Q 2.1) If 22 g of benzene is dissolved in 122 g of carbon tetrachloride, determine the mass percentage of carbon tetrachloride (CCl_4) and benzene (C_6H_6).

Solution:

Mass percentage of Benzene (C_6H_6) = $\frac{Mass\ of\ C_6H_6}{Total\ mass\ of\ the\ solution}\ v \times\ 100$

= $\frac{Mass\ of\ C_6H_6}{Mass\ of\ C_6H_6 + Mass\ of\ CCl_4} \times\ 100$

= $\frac{22}{22+122} \times\ 100$

= 15.28%

Mass percentage of Carbon Tetrachloride (CCl_4) = $\frac{Mass\ of\ CCl_4}{Total\ mass\ of\ the\ solution} \times\ 100$

= $\frac{Mass\ of\ CCl_4}{Mass\ of\ C_6H_6 + Mass\ of\ CCl_4} \times\ 100$

= $\frac{122}{22+122} \times\ 100$

= 84.72%

Q 2.2) If benzene in solution containing 30% by mass in carbon tetrachloride, calculate the mole fraction of benzene.

Solution:

Assume the mass of benzene be 30 g in the total mass of the solution of 100 g.

Mass of CCl_4 = (100 – 30) g

= 70 g

Molar mass of benzene (C_6H_6) = (6 × 12 + 6 × 1) g mol^{-1}

= 78 g mol^{-1}

Therefore, Number of moles of C_6H_6 = $\frac{30}{78}$ mol

= 0.3846 mol

Molar mass of CCl_4 = 1 x 12 + 4 x 355 = 154 g mol^{-1}

Therefore, Number of moles of CCl_4 = $\frac{70}{154}$ mol

= 0.4545 mol

Thus, the mole fraction of C_6H_6 is given as:

$$\frac{Number\ of\ moles\ of\ C_6H_6}{Number\ of\ moles\ of\ C_6H_6 + Number\ of\ moles\ of\ CCl_4}$$

= $\frac{0.3846}{0.3846+0.4545}$

= 0.458

Q 2.3) Determine the molarity of each of the solutions given below:

(a) 30 g of Co $(NO)_3$. $6H_2O$ in 4.3 L of solution

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

Solution:

We know that,

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

(a) Molar mass of $Co(NO)_3$. $6H_2O$ = 59 + 2 (14 + 3 x 16) + 6 x 18 = 291 g mol^{-1}

Therefore, Moles of $Co(NO)_3$. $6H_2O$ = $\frac{30}{291}$ mol

= 0.103 mol

Therefore, molarity = $\frac{0.103\ mol}{4.3\ L}$

= 0.023 M

(b) Number of moles present in 1000 mL of 0.5 M H_2SO_4 = 0.5 mol

Therefore, Number of moles present in 30 mL of 0.5 M H_2SO_4 = $\frac{0.5\times30}{1000}$ mol

= 0.015 mol

Therefore, molarity = $\frac{0.015}{0.5\ L}\ mol$

= 0.03 M

Q 2.4) To make 2.5 kg of 0.25 molar aqueous solution, determine the mass of urea (NH_2CONH_2) that is required.

Solution:

Molar mass of urea (NH_2CONH_2) = 2(1 × 14 + 2 × 1) + 1 × 12 + 1 × 16 = 60 g mol^{-1}

0.25 molar aqueous solution of urea means:

1000 g of water contains 0.25 mol = (0.25 × 60) g of urea = 15 g of urea

That is,

(1000 + 15) g of solution contains 15 g of urea

Therefore, 2.5 kg (2500 g) of solution contains = $\frac{15 \times 2500}{1000+15}\ g$

= 36.95 g

= 37 g of urea (approx.)

Hence, mass of Urea required is 37 g.

Q 2.5) If 1.202 g mL^{-1} is the density of 20% aqueous KI, determine the following:

(a) Molality of KI

(b) Molarity of KI

(c) Mole fraction of KI

Solution:

(a) Molar mass of KI = 39 + 127 = 166 g mol^{-1}

20% aqueous solution of KI means 20 g of KI is present in 100 g of solution.

That is,

20 g of KI is present in (100 − 20) g of water = 80 g of water

Therefore, molality of the solution = $\frac{Moles\ of\ KI}{Mass\ of\ water\ in\ kg}$

= $\frac{\frac{20}{166}}{0.08}\ m$

= 1.506 m

= 1.51 m (approx.)

(b) It is given that the destiny of the solution = 1.202 $g\ mL^{-1}$

Volume of 100 g solution = $\frac{Mass}{Density}$

= $\frac{100\ g}{1.202\ g\ mL^{-1}}$

= 83.19 mL

= $83.19 \times\ 10^{-3}\ L$

Therefore, molarity of the solution = $\frac{\frac{20}{166}\ mol}{83.19\times10^{-3}\ L}$

= 1.45 M

(c) Moles of KI = $\frac{20}{166}$ = 0.12 mol

Moles of water = $\frac{80}{18}$ = 4.44 mol

Therefore, mole = $\frac{Moles\ of\ KI}{Moles\ of\ KI+Moles\ of\ water}$

Fraction of KI = $\frac{0.12}{0.12+4.44}$

= 0.0263

Q 2.6) Calculate Henry's law constant when the solubility of H_2S (a toxic gas with rotten egg like smell) in water at STP is 0.195 m

Solution:

It is given that the solubility of H_2S in water at STP is 0.195 m, i.e., 0.195 mol of H_2S is dissolve in 1000 g of water.

Moles of water = $\frac{1000\ g}{18\ g\ mol^{-1}}$

= 55.56 mol

Therefore, Mole fraction of H_2S, x = $\frac{Moles\ of\ H_2S}{Moles\ of\ H_2S + Moles\ of\ water}$

= $\frac{0.195}{0.195+55.56}$

= 0.0035

At STP, pressure (p) = 0.987 bar

According to Henry's law: p = K_H x

=> $K_H = \frac{p}{x}$

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

= 282 bar

Q 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.

Solution:

Total amount of solute present in the mixture is given by,

$$300 \times \frac{25}{100} + 400 \times \frac{40}{100}$$

= 75 + 160

= 235 g

Total amount of solution = 300 + 400 = 700 g

Therefore, mass percentage of the solute in the resulting solution = $\frac{235}{700} \times 100$

= 33.57%

And, mass percentage of the solvent in the resulting solution is:

= (100 – 33.57) %

= 66.43%

Q 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.

Solution:

It is given that:

P_A° = 450 mm of Hg

P_B° = 700 mm of Hg

P_{total} = 600 mm of Hg

According to Raoult's law:

$$P_A = P_A^\circ x_A \quad P_B = P_B^\circ x_B = P_B^\circ (1 - x_A)$$

Therefore, total pressure, $P_{total} = P_A + P_B$

=> $P_{total} = P_A^\circ x_A + P_B^\circ (1 - x_A)$

=> $P_{total} = P_A^\circ x_A + P_B^\circ - P_B^\circ x_A$

=> $P_{total} = (P_A^\circ - P_B^\circ) x_A + P_B^\circ$

=> 600 = (450 – 700) x_A + 700

=> $-100 = -250x_A$

=> $x_A = 0.4$

Therefore, $x_B = 1 - x_A$ = 1 − 0.4 = 0.6

Now, $P_A = P_A^\circ x_A$

= 450 x 0.4 = 180 mm of Hg

$P_B = P_B^\circ x_B$

= 700 x 0.6 = 420 mm of Hg

Now, in the vapour phase: Mole fraction of liquid A = $\frac{P_A}{P_A + P_B}$

= $\frac{180}{180+420}$

= $\frac{180}{600}$

= 0.30

And, mole fraction of liquid B = 1 − 0.30 = 0.70

Q 2.9) Find the vapor pressure of water and its relative lowering in the solution which is 50 g of urea (NH_2CONH_2) dissolved in 850 g of water. (Vapor pressure of pure water at 298 K is 23.8 mm Hg)

Solution:

It is given that vapour pressure of water, P_1° = 23.8 mm of Hg

Weight of water taken, w_1 = 850 g

Weight of urea taken, w_2 = 50 g

Molecular weight of water, M_1 = 18 g mol^{-1}

Molecular weight of urea, M_2 = 60 g mol^{-1}

Now, we have to calculate vapour pressure of water in the solution. We take vapour pressure as p_1.

Now, from Raoult's law, we have:

$$\frac{P_1^\circ - P_1}{P_1^\circ} = \frac{n_2}{n_1+n_2}$$

=> $\frac{P_1^\circ - P_1}{P_1^\circ} = \frac{\frac{w_2}{M_2}}{\frac{w_1}{M_1}+\frac{w_2}{M_2}}$

=> $\frac{23.8 - P_1}{23.8} = \frac{\frac{50}{60}}{\frac{850}{18}+\frac{50}{60}}$

=> $\frac{23.8 - P_1}{23.8} = \frac{0.83}{47.22+0.83}$

=> $\frac{23.8 - P_1}{23.8} = 0.0173$

=> P_1 = 23.4 mm of Hg

Hence, the vapour pressure of water in the given solution is 23.4 mm of Hg and its relative lowering is 0.0173.

Q 2.10) How much of sucrose is to be added to 500 g of water such that it boils at 100°C if the molar elevation constant for water is 0.52 K kg mol^{-1} and the boiling point of water at 750 mm Hg is 99.63°C?

Solution:

Here, elevation of boiling point ΔT_b = (100 + 273) − (99.63 + 273)

= 0.37 K

Mass of water, w_1 = 500 g

Molar mass of sucrose ($C_{12}H_{22}O_{11}$), M_2 = 11 x 12 + 22 x 1 + 11 x 16

= 342 g mol^{-1}

Molar elevation constant, K_b = 0.52 K kg mol^{-1}

We know that:

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

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

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

= 121.67 g (approximately)

Hence, the amount of sucrose that is to be added is 121.67 g

Q 2.11) To lower the melting point of 75 g of acetic acid by 1.5^{0}C, how much mass of ascorbic acid is needed to be dissolved in the solution where K_t = 3.9 K kg mol^{-1}?

Solution:

Mass of acetic acid (w_1) = 75 g

Molar mass of ascorbic acid ($C_6H_8O_6$), M_2 = 6 x 12 + 8 x 1 + 6 x 16 = 176 g mol^{-1}

Lowering the melting point ΔT_f = 1.5 K

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 (approx)

Hence, the amount of ascorbic acid needed to be dissolved is 5.08 g.

Q 2.12) If a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C, calculate the osmotic pressure in Pascal exerted by it?

Solution:

It is given that:

Volume of water (V) = 450 mL = 0.45 L

Temperature (T) = 37 + 273 = 310 K

Number of moles of the polymer, n = $\frac{1}{185000}$ mol

We know that:

Osmotic pressure, $\pi = \frac{n}{V} RT$

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

= 30.98 Pa

= 31 Pa (approx)

Q 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?

Solution:

Molar mass of ethane (C_2H_6) = 2 x 12 + 6 x 1 = 30 g mol^{-1}

Therefore, number of moles present in $6.56 \times 10^{-2}\ g$ of ethane = $\frac{6.56\times10^{-2}}{30}$

= $2.187 \times 10^{-3}\ mol$

Let 'x' be the number of moles of the solvent, According to Henry's law,

$p = K_H x$

=> 1 bar = $K_H \cdot \frac{2.187\times10^{-3}}{2.187\times10^{-3}+x}$

=> 1 bar = $K_H . \frac{2.187 \times 10^{-3}}{x}$

=> $K_H = \frac{x}{2.187 \times 10^{-3}}$ bar (Since x >> 2.187×10^{-3})

Number of moles present in 5×10^{-2} g of ethane = $\frac{5 \times 10^{-2}}{30}$ mol

= 1.67×10^{-3} mol

According to Henry's law,

$p = K_H x$

= $\frac{x}{2.187 \times 10^{-3}} \times \frac{1.67 \times 10^{-3}}{(1.67 \times 10^{-3}) + x}$

= $\frac{x}{2.187 \times 10^{-3}} \times \frac{1.67 \times 10^{-3}}{x}$ (Since, x>> 1.67×10^{-3})

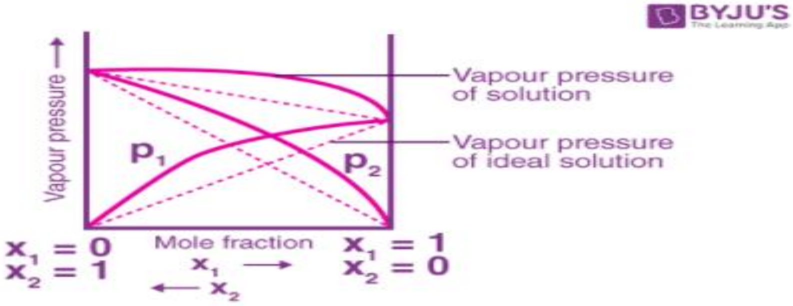
= 0.764 bar

Hence, partial pressure of the gas shall be 0.764 bar.

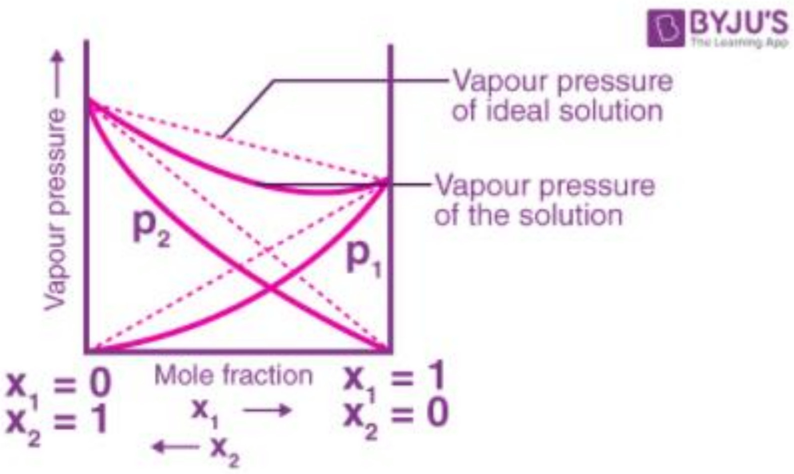
Q 2.14) What is meant by positive and negative deviations from Raoult's law and how is the sign of Δ_{sol} H related to positive and negative deviations from Raoult's law?

Solution:

According to Raoult's law the partial vapour pressure of each volatile component in any solution is directly proportional to its mole fraction. The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions. The solutions that do not obey Raoult's law (non-ideal solutions) have vapour pressures either higher or lower than that predicted by Raoult's law. If the vapour pressure is higher, then the solution is said to exhibit positive deviation, and if it is lower, then the solution is said to exhibit negative deviation from Raoult's law.



Vapour pressure of a two-component solution showing positive deviation from Raoult's law



Vapour pressure of a two-component solution showing negative deviation from Raoult's law

In the case of an ideal solution, the enthalpy of the mixing of the pure components for forming the solution is zero.

$$\Delta_{sol} H = 0$$

In the case of solutions showing positive deviations, absorption of heat takes place.

$$\therefore \ \Delta_{sol} H = Positive$$

In the case of solutions showing negative deviations, evolution of heat takes place.

$$\therefore \ \Delta_{sol} H = Negative$$

Q 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?

Solution:

Vapour pressure of the solution at normal boiling point, p_1 = 1.004 bar

Vapour pressure of pure water at normal boiling point, p_1° = 1.013 bar

Mass of solute, w_2 = 2 g

Mass of solvent (water), M_1 = 18 g mol^{-1}

According to Raoult's law,

$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{w_2 \times M_1}{M_2 \times w_1}$

=> $\frac{1.013 - 1.004}{1.013} = \frac{2 \times 18}{M_2 \times 98}$

=> $\frac{0.009}{1.013} = \frac{2 \times 18}{M_2 \times 98}$

=> $M_2 = \frac{1.013 \times 2 \times 18}{0.009 \times 98}$

= 41.35 g mol^{-1}

Hence, 41.35 g mol^{-1} is the molar mass of the solute.

Q 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?

Solution:

Vapour pressure of heptanes, p_1° = 105.2 KPa

Vapour pressure of octane, p_2° = 46.8 KPa

We know that,

Molar mass of heptanes (C_7H_{16}) = 7 x 12 + 16 x 1 = 100 g mol^{-1}

Therefore, number of moles of heptane = $\frac{26}{100}$ = 0.26 mol

Molar mass of octane (C_8H_{18}) = 8 x 12 + 18 x 1 = 114 g mol^{-1}

Therefore, number of moles of octane = $\frac{35}{114}$ = 0.31 mol

Mole fraction of heptane, $x_1 = \frac{0.26}{0.26+0.31}$ = 0.456

And, mole fraction of octane, $x_2 = 1 – 0.456$ = 0.544

Now, partial pressure of heptane, $p_1 = x_1 p_1^{\circ}$

= 0.456 x 105.2

= 47.97 kPa

Partial pressure of octane, $p_2 = x_2 p_2^{\circ}$

= 0.544 x 46.8

= 25.46 kPa

Hence, vapour pressure of solution, $p_{total} = p_1 + p_2$

= 47.97 + 25.46

= 73.43 kPa

Q 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.

Solution:

1 molal solution means 1 mol of the solute is present in 100 g of the solvent (water).

Molar mass of water = 18 g mol^{-1}

Therefore, number of moles present in 1000 g of water = $\frac{1000}{18}$

= 55.56 mol

Therefore, mole fraction of the solute in the solution is

$x_2 = \frac{1}{1+55.56}$ = 0.0177

It is given that,

Vapour pressure of water, p_1° = 12.3 kPa

Applying the relation, $\frac{p_1^\circ - p_1}{p_1^\circ} = x_2$

=> $\frac{12.3 - p_1}{12.3}$ = 0.0177

=> 12.3 – p_1 = 0.2177

=> p_1 = 12.0823

= 12.08 kPa (approx)

Hence, the vapour pressure of the solution is 12.08 kPa.

Q 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%?

Solution:

Let p_1° be the vapour pressure of pure octane.

Then, after dissolving the non-volatile solute the vapour pressure of octane is

$\frac{80}{100}\, p_1^\circ = 0.8\, p_1^\circ$

Molar mass of solute, M_2 = 40 g mol^{-1}

Mass of octane, w_1 = 114 g

Molar mass of octane, (C_8H_{18}), M_1 = 8 x 12 + 18 x 1 = 114 g mol^{-1}

Applying the relation,

$\frac{p_1^\circ - p_1}{p_1^\circ} = \frac{w_2 \times M_1}{M_2 \times w_1}$

=> $\frac{p_1^\circ - 0.8 p_1^\circ}{p_1^\circ} = \frac{w_2 \times 114}{40 \times 114}$

=> $\frac{0.2\, p_1^\circ}{p_1^\circ} = \frac{w_2}{40}$

=> 0.2 = $\frac{w_2}{40}$

=> w_2 = 8 g

Hence, the required mass of the solute is 8 g.

Q 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.

Solution:

(i) Let, the molar mass of the solute be M g mol^{-1}

Now, the number of moles of solvent (water), $n_1 = \frac{90\ g}{18\ g\ mol^{-1}}$ = 5 mol

And, the number of moles of solute, $n_2 = \frac{30\ g}{M\ mol^{-1}} = \frac{30}{M}\ mol$

p_1 = 2.8 kPa

Applying the relation:

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

$$\Rightarrow \frac{p_1^\circ - 2.8}{p_1^\circ} = \frac{\frac{30}{M}}{5 + \frac{30}{M}}$$

$$\Rightarrow 1 - \frac{2.8}{p_1^\circ} = \frac{\frac{30}{M}}{\frac{5M+30}{M}}$$

$$\Rightarrow 1 - \frac{2.8}{p_1^\circ} = \frac{30}{5M+30}$$

$$\Rightarrow \frac{2.8}{p_1^\circ} = 1 - \frac{30}{5M+30}$$

$$\Rightarrow \frac{2.8}{p_1^\circ} = \frac{5M+30-30}{5M+30}$$

$$\Rightarrow \frac{2.8}{p_1^\circ} = \frac{5M}{5M+30}$$

$$\Rightarrow \frac{p_1^\circ}{2.8} = \frac{5M+30}{5M} \qquad \text{(i)}$$

After the addition of 18 g of water:

$$n_1 = \frac{90+18g}{18} = 6\ mol \quad p_1 = 2.9 \text{ kPa}$$

Again applying the relation:

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

$$=> \frac{p_1^\circ - 2.9}{p_1^\circ} = \frac{\frac{30}{M}}{6+\frac{30}{M}}$$

$$=> 1 - \frac{2.9}{p_1^\circ} = \frac{\frac{30}{M}}{\frac{6M+30}{M}}$$

$$=> 1 - \frac{2.9}{p_1^\circ} = \frac{30}{6M+30}$$

$$=> \frac{2.9}{p_1^\circ} = 1 - \frac{30}{6M+30}$$

$$=> \frac{2.9}{p_1^\circ} = \frac{6M+30-30}{6M+30}$$

$$=> \frac{2.9}{p_1^\circ} = \frac{6M}{6M+30}$$

$$=> \frac{p_1^\circ}{2.9} = \frac{6M+30}{6M} \qquad \text{(ii)}$$

Dividing equation (i) by (ii), we have:

$$\frac{2.9}{2.8} = \frac{\frac{5M+30}{5M}}{\frac{6M+30}{6M}}$$

$$=> \frac{2.9}{2.8} \times \frac{6M+30}{6} = \frac{5M+30}{5}$$

$$=> 2.9 \times 5 \times (6M + 30) = 2.8 \times 6 \times (5M + 30)$$

=> 87M + 435 = 84M + 504

=> 3M = 69

=> M = 23 g mol^{-1}

Therefore, 23 g mol^{-1} is the molar mass of the solute.

(ii) Putting the value of 'M' in equation (i), we have:

$$\frac{p_1^\circ}{2.8} = \frac{5\times23+30}{5\times23}$$

=> $\frac{p_1^\circ}{2.8} = \frac{145}{115}$

=> p_1° = 3.53 kPa

Hence, 3.53 kPa is the vapour pressure of water at 298 K.

Q 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

Solution:

ΔT_f = 273.15 – 271 = 2.15 K

Molar mass of sugar ($C_{12}H_{22}O_{11}$) = 12 x 12 + 22 x 1 + 11 x 16 = 342 g mol^{-1}

5% solution (by mass) of cane sugar in water means 5 g of cane sugar is present in (100 – 5)g = 95 g of water.

Now, number of moles of cane sugar = $\frac{5}{342}$ mol = 0.0146 mol

Therefore, molality of the solution,

$$m = \frac{0.0146\ mol}{0.095\ kg} = 0.1537\ mol\ kg^{-1}$$

Applying the relation,

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

=> $K_f = \frac{\Delta T_f}{m}$

= $\frac{2.15\ K}{0.1537\ mol\ kg^{-1}}$

= 13.99 K kg mol^{-1}

Molar mass of glucose ($C_6H_{12}O_6$) = 6 x 12 + 12 x 1 + 6 x 16 = 180 g mol^{-1}

5% glucose in water means 5 g of glucose is present in (100 – 5) g = 95 g of water.

Therefore, number of moles of glucose = $\frac{5}{180}$ mol = 0.0278 mol

Therefore, molality of the solution, m = $\frac{0.0278\ mol}{0.095\ kg}$

= 0.2926 mol kg^{-1}

Applying the relation:

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

= $13.99\ K\ kg\ mol^{-1} \times 0.2926\ mol\ kg^{-1}$

= 4.09 K (approx)

Hence, the freezing point of 5 % glucose solution is (273.15 – 4.09) K = 269.06 K.

Q 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 K kg mol^{-1}. Calculate atomic masses of A and B.

Solution:

We know that,

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

Then, $M_{AB_2} = \frac{1000 \times 1 \times 5.1}{2.3 \times 20}$

= 110.87 g mol^{-1} $M_{AB_4} = \frac{1000 \times 1 \times 5.1}{1.3 \times 20}$

= 196.15 g mol^{-1}

Now, we have the molar masses of AB_2 and AB_4 as 110.87 g mol^{-1} and 196.15 g mol^{-1} respectively.

Let the atomic masses of A and B be x and y respectively.

Now, we can write:

x + 2y = 110.87 ...(i)

x + 4y = 196.15 ...(ii)

Subtracting equation (i) from (ii), we have

2y = 85.28

=> y = 42.64

Putting the value of 'y' in equation (1), we have:

x + 2 (42.64) = 110.87

=> x = 25.59

Hence, the atomic masses of A and B are 25.59 u and 42.64 u respectively.

Q 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?

Solution:

Given:

T = 300 K

n = 1.52 bar

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

Applying the relation, n = CRT

=> C = $\frac{n}{RT}$

= $\frac{1.52\ bar}{0.083\ bar\ L\ K^{-1}\ mol^{-1} \times 300\ K}$

= 0.061 mol

Since the volume of the solution is 1 L, the concentration of the solution would be 0.061 M.

Q 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).

Solution:

(i) Van der Wall's forces of attraction.

(ii) Van der Wall's forces of attraction.

(iii) Ion-dipole interaction.

(iv) Dipole-dipole interaction.

(v) Dipole-dipole interaction.

Q 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.

Solution:

n-octane is a non-polar solvent. Therefore, the solubility of a non-polar solute is more than that of a polar solute in the n-octane.

The order of increasing polarity is:

Cyclohexane < CH_3CN < CH_3OH < KCl

Therefore, the order of increasing solubility is:

KCl < CH_3OH < CH_3CN < Cyclohexane

Q 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.

Solution:

(i) Phenol (C_6H_5OH) has the polar group −OH and non-polar group –C_6H_5. Thus, phenol is partially soluble in water.

(ii) Toluene ($C_6H_5-CH_3$) has no polar groups. Thus, toluene is insoluble in water.

(iii) Formic acid (HCOOH) has the polar group −OH and can form H-bond with water.

Thus, formic acid is highly soluble in water.

(iv)Ethylene glycol has a polar −OH group and can form H−bond. Thus, it is highly soluble in water.

(v) Chloroform is insoluble in water.

(vi)Pentanol ($C_5H_{11}OH$) has a polar −OH group, but it also contains a very bulky nonpolar $-C_5H_{11}$ group. Thus, pentanol is partially soluble in water.

Q 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

Solution:

Number of moles present in 92 g of Na^+ ions = $\frac{92\ g}{23\ g\ mol^{-1}}$

= 4 mol

Therefore, molality of Na^+ ions in the lake = $\frac{4\ mol}{1\ kg}$

= 4 m

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

Solution:

Solubility product of CuS, $K_{sp} = 6 \times 10^{-16}$

Let s be the solubility of CuS in mol L^{-1}.

$$CuS \leftrightarrow Cu^{2+} + S^{2-}$$

s s

Now,

$$K_{sp} = [Cu^{2+}] + [S^{2-}]$$

= s x s

= s^2

Then, we have, $K_{sp} = s^2 = 6 \times 10^{-16}$

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

= $2.45 \times 10^{-8}\ mol\ L^{-1}$

Hence, $2.45 \times 10^{-8}\ mol\ L^{-1}$ is the maximum molarity of CuS in an aqueous solution.

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

Solution:

6.5 g of $C_9H_8O_4$ is dissolved in 450 g of CH_3CN.

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

Therefore, mass percentage of $C_9H_8O_4$ = $\frac{6.5}{456.5} \times 100$

= 1.424%

Q 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 1.5×10^{-3} m aqueous solution required for the above dose.

Solution:

The molar mass of nalorphene ($C_{19}H_{21}NO_3$) = 19 x 12 + 21 x 1 + 1 x 14 + 3 x 16 = 311 g mol^{-1}

In $1.5 \times 10^{-3}\ m$ aqueous solution of nalorphene,

1 kg (1000 g) of water contains $1.5 \times 10^{-3}\ mol$ = $1.5 \times 10^{-3} \times 311$ g

= 0.4665 g

Therefore, total mass of the solution = (1000 + 0.4665) g = 1000.4665 g

This implies that the mass of the solution containing 0.4665 g of nalorphene is 1000.4665 g.

Therefore, the mass of the solution containing 1.5 mg of nalorphene is:

$\frac{1000.4665 \times 1.5 \times 10^{-3}}{0.4665}$ g

= 3.22 g

Hence, 3.22 g is the required mass of aqueous solution.

Q 2.30) Calculate the amount of benzoic acid (C_6H_5COOH) required for preparing 250 mL of 0.15 M solution in methanol.

Solution:

0.15 M solution of benzoic acid in methanol means,

1000 mL of solution contains 0.15 mol of benzoic acid

Therefore, 250 mL of solution contains $\frac{0.15 \times 250}{1000}$ mol of benzoic acid

= 0.0375 mol of benzoic acid

Molar mass of benzoic acid (C_6H_5COOH) = 7 x 12 + 6 x 1 + 2 x 16 = 122 g mol^{-1}

Hence, required benzoic acid = 0.0375 mol x 122 g mol^{-1} = 4.575 g

Q 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:

Among H, Cl, and F, H is least electronegative while F is most electronegative. Then, F can withdraw electrons towards itself more than Cl and H. Thus, trifluoroacetic acid can easily lose H^+ ions i.e., trifluoroacetic acid ionizes to the largest extent. Now, the more ions produced, the greater is the depression of the freezing point. Hence, the depression in the freezing point increases in the order:

Acetic acid < trichloroacetic acid < trifluoroacetic acid

Q 2.32) Calculate the depression in the freezing point of water when 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water. $K_a = 1.4 \times 10^{-3}$, $K_f = 1.86$ K kg mol^{-1}

Solution:

Molar mass of $CH_3CH_2CHClCOOH$ = 15 + 14 + 13 + 35.5 + 12 + 16 + 16 + 1

= 122.5 g mol^{-1}

Therefore, No. of moles present in 10 g of $CH_3CH_2CHClCOOH$ = $\frac{10\ g}{122.5\ g\ mol^{-1}}$

= 0.0816 mol

It is given that 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water.

Therefore, Molality of the solution, $CH_3CH_2CHClCOOH$ = $\frac{0.0186}{250} \times 1000$

= 0.3264 mol kg^{-1}

Let 'a' be the degree of dissociation of $CH_3CH_2CHClCOOH$.

$CH_3CH_2CHClCOOH$ undergoes dissociation according to the following equation:

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

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

Since a is very small with respect to 1, $1-a \approx\ 1\ \ K_a = \frac{C\alpha^2}{1}$

Now,

=> $K_a = C\alpha^2$

=> $\alpha = \sqrt{\frac{K_a}{C}}$

= $\sqrt{\frac{1.4\times10^{-3}}{0.3264}}\quad (\because\ K_a = 1.4\times\ 10^{-3})$

= 0.0655

Again,

Total moles of equilibrium = 1 − a + a + a = 1 + a

$\therefore\ i = \frac{1+\alpha}{1}$

= $1+\ \alpha$

= 1 + 0.0655

= 1.0655

Hence, the depression in the freezing point of water is given as:

$\Delta T_f = i.K_f m$

= $1.0655\times\ 1.86\ K\ kg\ mol^{-1}\times\ 0.3264\ mol\ kg^{-1}$

= 0.65 K

Q 2.33) 19.5 g of CH_2 FCOOH 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.

Solution:

Given:

w_1 = 500 g

w_2 = 19.5 g

K_f = 1.86 K kg mol^{-1} ΔT_f = 1 K

We know that:

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

= $\frac{1.86\ K\ kg\ mol^{-1} \times 19.5\ g \times 1000\ g\ kg^{-1}}{500\ g \times 1\ K}$

= $72.54\ g\ mol^{-1}$

Therefore, observed molar mass of CH_2FCOOH, $(M_2)_{obs} = 72.54\ g\ mol^{-1}$

The calculated molar mass of CH_2FCOOH,

$(M_2)_{cal}$ = 14 + 19 + 12 + 16 + 16 + 1 = 78 g mol^{-1}

Therefore, van't Hoff factor, $i = \frac{(M_2)_{cal}}{(M_2)_{obs}}$ is:

= $\frac{78\ g\ mol^{-1}}{72.54\ g\ mol^{-1}}$

= 1.0753

Let 'a' be the degree of dissociation of CH_2FCOOH

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

=> i = 1 + α

=> α = i – 1

= 1.0753 – 1

= 0.0753

Now, the value of K_a is given as:

$$K_a = \frac{[CH_2FCOO^-][H^+]}{[CH_2FCOOH]}$$

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

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

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

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

= 0.5 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 (approx)

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

Q 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:

Vapour pressure of water, p_1^0 = 17.535 mm of Hg

Mass of glucose, w_2 = 25 g

Mass of water, w_1 = 450 g

We know that,

Molar mass of glucose ($C_6H_{12}O_6$), M_2 = 6 x 12 + 12 x 1 + 6 x 16 = 180 g mol^{-1}

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

Then, number of moles of glucose, $n_2 = \frac{25}{180\ g\ mol^{-1}}$

= 0.139 mol

And, number of moles of water, $n_1 = \frac{450\ g}{18\ g\ mol^{-1}}$

= 25 mol

We know that,

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

=> $\frac{17.535-p_1}{17.535} = \frac{0.139}{0.139+25}$

=> $17.535-p_1 = \frac{0.139\times17.535}{25.139}$

=> $17.535-p_1 = 0.097$

=> $p_1 = 17.44$ mm of Hg

Hence, 17.44 mm of Hg is the vapour pressure of water.

Q 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

Solution:

Given:

p = 760 mm Hg

$k_H = 4.27\times10^5$ mm Hg

According to Henry's law,

$p = k_H x$

$\Rightarrow x = \frac{p}{k_H}$

$= \frac{760\ mm\ Hg}{4.27 \times 10^5\ mm\ Hg}$

$= 177.99 \times 10^{-5}$

$= 178 \times 10^{-5}$ (approx)

Hence, 178×10^{-5} is the mole fraction of methane in benzene.

Q 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 torrs. 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, $n_A = \frac{100}{140}$ = 0.714 mol

Number of moles of liquid B, $n_B = \frac{1000}{180}$ = 5.556 mol

Then, mole fraction of A, $x_A = \frac{n_A}{n_A + n_B}$

$= \frac{0.714}{0.714 + 5.556}$

= 0.114

And, mole fraction of B, x_B = 1 − 0.114 = 0.886

Vapour pressure of pure liquid B, p_B° = 500 torr

Therefore, vapour pressure of liquid B in the solution,

$p_B = p_B^\circ x_B$

= 500 x 0.886

= 443 torr

Total vapour pressure of the solution, p_{total} = 475 torr

Therefore, Vapour pressure of liquid A in the solution,

$p_A = p_{total} - p_B$

= 475 – 443

= 32 torr

Now, $p_A = p_A^{\circ} x_A$

=> $p_A^{\circ} = \frac{p_A}{x_A}$

= $\frac{32}{0.114}$

= 280.7 torr

Hence, 280.7 torr is the vapour pressure of pure liquid A.

Q 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}, $p_{chloroform}$, and $p_{acetone}$ as a function of $x_{acetone}$. The experimental data observed for different compositions of mixture is:

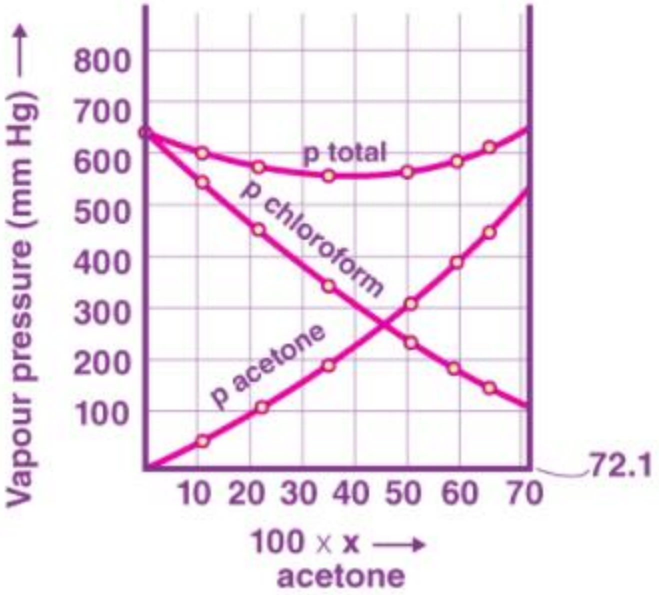
$100 \times x_{acetone}$	0	11.8	23.4	36.0	50.8	58.2	64.5	72.1
$p_{acetone}$ / mm Hg	0	54.9	110.1	202.4	322.7	405.9	454.1	521.1
$p_{chloroform}$ / mm Hg	632.8	548.1	469.4	359.7	257.7	193.6	161.2	120.7

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

Solution:

From the question, we have the following data

$100 \times x_{acetone}$	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
p_{total} (mm Hg)	632.8	603.0	579.5	562.1	580.4	599.5	615.3	641.8



It can be observed from the graph that the plot for the p_{total} of the solution curves downwards. Therefore, the solution shows a negative deviation from the ideal behaviour.

Q 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.

Solution:

Molar mass of benzene (C_6H_6) = 6 x 12 + 6 x 1 = 78 g mol^{-1}

Molar mass of toluene ($C_6H_5CH_3$) = 7 x 12 + 8 x 1 = 92 g mol^{-1}

Now, number of moles present in 80 g of benzene = $\frac{80}{78}$ = 1.026 mol

And, number of moles present in 100 g of toluene = $\frac{100}{92}$ = 1.087 mol

Therefore, Mole fraction of benzene, $x_b = \frac{1.026}{1.026+1.087}$ = 0.486

And, mole fraction of toluene, x_t = 1 – 0.486 = 0.514

It is given that vapour pressure of pure benzene, p_b° = 50.71 mm Hg

And, vapour pressure of pure toluene, p_t° = 32.06 mm Hg

Therefore, partial pressure of benzene, $p_b = x_b \times p_b^\circ$

= 0.486 x 50.71

= 24.645 mm Hg

And, partial vapour pressure of toluene, $p_t = x_t \times p_t^\circ$

= 0.514 x 32.06

= 16.479 mm Hg

Hence, mole fraction of benzene in vapour phase is given by:

$\frac{p_b}{p_b+p_t}$

= $\frac{24.645}{24.645+16.479}$

= $\frac{24.645}{41.124}$

= 0.599

= 0.6 (approx)

Q 2.39) The air is a mixture of a number of 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.

Solution:

Percentage of oxygen in air = 20 %

Percentage of nitrogen in air = 79 %

Also, it is given that water is in equilibrium with air at a total pressure of 10 atm, that is (10 x 760) mm Hg = 7600 mm Hg

Therefore,

Partial pressure of oxygen, $p_{O_2} = \frac{20}{100} \times 7600$ mm Hg

= 1520 mm Hg

Partial pressure of nitrogen, $p_{N_2} = \frac{79}{100} \times 7600$

= 6004 mm Hg

For oxygen:

$p_{O_2} = K_H . x_{O_2}$

=> $x_{O_2} = \frac{p_{O_2}}{K_H}$

= $\frac{1520\ mm\ Hg}{3.30 \times 10^7\ mm\ Hg}$ $(Given\ K_H = 3.30 \times 10^7\ mm\ Hg)$

= 4.61×10^{-5}

For nitrogen:

$p_{N_2} = K_H . x_{N_2}$

=> $x_{N_2} = \frac{p_{N_2}}{K_H}$

= $\frac{6004\ mm\ Hg}{6.51 \times 10^7\ mm\ Hg}$

= 9.22×10^{-5}

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

Q 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,

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

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

=> $w = \frac{\pi MV}{iRT}$ π = 0.75 atm

V = 2.5 L

i = 2.47

T = (27 + 273) = 300 K

Here,

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

M = 1 x 40 + 2 x 35.5

= 111 g mol^{-1}

Therefore, w = $\frac{0.75\times111\times2.5}{2.47\times0.0821\times300}$

= 3.42 g

Hence, 3.42 g is the required amount of $CaCl_2$.

Q 2.41) Determine the osmotic pressure of a solution prepared by dissolving 25 mg of K_2SO_4 in 2 litres of water at 25° C, assuming that it is completely dissociated.

Solution:

When K_2SO_4 is dissolved in water, $K^+ \ and \ SO_4^{2-}$ ions are produced.

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

Total number of ions produced = 3

Therefore, i = 3

Given:

w = 25 mg = 0.025 g

V = 2 L

T = 25^0C = (25 + 273) = 298 K

Also, we know that:

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

M = (2 x 39) + (1 x 32) + (4 x 16) = 174 g mol^{-1}

Applying the following relation,

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

= $i \frac{w}{M} \frac{1}{v} RT$

= $3 \times \frac{0.025}{174} \times \frac{1}{2} \times 0.0821 \times 298$

= $5.27 \times 10^{-3} \ atm$