

Chapter: Solutions

Intext Questions

Question 2.1

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

$$\begin{aligned}
 C_6H_6 \text{ mass percentage} &= \frac{\text{Mass of } C_6H_6}{\text{Total mass of the solution}} \times 100\% \\
 &= \frac{\text{Mass of } C_6H_6}{\text{Total mass of the solution}} \times 100\% \\
 &= \frac{22}{22+122} \times 100\% \\
 &= 15.28\%
 \end{aligned}$$

$$\begin{aligned}
 CCl_4 \text{ mass percentage} &= \frac{\text{Mass of } CCl_4}{\text{Total mass of the solution}} \times 100\% \\
 &= \frac{\text{Mass of } CCl_4}{\text{mass of } C_6H_6 + \text{Mass of } CCl_4} \times 100\% \\
 &= \frac{122}{22+122} \times 100\%
 \end{aligned}$$

On the other hand,

$$\begin{aligned}
 CCl_4 \text{ mass percentage} \\
 CCl_4 &= (100 - 15.28)\% \\
 &= 84.72\%
 \end{aligned}$$

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

Ans. Let the solution's total mass be 100g and the mass of benzene be 30g .

Carbon tetrachloride mass

$$\begin{aligned}
 &= (100 - 30) \\
 &= 70\text{g}
 \end{aligned}$$

Benzene's molar mass

$$\begin{aligned}
 (C_6H_6) &= (6 \times 12 + 6 \times 1) \text{ g mol}^{-1} \\
 &= 78 \text{ g mol}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \text{The number of } CCl_4 \text{ moles} &= \frac{70}{154} \text{ mol} \\
 &= 0.4545 \text{ mol}
 \end{aligned}$$

As a result, the mole fraction of C_6H_6 is:

$$\begin{aligned}
 &\frac{\text{Number of moles of } C_6H_6}{\text{Number of moles of } C_6H_6 + \text{Number of moles of } CCl_4} \\
 &= \frac{0.3846}{0.3846 + 0.4545} \\
 &= 0.458
 \end{aligned}$$

2.3 Calculate the molarity of each of the following solutions:

(a) 30g of $Co(NO_3)_2 \cdot 6H_2O$ in 4.3 l of solution

(b) 30ml of 0.5 M H_2SO_4 diluted to 500 ml.

Ans. Molarity is determined by:

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

(a) Molarity of the mass

$$\begin{aligned}
 Co(NO_3)_2 \cdot 6H_2O &= 59 + 2(14 + 3 \times 16) + 6 \times 18 \\
 &= 291 \text{ g mol}^{-1}
 \end{aligned}$$

$$Co(NO_3)_2 \cdot 6H_2O = \frac{30}{291} \text{ mol}$$

As a result, Moles of = 0.103 mol

Hence, the molarity is

$$\begin{aligned}
 &= \frac{0.015}{0.5 \text{ L}} \text{ mol} \\
 &= \frac{0.015}{0.5 \text{ L}} \text{ mol} \\
 &= 0.03 \text{ M}
 \end{aligned}$$

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

Ans. The urea molar mass

$$\begin{aligned}
 (\text{NH}_2\text{CONH}_2) &= 2(1 \times 14 + 2 \times 1) + 1 \times 12 + 1 \times 16 \\
 &= 60 \text{ g mol}^{-1}
 \end{aligned}$$

A 0.25 molar urea aqueous solution equals:

0.25 mol of sodium chloride is present in 1000 g of water = (0.25×60) g of urea = 15 g of urea.

15 g of urea is present in 1000 + 15 g of solution.

As a result, 2.5 kg (2500 g) of solution

$$\begin{aligned}
 &= \frac{15 \times 2500}{1000 + 15} \text{ g} \\
 &= 36.95 \text{ g} \\
 &= 37 \text{ g of urea}
 \end{aligned}$$

As a result, the needed urea mass is 37 g .

2.5 Calculate (a) molality (b) molarity and (c) mole fraction of KI if the density of 20% (mass/mass) aqueous KI is 1.202 g mL^{-1}

Ans. (a) KI's molar mass = $\text{KI} = 39 + 127 = 166 \text{ g mol}^{-1}$

A 20% (mass/mass) aqueous solution of KI means there are 20 g of KI in 100 g of solution.

That is, there are 20 g of KI in 100 g of water. = 80 g of water

As a result, the molality of the solution is important.

$$\begin{aligned}
 &= \frac{\text{Moles of KI}}{\text{Mass of water in kg}} \\
 &= \frac{20}{166} \text{ m} \\
 &= 0.08 \text{ m} \\
 &= 1.506 \text{ m} \\
 &= 1.51
 \end{aligned}$$

(b) The density of the solution is assumed = 1.202 g mL^{-1}

$$100 \text{ g solution volume} = \frac{\text{Mass}}{\text{Density}}$$

$$\begin{aligned}
 &= \frac{100 \text{ g}}{1.202 \text{ g mL}^{-1}} \\
 &= 83.19 \text{ mL} \\
 &= 83.19 \times 10^{-3} \text{ L}
 \end{aligned}$$

As a result, the molarity of the solution is important.

$$\begin{aligned}
 &= \frac{\frac{20}{166} \text{ mol}}{83.19 \times 10^{-3} \text{ L}} \\
 &= 1.45 \text{ M}
 \end{aligned}$$

(c) KI's moles

The water moles

Hence,

$$\begin{aligned}
 &= \frac{20}{166} = 0.12 \text{ mol} \\
 &= \frac{0.12}{0.12 + 4.44} \\
 &= \frac{80}{18} = 4.44 \text{ mol}
 \end{aligned}$$

2.6 H_2S , 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. H_2S has a solubility of 0.195 m in water at STP, which means that 0.195 mol of H_2S is dissolved in 1000 g of water.

The water moles

$$\begin{aligned}
 &= \frac{1000 \text{ g}}{18 \text{ g mol}^{-1}} \\
 &= 55.56 \text{ mol}
 \end{aligned}$$

H_2S mole fraction

$$\begin{aligned}
 &= \frac{\text{Moles of } \text{H}_2\text{S}}{\text{Moles of } \text{H}_2\text{S} + \text{Moles of water}} \\
 &= \frac{0.195}{0.195 + 55.56} \\
 &= 0.0035
 \end{aligned}$$

Pressure (p) = 0.987 bar at STP

The following is Henry's law:

$$K_H X$$

$$K_H = \frac{P}{x}$$

$$\frac{0.987}{0.0035} \text{ bar}$$

$$= 282 \text{ bar}$$

2.7 Henry's law constant for CO_2 in water is $1.67 \times 10^8 \text{ Pa}$ 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. Given

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

$$P_{\text{CO}_2} = 2.5 \text{ atm} = 2.5 \times 1.01325 \times 10^5 \text{ Pa}$$

$$= 2.533125 \times 10^5 \text{ pa}$$

Henry's law

$$P_{\text{CO}_2} = K_H x$$

$$= x = \frac{P_{\text{CO}_2}}{K_H}$$

$$= \frac{2.533125 \times 10^5}{1.67 \times 10^8}$$

$$= 0.00152$$

Can also be written as

$$x = \frac{n_{\text{CO}_2}}{n_{\text{CO}_2} + n_{\text{H}_2\text{O}}} \approx \frac{n_{\text{CO}_2}}{n_{\text{H}_2\text{O}}}$$

n_{CO_2} is insignificant in comparison to $n_{\text{H}_2\text{O}}$

We might write: [Neglecting the amount of soda present] The volume of water in 500 mL of soda water = 500 mL

500 mL water = 500 g water

$$= \frac{500}{18} \text{ moles of water}$$

27.78 mol

Here,

$$\frac{n_{\text{CO}_2}}{n_{\text{H}_2\text{O}}} = x$$

$$\frac{n_{\text{CO}_2}}{27.78} = 0.00152$$

$$n_{\text{CO}_2} = 0.042 \text{ mol}$$

As a result, the amount of CO_2 in 500 mL of soda water

$$= (0.042 \times 44) \text{g}$$

$$= 1.848 \text{ g}$$

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

Ans. Given

$$p_A^0 = 450 \text{ mm of Hg}$$

$$p_B^0 = 700 \text{ mm of Hg}$$

$$p_{\text{total}} = 600 \text{ mm of Hg}$$

$$p_A = p_A^0 x_A$$

$$p_B = p_B^0 x_B = p_B^0 (1 - x_A)$$

Hence, the total pressure

$$p_{\text{total}} = p_A + p_B$$

$$x_B = 1 - x_A$$

From Raoult's law, we get

$$p_{\text{total}} = p_A^0 x_A + p_B^0 (1 - x_A)$$

$$p_{\text{total}} = p_A^0 x_A + p_B^0 - p_A^0 x_A$$

$$p_{\text{total}} = p_{\text{total}} = (p_A^0 - p_B^0) x_A + p_B^0$$

$$\Rightarrow 600 = (450 - 700) x_A + 700$$

$$\Rightarrow -100 = -250 x_A$$

$$\Rightarrow x_A = 0.4$$

As a result,

$$= 1 - 0.4$$

$$= 0.6$$

Here,

$$\begin{aligned}
 p_A &= p_A^0 x_A \\
 &= 450 \times 0.4 = 180 \text{ mm of Hg}
 \end{aligned}$$

$$\begin{aligned}
 p_B &= p_B^0 x_B \\
 &= 700 \times 0.6 \\
 &= 420 \text{ mm of Hg}
 \end{aligned}$$

Now we're in the vapour phase: liquid A mole fraction

$$\begin{aligned}
 &= \frac{p_A}{p_A + p_B} \\
 &= \frac{180}{180 + 420} \\
 &= \frac{180}{600} \\
 &= 0.30
 \end{aligned}$$

In addition, the mole fraction of liquid

$$\begin{aligned}
 B &= 1 - 0.30 \\
 &= 0.70
 \end{aligned}$$

2.9 Vapour pressure of pure water at 298 K is 23.8 mm 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. It is assumed that the vapour pressure of water is equal to 23.8 mm Hg.

Water taken in weight, $w_1 = 850\text{g}$

Taken urea weight, $w_2 = 50\text{g}$

Water's molecular weight, $M_1 = 18 \text{ g mol}^{-1}$

Urea molecular weight, $M_2 = 60 \text{ g mol}^{-1}$

We must now determine the vapour pressure of water in the solution. We use p_1 to represent vapour pressure.

As a result of Raoult's law, we now have:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2}$$

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{\frac{w_2}{M_2}}{\frac{w_1}{M_1} + \frac{w_2}{M_2}}$$

$$= \frac{23.8 - p_1}{23.8} = \frac{\frac{50}{60}}{\frac{850}{18} + \frac{50}{60}}$$

$$= \frac{23.8 - p_1}{23.8} = \frac{0.83}{47.22 + 0.83}$$

$$= \frac{23.8 - p_1}{23.8} = 0.0173$$

$$p_1 = 23.4 \text{ mm of Hg}$$

As a result, the water vapour pressure in the provided solution is 23.4 mm of Hg, with a relative lowering of 0.0173.

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. Molal elevation constant for water is 0.52 K kg mol⁻¹.

Ans. The boiling point is raised in this case.

$$\Delta T_b = (100 + 273) - (99.63 + 273)$$

$$= 0.37 \text{ K}$$

$$\text{Water volume} = w_1 = 500 \text{ g}$$

$$\text{Sucrose molar mass } (C_{12}H_{22}O_{11}), M_2 = 12 \times 12 + 22 \times 1 + 11 \times 16$$

$$= 342 \text{ g mol}^{-1}$$

$$\text{Constant of molal elevation } K_b = 0.52 \text{ k kg mol}^{-1}$$

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

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

$$= \frac{0.37 \times 342 \times 500}{0.52 \times 1000}$$

$$= 121.67 \text{ g}$$

As a result, 121.67 g of sucrose must be supplied.

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 $1.5^\circ C$. $K_f = 3.9 K Kg mol^{-1}$.

Ans. The amount of acetic acid in a certain volume, $w_1 = 75 g$

Ascorbic acid molar mass, $C_6H_8O_6$

$$M_2 = 6 \times 12 + 8 \times 1 + 6 \times 16$$

$$= 176 g mol^{-1}$$

Melting point reduction, here, $\Delta T_f = 1.5 K$

As we know that,

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

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

$$= \frac{1.5 \times 176 \times 75}{3.9 \times 1000}$$

$$= 5.08 g$$

As a result, 5.08 g of ascorbic acid must be dissolved.

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 $37^\circ C$.

Ans. Given

Amount of water = $V = 450 mL = 0.45$

Temperature, $T = (37 + 273) K = 310 K$

The number of polymer moles, $n = \frac{1}{185000} mol$

As we know that,

Osmotic pressure,

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

$$= \frac{1}{185000} mol \times \frac{1}{0.45} \times 8.314 \times 10^3 Pa L K^{-1} mol^{-1} \times 310 K$$

$$= 30.98 Pa$$

$$= 31 Pa$$

Example solutions

(i) Mass percentage (w/w): The mass percentage of a component of a solution is defined as:

Mass % of a component

$$= \frac{\text{Mass of the component in the solution}}{\text{Total \% of a component}} \times 100$$

If a solution is characterised as containing 10% glucose in water by mass, it indicates that 10 g of glucose is dissolved in 90 g of water, yielding a 100 g solution. In industrial chemical applications, mass percentage concentration is widely employed. Commercial bleaching solutions, for example, comprise 3.62 mass percent sodium hypochlorite in water.

(ii) Volume percentage (V/V): The volume percentage is defined as:

$$\text{Volume \% of a component} = \frac{\text{Volume of the component}}{\text{Total volume of a solution}} \times 100$$

For example, a ten percent ethanol solution in water means that ten millilitres of ethanol are dissolved in one hundred millilitres of water. This unit is widely used to express liquid-based solutions. In autos, for instance, a 35 percent (v/v) solution of ethylene glycol, an antifreeze, is used to keep the engine cool.

The antifreeze reduces the freezing point of water to 255.4K (−17.6°C) at this concentration.

(iii) Mass by volume % (w/V): Mass by volume percentage is another unit often used in medicine and pharmacy. It refers to the amount of solute dissolved in 100 millilitres of solution.

(iv) Parts of a million: When a solute is present in trace amounts, the concentration is expressed in parts per million (ppm), which is defined as:

$$\text{Parts per million} = \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 100$$

Concentration in parts per million can be expressed as mass to mass, volume to volume, or mass to volume, just as it can be stated as a percentage. The dissolved oxygen (O_2) content of a litre of sea water (weighing 1030 g) is around 6 10^{-3} g. 5.8 g per 106 g (5.8 ppm) of sea water is another way to indicate such a low concentration. Pollutant concentrations in water or the atmosphere are frequently reported in terms of g mL^{-1} or ppm.

(v) portion of a molecule: The common symbol for mole fraction is x , and the component is denoted by the subscript on the right-hand side of x .

It is defined as follows:

$$\text{Mole fraction of a component} = \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}}$$

If the amount of moles of A and B in a binary mixture is n_A and n_B , respectively, the mole fraction of A will be

$$x_A = \frac{n_A}{n_A + n_B}$$

We have the following for a solution with a certain number of components:

$$x_1 = \frac{n_1}{n_1 + n_2 + \dots + n_i} = \frac{n_1}{\sum n_i}$$

It can be proven that the total of all mole fractions in each solution equals unity, i.e.

$$x_1 + x_2 + \dots + x_i = 1$$

The mole fraction unit is extremely useful for linking some physical properties of solutions, such as vapour pressure to solution concentration, and for illustrating calculations involving gas mixtures.

Examples

Example 2.1 Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in a solution containing 20% of $C_2H_6O_2$ by mass.

Ans. Assume that we have 100 g of solution (any amount of solution will get the same results). Ethylene glycol (20 g) and water (80 g) will be in the solution.

Molar mass of ($C_2H_6O_2$) = $12 \times 2 + 1 \times 6 + 16 \times 2 = 62 \text{ g mol}^{-1}$.

$$\text{Moles of } C_2H_6O_2 = \frac{20\text{g}}{62 \text{ g mol}^{-1}} = 0.322 \text{ mol}$$

$$\text{Moles of water} = \frac{80\text{g}}{18 \text{ g mol}^{-1}} = 4.444 \text{ mol}$$

$$x_{\text{glycerol}} = \frac{\text{moles of } C_2H_6O_2}{\text{Moles of } C_2H_6O_2 + \text{moles of } H_2O}$$

$$= \frac{0.322 \text{ mol}}{0.322 \text{ mol} + 4.444 \text{ mol}} = 0.068$$

$$x_{\text{water}} = \frac{4.444 \text{ mol}}{0.322 \text{ mol} + 4.444 \text{ mol}} = 0.932$$

The mole fraction of water can also be computed using the following formula:

$$1 - 0.068 = 0.932$$

(vi) Molarity : The number of moles of solute dissolved in one litre (or one cubic decimetre) of solution is known as molarity (M).

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

A 0.25 mol L^{-1} (or 0.25 M) solution of NaOH , for example, signifies that 0.25 mol of NaOH has been dissolved in one litre of water (or one cubic decimetre).

Example 2.2 Calculate the molarity of a solution containing 5 g of NaOH in 450 mL solution.

Solution:

$$\text{Moles of NaOH} = \frac{5 \text{ g}}{40 \text{ g mol}^{-1}} = 0.125 \text{ mol}$$

In litres, the volume of the solution = $450 \text{ mL}/1000 \text{ mL L}^{-1}$

Using 2.8 equation

$$\begin{aligned}
 &= \frac{0.125 \text{ mol} \times 1000 \text{ mL L}^{-1}}{450 \text{ mL}} = 0.278 \text{ M} \\
 &= 0.278 \text{ mol L}^{-1}
 \end{aligned}$$

$$\text{Molarity} = 0.278 \text{ mol dm}^{-3}$$

Example 2.3 Calculate molality of 2.5 g of ethanoic acid (CH_3COOH) in 75 g of benzene.

Molar mass of $\text{C}_2\text{H}_4\text{O}_2$: $12 \times 2 + 1 \times 4 + 16 \times 2 = 60 \text{ g mol}^{-1}$

$$\text{Moles of } \text{C}_2\text{H}_4\text{O}_2 = \frac{2.5 \text{ g}}{60 \text{ g mol}^{-1}} = 0.0417 \text{ mol}$$

Mass of benzene in kg $75 \text{ g}/1000 \text{ g kg}^{-1} = 75 \times 10^{-3} \text{ kg}$

$$\begin{aligned}
 \text{Molality of } \text{C}_2\text{H}_4\text{O}_2 &= \frac{\text{Moles of } \text{C}_2\text{H}_4\text{O}_2}{\text{kg of benzene}} = \frac{0.0417 \text{ mol} \times 1000 \text{ g kg}^{-1}}{75 \text{ g}} \\
 &= 0.556 \text{ mol kg}^{-1}
 \end{aligned}$$

Example 2.4 If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 k bar.

Ans. The mole fraction in aqueous solution is related to the solubility of gas. Henry's law is used to compute the mole fraction of gas in the solution. Therefore,

$$x(\text{Nitrogen}) = \frac{p(\text{nitrogen})}{K_H} = \frac{0.987 \text{ bar}}{76,480 \text{ bar}} = 1.29 \times 10^{-5}$$

Because 1 litre of water contains 55.5 mol of it, if n is the number of moles of N_2 in the solution,

$$x(\text{Nitrogen}) = \frac{n \text{ mol}}{n \text{ mol} + 55.5 \text{ mol}} = \frac{n}{55.5} = 1.29 \times 10^{-5}$$

(n in the denominator is ignored because it is 55.5)

$$\text{Hence, } n = 1.29 \times 10^{-5} \times 55.5 \text{ mol} = 7.16 \times 10^{-4} \text{ mol}$$

$$\frac{7.16 \times 10^{-4} \text{ mol} \times 1000 \text{ mmol}}{1 \text{ mol}} = 0.716 \text{ mmol}$$

Example 2.5 Vapour pressure of chloroform (CHCl_3) and dichloromethane (CH_2Cl_2) at 298 K are 200 mm Hg and 415 mm Hg respectively. (

i) Calculate the vapour pressure of the solution prepared by mixing 25.5 g of (CHCl_3) and 40 g of (CH_2Cl_2) at 298 K and, (ii) mole fractions of each component in vapour phase

(i) Molar mass of $\text{CH}_2\text{Cl}_2 = 12 \times 1 + 1 \times 2 + 35.5 \times 2 = 85 \text{ g mol}^{-1}$

Molar mass of $\text{CHCl}_3 = 12 \times 1 + 1 \times 1 + 35.5 \times 3 = 119.5 \text{ g mol}^{-1}$

$$\text{Moles of } \text{CH}_2\text{Cl}_2 = \frac{40 \text{ g}}{85 \text{ g mol}^{-1}} = 0.47 \text{ mol}^{-1}$$

$$\text{Moles of } \text{CHCl}_3 = \frac{25.5 \text{ g}}{119.5 \text{ g mol}^{-1}} = 0.213 \text{ mol}$$

$$\text{Moles in total} = 0.47 + 0.213 = 0.683 \text{ mol}$$

$$x_{\text{CH}_2\text{Cl}_2} = \frac{0.47 \text{ mol}}{0.683 \text{ mol}} = 0.688$$

$$x_{\text{CHCl}_3} = 1.00 - 0.688 = 0.312$$

Using the equation 2.16

$$p_{\text{total}} = p_1^0 + (p_2^0 - p_1^0) x_2 = 200 + (415 - 200) \times 0.688 = 200 + 147.9 = 347.9 \text{ mm Hg}$$

(ii) Making use of the relationship (2.19) $y_1 = p/p_{\text{total}}$ In the gas phase, we can determine the mole fraction of the components (y_1).

$$p_{\text{CH}_2\text{Cl}_2} = 0.688 \times 415 \text{ mm Hg} = 285.5 \text{ mm Hg}$$

$$p_{\text{CHCl}_3} = 0.312 \times 200 \text{ mm Hg} = 62.4 \text{ mm Hg}$$

$$y_{\text{CH}_2\text{Cl}_2} = 285.5 \text{ mm Hg} / 347.9 \text{ mm Hg} = 0.82$$

$$y_{\text{CHCl}_3} = 62.4 \text{ mm Hg} / 347.9 \text{ mm Hg} = 0.18$$

Note: Because CH_2Cl_2 is more volatile than CHCl_3

$\left[p_{\text{CH}_2\text{Cl}_2}^0 = 415 \text{ mm Hg and } p_{\text{CHCl}_3}^0 = 200 \text{ mm Hg} \right]$ and the vapour phase is richer in CH_2Cl_2 $\left[y_{\text{CH}_2\text{Cl}_2} = 0.82 \text{ and } y_{\text{CHCl}_3} = 0.18 \right]$

As a result, the vapour phase will always be rich in the component that is more volatile at equilibrium.

Example 2.6 The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.5 g when added to 39.0 g of benzene (molar mass 78 g mol⁻¹). Vapour pressure of the solution, then, is 0.845 bar. What is the molar mass of the solid substance?

Ans. The following are the various quantities that we are aware of:

$$p_1^0 = 0.850 \text{ bar; } p = 0.845 \text{ bar; } M_1 = 78 \text{ g mol}^{-1}; w_2 = 0.5 \text{ g; } w_1 = 39 \text{ g}$$

We get by substituting these numbers in equation (2.28).

$$\frac{0.850 \text{ bar} - 0.845 \text{ bar}}{0.850 \text{ bar}} = \frac{0.5 \text{ g} \times 78 \text{ g mol}^{-1}}{M_2 \times 39 \text{ g}}$$

$$\text{Thus, } M_2 = 170 \text{ g mol}^{-1}$$

Example 2.7 18 g of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, is dissolved in 1 kg of water in a saucepan. At what temperature will water boil at 1.013 bar? K_b for water is $0.52 \text{ K kg mol}^{-1}$.

$$\text{Glucose molecules} = 18 \text{ g} / 180 \text{ g mol}^{-1} = 0.1 \text{ mol}$$

$$\text{The amount of solvent in kilograms} = 1 \text{ kg}$$

$$\text{As a result, the molality of glucose solution} = 0.1 \text{ mol kg}^{-1}$$

Changes in the boiling point of water

$$\Delta T_b = K_b \times m = 0.52 \text{ K kg mol}^{-1} \times 0.1 \text{ mol kg}^{-1} = 0.052 \text{ K}$$

The boiling point of solution will be $373.15 + 0.052 = 373.202 \text{ K}$, because water boils at 373.15 K at 1.013 bar pressure.

Example 2.8 The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute. K_b for benzene is $2.53 \text{ K kg mol}^{-1}$

The difference (ΔT_b) between the boiling point and the temperature

$$= 354.11 \text{ K} - 353.23 \text{ K} = 0.88 \text{ K}$$

by substituting these numbers in equation (2.33), we get

$$M_2 = \frac{2.53 \text{ K kg mol}^{-1} \times 1.8 \text{ g} \times 1000 \text{ g kg}^{-1}}{0.88 \text{ K} \times 90 \text{ g}} = 58 \text{ g mol}^{-1}$$

As a result, the solute's molar mass $M_2 = 58 \text{ g mol}^{-1}$

Example 2.9 45 g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) is mixed with 600 g of water. Calculate

- the freezing point depression and
- the freezing point of the solution.

Ans. The molality is connected to freezing point, the molality of the solution in relation to ethylene glycol is important. = $\frac{\text{moles of ethylene glycol}}{\text{mass of water in kilogram}}$

$$\text{Moles of ethylene glycol} = \frac{45 \text{ g}}{62 \text{ g mol}^{-1}} = 0.73 \text{ mol}$$

$$\text{Water mass in kilograms} = \frac{600 \text{ g}}{1000 \text{ g kg}^{-1}} = 0.6 \text{ kg}$$

$$\text{As a result, the molality of ethylene glycol} = \frac{0.73 \text{ mol}}{0.60 \text{ kg}} = 1.2 \text{ mol kg}^{-1}$$

As a result of the freezing point depression,

$$\Delta T_f = 1.86 \text{ K kg mol}^{-1} \times 1.2 \text{ mol kg}^{-1} = 2.2 \text{ K}$$

$$\text{The aqueous solution's freezing point} = 273.15 \text{ K} - 2.2 \text{ K} = 270.95 \text{ K}$$

Example 2.10 1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant of benzene is $5.12 \text{ K kg mol}^{-1}$. Find the molar mass of the solute.

Ans. We get by substituting the values of the individual terms in equation (2.36):

$$M_2 = \frac{5.12 \text{ K kg mol}^{-1} \times 1.00 \text{ g} \times 1000 \text{ g kg}^{-1}}{0.40 \times 50 \text{ g}} = 256 \text{ g mol}^{-1}$$

As a result, the solute's molar mass = 256 g mol^{-1}

Example 2.11 200 cm³ of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be 2.57×10^{-3} bar. Calculate the molar mass of the protein.

Ans. The following are the various quantities that we are aware of: $\Pi = 2.57 \times 10^{-3}$ bar,

$$V = 200 \text{ cm}^3 = 0.200 \text{ litre}$$

$$T = 300 \text{ K}$$

$$R = 0.083 \text{ L bar mol}^{-1} \text{ K}^{-1}$$

Equation (2.42) is obtained by substituting these values.

$$M_2 = \frac{1.26 \text{ g} \times 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{2.57 \times 10^{-3} \text{ bar} \times 0.200 \text{ L}} = 61,022 \text{ g mol}^{-1}$$

Example 2.12 2 g of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is $4.9 \text{ K kg mol}^{-1}$. What is the percentage association of acid if it forms dimer in solution?

Ans. Given,

$$w_2 = 2 \text{ g}; K_f = 4.9 \text{ K kg mol}^{-1}; w_1 = 25 \text{ g}$$

$$\Delta T_f = 1.62 \text{ K}$$

When these values are substituted in equation (2.36), we get:

$$M_2 = \frac{4.9 \text{ K kg mol}^{-1} \times 2 \text{ g} \times 1000 \text{ g kg}^{-1}}{25 \text{ g} \times 1.62 \text{ K}} = 241.98 \text{ g mol}^{-1}$$

As a result, benzoic acid's experimental molar mass in benzene is

$$= 241.98 \text{ g mol}^{-1}$$

Consider the acid's equilibrium, which is as follows:



If x denotes the degree of solute association, we would have $(1-x)$ mol of benzoic acid in

unassociated form and $\frac{x}{2}$ as associated moles of benzoic acid at equilibrium.

As a result, at equilibrium, the total number of moles of particles is:

$$1-x + \frac{x}{2} = 1 - \frac{x}{2}$$

Thus, at equilibrium, the total number of moles of particles equals van't Hoff factor i .

$$\text{But } i = \frac{\text{Normal molar mass}}{\text{Abnormal molar mass}}$$

$$= \frac{122 \text{ g mol}^{-1}}{241.98 \text{ g mol}^{-1}} \quad \text{or}$$

$$\text{or } \frac{x}{2} = 1 - \frac{122}{241.98} = 1 - 0.504 = 0.496$$

$$\text{or } x = 2 \times 0.496 = 0.992$$

Example 2.13 0.6 mL of acetic acid (CH_3COOH), having density 1.06 g mL^{-1} , is dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was 0.0205°C . Calculate the van't Hoff factor and the dissociation constant of acid.

Ans. Amount of acetic acid in moles

$$= \frac{1 \times 0.6 \text{ mL} \times 1.06 \text{ g mL}^{-1}}{60 \text{ g mol}^{-1}} = 0.0106 \text{ mol} = n$$

$$\text{Molality} = \frac{0.0106 \text{ mol}}{1000 \text{ mL} \times 1 \text{ g mL}^{-1}} = 0.0106 \text{ mol kg}^{-1}$$

Using equation (2.35)

$$\Delta T_f = 1.86 \text{ K kg mol}^{-1} \times 0.0106 \text{ mol kg}^{-1} = 0.0197 \text{ K}$$

$$\text{van't Hoff Factor } (i) = \frac{\text{Observed freezing point}}{\text{Calculated freezing point}} = \frac{0.0205 \text{ K}}{0.0197 \text{ K}} = 1.041$$

Acetic acid is a weak electrolyte that dissociates into two ions per molecule: acetate and hydrogen ions. We would have $n(1-x)$ moles of undissociated acetic acid, nx moles of CH_3COO^- , and nx moles of H^+ ions if x is the degree of dissociation of acetic acid.



$$\begin{array}{ccc} n \text{ mol} & 0 & 0 \\ n(1-x) & nx \text{ mol} & nx \text{ mol} \end{array}$$

As a result, the total moles of particles are:

$$n(1-x+x+x) = n(1+x)$$

$$i = \frac{n(1+x)}{n} = 1+x = 1.041$$

As a result, the degree of acetic acid dissociation $= x = 1.041 - 1.000 = 0.041$

$$[\text{CH}_3\text{COOH}] = n(1 - x) = 0.0106 (1 - 0.041),$$

$$[\text{CH}_3\text{COO}^-] = nx = 0.0106 \times 0.041,$$

Then, $[\text{H}^+] = nx = 0.0106 \times 0.041.$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{0.0106 \times 0.041 \times 0.0106 \times 0.041}{0.0106 (1.00 - 0.041)}$$

$$= 1.86 \times 10^{-5}$$

Exercises

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

Answer. The term "solution" refers to a homogenous mixture of two or more components.

There are three different sorts of solutions available.

(i) Gaseous solution: The solute can be liquid, solid, or gas, and the solvent is a gas.

A blend of oxygen and nitrogen gases, for example.

(ii) Liquid solution: The solute might be a gas, liquid, or solid, and the solvent is a liquid.

A solution of ethanol in water, for example.

(iii) Solid solution: In a solid solution, the solvent is solid. The solute can be in the form of a gas, liquid, or solid.

A copper solution in gold, for example.

2.2 Give an example of a solid solution in which the solute is a gas

Answer. Solutions are two or more component homogeneous mixes (composition and attributes are consistent throughout the mixture).

Solvent is the term for a component that is present in significant quantities.

The physical condition of the solution is determined by the solvent.

Solutes are any components other than the solvent that are present in a solution.

There are three sorts of solutions, depending on the physical state of the solvent: gaseous, liquids, and solids.

Palladium in Hydrogen is an example of a solid solution including a gas as the solute.

Palladium is the solid solvent in this case, and Hydrogen is the gaseous solute.

This is a binary solution in this example (i.e., consisting of two components).

Palladium contains hydrogen, which is the answer to this question.

2.3 Define the following terms:

- (i) Mole fraction
- (ii) Molality
- (iii) Molarity
- (iv) Mass percentage

Answer. (i) mole fraction

It's the ratio of a component's number of moles to the overall number of moles in the combination. It is represented by the symbol.

(ii) Molality

It is defined as the number of moles of solute per kilogramme of solvent. It's the number of moles of solute divided by the mass of solvent in kilogrammes.

(iii) Molarity

The number of moles of solute per litre of solution is known as the solute concentration. The number of moles of solute to the volume of solution in litre is the ratio.

(iv) Mass proportion

One technique to indicate the concentration of an element in a compound or a component in a mixture is to use the mass percentage. The mass percentage is computed by dividing the mass of a component by the total mass of the combination and multiplying the result by 100%.

2.4 Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g mL^{-1} ?

Answer. Nitric acid has a molar mass of 63 g/mol.

The nitric acid employed in the lab is 68 percent by mass in aqueous solution, according to the manufacturer.

68 g of nitric acid is contained in 100 g of solution, or $\frac{68}{63} = 1.079$ moles of nitric acid.

The solution has a density of 1.504 g/mL

100 g of solution is equal to $\frac{100}{1.504} = 66.5 \text{ mL}$ or 0.0665 L .

The number of moles of nitric acid present in 1 litre of solution is known as the molarity of the solution.

$$\frac{1.079}{0.0665} = 16.22 \text{ M}$$

As a result, the molarity must be 16.22 g/mL.

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 mL^{-1} , then what shall be the molarity of the solution?

Answer. A 10% w/w glucose solution includes 10 grammes of glucose per 100 grams of solution, with 90 grams of water.

(i) Molality refers to the quantity of moles of glucose in one kilogram of water. The ratio of glucose's mass (10 g) to its molar mass (180 g/mol) is the number of moles of glucose.

$$\text{Molality} = \frac{10}{180 \times 0.090} = 0.618 \text{ m}$$

(ii) Molarity is defined as the ratio of the number of moles of glucose in a solution to the volume of the solution (in L).

The volume of the solution is 1.20 g/mL because the density of the solution is 1.20 g/mL.

$$\frac{100}{1.20 \times 1000} \text{ L}$$

$$\text{Molarity} = \frac{10}{180 \times \frac{100}{1.20 \times 1000}} = 0.667 \text{ M}$$

$$\text{(iii) The number of glucose moles} = \frac{10}{180} = 0.0556$$

$$\text{The number of water moles} = \frac{90}{18} = 5.0$$

$$\text{Glucose mole fraction} = \frac{0.0556}{0.0556 + 5.0} = 0.011$$

$$\text{Water's mole fraction} = 1 - 0.011 = 0.989$$

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?

Answer.

Allow for X g of sodium carbonate and 1 g of sodium bicarbonate in the mixture.

Sodium carbonate and sodium bicarbonate have molar weights of 106 g/mol and 84 g/mol, respectively.

Sodium carbonate and sodium bicarbonates have the same amount of moles $\frac{x}{106}$ & $\frac{1-x}{84}$

Because the combination is equimolar,

$$\begin{aligned}\frac{x}{106} &= \frac{1-x}{84} \\ 84x &= 106 - 106x \\ 190x &= 106 \\ x &= 0.5579\end{aligned}$$

$$\text{Number of sodium carbonate moles} = \frac{0.5579}{106} = 0.005263$$

$$\text{The amount of sodium hydrogen carbonate in moles} = \frac{1-0.5579}{84} = 0.005263$$

One mol of sodium carbonate reacts with two mol of HCl, while one mol of sodium bicarbonate reacts with one mol of HCl.

The total number of moles of HCl required to neutralise the mixture
 $= 2 \times 0.005263 + 0.005263 = 0.01578$ moles

$$\text{A volume of 0.1 M HCl is needed} = \frac{0.01578}{0.1} = 0.158\text{L} = 158 \text{ mL.}$$

2.7 A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.

Answer. Given that a solution is made by combining 300 g of 25% solution with 400 g of 40% solution by mass.

$$\text{Solution mass total} = 300 + 400 = 700 \text{ g}$$

$$\text{Solute mass} = 0.25 \times 300 + 0.40 \times 400 = 75 + 160 = 235 \text{ g}$$

$$\text{The solution's mass \%} = \frac{235}{700} \times 100 = 33.6\%$$

As a result, the final solution's mass percentage is 33.6%.

2.8 An antifreeze solution is prepared from 222.6 g of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL^{-1} , then what shall be the molarity of the solution?

Answer. Ethylene glycol is a solvent, while water is a solute, because there is too much of it. Water has a molar mass of 18 g/mol.

$$\text{The number of moles of a substance} = \frac{200}{18} = 11.11 \text{ moles}$$

The amount of moles of solute in one kilogramme of solvent is referred to as molality.

0.2226 kg is equal to 222.6 g of ethylene glycol.

$$\text{Therefore, Molality} = \frac{11.11}{0.2226} = 49.9 \text{ m}$$

$$\text{Solution mass total} = 222.6 + 200 = 422.6 \text{ g}$$

$$\text{Density of the liquid} = 1.072 \text{ g/mL}$$

$$\text{the volume of the solution} = \frac{\text{Mass}}{\text{Density}} = \frac{422.6}{1.072} = 394 \text{ ml or } 0.394 \text{ L}$$

The number of moles of solute in 1 litre of solution is referred to as molarity.

$$\text{Molarity} = \frac{11.11}{0.394} = 28.2 \text{ M}$$

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

Ans. In 1000,000 g of solution, 15 ppm equals 15 g chloroform.

$$\text{(i) Mass percentage} = \frac{\text{Mass of chloroform}}{\text{Mass of solution}} \times 100$$

$$\text{Mass percentage} = \frac{15}{1000,000} \times 100 = 1.5 \times 10^{-3} \%$$

(ii) Molality

$$\frac{\text{Mass of chloroform}}{\text{Molar mass of chloroform} \times (\text{Mass of solution} - \text{mass of chloroform})} \times 1000 \text{ (all masses in g)}$$

$$\text{Molality} = \frac{15}{119.5 \times (1000,000 - 15)} \times 1000 = 1.255 \times 10^{-4} \text{ m.}$$

2.10 What role does the molecular interaction play in a solution of alcohol and water?

Answer. The lower members of the alcohol family are very soluble in water, but as the molecular weight increases, so does the solubility. The creation of hydrogen bonds (Hydrogen bonding) between alcohols and water molecules accounts for the solubility of lesser alcohols in water.

When the size of an alcohol molecule grows larger, the alkyl groups get larger, preventing hydrogen bonds with water from forming, and therefore the solubility decreases as the length of a carbon chain grows longer. Furthermore, the interaction between the molecules of alcohol and water is weaker than the interaction between alcohol and water. As a result, when alcohol and water are mixed, the intermolecular connections weaken, allowing molecules to escape more easily. This raises the solution's vapour pressure, which lowers the boiling point of the resultant solution.

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

Answer. When the temperature is raised or lowered, the reaction's equilibrium changes backwards, and heat is utilised in the process, making the gases less soluble in liquids.

As a result of the shift in equilibrium direction as the temperature rises, the gases become less soluble in liquids.

2.12 State Henry's law and mention some important applications

Answer. When the temperature is held constant, Henry's law states that the amount of gas dissolved in a liquid is directly proportional to the partial pressure of that gas above the liquid. Henry's law constant is the proportionality constant.

Henry's law of applications.

In carbonated soft drinks, Henry's law states that when the bottle is opened, part of the gas escapes, resulting in a distinct pop. The lower pressure above the liquid causes carbon dioxide to escape in the form of bubbles.

The amount of oxygen that dissolves in the bloodstream is precisely proportional to the partial pressure of oxygen in the alveolar air, according to Henry's law in respiration.

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

Answer. The solubility of a gas in a liquid is directly proportional to its pressure, according to Henry's law.

$$X = K_h \times P$$

X is the gas's mole fraction, K_h is the Henry's law constant, and P is the gas's partial pressure.

Ethane's mole fraction will similarly be proportional to its mass.

$$W/P = W'/P'$$

The partial pressure of ethane in first solution is P , while the mass of ethane in first solution is W .

The partial pressure of ethane in second solution is P' , while the mass of ethane in second solution is W' .

$$6.56 \times 10^{-3} \times P' = 5.00 \times 10^{-2} \times 1$$

$$P' = 7.6$$

As a result, the gas partial pressure will be 7.6 bar.

2.14 What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{\text{mix}} H$ related to positive and negative deviations from Raoult's law?

Answer. When the total vapour pressure of a solution exceeds the corresponding vapour pressure in an ideal solution, a positive departure from Raoult's law occurs.

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

$\Delta_{\text{mix}} H$ has a positive sign when there is a positive deviation from Raoult's law.

$\Delta_{\text{mix}} H$ has a negative sign for a negative divergence from Raoult's law.

2.15 An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute?

Answer. Pure water has a vapour pressure of 1 atm (1.013 bar) at boiling point.

The solution has a vapour pressure of 1.004 bar.

The solute has a mass of 2 g.

The solution has a mass of 100 g.

The mass of the solvent is $100 - 2 = 98$ g

Using Raoult's law, we arrive at

$$\frac{P^0 - P}{P} = x_2 = \frac{M_2 W_1}{W_2 M_1}$$

$$\frac{1.013 - 1.004}{1.013} = \frac{2 \times 18}{M_2 \times 98} \Rightarrow M_2 = 41.35 \text{ g/mol}$$

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 g of octane?

Answer. Heptane and octane have molar weights of 100 g/mol and 114 g/mol, respectively.

26 g of heptane is equal to $\frac{26}{100} = 0.26$ moles

35 g of octane is equal to $\frac{35}{114} = 0.31$ moles

Heptane mole fraction $\chi = \frac{0.26}{0.26+0.31} = 0.456$

Octane mole fraction $\chi' = 1 - 0.456 = 0.544$

Heptane partial pressure $p = 0.456 \times 105.2 = 47.97$ kPa

octane partial pressure $p' = 0.544 \times 46.8 = 25.46$ kPa

Solution's vapour pressure $P = p + p' = 47.97 + 25.46 = 73.43$ 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.

Answer. At 300 K, the vapour pressure of water is 12.3 kPa. The vapour pressure of a 1 molal solution of a non-volatile solute in it must be calculated. 1 mole of solute is contained in 1000 g of water. Water has a molar mass of 18 g/mol.

The number of water moles $= \frac{1000}{18} = 55.56$ mol

The solute in the solution has a mole fraction of $x = \frac{1}{1+55.56} = 0.0177$.

The mole fraction of solute equals the relative decrease in vapour pressure.

$$\frac{p^0 - p}{p^0} = x$$

$$\frac{12.3 - p}{12.3} = 0.0177$$

$$p = 12.08 \text{ kPa}$$

2.18 Calculate the mass of a non-volatile solute (molar mass 40 g mol⁻¹) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

Answer. Let p be the pure octane vapour pressure. The solution's vapour pressure will be

$$\frac{80}{100}p = 0.8 p.$$

Solute molar mass (M) and octane molar mass (m) are 40 g/mol and 114 g/mol, respectively. Octane has a mass of 114 g.

$$\frac{p-p'}{p} = \frac{Wm}{Mw}$$

$$\frac{p-0.8p}{p} = \frac{W \times 114}{40 \times 114}$$

$$W = 8\text{g}$$

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

- (i) molar mass of the solute
- (ii) vapour pressure of water at 298 K.

Answer. Solute weight $W_B = 30$ g,

Water weight $W_A = 90$ g,

Solution's vapour pressure $P_A = 2.8$ kPa

Raoult's law states that
$$\frac{P_A^0 - P_A}{P_A^0} = XB \approx \frac{W_B M_A}{M_B W_A}$$

$$\frac{P_A^0 - 2.8}{P_A^0} = \frac{30 \times 18}{M_B \times 90}$$

$$\frac{2.8}{P_A^0} = \frac{M_B - 6}{M_B} \dots (1)$$

After water addition

Solute weight + water weight

$$90 + 18 = 108 \text{ g}$$

Raoult's law states that

$$\frac{P_A^0 - P_A}{P_A^0} = XB \approx \frac{W_B M_A}{M_B W_A}$$

$$\frac{P_A^0 - 2.9}{P_A^0} = \frac{30 \times 18}{M_B \times 108}$$

$$\frac{2.8}{P_A^0} = \frac{M_B - 5}{M_B} \dots (2)$$

On division of equation 1 and 2

$$\frac{2.8}{2.9} = \frac{M_B - 6}{M_B - 5}$$

$$M_B = 34 \text{ g/mol}$$

We get the following results by substituting the values of M_B in equation (1).

$$\frac{2.8}{P_A^0} = \frac{34 - 6}{34}$$

$$P_A^0 = 3.4 \text{ kPa}$$

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

Answer. Glucose and sucrose have molar weights of 180 g/mol and 342 g/mol, respectively.

A 5 percent solution is made by dissolving 5 grams of solute in 95 grammes of solvent to make 100 grams of solution. The difference between the freezing point of pure solvent (water) and the freezing point of the solution is the depression in the freezing point.

The following expression gives the decrease in the freezing point.

$$\Delta T_f = K_f \times \left(\frac{w}{m} \times \frac{1000}{W} \right)$$

Substitute the values for cane sugar

$$(273.15 \text{ K} - 271 \text{ K}) = K_f \times \left(\frac{5}{342} \times \frac{1000}{95} \right)$$

Now, substitute the values for glucose

$$\Delta T_f = K_f \times \left(\frac{5}{180} \times \frac{1000}{95} \right)$$

Divide the values of cane sugar and glucose

$$\frac{\Delta T_f}{2.15} = \frac{342}{180}$$

On rearranging

$$\Delta T_f = \frac{342}{180} \times 2.15$$

$$= 4.09 \text{ K}$$

To get the freezing point of 5 percent glucose solution, subtract the depression in the freezing point of 5 percent glucose solution from the freezing point of water:

$$273.15 \text{ K} - 4.09 \text{ K} = 269.06 \text{ K}$$

The freezing point of a 5% glucose solution is thus 269.06 K.

2.21 Two elements A and B form compounds having formula AB_2 and AB_4 . When dissolved in 20 g 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 $5.1 \text{ K kg mol}^{-1}$. Calculate atomic masses of A and B.

Answer.

Using the formula

$$M_B = \frac{K_f W_B \times 1000}{W_A \Delta T_f}$$

$$\Delta T_f = 2.3 \text{ K}, W_B = 1.0 \text{ g}, W_A = 20.0 \text{ g}, K_f = 5.1 \text{ K kg/mol}$$

$$M_B = 20.0 \times 2.3 \times 5.1 \times 1000 = 110.87 \text{ g/mol}$$

In case AB_4

$$\Delta T_f = 1.3 \text{ K}, W_B = 1.0 \text{ g}, W_A = 20.0 \text{ g}$$

$$M_B = \frac{5.1 \times 1.0 \times 1000}{20.0 \times 1.3} = 196.15 \text{ g/mol}$$

The atomic masses of A and B, respectively, are a g/mol and b g/mol.

$$M_{AB_2} = a + 2b = 110.87 \dots (i)$$

$$M_{AB_4} = a + 4b = 196.15 \dots (ii)$$

Subtract equation (ii) from (i)

$$-2b = -85.28$$

Atomic mass of B = $b = 42.64$

We get by substituting the values of b in equation I

$$a + 2 \times 42.64 = 110.87$$

Atomic mass of A = 25.59 g/mol.

As a result, the atomic masses of A and B is 25.59 g/mol and 42.64 g/mol, respectively.

2.22 At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bars at the same temperature, what would be its concentration?

Answer. The connection between osmotic pressure and molar concentration is equal to $\Pi = CRT$, according to the van't Hoff equation. The ideal gas constant is R, while the absolute temperature is T.

$$C_1 = \frac{36}{180} M$$

$$\Pi_1 = 4.98 \text{ bar}$$

$$C_2 = ?$$

$$\Pi_2 = 1.52 \text{ bar}$$

$$4.98 = 18036 RT \dots\dots (i)$$

$$1.52 = C_2 RT \dots\dots (ii)$$

$$\frac{C_2 \times 180}{36} = \frac{1.52}{4.98}$$

$$C_2 = 0.061 M$$

As a result, the concentration of the second solution is 0.061 M

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) $NaClO_4$ and water

(iv) methanol and acetone

(v) acetonitrile (CH_3CN) and acetone (C_3H_6O).

Answer. The following are the most important types of intermolecular attractive interactions in the supplied pairs:

(i) Van der waals interactions

(ii) Van der waals interactions

(iii) Ion dipole interactions

(iv) Hydrogen bonding

(v) 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, CH₃OH, CH₃CN.

Answer. Non-polar n-octane can dissolve non-polar solutes. It is unable of dissolving polar (or ionic) solutes.

Cyclohexane is a non-polar substance. As a result, it is easily soluble in n-octane.

Methanol and acetonitrile are polar and soluble in n-octane only in extremely small amounts.

Because KCl is an ionic molecule, it is insoluble in n-octane.

The following is the increasing order of solubility in n-octane:



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

Answer. (i) Phenol is only slightly water soluble.

(ii) Toluene is insoluble in water.

(iii) Formic acid is soluble in water.

(iv) Ethylene glycol dissolves in water.

(v) Chloroform is insoluble in water.

(vi) Pentanol is water soluble to a degree.

2.26 If the density of some lake water is 1.25g mL⁻¹ and contains 92 g of Na⁺ ions per kg of water, calculate the molarity of Na⁺ ions in the lake.

Answer. Mass of sodium ions = 92 g

Sodium ions' molar mass = 23 g/mol

The number of sodium ions in a mole = $\frac{92\text{g}}{23\text{g/mol}} = 4$

Water mass = 1 kg

$$\text{Molality} = \frac{\text{number of moles of sodium ions}}{\text{Mass of water (in kg)}} = \frac{4}{1} = 4m$$

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

Answer.

$$\text{CuS, } K_{sp} \text{ of CuS's solubility product} = 6 \times 10^{-16}$$

If the solubility is s , then $\text{CuS} = \text{Cu}^{2+} + \text{S}^{2-}$

$$\text{Hence, } K_{sp} = \{ \text{Cu}^{2+} \} \{ \text{S}^{2-} \}$$

Or

$$K_{sp} = s \times s$$

Or

$$s = \sqrt{K_{sp}} = \sqrt{6} \times 10^{-16}$$

$$= 2.45 \times 10^{-8} \text{ M}$$

2.28 Calculate the mass percentage of aspirin ($\text{C}_9\text{H}_8\text{O}_4$) in acetonitrile (CH_3CN) when 6.5 g of ($\text{C}_9\text{H}_8\text{O}_4$) is dissolved in 450 g of (CH_3CN).

Answer.

$$\text{Mass percent of aspirin} = \frac{\text{Mass of aspirin}}{\text{Mass of aspirin} + \text{Mass of acetonitrile}} \times 100$$

$$= \frac{6.5}{6.5 + 450} \times 100 = 1.424\%$$

2.29 Nalorphene ($\text{C}_{19}\text{H}_{21}\text{NO}_3$), like morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the mass of 1.5×10^{-3} m aqueous solution required for the above dose.

Answer.

$$w_B = 1.5 \times 10^{-3} \text{ g}$$

$$M_B = 19 \times 12 + 21 \times 1 + 14 + 3 \times 16 = 311$$

As we know that

$$m = \frac{w_B / MB}{w_A} \times 1000$$

$$1.5 \times 10^{-3} = \frac{1.5 \times 10^{-3} / 311}{w_A} \times 1000$$

$$w_A = \frac{1.5 \times 10^{-3}}{311 \times 1.5 \times 10^{-3}} \times 1000$$

$$= \frac{1000}{311} = 3.2 \text{ g.}$$

2.30 Calculate the amount of benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) required for preparing 250 mL of 0.15 M solution in methanol.

Answer. Required number of moles of benzoic acid = $0.15 \times \frac{250}{1000} = 0.0375$ moles

Benzoic acid molar mass = $7(12) + 6(1) + 2(16) = 84 + 6 + 32 = 122$ g/mol

Benzoic acid (mass) is necessary. = $122 \times 0.0375 = 4.575$ 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.

Ans. The acid strength and degree of dissociation increase when highly electron withdrawing groups are present on the alpha C atom of acetic acid. This raises the vant Hoff factor I and decreases the freezing point depression. Because fluorine is the greatest electron withdrawing element in nature, trifluoroacetic acid is the most acidic. As a result, trifluoroacetic acid exhibits the greatest decrease in freezing point.

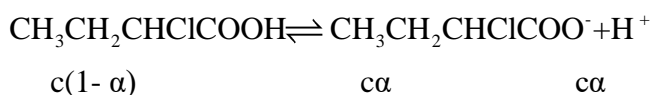
2.32 Calculate the depression in the freezing point of water when 10 g $\text{CH}_3\text{CH}_2\text{CHClCOOH}$ is added to 250 g of water. $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86 \text{ K kg mol}^{-1}$.

Ans. 2-Chlorobutanoic acid has a molar mass of 122.5 g/mol

The total number of moles = $\frac{10}{122.5} = 0.0816$ mol

The solution's molality = $\frac{0.0816 \times 1000}{250} = 0.3265$ m

Let α be the initial concentration and α be the degree of dissociation. After dissociation, the concentration is as illustrated.

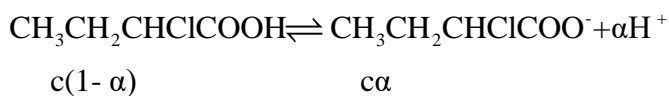


The expression for the equilibrium constant is

$$K = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = c\alpha^2$$

$$\alpha = \sqrt{\frac{K}{c}} = \sqrt{\frac{1.4 \times 10^{-3}}{0.3265}} = 0.065$$

The vant Hoff factor is calculated as follows:



$$i = \frac{1-\alpha + \alpha + \alpha}{1} = 1 + \alpha = 1 + 0.065 = 1.065$$

In the freezing point, there is a depression. $\Delta T_f = iK_f m = 1.065 \times 1.86 \times 0.3265 = 0.647^\circ$

2.33 19.5 g of CH₂FCOOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.00 C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

Answer. The molecular mass of fluoroacetic acid is 78 g/mol.

The number of fluoroacetic acid moles is $\frac{19.5}{78} = 0.25$.

The amount of moles of solute in one kilogram of solvent is referred to as molality.

$$\text{Molality} = \frac{0.25}{\frac{500}{1000}} = 0.50m$$

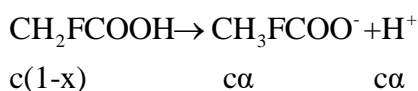
The freezing point has been lowered by a calculated amount.

$$\Delta T_f = K_f \times m = 1.86 \times 0.50 = 0.93 \text{ K}$$

The ratio of observed freezing point depression to calculated freezing point depression is known as the Van't Hoff factor.

$$i = \frac{1.0}{0.93} = 1.0753$$

Let c be the fluoro acetic acid concentration at the start and be the degree of dissociation.



Number of moles in total

$$= c(1 - \alpha) + c\alpha + c\alpha = c(1 + \alpha)$$

$$i = \frac{c(1 - \alpha)}{c} = 1 + \alpha = 1.0753$$

$$\alpha = 0.0753$$

$$[\text{CH}_2\text{FCOO}^-] = [\text{H}^+] = c\alpha = 0.50 \times 0.0753 = 0.03765$$

$$[\text{CH}_2\text{FCOOH}] = c(1 - \alpha) = 0.50(1 - 0.0753) = 0.462$$

$$K_a = \frac{[\text{CH}_2\text{FCOO}^-][\text{H}^+]}{[\text{CH}_2\text{FCOOH}]}$$

$$K_a = \frac{0.03765 \times 0.03765}{0.462}$$

$$K_a = 3.07 \times 10^{-3}$$

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.

Answer. Number of moles present in glucose = $\frac{25}{180} = 0.139$

The number of water moles = $\frac{450}{18} = 25$

Glucose mole fraction = $\frac{0.139}{0.139 + 25} = 0.0055$

The reduction in vapour pressure is proportional to the mole fraction.

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

$$\frac{17.535 - P}{17.535} = 0.0055$$

$$P = 17.438$$

As a result, a solution's vapour pressure is 17.438 mm Hg.

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

Answer.

$$K_H = 4.27 \times 10^5 \text{ mm Hg (at 298 K)}$$

$$p = 760 \text{ mm}$$

Using Henry's law

$$p = K_H x,$$

x is Methane solubility (mole fraction)

$$x = K_H p = (4.27 \times 10^5 \text{ mm})(760 \text{ mm})$$

$$= 1.78 \times 10^{-3}$$

2.36 100 g of liquid A (molar mass 140 g mol⁻¹) was dissolved in 1000 g of liquid B (molar mass 180 g 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

Answer.

Given

$$P_T = 475, W_A = 100 \text{ g}, M_A = 140, P_B^0 = 500$$

$$W_B = 1000 \text{ g}, M_B = 180, P_A^0, P_A = ?$$

$$P_T = P_A^0 X_A + P_B^0 X_B \rightarrow (1) \text{ \& } X_A + X_B = 1 \rightarrow (2)$$

$$\Rightarrow \frac{X_B}{X_A} = \frac{W_B M_A}{W_A M_B} = \frac{1000 \times 140}{100 \times 180} = 7.78$$

$$X_B = 7.78 X_A$$

X_B on substitution (2)

$$X_A + 7.78 X_A = 1$$

$$X_A = 0.113 \text{ \& hence } X_B = 1 - 0.113 = 0.886$$

$$475 = P_A^0(0.113) + 500(0.886)$$

$$\Rightarrow 0.113 P_A^0 = 32 \Rightarrow P_A^0 = \frac{32}{0.113} = 283.18 \text{ torr}$$

Substitution of X_A and X_B

$$475 = P_A^0(0.113) + 500(0.886)$$

$$\Rightarrow 0.113 P_A^0 = 32 \Rightarrow P_A^0 = \frac{32}{0.113} = 283.18 \text{ torr}$$

$$475 = P_A^0(0.113) + 500(0.886)$$

$$\Rightarrow 0.113 P_A^0 = 32 \Rightarrow P_A^0 = \frac{32}{0.113} = 283.18 \text{ torr}$$

$$\begin{aligned}
 P_A &= P_A^0(1 - X_B) = P_A^0 X_A \\
 &= 283.18 \times 0.113 \\
 &= 31.999 \text{ torr}
 \end{aligned}$$

2.37 Vapour pressures of pure acetone and chloroform at 328 K are 741.8 mm Hg and 632.8 mm Hg respectively. If they form ideal solution over the entire range of composition,

P_{total} , $P_{\text{chloroform}}$, and p_{acetone} as a function of X_{acetone} . The experimental data observed for different compositions of mixture is:

$100x_{\text{acetone}}$	0	11.8	23.4	36.0	50.8	58.3	64.5	72.1
$p_{\text{acetone}}/\text{mm Hg}$	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{\text{chloroform}}/\text{mm Hg}$	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

Answer.

$100x_{\text{acetone}}$	0	11.8	23.4	36.0	50.8	58.3	64.5	72.1
$p_{\text{acetone}}/\text{mm Hg}$	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{\text{chloroform}}/\text{mm Hg}$	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7
P_{total}	632.8	603.0	579.5	562.1	580.4	599.5	615.3	641.8

P_{total} plot shows a declining trend. This implies a departure 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 80 g of benzene is mixed with 100 g of toluene.

Ans. The number of moles is the mass to molar mass ratio. Benzene and toluene have molar weights of 78 g/mol and 92 g/mol, respectively.

$$\text{Benzene moles} = \frac{80}{78} = 1.026$$

$$\text{The number of toluene moles} = \frac{100}{92} = 1.087$$

$$X_B = \frac{1.026}{1.026 + 1.087} = 0.486$$

Benzene mole fraction,

$$X_T = 1 - 0.486 = 0.514$$

Toluene mole fraction

$$P_B = P_B^0 \times X_B = 50.71 \times 0.486 = 24.65 \text{ mm Hg}$$

$$P_T = P_T^0 \times X_T = 32.06 \times 0.514 = 16.48 \text{ mm of Hg}$$

$$\text{Vapour pressure} = 24.65 + 16.48 = 41.13 \text{ mm Hg}$$

The mole fraction of benzene in the vapour phase is:

$$Y_B = \frac{24.65}{41.13} = 0.60$$

2.39 The air is a mixture of a few gases. The major components are oxygen and nitrogen with 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 the Henry's law constants for oxygen and nitrogen at 298 K are 3.30×10^7 mm and 6.51×10^7 mm respectively, calculate the composition of these gases in water.

Ans. Air over water has a vapour pressure of 10 atm.

The nitrogen partial pressure

$$= P_{N_2} = \frac{79 \times 10}{100} = 7.9 \text{ atm} = 7.9 \times 760 \text{ mm Hg} = 6004 \text{ mm Hg}$$

$$\text{The oxygen partial pressure } P_{O_2} = \frac{20 \times 10}{100} = 2.0 \text{ atm} = 2.0 \times 760 \text{ mm Hg} = 1520 \text{ mm Hg}$$

Using Henry's law

$$P_{N_2} = K_H(N_2) \times X_{N_2}$$

$$X_{N_2} = \frac{P_{N_2}}{K_H(N_2)} = \frac{6004}{6.51 \times 10^7} = 9.22 \times 10^{-5}$$

$$X_{O_2} = \frac{P_{O_2}}{K_H(O_2)} = \frac{1520}{3.30 \times 10^7} = 4.6 \times 10^{-5}$$

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

Answer. The osmotic pressure is calculated using Van't Hoff's equation.

$$\Pi = iCRT = \frac{i n B R T}{V}$$

The Van't Hoff factor is i , the molar concentration is C , the ideal gas constant is R , the temperature is T , the number of moles of calcium chloride is n_B , and the volume of the solution is V .

We now have the following values:

$$\pi = 0.75 \text{ atm}$$

$$V = 2.5 \text{ L}$$

$$i = 2.47$$

$$T = (27+273) \text{ K} = 300 \text{ K}$$

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

$$0.75 = \frac{2.47 \times n_B \times 0.0821 \times 300}{2.5}$$

$$n_B = 0.0308 \text{ mol}$$

Calcium chloride has a molar mass of 111 g/mol.

The amount of calcium chloride that has been dissolved

$$= 0.0308 \times 111 = 3.42 \text{ g.}$$

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.

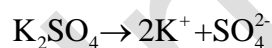
Answer. Given

$$\text{Mass of } K_2SO_4, w = 25 \text{ mg} = 0.025 \text{ g}$$

$$\text{Volume (V)} = 2 \text{ L}$$

$$T = 25 + 273 = 298 \text{ K}$$

The dissociation reaction of K_2SO_4



$$\text{Ions produced} = 2 + 1 = 3$$

Using osmotic pressure formula

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

$$\pi = i \cdot \frac{w}{MV} RT$$

R is Gas constant

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

Therefore, molar mass of K_2SO_4

On substitution

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