Q 2.1) If 22 g of benzene is dissolved in 122 g of carbon tetrachloride, determine the mass percentage of carbon tetrachloride $\left(\mathrm{CCl}_{4}\right)$ and benzene $\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)$.

Answer 2.1:
Mass percentage of Benzene $\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)=$

$$
\begin{aligned}
& \quad \frac{\text { Mass of } C_{6} H_{6}}{\text { Total mass of the solution }} v \times 100 \\
& = \\
& =\frac{\text { Mass of } C_{6} H_{6}}{\text { Mass of } C_{6} H_{6}+{\text { Mass of } \mathrm{CCl}_{4}} \times 100} \\
& = \\
& =15.28 \%
\end{aligned}
$$

Mass percentage of Carbon Tetrachloride $\left(\mathrm{CCl}_{4}\right)=$
$\frac{\text { Mass of } \mathrm{CCl}_{4}}{\text { Total mass of the solution }} \times 100$
$=$

$\frac{{\text { Mass of } \mathrm{CCl}_{4}}_{\text {Mass of } \mathrm{C}_{6} \mathrm{H}_{6}+{\mathrm{Mass} \mathrm{of} \mathrm{CCl}_{4}}^{2}} \times 100}{}$| $\frac{122}{22+122} \times 100$ |
| :--- |
| $84.72 \%$ |

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

Answer 2.2:
Assume the mass of benzene is 30 g in the total mass of the solution of 100 g .

Mass of $\mathrm{CCl}_{4}=(100-30) \mathrm{g}$
$=70 \mathrm{~g}$
Molar mass of benzene $\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)=(6 \times 12+6 \times 1) \mathrm{g}$

$$
\begin{aligned}
& \mathrm{mol}^{-1} \\
= & 78 \mathrm{~g} \\
& \mathrm{~mol}^{-1}
\end{aligned}
$$

Therefore, the number of moles of $\mathrm{C}_{6} \mathrm{H}_{6}=$

$$
\frac{30}{78}
$$

mol
$=0.3846 \mathrm{~mol}$
Molar mass of $\mathrm{CCl}_{4}=1 \times 12+4 \times 355=154 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

Therefore, the number of moles of $\mathrm{CCl}_{4}=$

$$
\frac{70}{154}
$$

mol
$=0.4545 \mathrm{~mol}$
Thus, the mole fraction of $\mathrm{C}_{6} \mathrm{H}_{6}$ is given as

$$
\begin{aligned}
& \quad \frac{\text { Number of moles of } C_{6} H_{6}}{\text { Number of moles of } C_{6} H_{6}+\text { Number of moles of } \mathrm{CCl}_{4}} \\
& = \\
& \\
& =0.388 \\
& =0.3846+0.4545
\end{aligned}
$$

Q 2.3) Determine the molarity of each of the solutions given below:
(a) $\mathbf{3 0} \mathbf{g}$ of $\mathbf{C o}(\mathrm{NO})_{3} .6 \mathrm{H}_{2} \mathrm{O}$ in 4.3 L of solution.
(b) 30 mL of $0.5 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}$ diluted to 500 mL .

Answer 2.3:
We know that,
Molarity $=$

## $\frac{\text { Moles of Solute }}{\text { Volume of solution in litre }}$

(a) Molar mass of $\mathrm{Co}(\mathrm{NO})_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}=59+2(14+3 \times 16)+6 \times 18=291 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

Therefore, the moles of $\mathrm{Co}(\mathrm{NO})_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}=$

$$
\frac{30}{291}
$$

mol
$=0.103 \mathrm{~mol}$
Therefore, molarity $=$
$\frac{0.103 \mathrm{~mol}}{4.3 \mathrm{~L}}$
$=0.023 \mathrm{M}$
(b) Number of moles present in 1000 mL of $0.5 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}=0.5 \mathrm{~mol}$

Therefore, the number of moles present in 30 mL of $0.5 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}=$

$$
\begin{aligned}
& \frac{0.5 \times 30}{1000} \mathrm{~mol} \\
= & 0.015 \mathrm{~mol}
\end{aligned}
$$

Therefore, molarity $=$
$\frac{0.015}{0.5 L} \mathrm{~mol}$
$=0.03 \mathrm{M}$
Q 2.4) To make 2.5 kg of 0.25 molar aqueous solution, determine the mass of urea $\left(\mathrm{NH}_{2} \mathbf{C O N H}_{2}\right)$ that is required.
Answer 2.4:
Molar mass of urea $(\mathrm{NH} 2 \mathrm{CONH} 2)=2(1 \times 14+2 \times 1)+1 \times 12+1 \times 16=60 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

0.25 molar aqueous solution of urea means

1000 g of water contains $0.25 \mathrm{~mol}=(0.25 \times 60) \mathrm{g}$ of urea $=15 \mathrm{~g}$ of urea

That is,
$(1000+15) \mathrm{g}$ of solution contains 15 g of urea
Therefore, $2.5 \mathrm{~kg}(2500 \mathrm{~g})$ of solution contains $=$

$$
\frac{15 \times 2500}{1000+15} g
$$

$=36.95 \mathrm{~g}$
$=37 \mathrm{~g}$ of urea (approx.)
Hence, the mass of Urea required is 37 g .

Q 2.5) If $1.202 \mathrm{~g}^{m L^{-1}}$ is the density of $20 \%$ aqueous KI, determine the following:
(a) Molality of KI
(b) Molarity of KI
(c) Mole fraction of KI

Answer 2.5:
(a) Molar mass of $\mathrm{KI}=39+127=166 \mathrm{~g}$

$$
m^{-1}
$$

$20 \%$ 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 $(100-20) \mathrm{g}$ of water $=80 \mathrm{~g}$ of water.
Therefore, molality of the solution $=$

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

(b) It is given that the destiny of the solution $=1.202$

$$
g m L^{-1}
$$

Volume of 100 g solution $=$

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

Therefore, the molarity of the solution $=$

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

(c) Moles of $\mathrm{KI}=$

$$
\begin{aligned}
& \frac{20}{166} \\
= & 0.12 \mathrm{~mol}
\end{aligned}
$$

Moles of water $=\frac{80}{18}$
$=4.44 \mathrm{~mol}$
Therefore, mole $=$

$$
\frac{\text { Moles of KI }}{\text { Moles of KI Moles of water }}
$$

Fraction of $\mathrm{KI}=$
$\frac{0.12}{0.12+4.44}$
$=0.0263$

Q 2.6) Calculate Henry's law constant when the solubility of $H_{2} S$ (a toxic gas with a rotten egg-like smell) in water at STP is $\mathbf{0 . 1 9 5}$ m

Answer 2.6:
It is given that the solubility of $\mathrm{H}_{2} \mathrm{~S}$ in water at STP is 0.195 m , i.e., 0.195 mol of $\mathrm{H}_{2} \mathrm{~S}$ is dissolved in 1000 g of water.
Moles of water $=$

$$
\frac{1000 \mathrm{~g}}{18 \mathrm{gmol}{ }^{-1}}
$$

$=55.56 \mathrm{~mol}$
Therefore, the mole fraction of $\mathrm{H}_{2} \mathrm{~S}, \mathrm{x}=$

$$
\begin{aligned}
& \frac{\text { Moles of } \mathrm{H}_{2} \mathrm{~S}}{\text { Moles of } \mathrm{H}_{2} \mathrm{~S}+\text { Moles of water }} \\
&= \\
& \frac{0.195}{0.195+55.56} \\
&= 0.0035
\end{aligned}
$$

At STP, pressure $(\mathrm{p})=0.987$ bar
According to Henry's law, $\mathrm{p}=$

$$
\begin{aligned}
& K_{H} \\
& \mathrm{x} \\
& => \\
& K_{H}=\frac{P}{x} \\
& = \\
& \frac{0.987}{0.0035} \text { bar } \\
& =282 \text { bar }
\end{aligned}
$$

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.

## Answer 2.7:

The total amount of solute present in the mixture is given by,
$300 \times \frac{25}{100}+400 \times \frac{40}{100}$
$=75+160$
$=235 \mathrm{~g}$
Total amount of solution $=300+400=700 \mathrm{~g}$
Therefore, mass percentage of the solute in the resulting solution $=$
$\frac{235}{700} \times 100$
$=33.57 \%$
And the 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 the total vapour pressure is 600 mm Hg . Also, find the composition of the vapour phase.

Answer 2.8:
It is given that
$P_{A}^{\circ}$
$=450-\mathrm{mm}$ of Hg
$P_{B}^{\circ}$
$=700 \mathrm{~mm}$ of Hg
$P_{\text {total }}$
$=600 \mathrm{~mm}$ of Hg
According to Raoult's law,

$$
\begin{aligned}
& P_{A}=P_{A}^{\circ} x_{A} \\
& P_{B}=P_{B}^{\circ} x_{B}=P_{B}^{\circ}\left(1-x_{A}\right)
\end{aligned}
$$

Therefore, total pressure,

$$
\begin{aligned}
& P_{\text {total }}=P_{A}+P_{B} \\
& \Rightarrow \\
& P_{\text {total }}=P_{A}^{\circ} x_{A}+P_{B}^{\circ}\left(1-x_{A}\right) \\
& \Rightarrow \\
& P_{\text {total }}=P_{A}^{\circ} x_{A}+P_{B}^{\circ}-P_{B}^{\circ} x_{A} \\
& \Rightarrow \\
& P_{\text {total }}=\left(P_{A}^{\circ}-P_{B}^{\circ}\right) x_{A}+P_{B}^{\circ} \\
& \Rightarrow 600=(450-700) \mathrm{x}_{A}+700 \\
& \Rightarrow-100=-250 \mathrm{x}_{\wedge} \\
& \Rightarrow \mathrm{x}_{\wedge}=0.4
\end{aligned}
$$

Therefore,

$$
x_{B}=1-x_{A}=1-0.4=0.6
$$

Now,

$$
\begin{gathered}
P_{A}=P_{A}^{\circ} x_{A} \\
=450 \times 0.4=180 \mathrm{~mm} \text { of } \mathrm{Hg} \\
P_{B}=P_{B}^{\circ} x_{B} \\
=700 \times 0.6=420 \mathrm{~mm} \text { of } \mathrm{Hg}
\end{gathered}
$$

Now, in the vapour phase, the mole fraction of liquid $\mathrm{A}=$

$$
\begin{aligned}
& \frac{P_{A}}{P_{A}+P_{B}} \\
& = \\
& \frac{180}{180+420} \\
& = \\
& \frac{180}{600} \\
& =0.30
\end{aligned}
$$

And, mole fraction of liquid $B=1-0.30=0.70$
Q 2.9) Find the vapour pressure of water and its relative lowering in the solution which is 50 g of urea $\left(\mathrm{NH}_{2} \mathrm{CONH}_{2}\right)$ dissolved in 850 g of water (Vapor pressure of pure water at 298 K is 23.8 mm Hg ).

Answer 2.9:
It is given that vapour pressure of water,

$$
P_{1}^{\circ}
$$

$=23.8 \mathrm{~mm}$ of Hg
Weight of water taken,
$\boldsymbol{w}_{1}=850 \mathrm{~g}$
Weight of urea taken,
$w_{2}=50 \mathrm{~g}$
Molecular weight of water,

$$
\begin{aligned}
& M_{1} \\
& =18 \mathrm{~g} \\
& \mathrm{~mol}^{-1}
\end{aligned}
$$

Molecular weight of urea,

$$
\begin{aligned}
& M_{2} \\
& =60 \mathrm{~g} \\
& \mathrm{~mol}^{-1}
\end{aligned}
$$

Now, we have to calculate the vapour pressure of water in the solution. We take vapour pressure as $\mathrm{p}_{1}$.
Now, from Raoult's law, we have

$$
\begin{aligned}
& \frac{P_{1}^{o}-P_{1}}{P_{1}^{o}}=\frac{n_{2}}{n_{1}+n_{2}} \\
& \Rightarrow \\
& \frac{P_{1}^{o}-P_{1}}{P_{1}^{o}}=\frac{\frac{w_{2}}{M_{2}}}{\frac{w_{1}}{M_{1}}+\frac{w_{2}}{M_{2}}} \\
& \Rightarrow> \\
& \frac{23.8-P_{1}}{23.8}=\frac{\frac{50}{60}}{\frac{850}{18}+\frac{50}{60}} \\
& \Rightarrow \\
& \frac{23.8-P_{1}}{23.8}=\frac{0.83}{47.22+0.83} \\
& \Rightarrow \\
& \frac{23.8-P_{1}}{23.8}=0.0173 \\
& \Rightarrow \\
& => \\
& P_{1} \\
& =23.4 \mathrm{~mm} \text { of } \mathrm{Hg}
\end{aligned}
$$

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 $100^{\circ} \mathrm{C}$ if the molar elevation constant for water is $0.52 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}$ and the boiling point of water at 750 mm Hg is $99.63^{\circ} \mathbf{C}$ ?

Answer 2.10:
Here, elevation of boiling point
$\Delta T_{b}$

$$
\begin{aligned}
& =(100+273)-(99.63+273) \\
& =0.37 \mathrm{~K}
\end{aligned}
$$

Mass of water,

$$
w_{1}=500 \mathrm{~g}
$$

Molar mass of sucrose $\left(\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}\right)$,

## $M_{2}$

$=11 \times 12+22 \times 1+11 \times 16$
$=342 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

Molar elevation constant, $\mathrm{K}_{\mathrm{b}}=0.52 \mathrm{~K} \mathrm{~kg}$

$$
\mathrm{mol}^{-1}
$$

We know that

$$
\begin{aligned}
& \Delta T_{b}=\frac{K_{b} \times 1000 \times w_{2}}{M_{2} \times w_{1}} \\
& => \\
& w_{2}=\frac{\Delta T_{b} \times M_{2} \times w_{1}}{K_{b} \times 1000} \\
& = \\
& \frac{0.37 \times 342 \times 500}{0.52 \times 1000} \\
& =121.67 \mathrm{~g} \text { (approximately) }
\end{aligned}
$$

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 $1.5^{\circ} \mathrm{C}$, how much mass of ascorbic acid is needed to $\mathrm{mol}^{-1}$
be dissolved in the solution where $K_{t}=3.9 \mathrm{~K} \mathrm{~kg}$ ?

Answer 2.11:
Mass of acetic acid $\left(\mathrm{w}_{\mathrm{t}}\right)=75 \mathrm{~g}$
Molar mass of ascorbic acid $\left(\mathrm{C}_{6} \mathrm{H}_{8} \mathrm{O}_{6}\right), \mathrm{M}_{2}=6 \times 12+8 \times 1+6 \times 16=176 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

Lowering the melting point

## $\Delta T_{f}$

$=1.5 \mathrm{~K}$
We know that

$$
\begin{aligned}
& \Delta T_{f}=\frac{K_{f} \times w_{2} \times 1000}{M_{2} \times w_{1}} \\
& => \\
& w_{2}=\frac{\Delta T_{f} \times M_{2} \times w_{1}}{K_{f} \times 1000} \\
& = \\
& \frac{1.5 \times 176 \times 75}{3.9 \times 1000} \\
& =5.08 \mathrm{~g} \text { (approx) }
\end{aligned}
$$

Hence, the amount of ascorbic acid needed to be dissolved is 5.08 g .
Q 2.12) If a solution is prepared by dissolving 1.0 g of polymer of molar mass $185,000 \mathrm{in} 450 \mathrm{~mL}$ of water at $37^{\circ} \mathrm{C}$, calculate the osmotic pressure in Pascal exerted by it.

Answer 2.12:
It is given that
Volume of water $(\mathrm{V})=450 \mathrm{~mL}=0.45 \mathrm{~L}$
Temperature $(\mathrm{T})=37+273=310 \mathrm{~K}$
Number of moles of the polymer, $n=$

$$
\frac{1}{185000}
$$

mol

We know that
Osmotic pressure,

$$
\begin{aligned}
& \quad \pi=\frac{n}{V} R T \\
& = \\
& \quad \frac{1}{185000} \mathrm{~mol} \times \frac{1}{0.45 \mathrm{~L}} \times 8.314 \times 10^{3} \mathrm{PaL} \mathrm{~K} \\
& =30.98 \mathrm{~Pa} \\
& =31 \mathrm{~Pa} \text { (approx })
\end{aligned}
$$

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

Answer 2.13:

Molar mass of ethane $\left(\mathrm{C}_{2} \mathrm{H}_{6}\right)=2 \times 12+6 \times 1=30 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

Therefore, number of moles present in

$$
\begin{aligned}
& 6.56 \times 10^{-2} g \\
& \text { of ethane }= \\
& \frac{6.56 \times 10^{-2}}{30} \\
& = \\
& 2.187 \times 10^{-3} \mathrm{~mol}
\end{aligned}
$$

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

$$
\begin{aligned}
& p=K_{H x} \\
& \Rightarrow 1 \mathrm{bar}= \\
& K_{H} \cdot \frac{2.187 \times 10^{-3}}{2.187 \times 10^{-3}+x} \\
& \Rightarrow 1 \mathrm{bar}= \\
& K_{H \cdot} \frac{2.187 \times 10^{-3}}{x} \\
& => \\
& K_{H}=\frac{x}{2.187 \times 10^{-3}} \\
& \text { bar } \quad\left(\text { Since } \ggg>10^{-3}\right. \\
& 2.187 \times 10^{-3} \\
& )
\end{aligned}
$$

The number of moles present in

$$
\begin{aligned}
& 5 \times 10^{-2} \\
& \mathrm{~g} \text { of ethane }= \\
& \frac{5 \times 10^{-2}}{30} \\
& \mathrm{~mol} \\
& =
\end{aligned}
$$

$$
1.67 \times 10^{-3} \mathrm{~mol}
$$

According to Henry's law,

```
p= KH
=
    \frac{x}{2.187\times1\mp@subsup{0}{}{-3}}\times\frac{1.67\times1\mp@subsup{0}{}{-3}}{(1.67\times1\mp@subsup{0}{}{-3})+x}
=
\frac{x}{2.187\times1\mp@subsup{0}{}{-3}}\times\frac{1.67\times1\mp@subsup{0}{}{-3}}{x}
    (Since, x>>
1.67\times10-3
)
\(=0.764 \mathrm{bar}\)
```

Hence, the 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
$\Delta_{\text {sol }} H$ 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.

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

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

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

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

## $\therefore \Delta_{\text {sol }} H=$ 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?

Answer 2.15:
Vapour pressure of the solution at normal boiling point,

$$
p_{1}=1.004 \mathrm{bar}
$$

Vapour pressure of pure water at normal boiling point,

$$
p_{1}^{\circ}=1.013 \mathrm{bar}
$$

Mass of solute, $\mathrm{w}_{2}=2 \mathrm{~g}$
Mass of solvent (water), $\mathrm{M}_{1}=18 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

According to Raoult's law,

$$
\begin{aligned}
& \frac{p_{1}^{\mathrm{o}}-p_{1}}{p_{1}^{\mathrm{o}}}=\frac{w_{2} \times M_{1}}{M_{2} \times w_{1}} \\
& => \\
& \frac{1.013-1.004}{1.013}=\frac{2 \times 18}{M_{2} \times 98} \\
& \Rightarrow \\
& \frac{0.009}{1.013}=\frac{2 \times 18}{M_{2} \times 98} \\
& => \\
& M_{2}=\frac{1.013 \times 2 \times 18}{0.009 \times 98} \\
& =41.35 \mathrm{~g}
\end{aligned}
$$

## $\mathrm{mol}^{-1}$

Hence, 41.35 g

## $\mathrm{mol}^{-1}$

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?

Answer 2.16:
Vapour pressure of heptanes,

$$
p_{1}^{\circ}=105.2 \mathrm{kPa}
$$

Vapour pressure of octane,

$$
p_{2}^{\circ}=46.8 \mathrm{kPa}
$$

We know that,
The molar mass of heptanes $\left(\mathrm{C}_{7} \mathrm{H}_{16}\right)=7 \times 12+16 \times 1=100 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

Therefore, the number of moles of heptane $=$

$$
\frac{26}{100}
$$

$=0.26 \mathrm{~mol}$
The molar mass of octane $\left(\mathrm{C}_{8} \mathrm{H}_{18}\right)=8 \times 12+18 \times 1=114 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

Therefore, the number of moles of octane $=$
$\frac{35}{114}$
$=0.31 \mathrm{~mol}$
The mole fraction of heptane,

$$
\begin{aligned}
& x_{1}=\frac{0.26}{0.26+0.31} \\
= & 0.456
\end{aligned}
$$

And, the mole fraction of octane,

$$
\begin{aligned}
& x_{2}=1-0.456 \\
= & 0.544
\end{aligned}
$$

Now, the partial pressure of heptane,

$$
p_{1}=x_{1} p_{1}^{\circ}
$$

$=0.456 \times 105.2$
$=47.97 \mathrm{kPa}$

Partial pressure of octane,

$$
p_{2}=x_{2} p_{2}^{\circ}
$$

$=0.544 \times 46.8$
$=25.46 \mathrm{kPa}$
Hence, vapour pressure of solution,

$$
p_{\text {total }}=p_{1}+p_{2}
$$

$=47.97+25.46$
$=73.43 \mathrm{kPa}$
Q 2.17) The vapour pressure of water is 12.3 kPa at 300 K . Calculate the 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).
The molar mass of water $=18 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

Therefore, the number of moles present in 1000 g of water $=$

## $\frac{1000}{18}$

$=55.56 \mathrm{~mol}$
Therefore, the 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,

$$
p_{1}^{\circ}=12.3 \mathrm{kPa}
$$

Applying the relation,

$$
\begin{aligned}
& \frac{p_{1}^{\mathrm{p}}-p_{1}}{p_{1}^{\circ}}=x_{2} \\
&=> \\
& \frac{12.3-p_{1}}{12.3} \\
&= 0.0177 \\
& \Rightarrow 12.3-\mathrm{p}_{1}=0.2177 \\
& \Rightarrow \mathrm{p}_{1}=12.0823 \\
&= 12.08 \mathrm{kPa} \text { (approx) }
\end{aligned}
$$

Hence, the vapour pressure of the solution is 12.08 kPa .
Q 2.18) Calculate the mass of a non-volatile solute (molar mass $40 \mathrm{~g} \mathrm{~mol}^{-1}$ ) which should be dissolved in 114 g octane to reduce its vapour pressure to $\mathbf{8 0 \%}$.

Answer 2.18:

Let $p_{1}^{\circ}$ be the vapour pressure of pure octane.
Then, after dissolving the non-volatile solute, the vapour pressure of octane is

$$
\frac{80}{100} p_{1}^{\circ}=0.8 p_{1}^{\circ}
$$

The molar mass of solute, $\mathrm{M}_{2}=40 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

The mass of octane, $\mathrm{w}_{1}=114 \mathrm{~g}$
The molar mass of octane, $\left(\mathrm{C}_{8} \mathrm{H}_{18}\right), \mathrm{M}_{1}=8 \times 12+18 \times 1=114 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

Applying the relation,

$$
\begin{aligned}
& \frac{p_{1}^{o}-p_{1}}{p_{1}^{o}}=\frac{w_{2} \times M_{1}}{M_{2} \times w_{1}} \\
& =>
\end{aligned}
$$

$$
\frac{p_{1}^{o}-0.8 p_{1}^{o}}{p_{1}^{\circ}}=\frac{w_{2} \times 114}{40 \times 114}
$$

$$
\Rightarrow
$$

$$
\frac{0.2 p_{1}^{\mathrm{o}}}{p_{1}^{\mathrm{o}}}=\frac{w_{2}}{40}
$$

$$
\Rightarrow 0.2=
$$

$$
\frac{w_{2}}{40}
$$

$$
\Rightarrow \mathrm{w}_{2}=8 \mathrm{~g}
$$

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 .

Answer 2.19:
(i) Let, the molar mass of the solute be Mg

$$
\mathrm{mol}^{-1}
$$

Now, the number of moles of solvent (water),

$$
\begin{aligned}
& \quad n_{1}=\frac{90 \mathrm{~g}}{18 \mathrm{~g} \mathrm{~mol}-1} \\
& =5 \mathrm{~mol}
\end{aligned}
$$

And, the number of moles of solute,

$$
\begin{aligned}
& \quad n_{2}=\frac{30 \mathrm{~g}}{M \mathrm{~mol}^{-1}}=\frac{30}{M} \mathrm{~mol} \\
& \mathrm{p}_{1}=2.8 \mathrm{kPa}
\end{aligned}
$$

Applying the relation:

$$
\begin{aligned}
& \frac{p_{1}^{\circ}-p_{1}}{p_{1}^{o}}=\frac{n_{2}}{n_{1}+n_{2}} \\
& \Rightarrow>
\end{aligned}
$$

$$
\frac{p_{1}^{\mathrm{o}}-2.8}{p_{1}^{\circ}}=\frac{\frac{30}{M}}{5+\frac{30}{M}}
$$

=>

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

=>

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

=>

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

=>

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

=>

$$
\begin{aligned}
& \frac{2.8}{p_{1}^{\circ}}=\frac{5 M+30-30}{5 M+30} \\
& \Rightarrow \\
& \frac{2.8}{p_{1}^{\circ}}=\frac{5 M}{5 M+30} \\
& \Rightarrow \\
& \frac{p_{1}^{o}}{2.8}=\frac{5 M+30}{5 M}
\end{aligned}
$$

(i)

After the addition of 18 g of water:

$$
\begin{aligned}
& n_{1}=\frac{90+18 g}{18}=6 \mathrm{~mol} \\
& p_{1}=2.9 k P a
\end{aligned}
$$

Again applying the relation:

$$
\begin{aligned}
& \frac{p_{1}^{\mathrm{o}}-p_{1}}{p_{1}^{\circ}}=\frac{n_{2}}{n_{1}+n_{2}} \\
& \text { => } \\
& \frac{p_{1}^{\sigma}-2.9}{p_{1}^{\sigma}}=\frac{\frac{30}{M}}{6+\frac{30}{M}} \\
& \text { => } \\
& 1-\frac{2.9}{p_{1}^{\mathrm{o}}}=\frac{\frac{30}{M}}{\frac{6 M+30}{M}} \\
& \text { => } \\
& 1-\frac{2.9}{p_{1}^{\circ}}=\frac{30}{6 M+30} \\
& \text { => } \\
& \frac{2.9}{p_{1}^{\circ}}=1-\frac{30}{6 M+30} \\
& \text { => } \\
& \frac{2.9}{p_{1}^{\circ}}=\frac{6 M+30-30}{6 M+30} \\
& \text { => } \\
& \frac{2.9}{p_{1}^{0}}=\frac{6 M}{6 M+30} \\
& \text { => } \\
& \frac{p_{1}^{\circ}}{2.9}=\frac{6 M+30}{6 M} \\
& \text { (ii) } \\
& \text { Dividing equation (i) by (ii), we have }
\end{aligned}
$$

$$
\begin{aligned}
& \frac{2.9}{2.8}=\frac{\frac{5 M+30}{65 M}}{\frac{6 M+30}{6 M}} \\
& \Rightarrow> \\
& \frac{2.9}{2.8} \times \frac{6 M+30}{6}=\frac{5 M+30}{5} \\
& \Rightarrow \\
& 2.9 \times 5 \times(6 M+30)=2.8 \times 6 \times(5 M+30) \\
& =>87 M+435=84 M+504 \\
& \Rightarrow 3 M=69 \\
& \Rightarrow M=23 \mathrm{~g} \\
& \mathrm{~mol}^{-1}
\end{aligned}
$$

Therefore, 23 g

$$
\mathrm{mol}^{-1}
$$

is the molar mass of the solute.
(ii) Putting the value of ' $M$ ' in equation (i), we have

$$
\begin{aligned}
& \frac{p_{1}^{\circ}}{2.8}=\frac{5 \times 23+30}{5 \times 23} \\
& => \\
& \frac{p_{1}^{\circ}}{2.8}=\frac{145}{115} \\
& => \\
& p_{1}^{\circ} \\
& =3.53 \mathrm{kPa} \\
& \text { Hence, } 3.53 \mathrm{kPa} \text { is the vapour pressure of water at } 298 \mathrm{~K} \text {. }
\end{aligned}
$$

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

## Answer 2.20:

$$
\begin{aligned}
& \Delta T_{f} \\
= & 273.15-271=2.15 \mathrm{~K}
\end{aligned}
$$

The molar mass of sugar $\left(\mathrm{C}_{12} \mathrm{H}_{22} \mathrm{O}_{11}\right)=12 \times 12+22 \times 1+11 \times 16=342 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

$5 \%$ solution (by mass) of cane sugar in water means 5 g of cane sugar is present in $(100-5) \mathrm{g}$
$=95 \mathrm{~g}$ of water.
Now, the number of moles of cane sugar $=$

$$
\frac{5}{342}
$$

$\mathrm{mol}=0.0146 \mathrm{~mol}$
Therefore, the molality of the solution,

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

Applying the relation,

$$
\Delta T_{f}=K_{f} \times m
$$

=>

$$
K_{f}=\frac{\Delta T_{f}}{m}
$$

$$
=
$$

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

$=13.99 \mathrm{Kkg}$

$$
\mathrm{mol}^{-1}
$$

The molar mass of glucose $\left(\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}\right)=6 \times 12+12 \times 1+6 \times 16=180 \mathrm{~g}$

## $\mathrm{mol}^{-1}$

$5 \%$ glucose in water means 5 g of glucose is present in $(100-5) \mathrm{g}=95 \mathrm{~g}$ of water.
Therefore, the number of moles of glucose $=$
$\frac{5}{5^{\frac{5}{180}}}$
$\mathrm{~mol}=0.0278 \mathrm{~mol}$
Therefore, the molality of the solution, $\mathrm{m}=$
$\frac{0.0278 \mathrm{~mol}}{0.095 \mathrm{~kg}}$
$=0.2926 \mathrm{~mol}$
$k g^{-1}$

Applying the relation:

$$
\Delta T_{f}=K_{f} \times m
$$

$$
=
$$

$13.99 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1} \times 0.2926 \mathrm{~mol} \mathrm{~kg}^{-1}$
$=4.09 \mathrm{~K}$ (approx)
Hence, the freezing point of the $5 \%$ glucose solution is $(273.15-4.09) \mathrm{K}=269.06 \mathrm{~K}$.
Q 2.21) Two elements $A$ and $B$ form compounds having formulas $A B_{2}$ and $A B_{4}$. When dissolved in 20 g of benzene $\left(C_{6} H_{6}\right)$, 1 g of $\mathrm{AB}_{2}$ lowers the freezing point by 2.3 K , whereas 1.0 g of $\mathrm{AB}_{4}$ lowers it by 1.3 K . The molar depression constant for benzene is $5.1 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}$. Calculate the 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,

$$
M_{A B_{2}}=\frac{1000 \times 1 \times 5.1}{2.3 \times 20}
$$

$$
=110.87 \mathrm{~g}
$$

$$
\mathrm{mol}^{-1}
$$

$M_{A B_{4}}=\frac{1000 \times 1 \times 5.1}{1.3 \times 20}$
$=196.15 \mathrm{~g}$
$\mathrm{mol}^{-1}$

Now, we have the molar masses of $\mathrm{AB}_{2}$ and $\mathrm{AB}_{4}$ as 110.87 g

$$
\begin{array}{lr}
\mathrm{mol}^{-1} & \text { and } 196.15 \mathrm{~g} \\
\mathrm{~mol}^{-1} & \\
& \text { respectively. }
\end{array}
$$

Let the atomic masses of A and B be x and y , respectively.
Now, we can write:
$x+2 y=110.87$
$x+4 y=196.15$
Subtracting equation (i) from (ii), we have
$2 \mathrm{y}=85.28$
=> $y=42.64$
Putting the value of ' $y$ ' in equation (1), we have
$x+2(42.64)=110.87$
$\Rightarrow \mathrm{x}=25.59$

Hence, the atomic masses of A and B are 25.59 u and 42.64 u , respectively.
Q 2.22) At $300 \mathrm{~K}, 36 \mathrm{~g}$ 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 $\mathbf{1 . 5 2}$ bars at the same temperature, what would be its concentration?

Answer 2.22:

Given:
$\mathrm{T}=300 \mathrm{~K}$
$\mathrm{n}=1.52$ bar
$\mathrm{R}=0.083 \mathrm{bar} \mathrm{L}$
$K^{-1} \mathrm{~mol}^{-1}$

Applying the relation, $n=C R T$
$\Rightarrow C=$

$=$
$\frac{1.52 \mathrm{bar}}{0.083 \text { bar } L \mathrm{~K}^{-1} \mathrm{~mol}^{-1} \times 300 \mathrm{~K}}$
$=0.061 \mathrm{~mol}$

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) $\mathrm{I}_{2}$ and $\mathrm{CCl}_{4}$
(iii) $\mathrm{NaClO}_{4}$ and water
(iv) methanol and acetone
(v) acetonitrile $\left(\mathrm{CH}_{3} \mathrm{CN}\right)$ and acetone $\left(\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}\right)$

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

Q 2.24) Based on solute-solvent interactions, arrange the following in order of increasing solubility in n-octane and explain. Cyclohexane, $\mathrm{KCl}, \mathrm{CH}_{3} \mathrm{OH}, \mathrm{CH}_{3} \mathrm{CN}$.

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 $<\mathrm{CH}_{3} \mathrm{CN}<\mathrm{CH}_{3} \mathrm{OH}<\mathrm{KCl}$
Therefore, the order of increasing solubility is
$\mathrm{KCl}<\mathrm{CH}_{3} \mathrm{OH}<\mathrm{CH}_{3} \mathrm{CN}<$ 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

Answer 2.25:
(i) Phenol $\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}\right)$ has the polar group -OH and non-polar group $-\mathrm{C}_{6} \mathrm{H}_{5}$. Thus, phenol is partially soluble in water.
(ii) Toluene $\left(\mathrm{C}_{6} \mathrm{H}_{5}-\mathrm{CH}_{3}\right)$ has no polar groups. Thus, toluene is insoluble in water.
(iii) Formic acid $(\mathrm{HCOOH})$ 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 $\left(\mathrm{C}_{5} \mathrm{H}_{11} \mathrm{OH}\right)$ has a polar -OH group, but it also contains a very bulky nonpolar $-\mathrm{C}_{5} \mathrm{H}_{11}$ group. Thus, pentanol is partially soluble in water.

Q 2.26) If the density of some lake water is $1.25 \mathrm{~g} \mathrm{~mL}^{-1}$ and contains 92 g of $\mathrm{Na}^{+}$ions per kg of water, calculate the molarity of $\mathbf{N a}^{+}$ions in the lake.

Answer 2.26:
The number of moles present in 92 g of $\mathrm{Na}^{+}$ions $=$
$\frac{92 \mathrm{~g}}{23 \mathrm{~g} \mathrm{~mol}^{-1}}$
$=4 \mathrm{~mol}$
Therefore, the molality of $\mathrm{Na}^{+}$ions in the lake $=$

$$
\begin{aligned}
& \frac{4 \mathrm{~mol}}{1 \mathrm{~kg}} \\
= & 4 \mathrm{~m}
\end{aligned}
$$

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

Answer 2.27:
Solubility product of CuS ,

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

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

$$
C u S \leftrightarrow C u^{2+}+S^{2-}
$$

Now,

S
S

$$
K_{s p}=\left[C u^{2+}\right]+\left[S^{2-}\right]
$$

$=\mathrm{s}^{2}$
Then, we have,

$$
\begin{aligned}
& K_{s p}=s^{2}=6 \times 10^{-16} \\
& => \\
& s=\sqrt{6 \times 10^{-16}} \\
& = \\
& 2.45 \times 10^{-8} \mathrm{~mol} \mathrm{~L} \\
& \text { Hence, } 2.45 \times 10^{-8} \mathrm{~mol} \mathrm{~L} \\
& \text { is the maximum molarity of } \mathrm{CuS} \text { in an aqueous solution. }
\end{aligned}
$$

Q 2.28) Calculate the mass percentage of aspirin $\left(\mathrm{C}_{9} \mathrm{H}_{8} \mathrm{O}_{4}\right)$ in acetonitrile $\left(\mathrm{CH}_{3} \mathrm{CN}\right)$ when 6.5 g of $\mathrm{C}_{9} \mathrm{H}_{8} \mathrm{O}_{4}$ is dissolved in 450 g of $\mathrm{CH}_{3} \mathrm{CN}$.

Answer 2.28:
6.5 g of $\mathrm{C}_{9} \mathrm{H}_{8} \mathrm{O}_{4}$ is dissolved in 450 g of $\mathrm{CH}_{3} \mathrm{CN}$.

Then, the total mass of the solution $=(6.5+450) \mathrm{g}=456.5 \mathrm{~g}$
Therefore, the mass percentage of $\mathrm{C}_{9} \mathrm{H}_{8} \mathrm{O}_{4}=$

$$
\frac{6.5}{456.5} \times 100
$$

$=1.424 \%$
Q 2.29) Nalorphene $\left(\mathrm{C}_{19} \mathrm{H}_{21} \mathrm{NO}_{3}\right)$, similar to morphine, is used to combat withdrawal symptoms in narcotic users. The dose of nalorphene generally given is $\mathbf{1 . 5} \mathbf{~ m g}$. Calculate the mass of $1.5 \times 10^{-3} \mathbf{m}$ aqueous solution required for the above dose.

Answer 2.29:
The molar mass of nalorphene $\left(\mathrm{C}_{19} \mathrm{H}_{21} \mathrm{NO}_{3}\right)=19 \times 12+21 \times 1+1 \times 14+3 \times 16=311 \mathrm{~g} \mathrm{~mol}^{-1}$
In $1.5 \times 10^{-3} m_{\text {aqueous solution of nalorphene, } 1 \mathrm{~kg}(1000 \mathrm{~g}) \text { of water contains }}$

$$
\begin{aligned}
& 1.5 \times 10^{-3} \mathrm{~mol} \\
& = \\
& 1.5 \times 10^{-3} \times 311
\end{aligned}
$$

$$
\mathrm{g}
$$

$$
=0.4665 \mathrm{~g}
$$

Therefore, total mass of the solution $=(1000+0.4665) \mathrm{g}=1000.4665 \mathrm{~g}$
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

```
        1000.4665\times1.5\times1\mp@subsup{0}{}{-3}
    g
=3.22g
```

Hence, 3.22 g is the required mass of the aqueous solution.
Q 2.30) Calculate the amount of benzoic acid $\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}\right)$ required for preparing 250 mL of 0.15 M solutions 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 $\frac{0.15 \times 250}{1000} \mathrm{~mol}$ of benzoic acid
$=0.0375 \mathrm{~mol}$ of benzoic acid
Molar mass of benzoic acid $\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}\right)=7 \times 12+6 \times 1+2 \times 16=122 \mathrm{~g} \mathrm{~mol}^{-1}$

Q 2.31) The depression in the 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 $\mathrm{H}, \mathrm{Cl}$, and $\mathrm{F}, \mathrm{H}$ is the least electronegative, while F is the most electronegative. Then, F can withdraw electrons towards itself more than Cl and H . Thus, trifluoroacetic acid can easily lose $\mathrm{H}^{+}$ions, i.e., trifluoroacetic acid ionises to the largest extent. Now, the more ions produced, the greater 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 $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHClCOOH}^{2}$ is added to 250 g of water. $\mathrm{K}_{\mathrm{a}}=1.4 \times \mathbf{1 0}^{-3}, \mathrm{~K}_{\mathrm{f}}=1.86 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}$

Answer 2.32:
Molar mass of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHCICOOH}=15+14+13+35.5+12+16+16+1$
$=122.5 \mathrm{~g} \mathrm{~mol}^{-1}$
Therefore, the number of moles present in 10 g of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHCICOOH}=$

$$
\begin{aligned}
& \frac{10 \mathrm{~g}}{122.5 \mathrm{~g} \mathrm{~mol}}{ }^{-1} \\
= & 0.0816 \mathrm{~mol}
\end{aligned}
$$

It is given that 10 g of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHCICOOH}$ is added to 250 g of water.
Therefore, the molality of the solution, $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHCICOOH}=$

$$
\frac{0.0186}{250} \times 1000
$$

$=0.3264 \mathrm{~mol} \mathrm{~kg}^{-1}$
Let ' $a$ ' be the degree of dissociation of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHCICOOH}$.
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHCICOOH}$ undergoes dissociation according to the following equation:

$$
\begin{aligned}
& \therefore K_{a}=\frac{C \alpha \cdot C \alpha}{C(1-\alpha)} \\
& = \\
& \frac{C \alpha^{2}}{1-\alpha}
\end{aligned}
$$

Since a is very small with respect to 1 ,

$$
\begin{aligned}
& 1-a \approx 1 \\
& K_{a}=\frac{C \alpha^{2}}{1}
\end{aligned}
$$

Now,
=>

$$
K_{a}=C \alpha^{2}
$$

=>

$$
\alpha=\sqrt{\frac{K_{a}}{C}}
$$

$$
=
$$

$$
\sqrt{\frac{1.4 \times 10^{-3}}{0.3264}} \quad\left(\because K_{a}=1.4 \times 10^{-3}\right)
$$

$$
=0.0655
$$

Again,

Total moles of equilibrium $=1-\mathrm{a}+\mathrm{a}+\mathrm{a}=1+\mathrm{a}$

$$
\begin{aligned}
& \therefore i=\frac{1+\alpha}{1} \\
& =
\end{aligned}
$$

$$
1+\alpha
$$

$=1+0.0655$
$=1.0655$

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

$$
\Delta T_{f}=i . K_{f} m
$$

$$
=
$$

$1.0655 \times 1.86 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1} \times 0.3264 \mathrm{~mol} \mathrm{~kg}^{-1}$
$=0.65 \mathrm{~K}$

Q 2.33) 19.5 g of $\mathrm{CH}_{2} \mathrm{FCOOH}$ is dissolved in 500 g of water. The depression in the freezing point of water observed is $\mathbf{1 . 0 0}$ C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.

Answer 2.33:
Given:
$\mathrm{w}_{1}=500 \mathrm{~g}$
$\mathrm{w}_{2}=19.5 \mathrm{~g}$
$\mathrm{K}_{\mathrm{f}}=1.86 \mathrm{~K} \mathrm{~kg}$
$\mathrm{mol}^{-1}$
$\Delta T_{f}$
$=1 \mathrm{~K}$
We know that

$$
\begin{aligned}
& M_{2}=\frac{K_{f} \times w_{2} \times 1000}{\Delta T_{f} \times w_{1}} \\
& = \\
& \frac{1.86 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}}{}+1 \times 19.5 \mathrm{~g} \times 1000 \mathrm{~g} \mathrm{~kg}^{-1} \\
& 500 \mathrm{~g} \times 1 \mathrm{~K}
\end{aligned} \quad .
$$

$72.54 \mathrm{~g} \mathrm{~mol}^{-1}$

Therefore, observed molar mass of $\mathrm{CH}_{2} \mathrm{FCOOH}$,

$$
\left(M_{2}\right)_{o b s}=72.54 \mathrm{~g} \mathrm{~mol}^{-1}
$$

The calculated molar mass of $\mathrm{CH}_{2} \mathrm{FCOOH}$,

$$
\begin{aligned}
& \left(M_{2}\right)_{c a l}=14+19+12+16+16+1=78 \mathrm{~g} \\
& \text { mol }^{-1}
\end{aligned}
$$

Therefore, van't Hoff factor,

$$
\begin{aligned}
& \quad i=\frac{\left(M_{2}\right)_{c a l}}{\left(M_{2}\right)_{o b s}} \\
& \text { is: } \\
& = \\
& \frac{78 \mathrm{~g} \mathrm{~mol}^{-1}}{72.54 \mathrm{~g} \mathrm{~mol}^{-1}} \\
& =1.0753
\end{aligned}
$$

Let ' $a$ ' be the degree of dissociation of $\mathrm{CH}_{2} \mathrm{FCOOH}$.

$$
\begin{aligned}
& \therefore i=\frac{C(1+\alpha)}{C} \\
& \Rightarrow \mathrm{i}=1+ \\
& \alpha \\
& \Rightarrow \\
& \\
& \\
& \alpha \\
& =\mathrm{i}-1 \\
& =1.0753-1 \\
& =0.0753
\end{aligned}
$$

Now, the value of $\mathrm{K}_{\mathrm{a}}$ is given as

$$
\begin{aligned}
& K_{a}=\frac{\left[\mathrm{CH}_{2} \mathrm{FCOO}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{CH}_{2} \mathrm{FCOOH}\right]} \\
& =
\end{aligned}
$$

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

$$
=
$$

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

Taking the volume of the solution as 500 mL , we have the concentration
$\mathrm{C}=$

$$
\frac{\frac{195}{78}}{500} \times 1000 M
$$

$=0.5 \mathrm{M}$
Therefore,

$$
\begin{aligned}
& K_{a}=\frac{C \alpha^{2}}{1-\alpha} \\
& = \\
& \frac{0.5 \times(0.0753)^{2}}{1-0.0753} \\
& = \\
& \frac{0.5 \times 0.00567}{0.9247} \\
& =0.00307 \text { (approx) } \\
& =3.07 \times 10-3
\end{aligned}
$$

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.

Answer 2.34:
Vapour pressure of water,

$$
P_{1}^{\circ}=17.535 \mathrm{~mm} \text { of } \mathrm{Hg}
$$

Mass of glucose, $\mathrm{w}_{2}=25 \mathrm{~g}$
Mass of water, $\mathrm{w}_{1}=450 \mathrm{~g}$
We know that,
Molar mass of glucose $\left(\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}\right), \mathrm{M}_{2}=6 \times 12+12 \times 1+6 \times 16=180 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

Molar mass of water, $\mathrm{M}_{1}=18 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

Then, the number of moles of glucose,

$$
n_{2}=\frac{25}{180 \mathrm{~g} \mathrm{~mol}^{-1}}
$$

$=0.139 \mathrm{~mol}$
And, the number of moles of water,

$$
n_{1}=\frac{450 \mathrm{~g}}{18 \mathrm{~g} \mathrm{~mol}^{-1}}
$$

$=25 \mathrm{~mol}$
We know that,

$$
\begin{aligned}
& \frac{p_{1}^{\circ}-p_{1}}{p_{1}^{\circ}}=\frac{n_{1}}{n_{2}+n_{1}} \\
& \Rightarrow \\
& \frac{17.535-p_{1}}{17.535}=\frac{0.139}{0.139+25} \\
& \Rightarrow \\
& 17.535-p_{1}=\frac{0.139 \times 17.535}{25.139} \\
& \Rightarrow \\
& 17.535-p_{1}=0.097 \\
& \quad \Rightarrow \\
& p_{1}=17.44 \\
& \text { mm of } \mathrm{Hg} \\
& \text { Hence, } 17.44 \mathrm{~mm} \text { of } \mathrm{Hg} \text { is the vapour pressure of water. }
\end{aligned}
$$

Q 2.35) Henry's law constant for the molality of methane in benzene at 298 K is $4.27 \times 10^{5} \mathbf{~ m m ~ H g}$. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg .

Answer 2.35:
Given:
$\mathrm{p}=760 \mathrm{~mm} \mathrm{Hg}$

$$
k_{H}=4.27 \times 10^{5} \mathrm{~mm} \mathrm{Hg}
$$

According to Henry's law,

$$
\begin{aligned}
& \mathrm{p}=\mathrm{k}_{\mathrm{H} \mathrm{X}} \\
& \Rightarrow \mathrm{x}= \\
& \frac{p}{k_{H}} \\
&= \\
& \frac{760 \mathrm{~mm} \mathrm{Hg}}{4.27 \times 10^{5} \mathrm{~mm} \mathrm{Hg}} \\
&= \\
& 177.99 \times 10^{-5} \\
&= \\
& \quad 178 \times 10^{-5} \\
& \begin{array}{l}
\text { (approx) } \\
\text { Hence, }
\end{array}
\end{aligned}
$$

## $178 \times 10-5$

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 $180 \mathrm{~g} \mathrm{~mol}^{-1}$ ). 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.

Answer 2.36:
Number of moles of liquid A,

$$
n_{A}=\frac{100}{140} \quad=0.714 \mathrm{~mol}
$$

Number of moles of liquid B,

$$
n_{B}=\frac{1000}{180}=5.556 \mathrm{~mol}
$$

Then, the mole fraction of A,

$$
\begin{aligned}
& x_{A}=\frac{n_{A}}{n_{A}+n_{B}} \\
& = \\
& \frac{0.714}{0.714+5.556} \\
& =0.114
\end{aligned}
$$

And, the mole fraction of B, $\mathrm{X}_{\mathrm{B}}=1-0.114=0.886$
Vapour pressure of pure liquid B,

$$
P_{B}^{\circ}=500 \text { torr }
$$

Therefore, the vapour pressure of liquid B in the solution,

$$
p_{B}=p_{B}^{\circ} x_{B}=500 \times 0.886
$$

$=443$ torr
Total vapour pressure of the solution,

$$
p_{\text {total }}=475 \text { torr }
$$

Therefore, the vapour pressure of liquid $A$ in the solution,

$$
p_{A}=p_{\text {total }}-p_{B}
$$

$=475-443$
$=32$ torr
Now,

$$
\begin{aligned}
& p_{A}=p_{A}^{\circ} x_{A} \\
& => \\
& p_{A}^{\circ}=\frac{p_{A}}{x_{A}} \\
& = \\
& \frac{32}{0.114} \\
& =280.7 \text { torr }
\end{aligned}
$$

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 the ideal solution over the entire range of composition, plot $\mathbf{p}_{\text {total, }}, \mathbf{p}_{\text {chloroform, }}$, and $\mathbf{p}_{\text {acetone }}$ as a function of $\mathbf{x}_{\text {acetone }}$. The experimental data observed for different compositions of the mixture is:

| $100 \times x_{\text {acetone }}$ | 0 | 11.8 | 23.4 | 36.0 | 50.8 | 58.2 | 64.5 | 72.1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $p_{\text {acetone }}$ <br> / mm Hg | 0 | 54.9 | 110.1 | 202.4 | 322.7 | 405.9 | 454.1 | 521.1 |
| $p_{\text {chloroform }}$ <br> $/ \mathrm{mm} \mathrm{Hg}$ | 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 a positive deviation or a negative deviation from the ideal solution.

Answer 2.37:

From the question, we have the following data

| $100 \times x_{\text {acetone }}$ | 0 | 11.8 | 23.4 | 36.0 | 50.8 | 58.2 | 64.5 | 72.1 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |


| $p_{\text {acetone }}$ <br> / mm Hg | 0 | 54.9 | 110.1 | 202.4 | 322.7 | 405.9 | 454.1 | 521.1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $p_{\text {chloroform }}$ $/ \mathrm{mm} \mathrm{Hg}$ | 632.8 | 548.1 | 469.4 | 359.7 | 257.7 | 193.6 | 161.2 | 120.7 |
| $p_{\text {total }}$ <br> ( 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 $P_{\text {total }}$ of the solution curves downwards. Therefore, the solution shows a negative deviation from the ideal behaviour.

Q 2.38) Benzene and toluene form the 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 the vapour phase if 80 g of benzene is mixed with 100 g of toluene.

Answer 2.38:

Molar mass of benzene $\left(\mathrm{C}_{6} \mathrm{H}_{6}\right)=6 \times 12+6 \times 1=78 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

Molar mass of toluene $\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{3}\right)=7 \times 12+8 \times 1=92 \mathrm{~g}$

$$
\mathrm{mol}^{-1}
$$

Now, the number of moles present in 80 g of benzene $=$

$$
\frac{80}{78}=1.026 \mathrm{~mol}
$$

And, the number of moles present in 100 g of toluene $=$

$$
\frac{100}{92}=1.087 \mathrm{~mol}
$$

Therefore, the mole fraction of benzene,

$$
x_{b}=\frac{1.026}{1.026+1.087}
$$

$=0.486$
And, the mole fraction of toluene,

$$
x_{t=1-0.486=0.514}
$$

It is given that the vapour pressure of pure benzene,

$$
p_{b}^{\circ}=50.71 \mathrm{~mm} \mathrm{Hg}
$$

And, the vapour pressure of pure toluene,

$$
p_{t}^{\circ}=32.06 \mathrm{~mm} \mathrm{Hg}
$$

Therefore, the partial pressure of benzene,

$$
p_{b}=x_{b} \times p_{b}^{\circ}=0.486 \times 50.71
$$

$=24.645 \mathrm{~mm} \mathrm{Hg}$
And, the partial vapour pressure of toluene,

$$
p_{t}=x_{t} \times p_{t}^{\circ}
$$

$=0.514 \times 32.06$
$=16.479 \mathrm{~mm} \mathrm{Hg}$
Hence, the mole fraction of benzene in the vapour phase is given by

$$
\begin{aligned}
& \frac{p_{b}}{p_{b}+p_{t}} \\
& = \\
& \frac{24.645}{24.645+16.479} \\
& = \\
& \frac{24.645}{41.124} \\
& =0.599 \\
& =0.6 \text { (approx) }
\end{aligned}
$$

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

## Answer 2.39:

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 $(10 \times 760) \mathrm{mm} \mathrm{Hg}=7600 \mathrm{~mm}$ Hg

Therefore,
Partial pressure of oxygen,

$$
\begin{aligned}
& \quad p_{O_{2}}=\frac{20}{100} \times 7600 \mathrm{~mm} \mathrm{Hg} \\
& =1520 \mathrm{~mm} \mathrm{Hg}
\end{aligned}
$$

Partial pressure of nitrogen,

$$
p_{N_{2}}=\frac{79}{100} \times 7600
$$

$=6004 \mathrm{~mm} \mathrm{Hg}$

$$
\begin{aligned}
& p_{O_{2}}=K_{H} \cdot x_{O_{2}} \\
& => \\
& x_{O_{2}}=\frac{p_{O_{2}}}{K_{H}} \\
& =
\end{aligned}
$$

$$
\frac{1520 \mathrm{~mm} \mathrm{Hg}}{3.30 \times 10^{7} \mathrm{~mm} \mathrm{Hg}}
$$

$$
\left(\text { Given } K_{H}=3.30 \times 10^{7} \mathrm{~mm} \mathrm{Hg}\right)
$$

$$
=4.61 \times 10-5
$$

For nitrogen:

$$
\begin{aligned}
& p_{N_{2}}=K_{H} \cdot x_{N_{2}} \\
& => \\
& x_{N_{2}}=\frac{p_{N_{2}}}{K_{H}} \\
& = \\
& \quad \frac{6004 \mathrm{~mm} \mathrm{Hg}}{6.51 \times 10^{7} \mathrm{~mm} \mathrm{Hg}} \\
& =9.22 \times 10-5 \\
& \text { Hence, }
\end{aligned}
$$

$4.61 \times 10^{-5}$
and
$9.22 \times 10^{-5}$
are the mole fractions of oxygen and nitrogen in the water.
Q 2.40) Determine the amount of $\mathrm{CaCl}_{2}(\mathbf{i}=2.47)$ dissolved in 2.5 litres of water such that its osmotic pressure is 0.75 atm at $27^{\circ} \mathrm{C}$.

Answer 2.40:
We know that,

Therefore, $\mathrm{w}=$

$$
\frac{0.75 \times 111 \times 2.5}{2.47 \times 0.0821 \times 300}
$$

$$
=3.42 \mathrm{~g}
$$

Hence, 3.42 g is the required amount of $\mathrm{CaCl}_{2}$.
Q 2.41) Determine the osmotic pressure of a solution prepared by dissolving 25 mg of $\mathrm{K}_{2} \mathrm{SO}_{4}$ in 2 litres of water at $25^{\circ} \mathrm{C}$, assuming that it is completely dissociated.

Answer 2.41:
When $\mathrm{K}_{2} \mathrm{SO}_{4}$ is dissolved in water,

$$
\begin{aligned}
& \pi=i \frac{n}{V} R T \\
& \text { => } \\
& \pi=i \frac{w}{M V} R T \\
& \text { => } \\
& w=\frac{\pi M V}{i R T} \\
& \pi \\
& =0.75 \mathrm{~atm} \\
& \mathrm{~V}=2.5 \mathrm{~L} \\
& \mathrm{i}=2.47 \\
& \mathrm{~T}=(27+273)=300 \mathrm{~K} \\
& \text { Here, } \\
& \mathrm{R}= \\
& 0.0821 \mathrm{Latm} K^{-1} \mathrm{~mol}^{-1} \\
& \mathrm{M}=1 \times 40+2 \times 35.5 \\
& =111 \mathrm{~g} \\
& \mathrm{~mol}^{-1}
\end{aligned}
$$

$\mathrm{K}^{+}$and $\mathrm{SO}_{4}^{2-}{ }_{\text {ions are produced. }}$

$$
\mathrm{K}_{2} \mathrm{SO}_{4} \rightarrow 2 \mathrm{~K}^{+}+\mathrm{SO}_{4}^{2-}
$$

Total number of ions produced $=3$
Therefore, $\mathrm{i}=3$

Given:
$\mathrm{w}=25 \mathrm{mg}=0.025 \mathrm{~g}$
$\mathrm{V}=2 \mathrm{~L}$
$\mathrm{T}=25^{\circ} \mathrm{C}=(25+273)=298 \mathrm{~K}$
Also, we know that
$\mathrm{R}=$
$0.0821 L^{\text {atm }} K^{-1} \mathrm{~mol}^{-1}$
$\mathrm{M}=(2 \times 39)+(1 \times 32)+(4 \times 16)=174 \mathrm{~g}$
$\mathrm{mol}^{-1}$

Applying the following relation,

$$
\begin{aligned}
& \pi=i \frac{n}{V} R T \\
& = \\
& i \frac{w}{M} \frac{1}{v} R T \\
& = \\
& 3 \times \frac{0.025}{174} \times \frac{1}{2} \times 0.0821 \times 298 \\
& =
\end{aligned}
$$

$$
5.27 \times 10^{-3} \mathrm{~atm}
$$

