## Class 12 Chemistry

## NCERT Solutions for Chapter 2 - Solutions

## Exercises

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

Sol: A solution is a homogeneous mixture of two or more chemically nonreacting substances. Types of solutions: There are nine types of solutions. Types of Solution Examples

## Gaseous solutions

(a) Gas in gas Air, mixture of $\mathrm{O}_{2}$ and $\mathrm{N}_{2}$, etc.
(b) Liquid in gas Water vapour
(c) Solid in gas Camphor vapours in N2 gas, smoke etc.

## Liquid solutions

(a) Gas in liquid CO2 dissolved in water (aerated water), and 02 dissolved in water, etc.
(b) Liquid in liquid Ethanol dissolved in water, etc.
(c) Solid in liquid Sugar dissolved in water, saline water, etc.

## Solid solutions

(a) Gas in solid Solution of hydrogen in palladium
(b) Liquid in solid Amalgams, e.g., $\mathrm{Na}-\mathrm{Hg}$
(c) Solid in solid Gold ornaments ( $\mathrm{Cu} / \mathrm{Ag}$ with Au )
2.2. Suppose a solid solution is formed between two substances, one whose particles are very large and the other whose particles are very small. What type of solid solution is this likely to be?
Sol: The solution likely to be formed is interstitial solid solution.
2.3 Define the following terms:
(i) Mole fraction
(ii) Molality
(iii) Molarity
(iv) Mass percentage

Sol: (i) Mole fraction: It is defined as the ratio of the number of moles of the solute to the total number of moles in the solution. If $A$ is the number of moles of solute dissolved in B moles of solvent, then Mole fraction of solute
$\left(X_{A}\right)=\frac{n_{A}}{n_{A}+n_{B}}$
Mole fraction of solvent $\left(X_{B}\right)=\frac{n_{B}}{n_{A}+n_{B}}$... (2)
Adding the above two equations, we get

$$
X_{A}+X_{B}=\frac{n_{A}}{n_{A}+n_{B}}+\frac{n_{B}}{n_{A}+n_{B}}=\frac{n_{A}+n_{B}}{n_{A}^{\prime}+n_{B}}=1
$$

i.e.,

$$
X_{A}+X_{B}=1
$$

$\therefore X_{A}=1-X_{B}$ or $X_{B}=1-X_{A}$
(ii) Molality: It is defined as die number of moles of a solute present in 1000 g (1kg) of a solvent.
Molality $(m)=\frac{\text { Number of moles of solute }}{\text { Weight of solvent in kg }}=\frac{n}{W}$
NOTE: Molality is considered better way of expressing concentration of solutions, as compared to molarity because molality does not change with change in temperature since the mass of solvent does not vary with temperature,
(iii) Molarity: It is defined as the number of moles of solute present in one litre of solution.
Molarity $(M)=$
$\frac{\text { Number of moles of solute }}{\text { Volume of Solution in litre }}=\frac{n}{V}$
$n=\frac{\text { Weight in grams }}{\text { Molecular weight of solute }}$
$\therefore M=\frac{\text { Weight in grams }}{\text { Volume of solution in litres }}$

$$
\times \frac{1}{\text { Molecular weight of solute }}
$$

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

$$
\begin{aligned}
& \therefore \text { Molarity }=\frac{\text { Strength }}{\text { Molecular weight of solute }} \\
& \text { or Strength }=\text { Molarity } \times \text { Molecular weight }
\end{aligned}
$$

NOTE: Molarity is the most common way of expressing concentration of a solution in laboratory. However, it has one disadvantage. It changes with temperature because volume of a solution alters due to expansion and contraction of the liquid with temperature.
(iv) Mass percentage: It is the amount of solute in grams present in 100 g of solution.

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

2.4. Concentrated nitric acid used in the laboratory work is $68 \%$ nitric acid by mass in aqueous solution. What should be the molarity of such a sample of acid if the density of the solution is $1.504 \mathrm{~g} \mathrm{~mL}^{-1}$ ?
Sol: Mass of $\mathrm{HNO}_{3}$ in solution $=68 \mathrm{~g}$
Molar mass of $\mathrm{HNO}_{3}=63 \mathrm{~g} \mathrm{~mol}^{-1}$
Mass of solution $=100 \mathrm{~g}$
Density of solution $=1.504 \mathrm{~g} \mathrm{~mL}^{-1}$
Volume of solution $=\frac{\text { Mass of solution }}{\text { Density of solution }}$

$$
=\frac{(100 \mathrm{~g})}{\left(1.504 \mathrm{~g} \mathrm{~mL}^{-1}\right)}=66.5 \mathrm{~mL}=0.0665 \mathrm{~L}
$$

Molarity of solution $(\mathrm{M})=\frac{\text { Mass of } \mathrm{HNO}_{3} / \text { Molar mass of } \mathrm{HNO}_{3}}{\text { Volume of solution in Litres }}$

$$
=\frac{\left(68 \mathrm{~g} / 63 \mathrm{~g} \mathrm{~mol}^{-1}\right)}{(0.0665 \mathrm{~L})}=16.23 \mathrm{~mol} \mathrm{~L}^{-1}=\mathbf{1 6 . 2 3 ~ M}
$$

2.5. A solution of glucose in water is labelled as $10 \% \mathrm{w} / \mathrm{w}$, what would be the molality and mole fraction of each component in the solution? If the density of solution is $1.2 \mathrm{~g} \mathrm{~m} \mathrm{~L}^{-1}$, then what shall be the molarity of the solution?
Sol: 10 percent w/w solution of glucose in water means 10 g glucose and 90 g of water.
Molar mass of glucose $=180 \mathrm{~g} \mathrm{~mol}^{-1}$ and molar mass of water $=18 \mathrm{~g} \mathrm{~mol}^{-1}$
$\therefore \quad 10 \mathrm{~g}$ of glucose $=\frac{10}{180}=0.0555$ moles
and 90 g of $\mathrm{H}_{2} \mathrm{O}=\frac{90}{18}=5$ moles
$\therefore$ Molality of solution

$$
\begin{aligned}
& =\frac{\text { Moles of solute } \times 1000}{\text { Mass of solution in grams }} \\
& =\frac{0.0555}{90} \times 1000=0.617 \mathrm{~m}
\end{aligned}
$$

Mole fraction of glucose

$$
\begin{aligned}
& =X_{g}=\frac{\text { No. of moles of glucose }}{\begin{array}{c}
\text { No. of moles }+\begin{array}{l}
\text { No. of moles } \\
\text { of glucose } \\
\text { of water }
\end{array}
\end{array}} \\
& =\frac{0.0555}{5+0.0555}=0.01
\end{aligned}
$$

Mole fraction of water

$$
\begin{aligned}
& =X_{w}=\frac{\text { No. of moles of water }}{\begin{array}{l}
\text { No. of moles } \\
\text { of glucose }
\end{array}+\begin{array}{l}
\text { No. of } \\
\text { moles of water }
\end{array}} \\
& =\frac{5}{5+0.0555}=0.99 .
\end{aligned}
$$

Volume of 100 g of solution

$$
=\frac{\text { Mass of solution }}{\text { Density }}=\frac{100}{1 \cdot 2}=83.33 \mathrm{~mL}
$$

$\therefore$ Molarity of solution $=\frac{0.0555}{83.33} \times 1000$

$$
=0.67 \mathrm{M}
$$

2.6. How many mL of 0.1 M HCl are required to react completely with 1 g mixture of $\mathrm{Na}_{2} \mathrm{CO}_{3}$ and $\mathrm{NaHCO}_{3}$ containing equimolar amounts of both?

Sol: Calculation of no. of moles of components in the mixture.
Let $x \mathrm{~g}$ of $\mathrm{Na}_{2} \mathrm{CO}_{3}$ is present in the mixture.
$\therefore(1-x) \mathrm{g}^{2} \mathrm{NaHCO}_{3}$ is present in the mixture.
Molar mass of $\mathrm{Na}_{2} \mathrm{CO}_{3}$
$=2 \times 23+12+3 \times 16=106 \mathrm{~g} \mathrm{~mol}^{-1}$
and molar mass of $\mathrm{NaHCO}_{3}$
$=23 \times 1+1+12+3 \times 16=84 \mathrm{~g} \mathrm{~mol}^{-1}$
No. of moles of $\mathrm{Na}_{2} \mathrm{CO}_{3}$ in $x \mathrm{~g}=\frac{x}{106}$
No. of moles of $\mathrm{NaHCO}_{3}$ in $(1-x) \mathrm{g}=(1-x) / 84$
As given that the mixture contains equimolar amounts of $\mathrm{Na}_{2} \mathrm{CO}_{3}$ and $\mathrm{NaHCO}_{3}$, therefore
$\frac{x}{106}=\frac{1-x}{84}$
$106-106 x=84 x$
$106=190 x$
$\therefore x=\frac{106}{190}=0.558 \mathrm{~g}$
$\therefore$ Nó. of moles of $\mathrm{Na}_{2} \mathrm{CO}_{3}$ present
$=\frac{0.558}{106}=0.00526$
and no. of moles of $\mathrm{NaHCO}_{3}$ present
$=\frac{1-0.558}{84}=0.00526$
Calculation of no. of moles of HCl required
$\mathrm{Na}_{2} \mathrm{CO}_{3}+2 \mathrm{HCl} \longrightarrow 2 \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}$
$\mathrm{NaHCO}_{3}+\mathrm{HCl} \longrightarrow \mathrm{NaCl}+\mathrm{H}_{2} \mathrm{O}+\mathrm{CO}_{2}$
As can be seen, each mole of $\mathrm{Na}_{2} \mathrm{CO}_{3}$ needs
2 moles of HCl ,
$\therefore 0.00526$ mole of $\mathrm{Na}_{2} \mathrm{CO}_{3}$ needs
$=0.00526 \times 2=0.01052 \mathrm{~mole}$
Each mole of $\mathrm{NaHCO}_{3}$ needs 1 mole of HCl .
$\therefore 0.00526$ mole of $\mathrm{NaHCO}_{3}$ needs
$=1 \times 0.00526=0.00526 \mathrm{~mole}$
Total amount of HCl needed will be
$=0.01052+0.00526=0.01578 \mathrm{~mole}$.
0.1 mole of 0.1 M HCl are present in 1000 mL of HCl
$\therefore \quad 0.01578$ mole of 0.1 M HCl will be present in
$=\frac{1000}{0.1} \times 0.01578=157.8 \mathrm{~mL}$.
2.7. Calculate the percentage composition in terms of mass of a solution obtained by mixing 300 g of a $25 \%$ and 400 g of a $40 \%$ solution by mass. Sol:

$$
\begin{aligned}
\text { Mass of one component in solution } & =\frac{(300 \mathrm{~g}) \times 25}{100}=75 \mathrm{~g} \\
\text { Mass of other component in solution } & =\frac{(400 \mathrm{~g}) \times 40}{100}=160 \mathrm{~g} \\
\text { Total mass of solute } & =(75+160) \mathrm{g}=235 \mathrm{~g} \\
\text { Total mass of solution } & =(300+400) \mathrm{g}=700 \mathrm{~g} \\
\% \text { of solute in the final solution } & =\frac{(235 \mathrm{~g})}{(700 \mathrm{~g})} \times 100=\mathbf{3 3 . 5 7} \\
\% \text { of solvent in the final solution } & =100-33.57=\mathbf{6 6 . 4 3}
\end{aligned}
$$

2.8. An antifreeze solution is prepared from 222.6 g of ethylene glycol, ( $\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}_{2}$ ) and 200 g of water. Calculate the molality of the solution. If the density of the solution is $1.072 \mathrm{~g} \mathrm{~mL}^{-1}$, then what shall be the molarity of the solution?
Sol:
Mass of solute $=222 \cdot 6 \mathrm{~g}$
Molar mass of solute, $\mathrm{C}_{2} \mathrm{H}_{4}(\mathrm{OH})_{2}$

$$
\begin{aligned}
& =12 \times 2+4+2(12+1)=62 \mathrm{~g} \mathrm{~mol}^{-1} \\
& \therefore \quad \text { Moles of solute }=\frac{222 \cdot 6}{62}=3.59
\end{aligned}
$$

Mass of solvent $=200 \mathrm{~g}$
$\therefore \quad$ Molality $=\frac{3.59}{200} \times 1000=17.95 \mathrm{~mol} \mathrm{~kg}^{-1}$
Total mass of solution $=422.6 \mathrm{~g}$
Volume of solution $=\frac{422 \cdot 6}{1 \cdot 072}=394.21 \mathrm{~mL}$.
$\therefore \quad$ Molarity $=\frac{3.59}{394.2} \times 1000=9.1 \mathrm{~mol} \mathrm{~L}^{-1}$
2.9. A sample of drinking water was found to be severely contaminated with chloroform $\left(\mathrm{CHCl}_{3}\right)$, supposed to be a carcinogen. The level of contamination was 15 ppm (by mass).
(i) express this in percent by mass.
(ii) determine the molality of chloroform in the water sample.

Sol: 15 ppm means 15 parts in million $\left(10^{6}\right)$ by mass in the solution.
$\therefore$ Percentage by mass $=\frac{15}{10^{6}} \times 100=15 \times 10^{-4} \%$
As only 15 g of chloroform is present in $10^{6} \mathrm{~g}$ of
the solution, mass of the solvent $=10^{6} \mathrm{~g}$
Molar mass of $\mathrm{CHCl}_{3}=12+1+3 \times 35.5$
$=119.5 \mathrm{~g} \mathrm{~mol}^{-1}$
Moles of $\mathrm{CHCl}_{3}=\frac{15}{119.5}$
$\therefore$ Molality $=\frac{15 / 119.5 \times 1000}{10^{6}}=1.25 \times 10^{-4} \mathrm{~m}$
2.10. What role does the molecular interaction play in solution of alcohol in water?
Sol: In case of alcohol as well as water, the molecules are interlinked by intermolecular hydrogen bonding. However, the hydrogen bonding is also present in the molecules of alcohol and water in the solution but it is comparatively less than both alcohol and water. As a result, the magnitude of attractive forces tends to decrease and the solution shows positive deviation from Raoult's Law. This will lead to increase in vapour pressure of the solution and also decrease in its boiling point.

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

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

Sol:
Henry's law: The solubility of a gas in a liquid at a particular temperature is directly proportional to the pressure of the gas in equilibrium with the liquid at that temperature.
or
The partial pressure of a gas in vapour phase is proportional to the mole fraction of the gas ( x ) in the solution. $\mathrm{p}=\mathrm{KHX}$
where KH is Henry's law constant.

## Applications of Henry's law :

(i) In order to increase the solubility of $\mathrm{CO}_{2}$ gas in soft drinks and soda water, the bottles are normally sealed under high pressure. Increase in pressure increases the solubility of a gas in a solvent according to Henry's Law. If the bottle is opened by removing the stopper or seal, the pressure on the surface of the gas will suddenly decrease. This will cause a decrease in the solubility of the gas in the liquid i.e. water. As a result, it will rush out of the bottle producing a hissing noise or with a fiz.
(ii) As pointed above, oxygen to be used by deep sea divers is generally diluted with helium inorder to reduce or minimise the painfril effects during decompression.
(iii) As the partial pressure of oxygen in air is high, in lungs it combines with haemoglobin to form oxyhaemoglobin. In tissues, the partial pressure of oxygen is comparatively low. Therefore, oxyhaemoglobin releases oxygen in order to carry out cellular activities.
2.13. The partial pressure of ethane over a solution containing $6.56 \times 10^{-3} \mathrm{~g}$ of ethane is 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?
Sol:
We know that, $m=K_{H} \times P$

$$
\begin{equation*}
\therefore \quad 6.56 \times 10^{-2} \mathrm{~g}=K_{H} \times 1 \mathrm{bar} \tag{i}
\end{equation*}
$$

$\therefore 5.00 \times 10^{-2} \mathrm{~g}=K_{H} \times P$
$K_{H}=6.56 \times 10^{-2} / 1 \mathrm{bar}$ (from i)
$K_{H}=5.00 \times 10^{-2} / p$ bar(from ii),
$\therefore \frac{6.56 \times 10^{-2}}{1}=\frac{5.00 \times 10^{-2}}{p}$
$\therefore P=\frac{5.00}{6.56}=0.762 \mathrm{bar}$.
2.14. According to Raoult's law, what is meant by positive and negative deviaitions and how is the sign of $\Delta_{\text {sol }} H$ related to positive and negative deviations from Raoult's law?
Sol: Solutions having vapour pressures more than that expected from Raoult's law are said to exhibit positive deviation. In these solutions solvent - solute interactions are weaker and $\Delta_{\text {sol }} H$ is positive because stronger $A-A$ or $B-B$ interactions are replaced by weaker $A-B$ interactions. Breaking of the stronger interactions requires more energy \& less energy is released on formation of
weaker interactions. So overall $\Delta_{\text {sol }} H$ is positive. Similarly $\Delta_{\text {sol }} V$ is positive i.e. the volume of solution is some what more than sum of volumes of solvent and solute.
So there is expansion in volume on solution formation.
Similarly in case of solutions exhibiting negative deviations, A - B interactions are stronger than A-A\&B-B. So weaker interactions are replaced by stronger interactions so , there is release of energy i.e. $\Delta_{\text {sol }} \mathrm{H}$ is negative.
2.15. An aqueous solution of 2 percent non-volatile solute exerts a pressure of 1.004 bar at the boiling point of the solvent. What is the molecular mass of the solute?
Sol:
According to Raoult's Law,

$$
\frac{\mathrm{P}_{\mathrm{A}}^{\circ}-\mathrm{P}_{\mathrm{S}}}{\mathrm{P}_{\mathrm{S}}}=\frac{n_{\mathrm{B}}}{n_{\mathrm{A}}}=\frac{\mathrm{W}_{\mathrm{B}}}{\mathrm{M}_{\mathrm{B}}} \times \frac{\mathrm{M}_{\mathrm{A}}}{\mathrm{~W}_{\mathrm{A}}}
$$

$$
\begin{aligned}
& \mathrm{P}_{\mathrm{A}}^{\circ}(\text { for water })=1.013 \mathrm{bar} ; \mathrm{P}_{\mathrm{S}}=1.004 \mathrm{bar} ; \mathrm{W}_{\mathrm{B}}=2 \mathrm{~g} ; \mathrm{W}_{\mathrm{A}}=100-2=98 \mathrm{~g} ; \\
& \mathrm{M}_{\mathrm{A}}=18 \mathrm{~g} \mathrm{~mol}^{-1} . \\
& \quad \frac{(1.013-1.004) \mathrm{bar}}{(1.004 \mathrm{bar})}=\frac{(2 \mathrm{~g}) \times\left(18 \mathrm{~g} \mathrm{~mol}^{-1}\right)}{\mathrm{M}_{\mathrm{B}} \times(98 \mathrm{~g})} \\
& \therefore \quad \mathrm{M}_{\mathrm{B}}=\frac{(2 \mathrm{~g}) \times\left(18 \mathrm{~g} \mathrm{~mol}^{-1}\right) \times(1.004 \mathrm{bar})}{(0.009 \mathrm{bar})) \times(98 \mathrm{~g})}=\mathbf{4 1 . 0} \mathrm{g} \mathrm{~mol}^{-1}
\end{aligned}
$$

2.16 Heptane and octane form an ideal solution. At 373 K , the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35.0 g of octane?
Sol.
Molar mass of heptane $\left(\mathrm{C}_{7} \mathrm{H}_{16}\right)$

$$
=7 \times 12+16=100 \mathrm{~g} \mathrm{~mol}^{-1}
$$

Molar mass of octane $\left(\mathrm{C}_{8} \mathrm{H}_{18}\right)$

$$
=8 \times 12+18=114 \mathrm{~g} \mathrm{~mol}^{-1}
$$

Moles of heptane present in mixture

$$
=\frac{26 \cdot 0}{100}=0.26 \mathrm{~mol}
$$

Moles of octane present in mixture

$$
=\frac{35 \cdot 0}{114}=0.307 \mathrm{~mol}
$$

Mole fraction of heptane $x_{\mathrm{H}}$

$$
=\frac{0.26}{0.26+0.307}=0.458
$$

Mole fraction of octane, $x_{O}=(1-0.458)=0.542$
Vapour pressure of heptane $=x_{H} \times P^{\circ}$
$=0.458 \times 105.2 \mathrm{kPa}=48.18 \mathrm{kPa}$
Vapour pressure of octane $=x_{O} \times P^{0}$
$=0.542 \times 46.8 \mathrm{kPa} \dot{=} 25.36 \mathrm{kPa}$
Vapour pressure of mixture
$=48 \cdot 18+25 \cdot 36=73.54 \mathrm{kPa}$.
2.17. The vapour pressure of water is 12.3 kPa at 300 K . Calculate vapour pressure of 1 molal solution of a non-volatile solute in it
Sol: 1 molal solution of solute means 1 mole of solute in 1000 g of the solvent.
Molar mass of water (solvent) $=18 \mathrm{~g} \mathrm{~mol}^{-1}$
$\therefore$ Moles of water $=\frac{1000}{18}=55.5$ moles.
$\therefore$ Mole fraction of solute $=\frac{1}{1+55.5}=0.0177$
Now, $\frac{P^{\circ}-P_{s}}{P^{\circ}}=x_{2}$
$\frac{12.3-P_{s}}{12.3}=0.0177$
$\Rightarrow P_{s}=12.08 \mathrm{kPa}$
2.18. Calculate the mass of a non-volatile solute (molecular mass $40 \mathrm{~g} \mathrm{~mol}^{-1}$ ) that should be dissolved in 114 g of octane to reduce its pressure to $\mathbf{8 0 \%}$.

## (C.B.S.E. Outside Delhi 2008)

Sol: According to Raoult's Law,

$$
\frac{\mathrm{P}_{\mathrm{A}}^{\circ}-\mathrm{P}_{\mathrm{S}}}{\mathrm{P}_{\mathrm{S}}}=\frac{n_{\mathrm{B}}}{n_{\mathrm{A}}}=\frac{\mathrm{W}_{\mathrm{B}}}{\mathrm{M}_{\mathrm{B}}} \times \frac{\mathrm{M}_{\mathrm{A}}}{\mathrm{~W}_{\mathrm{A}}}
$$

Let $\mathrm{P}_{\mathrm{A}}^{\circ}=1 \mathrm{~atm}, \mathrm{P}_{\mathrm{S}}=0.8 \mathrm{~atm} ; \mathrm{P}_{\mathrm{A}}^{\circ}-\mathrm{P}_{\mathrm{S}}=0.2 \mathrm{~atm} ; \mathrm{M}_{\mathrm{B}}=40 \mathrm{~g} \mathrm{~mol}^{-1} ; \mathrm{W}_{\mathrm{A}}=114 \mathrm{~g}$; $\mathrm{M}_{\mathrm{A}}\left(\mathrm{C}_{8} \mathrm{H}_{18}\right)=114 \mathrm{~g} \mathrm{~mol}^{-1}$.

$$
\begin{aligned}
W_{B} & =\frac{\left(\mathrm{P}_{\mathrm{A}}^{\circ}-\mathrm{P}_{\mathrm{S}}\right)}{\mathrm{P}_{\mathrm{S}}} \times \frac{\mathrm{M}_{\mathrm{B}} \times \mathrm{W}_{\mathrm{A}}}{\mathrm{M}_{\mathrm{A}}} \\
& =\frac{(0 \cdot 2 \mathrm{~atm})}{(0 \cdot 8 \mathrm{~atm})} \times \frac{\left(40 \mathrm{~g} \mathrm{~mol}^{-1}\right) \times(114 \mathrm{~g})}{\left(114 \mathrm{~g} \mathrm{~mol}^{-1}\right)}=\mathbf{1 0 . 0} \mathrm{g} .
\end{aligned}
$$

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 of vapour pressure becomes 2.9 kPa at 298 K .
Calculate
(i) molar mass of the solute.
(ii) vapour pressure of water at 298 K .

Sol: Let the molar mass of solute $=\mathrm{Mg} \mathrm{mol}^{-1}$
$\therefore$ Moles of solute present

$$
=\frac{30 \mathrm{~g}}{\mathrm{Mg} \mathrm{~mol}^{-1}}=\frac{30}{M} \mathrm{~mol}
$$

Moles of solvent present, ${ }^{\prime}\left(n_{1}\right)=\frac{90}{18}=5$ moles.

$$
\begin{gather*}
\therefore \quad \frac{P^{\circ}-P_{s}}{P^{\circ}}=\frac{n_{2}}{n_{1}+n_{2}} \\
\frac{P^{\circ}-2 \cdot 8}{P^{\circ}}=\frac{30 / M}{5+30 / M} \\
1-\frac{2 \cdot 8}{P^{\circ}}=\frac{30}{(5 M+30)} \\
1-\frac{30}{5 M+30}=\frac{2 \cdot 8}{P^{\circ}} \\
1-\frac{6}{M+6}=\frac{2.8}{P^{\circ}} \\
\frac{M+6-6}{M+6}=\frac{2 \cdot 8}{P^{\circ}} \\
\frac{M}{M+6}=\frac{2 \cdot 8}{P^{\circ}} \\
\frac{P^{\circ}}{2 \cdot 8}=1+\frac{6}{M} \tag{i}
\end{gather*}
$$

After adding 18 g of water,
Moles of water becomes
$=\frac{90+18}{18}=\frac{108}{18}=6 \mathrm{moles}$
$\therefore \frac{P^{\circ}-P_{s}}{P^{\circ}}=\frac{30 / M}{6+30 / M}$
$P_{s}$ New vapour pressure $=\mathbf{2 . 9} \mathbf{~ k P a}$

$$
\begin{align*}
& \frac{P^{\circ}-2 \cdot 9}{P^{\circ}}=\frac{30 M}{M(6 M+30)}=\frac{5}{M+5} \\
& 1-\frac{2 \cdot 9}{P^{\circ}}=\frac{5}{M+5} \\
& 1-\frac{5}{M+5}=\frac{2.9}{P^{\circ}} \\
& \frac{M+5-5}{M+5}=\frac{2.9}{P^{\circ}} \\
& \frac{P^{\circ}}{2 \cdot 9}=\frac{M+5}{M} \Rightarrow=1+\frac{5}{M} \\
& \frac{P^{\circ}}{2 \cdot 9}=1+\frac{5}{M} \tag{ii}
\end{align*}
$$

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

$$
\begin{aligned}
& \frac{2.9}{2.8}=\frac{1+6 / M}{1+5 / M} \\
& 2.9\left(1+\frac{5}{M}\right)=2.8\left(1+\frac{6}{M}\right) \\
& 2.9+\frac{2.9 \times 5}{M}=2.8+\frac{2.8 \times 6}{M} \\
& 2.9+\frac{14.5}{M}=2.8+\frac{16.8}{M} \\
& 0.1=\frac{16.8}{M}-\frac{14.5}{M}=\frac{2.3}{M} \\
& M=\frac{2.3}{0.1} \\
& M=23 \mathrm{~g}_{\mathrm{mol}} \\
& \hline 1
\end{aligned}
$$

Putting $M=23$, in equation ( $i$, we get,

$$
\begin{aligned}
& \frac{P^{\circ}}{2.8}=1+\frac{6}{23}=\frac{29}{23} \\
& P^{\circ}=\frac{29}{23} \times 2.8=3.53 \mathrm{kPa}
\end{aligned}
$$

2.20. A 5\% solution (by mass) of cane sugar in water has freezing point of 271 K. Calculate the freezing point of $5 \%$ glucose in water if freezing point of pure water is 273.15 K .
Sol: Mass of sugar in 5\% (by mass) solution means 5gin 100g of solvent (water)
Molar mass of sugar $=342 \mathrm{~g} \mathrm{~mol}^{-1}$
Molality of sugar solution $=\frac{5 \times 1000}{342 \times 100}=0.146$
$\therefore \Delta T_{f}$ for sugar solution $=273.15-271=2.15^{\circ}$
$\Delta T_{f}=K_{f} \times m$
$\Delta T_{f}=K_{f} \times 0.146 \Rightarrow K_{f}=2 \cdot 15 / 0.146$
Molality of glucose solution
$=\frac{5}{180} \times \frac{1000}{100}=0.278$
(Molar mass of glucose $=180 \mathrm{~g} \mathrm{~mol}^{-1}$ )
$\Delta T_{f}=K_{f} \times m=\frac{2.15}{0.146} \times 0.278=4.09^{\circ}$
$\therefore$ Freezing point of glucose solution
$=273.15-4.09=269.06 \mathrm{~K}$.
2.21. Two elements $A$ and $B$ form compounds having formula $A B_{2}$ and $A B_{4}$. When dissolved in 20 g of benzene $\left(\mathrm{C}_{6} \mathrm{H}_{6}\right), 1 \mathrm{~g}$ of $A B_{2}$ 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 atomic masses of $A$ and $B$. Sol:

Using the relation, $M_{2}=\frac{1000 \times k_{f} \times w_{2}}{w_{1} \times \Delta T_{f}}$

$$
\begin{aligned}
\therefore \quad M_{A B_{2}} & =\frac{1000 \times 5.1 \times 1}{20 \times 2.3}=110.87 \mathrm{~g} \mathrm{~mol}^{-1} \\
& M_{A B_{4}}
\end{aligned}=\frac{1000 \times 5.1 \times 1}{20 \times 1.3}=196.15 \mathrm{~g} \mathrm{~mol}^{-1} .
$$

Let the atomic masses of $A$ and $B$ are ' $p$ ' and ' $q$ ' respectively.
Then molar mass of $A B_{2}=\mathrm{p}+2 \mathrm{q}=110.87 \mathrm{~g} \mathrm{~mol}^{-1}$
And molar mass of
$A B_{4}=\mathrm{p}+4 \mathrm{q}=196.15 \mathrm{~g} \mathrm{~mol}^{-1}$
Substracting equation (ii) from equation (i), we
get $\quad 2 \mathrm{q}=85.28 \Rightarrow \mathrm{q}=42.64$
Putting $\mathrm{q}=42.64$ in equ. (i), we get

$$
\begin{aligned}
& p=110.87-85.28 \\
& p=25.59
\end{aligned}
$$

Thus, atomic mass of $A=25.59 \mathrm{~g} \mathrm{~mol}^{-1}$ and atomic mass of $B=42.64 \mathrm{~g} \mathrm{~mol}^{-1}$
2.22. At $300 \mathrm{~K}, 36 \mathrm{~g}$ glucose present per litre in its solution has osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bar at the same temperature, what would be its concentration?
Sol:

$$
\pi=\mathrm{CRT}=\frac{\mathrm{W}_{\mathrm{B}} \times \mathrm{R} \times \mathrm{T}}{\mathrm{M}_{\mathrm{B}} \times \mathrm{V}}
$$

For both the solutions, $\mathrm{R}, \mathrm{T}$ and V are constants
Ist case :

$$
(4.98 \text { bar })=\frac{(36 \mathrm{~g}) \times \mathrm{R} \times \mathrm{T}}{\left(180 \mathrm{~g} \mathrm{~mol}^{-1}\right) \times \mathrm{V}}
$$

Ind case: $\quad(1.52 \mathrm{bar})=\frac{\mathrm{W}_{\mathrm{B}} \times \mathrm{R} \times \mathrm{T}}{\mathrm{M}_{\mathrm{B}} \times \mathrm{V}}$
Divide eqn. (ii) by eqn. (i),
or

$$
\begin{aligned}
\frac{(1.52 \mathrm{bar})}{(4.98 \mathrm{bar})} & =\frac{\mathrm{W}_{B}}{\mathrm{M}_{B}} \times(5 \mathrm{~mol}) \\
\frac{\mathrm{W}_{B}}{\mathrm{M}_{\mathrm{B}}} & =\frac{1.52}{4.98} \times \frac{1}{(5 \mathrm{~mol})}=0.0610 \mathrm{~mol}^{-1}
\end{aligned}
$$

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 ( $\mathrm{CH}_{3} \mathrm{CN}$ ) and acetone ( $\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}$ )

Sol: (i) Both w-hexane and n-octane are non-polar. Thus, the intermolecular interactions will be London dispersion forces.
(ii) Both $\mathrm{I}_{2}$ and $\mathrm{CCl}_{4}$ are non-polar. Thus, the intermolecular interactions will be London dispersion forces.
(iii) $\mathrm{NaClO}_{4}$ is an ionic compound and gives $\mathrm{Na}^{+}$and $\mathrm{ClO}_{4}^{-}$ions in the Solution. Water is a polar molecule. Thus, the intermolecular interactions will be iondipole interactions.
(iv) Both methanol and acetone are polar molecules. Thus, intermolecular interactions will be dipole-dipole interactions.
(v) Both $\mathrm{CH}_{3} \mathrm{CN}$ and $\mathrm{C}_{3} \mathrm{H}_{6} \mathrm{O}$ are polar molecules. Thus, intermolecular interactions will be dipole-dipole interactions.
2.24. Based on solute solvent interactions, arrange the following in order of increasing solubility in $n$-octane and explain. Cyclohexane, $\mathrm{KCl}, \mathrm{CH}_{3} \mathrm{OH}$, $\mathrm{CH}_{3} \mathrm{CN}$.
Sol: n -octane $\left(\mathrm{C}_{8} \mathrm{H}_{18}\right)$ is a non-polar liquid and solubility is governed by the principle that like dissolve like. Keeping this in view, the increasing order of solubility of different solutes is:
$\mathrm{KCl}<\mathrm{CH}_{3} \mathrm{OH}<\mathrm{CH}_{3} \mathrm{C}=\mathrm{N}<\mathrm{C}_{6} \mathrm{H}_{12}$ (cyclohexane).
2.25. Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water?
(i) phenol
(ii) toluene
(iii) formic acid
(iv) ethylene glycol
(v) chloroform
(vi) pentanol

Sol: (i) Phenol (having polar - OH group) - Partially soluble.
(ii) Toluene (non-polar) - Insoluble.
(iii) Formic acid (form hydrogen bonds with water molecules) - Highly soluble.
(iv) Ethylene glycol (form hydrogen bonds with water molecules) Highly soluble.
(v) Chloroform (non-polar)- Insoluble.
(vi) Pentanol (having polar -OH) - Partially soluble.
2.26. If the density of lake water is $1.25 \mathrm{~g} \mathrm{~mL}-1$, and it contains 92 g of $\mathrm{Na}^{+}$ions per kg of water, calculate the molality of $\mathrm{Na}^{+}$ions in the lake. (C.B.S.E. Outside Delhi 2008)

Sol:

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

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

Sol:

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

Maximum molarity of CuS in aqueous solution
means solubility of CuS.
Let the solubility of CuS be $S \mathrm{~mol} \mathrm{~L}^{-1}$
$\therefore \quad K_{\mathrm{sp}}=\left[\mathrm{Cu}^{2+}\right][\mathrm{S}]^{2-}$

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

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

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 CHO is dissolved in 450 g of CH 3 CN .
Solution:
Mass of aspirin $=6.5 \mathrm{~g}$
Mass of acetonitrile $=450 \mathrm{~g}$
Then, total mass of the solution $=(6.5+450) \mathrm{g}=456.5 \mathrm{~g}$
Therefore, mass percentage of $\mathrm{C}_{9} \mathrm{H}_{8} \mathrm{O}_{4}=6.5456 .5 \times 100 \%$
= 1.424\%
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. Dose of nalorphene generally given is 1.5 mg . Calculate the mass of $1.5 \times 10^{-3} \mathrm{~m}$ aqueous solution required for the above dose.

## Solution:

$1.5 \times 10^{-3} \mathrm{~m}$ aqueous solution of nalorphene means that $1.5 \times 10^{-3}$ mole of nalorphene is dissolved in 1 kg of water.
Molar mass of nalorphene, $\mathrm{C}_{19} \mathrm{H}_{21} \mathrm{NO}_{3}$
$=19 \times 12+21+14+3 \times 16=311 \mathrm{~g} \mathrm{~mol}^{-1}$
$\therefore 1.5 \times 10^{-3}$ mole of nalorphene
$=1.5 \times 10^{-3} \times 311 \mathrm{~g}=0.467 \mathrm{~g}$
$\therefore$ Mass of solution $=0.467+1000=1000 \cdot 467 \mathrm{~g}$.
For 0.467 g of nalorphene, mass of solution required $=1000.467 \mathrm{~g}$
For $1.5 \mathrm{mg}\left(1.5 \times 10^{-3} \mathrm{~g}\right)$ of nalorphene, mass of solution required
$=\frac{1000.467}{0.467} \times 1.5 \times 10^{-3}=3.21 \mathrm{~g}$.
2.30. Calculate the amount of benzoic acid $\left(\mathrm{C}_{5} \mathrm{H}_{5} \mathrm{COOH}\right)$ required for preparing $\mathbf{2 5 0} \mathrm{mL}$ of $\mathbf{0 . 1 5} \mathbf{~ M}$ solution in methanol.
Solution:

$$
\begin{aligned}
\text { Molarity }(\mathrm{M}) & =\frac{\text { Mass of solute } / \mathrm{molar} \text { mass }}{\text { Volume of solution in litres }} \\
\mathrm{M} & =0.15 \mathrm{M}=0.15 \mathrm{~mol} \mathrm{~L}^{-1} ; \\
\text { Molar mass of solute } & =7 \times 12+6 \times 1 \times 2 \times 16=122 \mathrm{~g} \mathrm{~mol}^{-1} ; \\
\text { Volume of solution } & =250 \mathrm{~mL}=0.25 \mathrm{~L} . \\
\left(0.15 \mathrm{~mol} \mathrm{~L}^{-1}\right) & =\frac{\text { Mass of solute }}{\left(122 \mathrm{~g} \mathrm{~mol}^{-1}\right) \times(0.25 \mathrm{~L})} \\
\text { Mass of solute } & =\left(0.15 \mathrm{~mol} \mathrm{~L}^{-1}\right) \times\left(122 \mathrm{~g} \mathrm{~mol}^{-1}\right) \times(0.25 \mathrm{~L})=\mathbf{4 . 5 7 5} \mathrm{g}
\end{aligned}
$$

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

## Solution:



Acetic acid Trichloroacetic acid Trifluoroacetic acid
Fluorine being more electronegative than chlorine has the highest electron withdrawing inductive effect. Thus, triflouroacetic acid is the strongest trichloroacetic acid is second most and acetic acid is the weakest acid due to absence of any electron withdrawing group. Thus, $\mathrm{F}_{3} \mathrm{CCOOH}$ ionizes to the largest extent while $\mathrm{CH}_{3} \mathrm{COOH}$ ionizes to minimum extent in water. Greater the extent of ionization greater is the depression in freezing point. Hence, the order of depression in freezing point will be $\mathrm{CH}_{3} \mathrm{COOH}<\mathrm{Cl}_{3} \mathrm{CCOOH}<\mathrm{F}_{3} \mathrm{CCOOH}$.
2.32. Calculate the depression in the freezing point of water when 10 g of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHClCOOH}$ is added to 250 g of water. $\mathrm{Ka}=1.4 \times 10^{-3} \mathrm{Kg}=1.86 \mathrm{~K} \mathrm{~kg}$ $\mathrm{mol}^{-1}$.

## Solution:

Mass of solute $\left(\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHClCOOH}\right)=10 \mathrm{~g}$
Molar mass of
$\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHClCOOH}=4 \times 12+7 \times 1+1 \times 35.5+2 \times 16=48+7+35.5+32$
$=122.5 \mathrm{~g} \mathrm{~mol}^{-1}$
\frac\{\text $\{$ Mass / Molar mass \}\}\{\text $\{$ Mass of solvent (Kg) \}\}= Mass / Molar mass Mass of solvent ( Kg ) [latex/latex]=[latex] $10 \mathrm{~g}(122.5 \mathrm{~g} \mathrm{~mol}-1) \times(0.25 \mathrm{Kg})$ $=0.326 \mathrm{~m}$
Let $\alpha$ be the degree of dissociation of $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHClCOOH}$ then

$$
\begin{aligned}
& \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHClCOOH} \rightleftharpoons \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHClCOO}^{-}+\mathrm{H}^{+} \\
& \text {Initial conc. } \\
& \text { At equilibrium } \\
& \mathrm{C} \mathrm{~mol}^{-1} \mathrm{Kg} \\
& \text { C ( } 1-\alpha \text { ) } \\
& { }^{0} \mathrm{C} \alpha \\
& \stackrel{0}{\mathrm{C}} \alpha \\
& \therefore \quad K_{a}=\frac{C \alpha . C \alpha}{C(1-\alpha)} \\
& =\frac{C \alpha^{2}}{1-\alpha} \quad[\because \text { considering }(1-\alpha)=1 \text { for dilute solution }] \\
& \text { Now, } \quad K_{a}=\frac{C \alpha^{2}}{1} \\
& \Rightarrow \quad K_{a}=C \alpha^{2} \\
& \Rightarrow \quad \alpha=\sqrt{\frac{K_{\alpha}}{C}} \\
& =\sqrt{\frac{1.4 \times 10^{-3}}{0.326}} \\
& \left(\because K_{a}=1.4 \times 10^{-3}\right) \\
& =0.0655
\end{aligned}
$$

| $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHClCOOH}$ | $\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CHClCOO}^{-}$ | $+\mathrm{H}^{+}$ |
| :---: | :---: | :---: |
| 1 | 0 | 0 |
| $1-\alpha$ | $\alpha$ | $\alpha$ |

Total no. of moles after dissociation $=1-\alpha+\alpha+\alpha$
$=1+\alpha$
Van't Hoff factor
Total no. of moles after dissociation
(i) $=\frac{\text { Total no. of moles after dissociation }}{\text { No. of moles before dissociation }}$
$\therefore i=1+\alpha 1$
$=1+\alpha$
$=1+0.0655$
$=1.0655$
Hence, the depression in the freezing point of water is given as:
$\Delta \mathrm{T}_{\mathrm{f}}=\mathrm{i} . \mathrm{K}_{\mathrm{f}} \mathrm{m}$
$=1.0655 \times 1.86 \mathrm{~kg} \mathrm{~mol}^{-1} \times 0.326 \mathrm{~mol} \mathrm{~kg}^{-1}$
$=0.65 \mathrm{~K}$
2.33. 19.5g of $\mathrm{CH}_{2} \mathrm{FCOOH}$ is dissolved in 500 g of water. The depression in the freezing point of water observed is $1.0^{\circ} \mathrm{C}$. Calculate the van's Hoff factor and dissociation constant of fluoroacetic acid.

## Solution:

Calculation of Van't Hoff factor (i)
Given, $\mathrm{w}_{1}=500 \mathrm{~g}=0.5 \mathrm{~kg}, \mathrm{w}_{2}=19.5 \mathrm{~g}, \mathrm{~K}_{\mathrm{f}}=1.86 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}, \Delta \mathrm{~T}_{\mathrm{f}}=1 \mathrm{~K}$
Molar mass of $\mathrm{CH}_{2} \mathrm{FCOOH}\left(\mathrm{M}_{2}\right)$
$=2 \times 12+3 \times 1+1 \times 19+2 \times 16$
$=24+3+19+32$
$=78 \mathrm{~g} \mathrm{~mol}^{-1}$
$\Delta T_{f}=i K_{f} m$

$$
\begin{align*}
i & =\frac{\Delta T_{f}}{K_{f} m}  \tag{i}\\
m & =\frac{w_{2}}{M_{2} \times w_{1}} \\
& =\frac{19.5 \mathrm{~g}}{\left(78 \mathrm{~g} \mathrm{~mol}^{-1}\right) \times(0.5 \mathrm{~kg})} \\
& =0.5 \mathrm{~mol} \mathrm{~kg}^{-1} \tag{ii}
\end{align*}
$$

From eq. (i), we get

$$
\begin{aligned}
i & =\frac{1}{\left(1.86 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}\right) \times\left(0.5 \mathrm{~mol} \mathrm{~kg}^{-1}\right)} \\
& =1.0753
\end{aligned}
$$

Calculation of dissociation constant, $\boldsymbol{K}_{\boldsymbol{a}}$
Let $\alpha$ be the degree of dissociation of $\mathrm{CH}_{2} \mathrm{FCOOH}$ then

Initial conc.
At equilibrium
$\mathrm{CH}_{2} \mathrm{FCOOH} \rightleftharpoons \mathrm{CH}_{2} \mathrm{FCOO}^{-}+\mathrm{H}^{+}$
$C \mathrm{~mol} \mathrm{~L}^{-1}$
$0 \quad 0$
$C(1-\alpha)$
$C \alpha$ $C \alpha$
Total $=C(1+\alpha)$
$\therefore \quad i=\frac{C(1+\alpha)}{C}$
$\Rightarrow \quad i=1+\alpha$
$\Rightarrow \quad \alpha=i-1$

$$
\begin{aligned}
& =1.0753-1 \\
& =0.0753
\end{aligned}
$$

Now,

$$
\begin{aligned}
K_{a} & =\frac{\left[\mathrm{CH}_{2} \mathrm{FCOO}^{-}\right]\left[\mathrm{H}^{+}\right]}{\left[\mathrm{CH}_{2} \mathrm{FCOOH}\right]} \\
& =\frac{C \alpha \cdot C \alpha}{C(1-\alpha)} \\
& =\frac{C \alpha^{2}}{1-\alpha}
\end{aligned}
$$

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

$$
\begin{aligned}
C & =\frac{\frac{19.5}{78}}{500} \times 1000 \mathrm{M} \\
& =0.5 \mathrm{M}
\end{aligned}
$$

Therefore, $\quad K_{a}=\frac{C \alpha^{2}}{1-\alpha}$

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

2.34. Vapour pressure of water at 293 K is $\mathbf{1 7 . 5 3 5} \mathbf{~ m m ~ H g}$. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in $\mathbf{4 5 0} \mathrm{g}$ of water.
Solution:
According to Raoult's Law,

$$
\begin{aligned}
\frac{\mathrm{P}_{\mathrm{A}}^{\circ}-\mathrm{P}_{\mathrm{S}}}{\mathrm{P}_{\mathrm{S}}} & =\frac{n_{\mathrm{B}}}{n_{\mathrm{A}}} \text { or } \frac{\mathrm{P}_{\mathrm{A}}^{\circ}}{\mathrm{P}_{\mathrm{S}}}-1=\frac{n_{\mathrm{B}}}{n_{\mathrm{A}}} \\
\frac{\mathrm{P}_{\mathrm{A}}^{\circ}}{\mathrm{P}_{\mathrm{S}}} & =1+\frac{n_{\mathrm{B}}}{n_{\mathrm{A}}}=1+\frac{\mathrm{W}_{\mathrm{B}}}{\mathrm{M}_{\mathrm{B}}} \times \frac{\mathrm{M}_{\mathrm{A}}}{\mathrm{~W}_{\mathrm{A}}} \\
\mathrm{~W}_{\mathrm{B}} & =25 \mathrm{~g} ; \mathrm{W}_{\mathrm{A}}=450 \mathrm{~g} ; \mathrm{M}_{\mathrm{B}}=180 \mathrm{~g} \mathrm{~mol}^{-1} ; \\
\mathrm{M}_{\mathrm{A}} & =18 \mathrm{~g} \mathrm{~mol}^{-1} ; \mathrm{P}_{\mathrm{A}}^{\circ}=17.535 \mathrm{~mm} \\
\frac{\mathrm{P}_{\mathrm{A}}^{\circ}}{\mathrm{P}_{\mathrm{S}}} & =1+\frac{(25 \mathrm{~g}) \times\left(18 \mathrm{~g} \mathrm{~mol}^{-1}\right)}{\left(180 \mathrm{~g} \mathrm{~mol}^{-1}\right) \times(450 \mathrm{~g})}=1+0.0055=1.0055 \\
\mathrm{P}_{\mathrm{S}}(\text { V.P of water in solution }) & =\frac{(17.535 \mathrm{~mm})}{(1.0055)}=17.44 \mathrm{~mm}
\end{aligned}
$$

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

## Solution:

Here, $\mathrm{p}=760 \mathrm{~mm} \mathrm{Hg}, \mathrm{K}_{\mathrm{H}}=4.27 \times 10^{5} \mathrm{~mm} \mathrm{Hg}$ (at 298 K )
According to Henry's law, $\mathrm{p}=\mathrm{K}_{\mathrm{Hx}}$
$\chi=\mathrm{pkH}$
$=760 \mathrm{mmHg} 4.27 \times 105 \mathrm{mmHg}$
$=177.99 \times 10^{-5}$
$=178 \times 10^{-5}$
Hence, the mole fraction of methane in benzene is $178 \times 10^{-5}$.
2.36. 100 g of liquid $A$ (molar mass $140 \mathrm{~g} \mathrm{~mol}^{-1}$ ) 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 torr. Calculate the vapour pressure of pure liquid $A$ and its vapour pressure in the solution if the total vapour pressure of the solution is 475 torr.

## Solution:

Number of moles of liquid $A, n_{A}=w 1 M 1=100140 \mathrm{~mol}=0.714 \mathrm{~mol}$
Number of moles of liquid $B, n_{B}=w 2 M 2=1000180 \mathrm{~mol}=5.556 \mathrm{~mol}$
Then, mole fraction of $A, \chi_{A}=n A n A+n B$
$=0.714 \mathrm{~mol}(0.714+5.556) \mathrm{mol}=0.114$
Mole fraction of $B, \chi_{B}=1-0.114=0.886$
Vapour pressure of pure liquid $B, p 0 B=500$ torr
Therefore, vapour pressure of liquid $B$ in the solution,
$P_{B}=p 0 B \chi_{B}$
$=500 \times 0.886$
$=443$ torr
Total vapour pressure of the solution, $\mathrm{p}_{\text {total }}=475$ torr
$\therefore$ Vapour pressure of liquid $A$ in the solution,
$P_{A}=P_{\text {total }}-P_{B}$
$=475-443$ = 32 torr
Now, $P_{A}=p 0 A \chi_{A}$
$\Rightarrow \mathrm{pAxA}=320.114$
$=280.7$ torr
Hence, the vapour pressure of pure liquid A is 280.7 torr.
2.37. Vapour pressures of pure acetone and chloroform at 328 K are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition, plot $P_{\text {total }}, P_{\text {chlroform }}$ and $P_{\text {acetone }}$ as a function of $\chi_{\text {acetone. }}$. The experimental data observed for different compositions of mixtures is:

| $\mathbf{1 0 0} \times \boldsymbol{x}_{\text {acetone }}$ | 0 | 11.8 | 23.4 | 36.0 | 50.8 | 58.2 | 64.5 | 72.1 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\boldsymbol{p}_{\text {acetone }} / \mathbf{m m} \mathbf{H g}$ | 0 | 54.9 | 110.1 | 202.4 | 322.7 | 405.9 | 454.1 | 521.1 |
| $\boldsymbol{p}_{\text {chloroform }} / \mathbf{m m ~ H g}$ | 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:


It can be observed from the graph that the plot for the ptotai of the solution curves downwards. Therefore, the solution shows negative deviation from the ideal behaviour.
2.38. Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and toluene at 300 K are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of toluene.

## Solution:

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 $\left(\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{CH}_{3}\right)=7 \times 12+8 \times 1=92 \mathrm{~g} \mathrm{~mol}^{-1}$
No. of moles present in 80 g of benzene $=8078 \mathrm{~mol}=1.026 \mathrm{~mol}$
No. of moles present in 100 g of toluene $=10092 \mathrm{~mol}=1.087 \mathrm{~mol}$
Mole fraction of benzene, $\chi_{\text {с6н6 }}=1.0261 .026+1.087=0.486$
$\therefore$ Mole fraction of toluene, $\chi_{\text {с6н5сн3 }} 5013=1-0.486=0.514$
It is given that vapour pressure of pure benzene, p0C6H6 $=50.71 \mathrm{~mm} \mathrm{Hg}$
Vapour pressure of pure toluene, $\mathrm{p} 0 \mathrm{C} 6 \mathrm{H} 5 \mathrm{CH} 3=32.06 \mathrm{~mm} \mathrm{Hg}$
Therefore, partial vapour pressure of benzene,
$P_{\text {total }}=\chi_{\text {c6 } 6} \times$ p0C6H6
$=0.486 \times 50.71$
$=24.645 \mathrm{~mm} \mathrm{Hg}$
Partial vapour pressure of toluene, $\mathrm{P}_{\text {с6Н5СН }}=\chi_{\text {с6Н5СН }} \times$ POC6H5CH3
$=0.514 \times 32.06$
$=16.479 \mathrm{~mm} \mathrm{Hg}$
Total vapour pressure of solution $(p)=24.645+16.479$
$=41.124 \mathrm{~mm} \mathrm{Hg}$
Mole fraction of benzene in vapour phase
$=\chi \mathrm{C} 6 \mathrm{H} 6 \times \mathrm{p} 0 \mathrm{C} 6 \mathrm{H} 6$ ptotal
$=0.486 \times(50.71) \mathrm{mm}(41.124) \mathrm{mm}$
$=0.599 \cong 0.6$
2.39. The air is a mixture of a number of gases. The major components are oxygen and nitrogen with an approximate proportion of $20 \%$ is to $\mathbf{7 9 \%}$ by volume at 298 K . The water is in equilibrium with air at a pressure of 10 atm. At 298 K if Henry's law constants for oxygen and nitrogen are $3.30 \times 10^{7} \mathbf{~ m m}$ and $6.51 \times 10^{7} \mathrm{~mm}$ respectively, calculate the composition of these gases in water.

## Solution:

Percentage of oxygen $\left(\mathrm{O}_{2}\right)$ in air $=20 \%$
Percentage of nitrogen $\left(\mathrm{N}_{2}\right)$ in air $=79 \%$
Also, it is given that water is in equilibrium with air at a total pressure of 10 atm that is, $(10 \times 760) \mathrm{mm}=7600 \mathrm{~mm}$
Therefore, partial pressure of oxygen,
$\mathrm{PO}_{2}=20100 \times 7600 \mathrm{~mm}$
$=1520 \mathrm{~mm} \mathrm{Hg}$
Partial pressure of nitrogen, $\mathrm{pN}_{2}=79100 \times 7600 \mathrm{~mm}$
$=6004 \mathrm{~mm} \mathrm{Hg}$
Now, according to Henry's law,
$p=K_{\text {H. }}$
For oxygen:

$$
\Rightarrow \begin{aligned}
p_{\mathrm{O}_{2}} & =K_{\mathrm{H}} \cdot \chi_{\mathrm{O}_{2}} \\
\chi_{\mathrm{O}_{2}} & =\frac{p_{\mathrm{O}_{2}}}{K_{\mathrm{H}}} \\
& =\frac{1520 \mathrm{~mm}}{3.30 \times 10^{7} \mathrm{~mm}} \\
& =4.61 \times 10^{-5}
\end{aligned}
$$

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

For nitrogen :

$$
\Rightarrow \quad \begin{aligned}
& p_{\mathrm{N}_{2}}=K_{\mathrm{H}} \cdot \chi_{\mathrm{N}_{2}} \\
& \chi_{\mathrm{N}_{2}}=\frac{p_{\mathrm{N}_{2}}}{K_{\mathrm{H}}}
\end{aligned}
$$

$6004 \mathrm{~mm} 6.51 \times 107 \mathrm{~mm}$
(Given $K_{H}=6.51 \times 10^{7} \mathrm{~mm}$ )
$=9.22 \times 10^{-5}$
Hence, the mole fractions of oxygen and nitrogen in water are $4.61 \times 10^{-5}$ and $9.22 \times 10^{-5}$ respectively.
2.40. Determine the amount of $\mathrm{CaCl}_{2}(i=2.47)$ dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at $27^{\circ} \mathrm{C}$.

## Solution:

We know that,
$\pi=\mathrm{i} T$
$\Rightarrow \pi=\mathrm{i} T$
$\Rightarrow \mathrm{w}=$
Given,
$\pi=0.75$ atm
$V=2.5 \mathrm{~L}$
$i=2.47$
$\mathrm{T}=(27+273) \mathrm{K}=300 \mathrm{~K}$
$\mathrm{R}=0.0821 \mathrm{~L} \mathrm{~atm} \mathrm{~K}^{-1} \mathrm{~mol}^{-}$
Molar mass of $\mathrm{CaCl}_{2}(\mathrm{M})=1 \times 40+2 \times 35.5=111 \mathrm{~g} \mathrm{~mol}^{-1}$
Therefore, $\mathrm{w}=0.75 \times 111 \times 2.52 .47 \times 0.0821 \times 300=3.42 \mathrm{~g}$
Hence the required amount of $\mathrm{CaCl}_{2}$ is 3.42 g
2.41. Determine the osmotic pressure of a solution prepared by dissolving 25 $\mathbf{m g}$ of $\mathrm{K}_{2} \mathrm{SO}_{4}$ in 2 litre of water at $25^{\circ} \mathrm{C}$, assuming that it is completely
dissociated. (C.B.S.E. 2013)

## Solution:

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

$\mathrm{K}_{2} \mathrm{SO}_{4}$ dissociates in water as :

$$
\mathrm{K}_{2} \mathrm{SO}_{4} \xrightarrow{(\mathrm{aq})} 2 \mathrm{~K}^{+}(\mathrm{aq})+\mathrm{SO}_{4}^{2-}(\mathrm{aq}) ; a=\frac{i-1}{n-1}
$$

a(for complete dissociation) $=1, n=3 ; 1=\frac{i-1}{3-1}$ or $i=2+1=3$
Step II. Calculation of osmotic pressure ( $\pi$ )
Osmotic pressure $(\pi)=i C R T=\frac{i W_{B} R T}{M_{B} \times V}$
$i=3 ; W_{B}=25 \mathrm{mg}=0.025 \mathrm{~g} ; \mathrm{M}_{\mathrm{B}}=2 \times 39+32+4 \times 16=174 \mathrm{~g} \mathrm{~mol}^{-1} ; \mathrm{V}=2 \mathrm{~L} ; \quad \mathrm{T}=25^{\circ} \mathrm{C}=298 \mathrm{~K} ;$ $\mathrm{R}=0.0821 \mathrm{Latm}^{-1} \mathrm{~mol}^{-1}$

$$
\begin{aligned}
\pi & \left.=\frac{(3) \times(0.025 \mathrm{~g}) \times\left(0.0821 \mathrm{~L} \mathrm{am} \mathrm{~K} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}\right) \times(298 \mathrm{~K})}{(174 \mathrm{~g} \mathrm{~mol}}{ }^{-1}\right) \times(2 \mathrm{~L}) \\
& =5.27 \times 10^{-3} \mathrm{~atm} .
\end{aligned}
$$

