2 litre of water at 25°C, assuming that it is completely dissociated. (C.B.S.E. 2013)**

Solution:

Step I. Calculation of Van't Hoff factor (i)

$K_2SO_4$ dissociates in water as :

$$K_2SO_4 \xrightarrow{(aq)} 2K^+(aq) + SO_4^{2-}(aq) \ ; \ \alpha = \frac{i-1}{n-1}$$

$$\alpha(\text{for complete dissociation}) = 1, n = 3 \ ; \ 1 = \frac{i-1}{3-1} \text{ or } i = 2 + 1 = 3$$

**Step II.** *Calculation of osmotic pressure* ($\pi$)

$$\text{Osmotic pressure } (\pi) = i\,C\,R\,T = \frac{i\,W_B\,RT}{M_B \times V}$$

$i = 3$ ; $W_B = 25$ mg $= 0{\cdot}025$ g ; $M_B = 2\times 39 + 32 + 4 \times 16 = 174$ g mol$^{-1}$; V = 2L ; T = 25°C = 298 K ;
R = 0·0821 L atm K$^{-1}$mol$^{-1}$

$$\pi = \frac{(3) \times (0{\cdot}025\text{g}) \times (0{\cdot}0821 \text{ L atm K}^{-1}\text{ mol}^{-1}) \times (298\text{K})}{(174 \text{ g mol}^{-1}) \times (2\text{L})}$$

$$= \mathbf{5{\cdot}27 \times 10^{-3}} \textbf{ atm.}$$

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