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

Answer 2.1:
A homogeneous mixture of two or more non-reacting substances whose composition varies within certain fixed limits, known as a solution. Generally, the component that is present in the largest quantity is known as *solvent*. Solvent determines the physical state in which solution exists. One or more components present in the solution other than solvent are called solutes.

When the solutions contains two, three or four components, it is known as binary, ternary or quaternary solutions respectively. On the basis of physical state of components, the solutions are of the following types:

1) When both solute and solvent are in solid state. Example: Alloys.
2) When solute is in solid and solvent is in liquid state. Example: Sugar or salt solutions.
3) When solute is in solid and solvent is in gaseous state. Example: iodine vapours in air.
4) When both solute and solvent are in liquid state. Example: alcohol in water.
5) When solute is in liquid and solvent is in solid state. Example: Zinc amalgam.
6) When solute is in liquid and solvent is in gaseous state. Example: water vapour in air.
7) When both solute and solvent are in gaseous state. Example: air.
8) When solute is in gaseous and solvent is in liquid state. Example: aerated drinks.
9) When solute is in gaseous and solvent is in solid state. Example: dissolve gas in mineral.

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

Answer 2.2:
Dissolved gases in minerals.

Question 2.3:
Define the following terms:
(i) Mole fraction   **(ii)** Molality   **(iii)** Molarity   **(iv)** Mass percentage.

Answer 2.3:
(i) Mole fraction: Commonly used symbol for mole fraction is x and subscript used on the right hand side of x denotes the component. It is defined as:

$$Mole\ fraction\ of\ a\ component = \frac{Number\ of\ moles\ of\ the\ component}{Number\ of\ moles\ of\ all\ the\ component}$$

(ii) Molality: Molality (m) is defined as the number of moles of the solute per kilogram (kg) of the solvent and is expressed as:

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

(iii) Molarity: Molarity (M) is defined as number of moles of solute dissolved in one litre (or one cubic decimetre) of solution.

$$Molarity\ (M)\ = \frac{Moles\ of\ solute}{Volume\ of\ solution\ in\ litre}$$

(iv) Mass percentage: The mass percentage of a component of a solution is defined as:

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

Question 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 2.4:
In 100 g of nitric acid (HNO_3) solution,
Mass of nitric acid (HNO_3) = 68 g
Molar mass of HNO_3 = 63 g/mol
Moles on 68 g of $HNO_3 = \frac{68}{63}$ mole = 1.079 mole

Density of solution = 1.504 g mL^{-1}

Therefore, volume of solution = $\frac{Mass\ of\ solution}{Density\ of\ solution} = \frac{100}{1.504} mL = 0.0665\ L$

Molarity of the solution = $\frac{Moles\ of\ solute}{Volume\ of\ solution\ in\ L} = \frac{1.079}{0.0665} M = 16.23\ M$

Question 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 2.5:
10% w/w means 10 g glucose is present in 100 g solution.

Mass of water = 100 – 10 = 90 g = 0.90 kg

10 g glucose = $\frac{10}{180}$ mol = 0.0555 moles

Number of moles in 90 g of H_2O = $\frac{90}{18}$ mol = 5 moles

Molality of the solution = $\frac{0.0555}{0.090} m = 0.617\ m$

Mole fraction of glucose = $\frac{0.0555}{5+0.0555} = 0.01$

Mole fraction of H_2O = 1 – 0.01 = 0.99

Volume of 100 g solution = $\frac{100}{1.2} mL = 83.33\ mL = 0.08333\ L$

Molarity = $\frac{0.0555\ mol}{0.08333\ L} = 0.67\ M$

Question 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 2.6:
Step 1: To calculate the number of moles of the components in the mixture:

Suppose mass of Na_2CO_3 present in the mixture = x g

Mass of $NaHCO_3$ present in the mixture = $(1 - x)$ g

Molar mass of Na_2CO_3 = $2 \times 23 + 12 + 3 \times 16 = 106$ g mol^{-1}

Molar mass of $NaHCO_3$ = $23 + 1 + 12 + 3 \times 16 = 84$ g mol^{-1}

Number of moles of Na_2CO_3 in x g = $\frac{x}{106}$

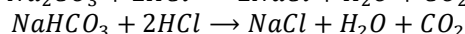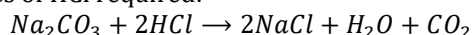Number of moles of $NaHCO_3$ in $(1 - x)$ g = $\frac{1-x}{84}$

As mixture contains equimolar amount of the two, therefore,

$$\frac{x}{106} = \frac{1-x}{84} \quad \Rightarrow 106 - 106x = 84x \quad \Rightarrow x = \frac{106}{106+84} = \frac{106}{190} g = 0.558\ g$$

Now, Number of moles of Na_2CO_3 = $\frac{0.558}{106} = 0.00526$

Number of moles of $NaHCO_3$ = $\frac{1-0.558}{84} = \frac{0.442}{84} = 0.00526$

Step 2: To calculate the number of moles of HCl required:
$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$
$$NaHCO_3 + 2HCl \longrightarrow NaCl + H_2O + CO_2$$

1 mole of Na_2CO_3 requires = 2 mole of HCl

Therefore, 0.00526 mole of Na2CO3 requires = 0.00526 × 2 moles = 0.01052 mole

1 mole of NaHCO3 requires = 1 mole of HCl

Therefore, 0.00526 mole of NaHCO3 requires = 0.00526 mole

Total HCl required = 0.01052 + 0.00526 = 0.01578 moles

Step 3: To calculate the volume of 0.1 M HCl:

0.1 mole of 0.1 M HCl are present in 1000 ml of HCl, therefore,

0.01578 mole of 0.1 M HCl will be present in = $\frac{1000}{0.1} \times 0.01578 = 157.8$ mL of HCl.

Question 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 2.7:
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 (w/w) of the solute in the resulting solution, $= \frac{235}{700} \times 100 \% = 33.57 \%$

And, mass percentage (w/w) of the solvent in the resulting solution = (100 − 33.57) % = 66.43%

Question 2.8:
An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_6O_2$) 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 2.8:
Mass of the solute, $C_2H_6O_2$ = 222.6 g
Molar mass of $C_2H_6O_2$ = 62 g mol^{-1}

Number of moles of solute $= \frac{222.6 \text{ g}}{62 \text{ g mol}^{-1}} = 3.59$

Mass of solvent = 200 g = 0.200 kg

Molality of the solution $= \frac{3.59 \text{ moles}}{0.200 \text{ kg}} = 17.95$

Total mass of the solution = 222.6 + 200 = 422.6 g

Volume of the solution $= \frac{Mass \ of \ solution}{Density \ of \ solution} = \frac{422.6 \text{ g}}{1.072 \text{ g mL}^{-1}} = 394.2$ mL = 0.3942 L

Molarity of the solution $= \frac{3.59 \text{ moles}}{0.3942 \text{ L}} = 9.11$ M

Question 2.9:
A sample of drinking water was found to be severely contaminated with chloroform (CHCl3) 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.

Answer 2.9:
15 ppm means 15 part in one million (10^6) parts by mass in the solution. Therefore,

Percentage by mass $= \frac{18}{10^6} \times 100 = 15 \times 10^{-4}$

Taking 15 g chloroform in 10^6 g of the solution, mass of the solvent = 10^6 g   [∵ Neglecting 15 g in comparison with 10^6 g]
Molar mass of CHCl3 = 12 + 1 + 3 × 35.5 = 119.5 g mol^{-1}

Therefore, molality $= \frac{\frac{15}{119.5}}{10^6} \times 100 = 1.25 \times 10^{-4}$ m

Question 2.10:
What role does the molecular interaction play in a solution of alcohol and water?
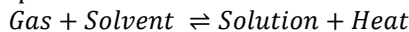
Answer 2.10:
There is strong intramolecular hydrogen bonding in alcohol molecules as well as water molecules separately. On mixing, intermolecular hydrogen bonding between alcohol and water molecules is comparatively week. Hence, they show positive deviations from ideal behaviour. As a result, the solution will have higher vapour pressure and lower boiling point than that of water and alcohol.

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

Answer 2.11:
Dissolution of gas in liquid is an exothermic process.
$$Gas + Solvent \rightleftharpoons Solution + Heat$$
As the temperature is increased, equilibrium shifts backward, according to Le Chatelier's Principle.

Question 2.12:
State Henry's law and mention some important applications?

Answer 2.12:
According to Henry's law, at a particular temperature, the solubility of a gas in given volume of a liquid is directly proportional to the pressure of the gas above the liquid.

$$m \propto p$$
$$m = kp$$

Where, k = Henry's constant.
Here, m and p represent the mass of the dissolved gas and pressure respectively.

Some important applications of Henry's law:

➢ To increase the solubility of CO^2 in soft drinks, the bottle is sealed under high pressure.

➢ Scuba divers face the problems of high concentration of dissolved gasses while breathing air at high pressure underwater. When the divers reach the surface, the pressure gradually decreases. This releases the dissolved gasses and leads to the formation of bubbles of nitrogen in blood. This blocks capillaries and creates a medical condition known bends which are painful and dangerous to life. To avoid bends, tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

➢ The partial pressure of oxygen at high altitudes is smaller than at the sea level. This results in low concentration of oxygen in the blood and tissues. Low blood oxygen causes climbers to become weak and unable to think. Such symptoms are known as anoxia.

Question 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 2.13:
Molar mass of ethane (C_2H_6) = 2 × 12 + 6 × 1 = 30 g mol^{-1}

∴ Number of moles present in 6.56×10^{-2} g of ethane $= \dfrac{6.56 \times 10^{-2}}{30} = 2.187 \times 10^{-3}$ mol

Let the number of moles of the solvent be x. According to Henry's law,
$p = K_H x$

$\Rightarrow 1\ bar = K_H . \dfrac{2.187 \times 10^{-3}}{2.187 \times 10^{-3} + x}$ $\qquad \Rightarrow 1\ bar = K_H . \dfrac{2.187 \times 10^{-3}}{x}$ $\qquad \left[\because x \gg 2.187 \times 10^{-3} \right]$

$\Rightarrow K_H = \dfrac{x}{2.187 \times 10^{-3}}\ bar$

Number of moles present in 5.00×10^{-2} g of ethane

$= \dfrac{5.00 \times 10^{-2}}{30} = 1.67 \times 10^{-3}$ mol

According to Henry's law,
$p = K_H x$

$= \dfrac{x}{2.187 \times 10^{-3}} \times \dfrac{1.67 \times 10^{-3}}{1.67 \times 10^{-3} + x}$

$= \dfrac{x}{2.187 \times 10^{-3}} \times \dfrac{1.67 \times 10^{-3}}{1.67 \times 10^{-3} + x}$ $\qquad \left[\because x \gg 1.67 \times 10^{-3} \right]$

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

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

Answer 2.14:
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.
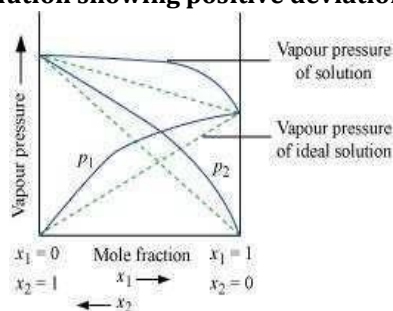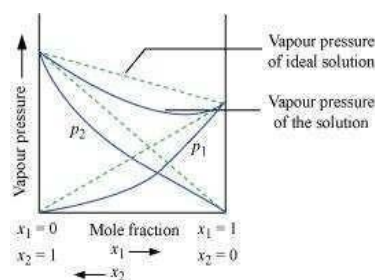
Vapour pressure of a two-component solution showing positive deviation from Raoult's law

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

Question 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 2.15:
Here, Vapour pressure of the solution at normal boiling point $(p_1) = 1.004$ bar
Vapour pressure of pure water at normal boiling point $(p_1^0) = 1.013$ bar
Mass of solute, $(w_2) = 2$ g and Mass of solvent (water), $(w_1) = 98$ g
Molar mass of solvent (water), $(M_1) = 18$ g mol^{-1} According to Raoult's law,

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

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

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

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

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

Question 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 2.16:
Vapour pressure of heptane $(p_1^0) = 105.2$ kPa
Vapour pressure of octane $(p_2^0) = 46.8$ kPa

We know that,

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

∴ Number of moles of heptane = $\frac{26}{100}$ mol = 0.26 mol

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

∴ Number of moles of octane = $\frac{35}{114}$ mol = 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, $p_1 = x_1 p_1^{0}$ = 0.456 × 105.2 = 47.97 kPa

Partial pressure of octane, $p_2 = x_2 p_2^{0}$ = 0.544 × 46.8 = 25.46 kPa

Hence, vapour pressure of solution, $p_{total} = p_1 + p_2$ = 47.97 + 25.46 = 73.43 kPa

Question 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 2.17:
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^{0} = 12.3 kPa

Applying the relation,

$\frac{p_1^{0} - p_1}{p_1^{0}} = x_2 \quad \Rightarrow \frac{12.3 - p_1}{12.3} = 0.0177$

⇒ 12.3 − p_1 = 0.2177 ⇒ p_1 = 12.0823 = 12.08 kPa (approximately)

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

Question 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 2.18:
Let the vapour pressure of pure octane be p_1^{0}.

Then, the vapour pressure of the octane after dissolving the non-volatile solute is $\frac{80}{100}p_1^{0} = 0.8 p_1^{0}$

Molar mass of solute, M_2 = 40 g mol^{-1} and mass of octane, w_1 = 114 g

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

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

$$\Rightarrow \frac{p_1^{0} - 0.8 p_1^{0}}{p_1^{0}} = \frac{w_2 \times 114}{40 \times 114}$$

$$\Rightarrow \frac{0.2 p_1^{0}}{p_1^{0}} = \frac{w_2}{40}$$

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

$$\Rightarrow w_2 = 8 \text{ g}$$

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

Question 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 2.19:

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

Now, the no. of moles of solvent (water), $n_1 = \frac{90\ g}{18\ g\ mol^{-1}} = 5$ mol and, the no. of moles of solute, $n_2 = \frac{30\ g}{M\ g\ mol^{-1}} = \frac{30}{M}$ mol

$p_1 = 2.8$ kPa, Applying the relation:

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

$$\Rightarrow \frac{p_1^0 - 2.8}{p_1^0} = \frac{\frac{30}{M}}{5 + \frac{30}{M}}$$

$$\Rightarrow 1 - \frac{2.8}{p_1^0} = \frac{\frac{30}{M}}{\frac{5M + 30}{M}}$$

$$\Rightarrow 1 - \frac{2.8}{p_1^0} = \frac{30}{5M + 30}$$

$$\Rightarrow \frac{2.8}{p_1^0} = 1 - \frac{30}{5M + 30}$$

$$\Rightarrow \frac{2.8}{p_1^0} = \frac{5M + 30 - 30}{5M + 30}$$

$$\Rightarrow \frac{2.8}{p_1^0} = \frac{5M}{5M + 30}$$

$$\Rightarrow \frac{p_1^0}{2.8} = \frac{5M + 30}{5M} \qquad (i)$$

After the addition of 18 g of water: $n_1 = \frac{90g + 18\ g}{18\ g\ mol^{-1}} = 6$ mol

$p_1 = 2.9$ kPa, Again, applying the relation:

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

$$\Rightarrow \frac{p_1^0 - 2.9}{p_1^0} = \frac{\frac{30}{M}}{6 + \frac{30}{M}}$$

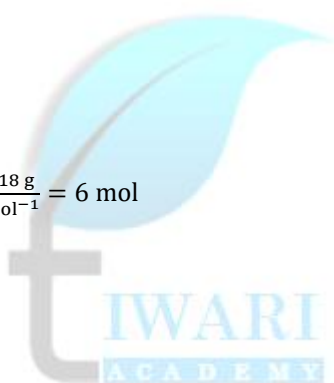$$\Rightarrow 1 - \frac{2.9}{p_1^0} = \frac{\frac{30}{M}}{\frac{6M + 30}{M}}$$

$$\Rightarrow 1 - \frac{2.9}{p_1^0} = \frac{30}{6M + 30}$$

$$\Rightarrow \frac{2.9}{p_1^0} = 1 - \frac{30}{6M + 30}$$

$$\Rightarrow \frac{2.9}{p_1^0} = \frac{6M + 30 - 30}{6M + 30}$$

$$\Rightarrow \frac{2.9}{p_1^0} = \frac{6M}{6M + 30}$$

$$\Rightarrow \frac{p_1^0}{2.9} = \frac{6M + 30}{6M} \qquad (ii)$$

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

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

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

$$\Rightarrow 2.9 \times 5 \times (6M+30) = 2.8 \times 6 \times (5M+30)$$
$$\Rightarrow 87M + 435 = 84M + 504$$
$$\Rightarrow 3M = 69$$
$$\Rightarrow M = 23\,u$$

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

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

$$\frac{p_1^0}{2.8} = \frac{5 \times 23 + 30}{5 \times 23}$$

$$\Rightarrow \frac{p_1^0}{2.8} = \frac{145}{115}$$

$$\Rightarrow p_1^0 = 3.53$$

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

Question 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.

Answer 2.20:
Here, ΔT_f = (273.15 – 271) K = 2.15 K
Molar mass of sugar ($C_{12}H_{22}O_{11}$) = 12 × 12 + 22 × 1 + 11 × 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, $m = \frac{0.0146 \text{ mol}}{0.095 \text{ kg}}$ = 0.1537 mol kg^{-1}

Applying the relation, $\Delta T_f = K_f \times m$
$$\Rightarrow K_f = \frac{\Delta T_f}{m} = \frac{2.15\,K}{0.1537 \text{ mol kg}^{-1}} = 13.99 \text{ K kg mol}^{-1}$$
Molar of glucose ($C_6H_{12}O_6$) = 6 × 12 + 12 × 1 + 6 × 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, $m = \frac{0.0278 \text{ mol}}{0.095 \text{ kg}}$ = 0.2926 mol kg^{-1}

Applying the relation, $\Delta T_f = K_f \times m$ = 13.99 K kg mol^{-1} × 0.2926 mol kg^{-1} = 4.09 K (approximately)
Hence, the freezing point of 5% glucose solution is (273.15 – 4.09) K= 269.06 K.

Question 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 Kkg mol^{-1}.
Calculate atomic masses of A and B.

Answer 2.21:

We know that, $M_2 = \frac{1000 \times w_2 \times k_f}{\Delta T_f \times w_1}$

Then,

$$M_{AB_2} = \frac{1000 \times 1 \times 5.1}{2.3 \times 20} = 110.87 \text{ g mol}^{-1}$$

$$M_{AB_4} = \frac{1000 \times 1 \times 5.1}{1.3 \times 20} = 196.15 \text{ g mol}^{-1}$$

Now, we have the molar masses of AB₂ and AB₄ 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 $x + 2 \times 42.64 = 110.87$
⇒ $x = 25.59$
Hence, the atomic masses of A and B are 25.59 u and 42.64 u respectively.

Question 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 2.22:

Here, T = 300 K π = 1.52 bar
R = 0.083 bar L K⁻¹ mol⁻¹ Applying the relation, π = CRT

$$\Rightarrow C = \frac{\pi}{RT} = \frac{1.52 \text{ bar}}{0.083 \text{ bar L K}^{-1} \times 300 \text{ K}} = 0.061 \text{ mol}$$

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

Question 2.23:

Suggest the most important type of intermolecular attractive interaction in the following pairs.
(i) n-hexane and n-octane
(ii) I₂ and CCl₄
(iii) NaClO₄ and water
(iv) methanol and acetone
(v) acetonitrile (CH₃CN) and acetone (C₃H₆O).

Answer 2.23:

(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.

Question 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 2.24:

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 < CH₃CN < CH₃OH < KCl
Therefore, the order of increasing solubility is: KCl < CH₃OH < CH₃CN < Cyclohexane

Question 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 2.25:
(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 (HO—___—OH) has 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 polar –OH group, but it also contains a very bulky nonpolar –C_5H_{11} group. Thus, pentanol is partially soluble in water.

Question 2.26:
If the density of some lake water is 1.25 g mL^{-1} and contains 92 g of Na$^+$ ions per kg of water, calculate the molality of Na$^+$ ions in the lake.

Answer 2.26:
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

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

Answer 2.27:
Solubility product of CuS, $K_{sp} = 6 \times 10^{-16}$ Let s be the solubility of CuS in mol L^{-1}.

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

Now, $K_{sp} = \left[Cu^{2+}\right]\left[S^{2-}\right]$
$= s \times s = s^2$
Then, we have, $K_{sp} = s^2 = 6 \times 10^{-16}$
$\Rightarrow s = \sqrt{6 \times 10^{-16}} = 2.45 \times 10^{-8}$ mol L^{-1}
Hence, the maximum molarity of CuS in an aqueous solution is 2.45×10^{-8} mol L^{-1}.

Question 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.

Answer 2.28:
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%

Question 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.

Answer 2.29:
The molar mass of Nalorphene ($C_{19}H_{21}NO_3$) is given as:
$19 \times 12 + 12 \times 1 + 1 \times 14 + 3 \times 16 = 311$ g mol^{-1}
In 1.5×10^{-3}m aqueous solution of nalorphene, 1 kg (1000 g) of water contains 1.5×10^{-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, 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, the mass of aqueous solution required is 3.22 g.

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

Answer 2.30:
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 × 12 + 6 × 1 + 2 × 16 = 122 g mol^{-1}
Hence, required benzoic acid = 0.0375 mol × 122 g mol^{-1} = 4.575 g

Question 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.

Answer 2.31:
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
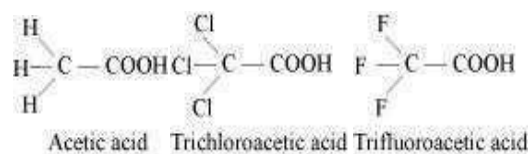
Question 2.32:
Calculate the depression in the freezing point of water when 10 g of $CH_3CH_2CHClCOOH$ is added to 250 g of water.
$K_a = 1.4 \times 10^{-3}$, $K_f = 1.86$ K kg mol^{-1}.

Answer 2.32:
Molar mass of $CH_3CH_2CHClCOOH$ = 15 + 14 + 13 + 35.5 + 12 + 16 + 16 + 1 = 122.5 g mol^{-1}
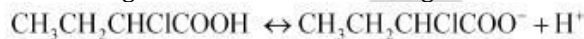
∴ No. of moles present in 10 g of $CH_3CH_2CHClCOOH = \frac{10\text{ g}}{122.5\text{ g mol}^{-1}} = 0.0816$ mol

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

∴ Molality of the solution, $\frac{0.0186}{250} \times 1000 = 0.3264$ mol kg^{-1}

Let α be the degree of dissociation of $CH_3CH_2CHClCOOH$.
$CH_3CH_2CHClCOOH$ undergoes dissociation according to the following equation:

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

Initial conc.	C mol L^{-1}	0	0
At equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$

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

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

Since α is very small with respect to 1, $1 - \alpha \approx 1$

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

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

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

$$= \sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} \quad (\because K_a = 1.4 \times 10^{-3})$$
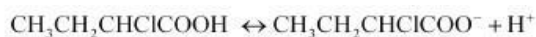
$$= 0.0655$$

Again,

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

Initial moles	1	0	0
At equilibrium	$1 - \alpha$	α	α

Total moles of equilibrium = $1 - \alpha + \alpha + \alpha$

= $1 + \alpha$

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

$$= 1 + \alpha$$

$$= 1 + 0.0655$$

$$= 1.0655$$

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

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

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

$$= 0.65\,K$$

Question 2.33:

19.5 g of CH₂FCOOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.0°C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

Answer 2.33:

It is given that:

$$w_1 = 500\,g$$

$$w_2 = 19.5\,g$$

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

$$\Delta T_f = 1\,K$$

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 mass of CH₂FCOOH, $(M_2)_{obs} = 72.54\,g\,mol^{-1}$

The calculated mass of CH₂FCOOH, $(M_2)_{cal} = 14 + 19 + 12 + 16 + 16 + 1 = 78\,g\,mol^{-1}$

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

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

$$= 1.0753$$

Let α be the degree of dissociation of CH₂FCOOH.

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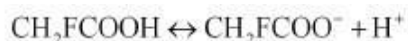
Initial conc.	C mol L^{-1}	0	0
At equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$	Total = $C(1+\alpha)$

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

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

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

$$= 1.0753 - 1$$

$$= 0.0753$$

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, $K_a = \dfrac{C\alpha^2}{1-\alpha}$

$$= \frac{0.5 \times (0.0753)^2}{1 - 0.0753}$$

$$= \frac{0.5 \times 0.00567}{0.9247}$$

$$= 0.00307\,(\text{approximately})$$

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

Question 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 2.34:
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 × 12 + 12 × 1 + 6 × 16 = 180 g mol^{-1}

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

Then, number of moles of glucose, $n_2 = \dfrac{25\ g}{180\ g\ mol^{-1}}$ = 0.139 mol

And, number of moles of water, $n_1 = \dfrac{450\ g}{18\ g\ mol^{-1}}$ = 25 mol

We know that,

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

$$\Rightarrow \dfrac{17.535 - p_1}{17.535} = \dfrac{0.139}{0.139 + 25}$$

$$\Rightarrow 17.535 - p_1 = \dfrac{0.139 \times 17.535}{25.139}$$

⇒ 17.535 − p_1 = 0.097

⇒ p_1 = 17.44 mm of Hg

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

Question 2.35:

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

Answer 2.35:

Here, p = 760 mm Hg k$_H$ = 4.27 × 10^5 mm Hg

According to Henry's law, $p = k_H x$

$$\Rightarrow x = \dfrac{p}{k_H} = \dfrac{760\ mm\ Hg}{4.27 \times 10^5\ mm\ Hg}$$

= 177.99 × 10^{-5}

= 178 × 10^{-5} (approximately)

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

Question 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 2.36:

Number of moles of liquid A, $n_A = \dfrac{100\ g}{140\ g\ mol^{-1}}$ = 0.714 mol

Number of moles of liquid B, $n_B = \dfrac{1000\ g}{180\ g\ mol^{-1}}$ = 5.556 mol

Then, mole fraction of A, $x_A = \dfrac{n_A}{n_A + n_B} = \dfrac{0.714}{0.714 + 50556}$ = 0.114

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

Vapour pressure of pure liquid B, p_B^0 = 500 torr

Therefore, vapour pressure of liquid B in the solution,

$p_B = p_B^0\ x_B$ = 500 × 0.886 = 443 torr

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

So, vapour pressure of liquid A in the solution,

$p_A = p_{tatal} - p_B$ = 475 − 443 = 32 torr

Now, $p_A = p_A^0\ x_A \Rightarrow p_A^0 = \dfrac{p_A}{x_A} = \dfrac{32}{0114}$ = 280.7 torr

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

Question 2.37:
Vapour pressure 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

Answer 2.37:
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_{tota}(mm Hg)	632.8	603.0	579.5	562.1	580.4	599.5	615.3	641.8
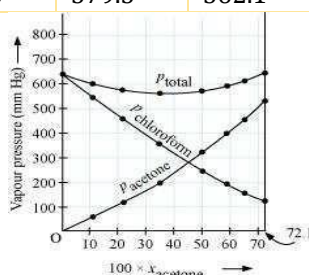
It can be observed from the graph that the plot for the p_{total} of the solution curves downwards. Therefore, the solution shows negative deviation from the ideal behaviour.

Question 2.38:
Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and naphthalene at 300 Kare 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.

Answer 2.38:
Molar mass of benzene $(C_6H_6) = 6 \times 12 + 6 \times 1 = 78$ g mol^{-1}
Molar mass of toluene $(C_6H_5CH_3) = 7 \times 12 + 8 \times 1 = 92$ g mol^{-1}

Now, no. of moles present in 80 g of benzene $= \frac{80}{78} = 1.026$ mol

And, no. 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, $p_b^0 = 50.71$ mm Hg
And, vapour pressure of pure toluene, $p_t^0 = 32.06$ mm Hg
Therefore, partial vapour pressure of benzene, $p_b = x_b \cdot p_b^0 = 0.486 \times 50.71 = 24.645$ mm Hg
And, partial vapour pressure of toluene, $p_t = x_t \cdot p_t^0 = 0.514 \times 32.06 = 16.479$ mm Hg
Hence, mole fraction of benzene in vapour phase is given by:
$$\frac{p_b}{p_b + p_t} = \frac{24.645}{24.645 + 16.479} = \frac{24.645}{41.124} = 0.599 = 0.6$$

Question 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 Kif the
Henry's law constants for oxygen and nitrogen are 3.30×10^7 mm and 6.51×10^7 mm respectively, calculate the composition of these gases in water.

Answer 2.39:
Percentage of oxygen (O₂) in air = 20 %

Percentage of nitrogen (N_2) in air = 79%

Also, it is given that water is in equilibrium with air at a total pressure of 10 atm, i.e., (10 × 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, $p_{N_2} = \frac{79}{100} \times 7600$ mm Hg = 6004 mmHg

Now, according to Henry's law: $p = K_H.x$

For oxygen: $p_{O_2} = K_H.x_{O_2}$

$\Rightarrow x_{O_2} = \frac{p_{O_2}}{K_H} = \frac{1520 \text{ mm Hg}}{3.30 \times 10^7 \text{ mm Hg}} = 4.61 \times 10^{-5}$ $\qquad$ [∵ $K_H = 3.30 \times 10^7$ mm Hg]

For nitrogen: $p_{N_2} = K_H.x_{N_2}$

$\Rightarrow x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{6004 \text{ mm Hg}}{6.51 \times 10^7 \text{ mm Hg}} = 9.22 \times 10^{-5}$

Hence, the mole fractions of oxygen and nitrogen in water are 4.61 ×10⁻⁵ and 9.22 × 10⁻⁵ respectively.

Question 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 2.40:
We know that,

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

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

$$\Rightarrow w = \frac{\pi MV}{iRT}$$

$\pi = 0.75 \text{ atm}$

$V = 2.5 \text{ L}$

$i = 2.47$

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

Here, R = 0.0821 L atm K⁻¹mol⁻¹ and M = 1 × 40 + 2 × 35.5 = 111g mol⁻¹

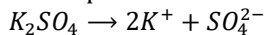Therefore, $w = \frac{0.75 \times 111 \times 2.5}{2.47 \times 0.0821 \times 300} = 3.42$ g

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

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

Answer 2.41:
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 = 25⁰C = (25 + 273) K = 298 K

Also, we know that:

R = 0.0821 L atm K⁻¹mol⁻¹ and M = (2 × 39) + (1 × 32) + (4 × 16) = 174 g mol⁻¹

Appling the following relation,

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

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

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

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