## LIQUID SOLUTION

## Vapour Pressure



The pressure exerted by the vapour (molecules in the vapour phase) over the surface of the liquid at the equilibrium at given temperature is called the vapour pressure of the liquid.

## Factors affecting vapour pressure

(i) Temperature :

Vapour pressure $\propto$ Temperature
The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called its boiling point.

(ii) Nature of liquid:

Vapour pressure of liquid $\propto \frac{1}{\begin{array}{c}\text { The strength of intermolecular forces } \\ \text { acting between molecules }\end{array}}$
For example, ethyl alcohol has higher vapour pressure because of the weak intermolecular forces acting between its molecules than water which has stronger intermolecular forces acting between water molecules of volatile liquid has lower boiling point than a non-volatile liquid.

## i) Vapour Pressure of a Solution Containing Non Volatile Solute - Raoult's Law

Raoult's Law : Acccording to this law, the partial pressure of any volatile constituent of a soltuion at a constant temperature is equal to the vapour pressure of pure constituent multiplied by the mole fraction of that constituent in the solution.

$$
\mathbf{P}_{\mathrm{A}} \propto \mathbf{X}_{\mathrm{A}} \Rightarrow \mathbf{P}_{\mathrm{A}}=\mathbf{P}_{\mathrm{A}}^{0} \mathbf{X}_{\mathrm{A}}
$$



Relative Lowering of vapour pressure: For a solution of a non-volatile solute in a liquid, the vapour pressure contribution by the non-volatile solute is negligible. Therefore, the partial vapour pressure of a solution containing a non-volatile solute is equal to the product of vapour pressure of the pure liquid (solvent $\mathrm{P}_{\mathrm{A}}^{\circ}$ ) and its mole fraction in the solution.
Let $X_{A}$ be the mole fraction of solvent $A$, then (Here $\mathrm{p}_{\mathrm{B}}^{0}=$ negligible as solute is non-volatile)

$$
\mathrm{P}_{\mathrm{A}}=\mathrm{P}_{\mathrm{A}}^{\circ} \mathrm{X}_{\mathrm{A}}
$$

If $X_{B}$ be the mole fraction of the solute $B$, then

$$
\mathrm{X}_{\mathrm{A}}+\mathrm{X}_{\mathrm{B}}=1 \Rightarrow \mathrm{X}_{\mathrm{A}}=1-\mathrm{X}_{\mathrm{B}}
$$

hence $P_{A}=P_{A}^{\circ}\left(1-X_{B}\right)=P_{A}^{\circ}-P_{A}^{\circ} X_{B} \Rightarrow \quad \mathbf{P}_{\mathbf{A}}^{\mathbf{0}} \mathbf{X}_{\mathbf{B}}=\mathbf{P}_{\mathbf{A}}^{\mathbf{0}}-\mathbf{P}_{\mathbf{A}}$
$\left(\mathrm{P}_{\mathrm{A}}^{0}-\mathrm{P}_{\mathrm{A}}\right.$ is known as lowering of vapour pressure)

$$
\frac{\mathbf{P}_{\mathbf{A}}^{\mathbf{o}}-\mathbf{P}_{\mathbf{A}}}{\mathbf{P}_{\mathbf{A}}^{\mathbf{0}}}=\mathbf{X}_{\mathbf{B}} \quad\left(\frac{\mathrm{P}_{\mathrm{A}}^{\circ}-\mathrm{P}_{\mathrm{A}}}{\mathrm{P}_{\mathrm{A}}^{\circ}} \text { is called relative lowering of vapour pressure, (RLVP)}\right)
$$

Therefore, Raoult's law states that the relative lowering of vapour pressure $\left(\frac{\mathrm{P}_{\mathrm{A}}^{\circ}-\mathrm{P}_{\mathrm{A}}}{\mathrm{P}_{\mathrm{A}}^{\circ}}\right)$, for a non-volatile solute is equal to the mole fraction of the solute when the solvent alone is volatile.

Example: $\quad$ The vapour pressure of pure water at $37^{\circ} \mathrm{C}$ is 47.1 torr. What is the vapour pressure of an aqueous solution at $37^{\circ} \mathrm{C}$ containing 20 g of glucose dissolved in 500 gm of water. Also calculate vapour pressure lowering.
Solution: $\quad \mathrm{n}_{\mathrm{H}_{2} \mathrm{O}}=\frac{500}{18}=27.78 \mathrm{~mol}, \quad \mathrm{n}_{\text {(glucose) }}=\frac{20}{180}=0.11 \mathrm{~mol}$

$$
\mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}=\frac{\mathrm{n}_{\mathrm{H}_{2} \mathrm{O}}}{\mathrm{n}_{\mathrm{H}_{2} \mathrm{O}}+\mathrm{n}_{\text {(glucose) }}}=\frac{27.78}{27.78+0.11}=\frac{27.78}{27.89}=0.996
$$

According to Raoult's law,
Vapour pressure of solution $\quad \mathrm{P}_{\mathrm{H}_{2} \mathrm{O}}=\mathrm{P}_{\mathrm{H}_{2} \mathrm{O}}^{\mathrm{O}} \mathrm{X}_{\mathrm{H}_{2} \mathrm{O}}=47.1 \times 0.996=46.9$ torr
Lowring of vapour pressure $\quad \mathrm{P}_{\mathrm{H}_{2} \mathrm{O}}^{\mathrm{o}}-\mathrm{P}_{\mathrm{H}_{2} \mathrm{O}}=47.1-46.9=0.2$ torr
Example: $\quad$ The vapour pressure of ethyl alcohol at $25^{\circ} \mathrm{C}$ is 59.2 torr. The vapour pressure of a solution of urea in ethyl alcohol is $\mathbf{5 1 . 3}$ torr. What is the molality of the solution?
Solution: Given: $\mathrm{P}_{\mathrm{A}}^{\mathrm{o}}=59.2$ torr, $\mathrm{pA}=51.3$ torr

$$
\begin{aligned}
\text { By RLVP } \Rightarrow & X_{\text {solute }}=\frac{7.9}{59.2}=.1334 \\
(\text { molality } m= & \frac{X_{B}}{X_{A}} \times \frac{1000}{M_{\text {solvent }}}=\frac{X_{B}}{\left(1-X_{B}\right)} \times \frac{1000}{M_{\text {solvent }}} \quad\left(X_{A}+X_{B}=1\right) \\
& m=\frac{0.1334}{0.8666} \times \frac{1000}{46}=3.346 \text { molal }
\end{aligned}
$$

## Practice Problems I

Q. 1 The vapour pressure of ether at $20^{\circ} \mathrm{C}$ is 442 mm . When 7.2 g of a solute is dissolved in 60 g ether, vapour pressure is lowered by 32 units. If molecular weight of ether is 74 then molecular weight of solute is -
(A) 113.77
(B) 150.35
(C) 116.23
(D) 190.26
Q. 2 The vapour pressure of pure benzene at $25^{\circ} \mathrm{C}$ is 639.7 mm of Hg and the vapour pressure of a solution of a solute in $\mathrm{C}_{6} \mathrm{H}_{6}$ at the same temperature is 631.9 mm of Hg . Molality of solution is
(A) $0.079 \mathrm{~mol} / \mathrm{kg}$ of solvent
(B) $0.256 \mathrm{~mol} / \mathrm{kg}$ of solvent
(C) $0.158 \mathrm{~mol} / \mathrm{kg}$ of solvent
(D) $0.316 \mathrm{~mol} / \mathrm{kg}$ of solvent
Q. 3 A 6\% (by weight) of non-volatile solute in isopentane at 300 K has a vapour pressure of 1426 mm Hg .20 g of isopentane is now added to the solution. The resulting solution has a vapour pressure of 1445 mm of Hg at the same temperature. Then :
(i) Molecular weight of solute is -
(A) 28.32
(B) 92.81
(C) 113.30
(D) 56.65
(ii) Vapour pressure of isopentane at 300 K is -
(A) 1541.68 mm
(B) 770.89 mm
(C) 1212.46 mm
(D) 981.32
mm
Q. 4 Find out the weight of solute (M. wt. 60) that is required to dissolve in 180 g water to reduce the vapour pressure to $4 / 5$ th of pure water
(A) 130 g
(B) 150 g
(C) 300 g
(D) 75 g
Q. 5 The molality of a solution containing a non-volatile solute if the vapour pressure is $2 \%$ below the vapour pressure of pure water, will be -
(A) 2.213
(B) 2.518
(C) 1.133
(D) 1.891
Q. 6 The weight of a non-volatile solute (m. wt. 40). Which should be dissolved in 114 g octane to reduce its vapour pressure to $80 \%$, is -
(A) 20 gm
(B) 10 gm
(C) 7.5 gm
(D) 5 gm
Q. 7 Twenty gram of a solute are added to 100 g of water at $25^{\circ} \mathrm{C}$. The vapour pressure of pure water i
23.76 mm Hg , vapour pressure of solution is 22.41 mm Hg . The mass of this solute that is required in 100 g water to reduce the vapour pressure to one-half of the pure water is -
(A) 333 g
(B) 666 g
(C) 166 g
(D) 256 g
Q. 8 Vapour pressure of pure water is 40 mm . If a non-volatile solute is added to it vapour pressure falls by 4 mm . Hence, molality of solution is -
(A) 6.173 molal
(B) 3.0864 molal
(C) 1.543 molal
(D) 0.772 molal
Q. 9 The vapour pressure of pure liquid solvent $A$ is 0.80 atm . When a non-volatile substance $B$ is added to the solvent, its vapour pressure drops to 0.60 atm ; mole fraction of the component B in the solution is
(A) 0.50
(B) 0.25
(C) 0.75
(D) 0.40
Q. 10 Vapour pressure of $\mathrm{CCl}_{4}$ at $25^{\circ} \mathrm{C}$ is 143 mm Hg . If 0.5 gm of non-volatile solute (mol. mass 65) is dissolved in $100 \mathrm{ml} \mathrm{CCl}_{4}$, then the vapour pressure of the solution at $25^{\circ} \mathrm{C}$ is -
[ Given : Density of $\mathrm{CCl}_{4}=1.58 \mathrm{~g} / \mathrm{cm}^{3}$ ]
(A) 141.93 mm
(B) 94.39 mm
(C) 199.34 mm
(D) 143.99 mm
Q. 11 Lowering of vapour pressure of 1.00 m solution of a non-volatile solute in a hypothetical solvent of molar mass 40 g at its normal boiling point, is -
(A) 29.23 torr
(B) 30.4 torr
(C) 35.00 torr
(D) 40.00 torr
Q. 12 The vapour pressure of a liquid decreases by 10 torr when a non-volatile solute is dissolved. The mole fraction of the solute in solution is 0.1 . What would be the mole fraction of the liquid if the decrease in vapour pressure is 20 torr, the same solute being dissolved -
(A) 0.2
(B) 0.9
(C) 0.8
(D) 0.6
Q. 13 The mole fraction of the solvent in the solution of a non-volatile solute is 0.980 . The relative lowering of vapour pressure is -
(A) 0.01
(B) 0.980
(C) 0.02
(D) 0.49
Q. 14 The vapour pressure of a solution of a non-volatile solute B in a solvent A is $95 \%$ of the vapour pressure of the solvent at the same temperature. If the molecular weight of the solvent is 0.3 times the molecular weight of the solute, what is the weight ratio of solvent to solute.
(A) 0.15
(B) 5.7
(C) 0.2
(D) none of these
Q. 15 The vapour pressure of water at room temperature is 23.8 mm Hg . The vapour pressure of an aqueous solution of sucrose with mole fraction 0.1 is equal to -
(A) 23.9 mm Hg
(B) 24.2 mm Hg
(C) 21.42 mm Hg
(D) 31.44 mm Hg
Q. 16 The vapour pressure of pure A is 10 torr and at the same temperature when 1 g of B is dissolved i
20 g of A, its vapour pressure is reduced to 9.0 torr. If the molecular mass of A is 200 amu , then the molecular mass of $B$ is -
(A) 100 amu
(B) 90 amu
(C) 75 amu
(D) 120 amu
Q. 17 The vapour pressure of pure benzene $\mathrm{C}_{6} \mathrm{H}_{6}$ at $50^{\circ} \mathrm{C}$ is 260 Torr. How many moles of nonvolatile solute per mole of benzene are required to prepare a solution of benzene having a vapour pressure of 167.0 Torr at $50^{\circ} \mathrm{C}$ ?
(A) 0.305 mol
(B) 0.605 mol
(C) 0.336 mol
(D) 0.663 mol
Q. 18 Lowering of vapour pressure due to a solute in 1 molal aqueous solution at $100^{\circ} \mathrm{C}$ is -
(A) 13.44 Torr
(B) 14.12 Torr
(C) 312 Torr
(D) 352 Torr
Q. 19 How many grams of sucrose must be added to 360 g of water to lower the vapour pressure by 1.19 mmHg at a temperature at which pressure of pure water is 25 mm Hg ?
(A) 342 g
(B) 360 g
(C) 375 g
(D) 380 g

## (ii) Vapour Pressure of a Solution Containing Two Volatile Liquids

Raoult's law states that the partial vapour pressure of a component of a solution of two miscible liquids A and B at a given temperature is equal to the product of the vapour pressure of the pure component at that temperature and its mole fraction in the solution.

Mathematical Expression: Let us assume that a solution has $n_{A}$ moles of liquid $A$ and $n_{B}$ moles of liquid $B$. Let $P_{A}^{\circ}$ be the vapour pressure of the pure liquid $A$ and $P_{B}^{\circ}$ is the vapour pressure of the pure liquid $B$.

Mole fraction of $A, X_{A}=\frac{n_{A}}{n_{A}+n_{B}}, \quad \quad$ Mole fraction of $B, X_{B}=\frac{n_{B}}{n_{A}+n_{B}}$ According to Raoult's law,

$$
P_{A}=P_{A}^{\circ} X_{A} \quad \text { (where } P_{A} \text { is the partial vapour pressure of liquid } A \text { in the solution) }
$$

Similarly, $P_{B}=P_{B}^{\circ} X_{B}\left(P_{B}\right.$ - partial vapour pressure of $B$ in the solution)
The total vapour pressure of an ideal solution containing components $A$ and $B$ is the sum of partial vapour pressures of all the components (Dalton's law of partial pressures)

$$
\begin{equation*}
\mathbf{P}=\mathbf{P}_{\mathbf{A}}+\mathbf{P}_{\mathbf{B}}=\mathbf{P}_{\mathbf{A}}^{\mathbf{0}} \mathbf{X}_{\mathbf{A}}+\mathbf{P}_{\mathbf{B}}^{\mathbf{0}} \mathbf{X}_{\mathbf{B}} \tag{1}
\end{equation*}
$$



$$
\begin{array}{ll}
\square \mathrm{X}_{\mathrm{A}}+\mathrm{X}_{\mathrm{B}}=1 & \Rightarrow \mathrm{X}_{\mathrm{A}}=1-\mathrm{X}_{\mathrm{B}} \\
\therefore \quad \mathrm{P}=\mathrm{P}_{\mathrm{A}}^{\mathrm{o}}\left(1-\mathrm{X}_{\mathrm{B}}\right)+\mathrm{P}_{\mathrm{B}}^{o} \mathrm{X}_{\mathrm{B}} & \Rightarrow \mathrm{P}_{\mathrm{A}}^{\mathrm{o}}-\mathrm{P}_{\mathrm{A}}^{o} \mathrm{X}_{\mathrm{B}}+\mathrm{P}_{\mathrm{B}}^{o} \mathrm{X}_{\mathrm{B}} \\
\mathbf{P}=\mathbf{P}_{\mathrm{A}}^{\mathrm{o}}+\left(\mathbf{P}_{\mathbf{B}}^{o}-\mathbf{P}_{\mathrm{A}}^{\mathrm{o}}\right) \mathbf{X}_{\mathrm{B}} & \tag{2}
\end{array}
$$

About relation shows that graph between P and XB is a straight line having slope $\mathbf{P}_{\mathbf{B}}^{\mathbf{o}}-\mathbf{P}_{\mathrm{A}}^{\mathbf{o}}$ and intercept $\mathbf{P}_{\mathbf{A}}{ }^{\circ}$
Similarly $\mathbf{P}=\mathbf{P}_{\mathbf{B}}^{\boldsymbol{o}}+\left(\mathbf{P}_{\mathbf{A}}^{\boldsymbol{0}}-\mathbf{P}_{\mathbf{B}}^{0}\right) \mathbf{X}_{\mathbf{A}}$
Above figure shows the relationship between partial vapour pressure and mole fraction of an ideal solution at constant temperature.

1. Straight line I represents the plot of vapour pressure of liquid $A\left(P_{A}\right)$ and its mole fraction $\left(X_{A}\right)$. According to Raoult's law this should be a straight line when
$X_{A}=0 \quad P_{A}=0$,
$\mathrm{X}_{\mathrm{A}}=1, \mathrm{P}_{\mathrm{A}}=\mathrm{P}_{\mathrm{A}}^{\circ}$
When mole fraction of liquid $A$ is $X_{A}=1$, the liquid $A$ is pure and its vapour pressure is equal to $P_{A}^{o}$ as shown by line (I)
2. Straight line II represents the plot of partial vapour pressure of liquid (B) $P_{B}$ and its mole fraction $\left(X_{B}\right)$. According to Raoult's law, this should be a straight line. when
$X_{B}=0 \quad P_{B}=0, \quad X_{B}=1, \quad P_{B}=P_{B}^{0}$
When mole fraction of liquid $B$ is $X_{B}=1$, the liquid $B$ is pure and its vapour pressure is equal to $P_{B}^{o}$ as shown by line (II).
3. Straight line (III) represents the total vapour pressure, P , of the solution for any composition and is given by the sum of the partial vapour pressure of liquids of A and B .
$\mathrm{P}=\mathrm{P}_{\mathrm{A}}+\mathrm{P}_{\mathrm{B}}$
Illustration 7. An aqueous solution containing 28\% by mass of a liquid A (mol. mass =140) has a vapour pressure of 160 mm at $37^{\circ} \mathrm{C}$. Find the vapour pressure of the pure liquid $A$. (The vapour pressure of water at $37^{\circ} \mathrm{C}$ is 150 mm .)
Solution : For two miscible liquids,

$$
\mathrm{P}_{\text {total }}=\mathrm{P}_{\mathrm{A}}+\mathrm{P}_{\mathrm{B}}=\mathrm{P}_{\mathrm{A}}^{\mathrm{o}} \mathrm{X}_{\mathrm{A}}+\mathrm{P}_{\mathrm{B}}^{\mathrm{o}} \mathrm{X}_{\mathrm{B}} \quad \mathrm{n}_{\mathrm{A}}=\frac{28}{140}=0.2
$$

Liquid B is water. Its mass is (100-28), i.e. 72.

$$
\mathrm{n}_{\mathrm{B}}=\frac{72}{18}=4.0
$$

Total number of moles $=0.2+4.0=4.2$
Given $\quad P_{\text {total }}=160 \mathrm{~mm}, \quad P_{B}^{0}=150 \mathrm{~mm}$
So

$$
\begin{aligned}
& 160=\frac{0.2}{4.2} \times \mathrm{P}_{\mathrm{A}}^{0}+\frac{4.0}{4.2} \times 5.0 \\
& \mathrm{p}_{\mathrm{A}}^{0}=\frac{17.15 \times 4.2}{0.2}=360.15 \mathrm{~mm}
\end{aligned}
$$

## Dalton's Law v/s Raoult's Law:

The composition of the vapour in equilibrium with the solution can be calculated applying Daltons' law of partial pressures. Let the mole fractions of vapours $A$ and $B$ be $Y_{A}$ and $Y_{B}$ respectively. Let $p_{A}$ and $p_{B}$ be the partial pressure of vaours A and $B$ respectively and total pressure $P$.


From Raoult's law $\quad \mathrm{P}=\mathrm{P}_{\mathrm{A}}^{\mathrm{o}} \mathrm{X}_{\mathrm{A}}+\mathrm{P}_{\mathrm{B}}^{\mathrm{o}} \mathrm{X}_{\mathrm{B}}$

$$
\mathrm{P}_{\mathrm{A}}=\mathrm{P}_{\mathrm{A}}^{\circ} \mathrm{X}_{\mathrm{A}} \text { and } \mathrm{P}_{\mathrm{B}}=\mathrm{P}_{\mathrm{B}}^{\circ} \mathrm{X}_{\mathrm{B}}
$$

From Dalton's law,
Partial pressure $=$ Mole fraction $\times$ Total pressure
For A $\quad P_{A}=y_{A} \times P$

$$
\begin{equation*}
\mathrm{P}_{\mathrm{A}}^{o} \mathrm{X}_{\mathrm{A}}=\mathrm{y}_{\mathrm{A}} \times \mathrm{P} \quad \Rightarrow \mathbf{y}_{\mathrm{A}}=\frac{\mathbf{P}_{\mathrm{A}}^{\mathbf{0}} \mathbf{X}_{\mathbf{A}}}{\mathbf{P}} \tag{1}
\end{equation*}
$$

Above formula is used for calculation of mole fraction of A in vapour phase
For B, $\quad P_{B}=y_{B} \times P$

$$
\begin{equation*}
\mathrm{P}_{\mathrm{B}}{ }^{\circ} \mathrm{X}_{\mathrm{B}}=\mathrm{y}_{\mathrm{B}} \times \mathrm{P} \quad \Rightarrow \mathbf{y}_{\mathbf{B}}=\frac{\mathbf{P}_{\mathbf{B}}^{\mathbf{0}} \mathbf{X}_{\mathbf{B}}}{\mathbf{P}} \tag{2}
\end{equation*}
$$

Above formula is used for calculation of mole fraction of $B$ in vapour phase
From (1), $X_{A}=\frac{P \times y_{A}}{P_{A}^{0}} \quad$ From (2) $X_{B}=\frac{P \times y_{B}}{P_{B}^{0}}$
on adding $\quad X_{A}+X_{B}=\frac{P \times y_{A}}{P_{A}^{o}}+\frac{P \times y_{B}}{P_{B}^{o}}=1$
$\Rightarrow \frac{\mathbf{1}}{\mathbf{P}}=\frac{\mathbf{y}_{\mathbf{A}}}{\mathbf{P}_{\mathbf{A}}^{\mathbf{0}}}+\frac{\mathbf{y}_{\mathbf{B}}}{\mathbf{P}_{\mathbf{B}}^{\mathbf{0}}}$

Above formula is used to calculate total vapour pressure when mole fractions are given in vapoure phase

## Avoid confusion

$\mathrm{P}=\mathrm{P}_{\mathrm{A}}^{\mathrm{o}} \mathrm{X}_{\mathrm{A}}+\mathrm{P}_{\mathrm{B}}^{\mathrm{o}} \mathrm{X}_{\mathrm{B}} \Rightarrow$ This formula is used to calculate total pressure when mole fraction are given in liquid phase
$\frac{1}{P}=\frac{y_{A}}{P_{A}^{o}}+\frac{y_{B}}{P_{B}^{o}} \Rightarrow$ This formula is used to calculate total pressure when mole fraction are given in vapour phase

Note: Thus, in case of ideal solution the vapour phase is phase is richer with more volatile component i.e., the one having relatively greater vapour pressure.

Example: The vapour pressures of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fracion of methanol in the vapour.

Solution: No. of moles of $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}=\frac{60}{46}=1.304$, No. of moles of $\mathrm{CH}_{3} \mathrm{OH}=\frac{40}{32}=1.25$
' $\mathrm{X}_{\mathrm{A}}$ ' of ethyl alcohol $=\frac{1.304}{1.304+1.25}=0.5107$
' $\mathrm{X}_{\mathrm{B}}$ ' of methyl alcohol $=\frac{1.25}{1.304+1.25}=0.4893$
Partial pressure of ethyl alcohol $=\mathrm{X}_{\mathrm{A}} \cdot \mathrm{P}_{\mathrm{A}}^{0}=0.5107 \times 44.5=22.73 \mathrm{~mm} \mathrm{Hg}$
Partial pressure of methyl alcohol $=X_{B} \cdot P_{B}{ }^{0}=0.4893 \times 88.7=\quad 43.40 \mathrm{~mm} \mathrm{Hg}$
Total vapour pressure of solution $=22.73+43.40=66.13 \mathrm{~mm} \mathrm{Hg}$
Mole fraction of methyl alcohol in the vapour $=\frac{\text { Partial pressure of } \mathrm{CH}_{3} \mathrm{OH}}{\text { Total vapour pressure }}$

$$
=\frac{43.40}{66.13}=0.6563
$$

## Practice Problems II

Q. 1 An aqueous solution containing liquid A (M. wt. $=128) 64 \%$ by weight has a V. P. of 145 mm . If the vapour pressure of water is 155 mm then vapour pressure of A at the same temperature will be -
(A) 205 mm
(B) 105 mm
(C) 185 mm
(D) 52.5 mm
Q. 2 The vapour pressure of pure ethylene bromide and propylene bromide are 170 and 127 mm of Hg at a temperature. Find out:
(i)The vapour pressure of ethylene bromide \& propyline bromide in a $60 \%$ by weight solution of ethylene bromide in propylene bromide at same temperature, is -
(A) $52.4 \mathrm{~mm}, 24.31 \mathrm{~mm}$
(C) $52.4 \mathrm{~mm}, 48.63 \mathrm{~mm}$
(C) $104.9 \mathrm{~mm}, 48.63 \mathrm{~mm}$
(D) $104.9 \mathrm{~mm}, 24.31 \mathrm{~mm}$
(ii) Total vapour pressure of solution, is -
(A) 153.53 mm
(B) 76.71 mm
(C) 101.03 mm
(D) 129.21 mm
Q. 3 Two liquids A and B form ideal solution at 300 K . The vapour pressure of a solution containing one mole of A and four mole of B is 560 mm of Hg . At the same temperature if one mole of B is taken out from the solution, the vapour pressure of solution decreases by 10 mm of Hg . Vapour pressures of A and B in pure state will be-
(A) 330,550
(B) 200,300
(C) 400, 600
(D) 800,1200
Q. 4 The vapour pressure of two volatile liquid mixture is $P_{T}=\left(5.3-2 X_{B}\right)$ in cm of Hg ; where $X_{B}$ is mole fraction of B in mixture. What are vapour pressure of pure liquids A and B ?
(A) 3.3 and 2.1 cm of Hg
(B) 2.3 and 3.3 cm of Hg
(C) 5.3 and 2.3 cm of Hg
(D) 5.3 and 3.3 cm of Hg
Q. 5 A mixture contains 1 mole volatile liquid $\mathrm{A}\left(\mathrm{P}_{\mathrm{A}}^{\mathrm{o}}=100 \mathrm{mg} \mathrm{Hg}\right)$ and 3 moles volatile liquid $\mathrm{B}\left(\mathrm{P}_{\mathrm{B}}^{\mathrm{o}}=\right.$ 80 mm ). If solution be haves ideally, total vapour pressure of the solution is approximately -
(A) 80 mmHg
(B) 85 mmHg
(C) 90 mmHg
(D) 92 mmHg
Q. 6 At $40^{\circ} \mathrm{C}$ the vapour pressure in torr of methanol and ethanol solution is $\mathrm{P}=119 \mathrm{x}+135$ where $x$ is the mole fraction of methanol, hence,
(A) vapour pressure of pure methanol is 119 torr
(B) vapour pressure of pure ethanol is 135 torr
(C) vapour pressure of equimolar mixture of each is 127 torr
(D) mixture is completely immiscible
Q. 7 Vapour pressure of pure A is 70 mm of Hg at $25^{\circ} \mathrm{C}$ it forms an ideal solution with B in which mole fraction of $A$ is 0.8 . If vapour pressure of solution is 84 mm of Hg at $25^{\circ} \mathrm{C}$, the vapour pressure of pure B at $25^{\circ} \mathrm{C}$ is -
(A) 1 atm
(B) 14 mm of Hg
(C) 140 mm of Hg
(D) 56 cm of Hg
Q. 8 Vapour pressure (in torr) of an ideal solution of two liquids $A$ and $B$ is given by: $P=52 \mathrm{X}_{\mathrm{A}}+114$ where $X_{A}$ is the mole fraction of $A$ in the mixture. The vapour pressure (in torr) of equimolar mixture of the two liquids will be -
(A) 166
(B) 83
(C) 140
(D) 280
Q. 9 Solution of two volatile liquids A and B obey Raoult's law. At a certain temperature, it is found that when the total vapour pressure above solution is 400 mm of Hg , the mole fraction of A in vapour phase is 0.45 and in liquid phase 0.65 then the vapour pressures of two pure liquids at the same temperature will be -
(A) $138.4 \mathrm{~mm}, 628.57 \mathrm{~mm}$
(B) $276.9 \mathrm{~mm}, 628.57 \mathrm{~mm}$
(C) $276.9 \mathrm{~mm}, 314.28 \mathrm{~mm}$
(D) $138.4 \mathrm{~mm}, 314.28 \mathrm{~mm}$
Q. 10 The vapour pressure of benzene and toluene at $20^{\circ} \mathrm{C}$ are 75 mm of Hg and 22 mm of Hg respectively. 23.4 g of benzene and 64.4 g of toluene are mixed. If two forms ideal solution, the mole fraction of benzene in vapour phase when vapours are in equilibrium with liquid mixture, is -
(A) $0.59,0.41$
(B) $0.25,0.75$
(C) $0.5,0.5$
(D) $0.35,0.65$
Q. 11 The vapour pressure of two liquids are 15000 and 30000 in a unit. When equimolar solution of liquids is made. Then the mole fraction of A and B in vapour phase will be -
(A) $\frac{2}{3}, \frac{1}{3}$
(B) $\frac{1}{3}, \frac{2}{3}$
(C) $\frac{1}{2}, \frac{1}{2}$
(D) $\frac{1}{4}, \frac{3}{4}$
Q. 12 At $30^{\circ} \mathrm{C}$, the vapour pressure of pure ether is 646 mm and of pure acetone is 283 mm . Find out the mole fraction of each component in vapour state for the solution of two having mole fraction of ether 0.50 . Assume ideal behaviour.
(A) $0.20,0.80$
(B) $0.799,0.201$
(C) $0.695,0.305$
(D) $0.535,0.465$
Q. 13 Benzene and toluene form an ideal solution. The vapour pressure of benzene and toluene are respectively 75 mm and 22 mm at $20^{\circ} \mathrm{C}$. If the mole fraction of benzene and toluene in vapour phase are 0.63 and 0.37 respectively, then :
(i) The vapour pressure of mixture is -
(A) 39.68 mm
(B) 79.32 mm
(C) 58.56 mm
(D) 29.24 mm
(ii) Mole fraction of benzene \& toluene in liquid phase is -
(A) $0.2,0.8$
(B) $0.63,0.37$
(C) $0.54,0.46$
(D) $0.33,0.67$
Q. 14 At $90^{\circ} \mathrm{C}$, the vapour pressure of toluene is 400 mm and that of xylene is 150 mm . The composition of liquid mixture that will boil at $90^{\circ} \mathrm{C}$ when the pressure of mixture is 0.5 atm , is -
(A) $0.8,0.2$
(B) $0.75,0.25$
(C) $0.92,0.08$
(D) $0.66,0.34$
Q. 15 V. P. of pure $A \quad \mathrm{p}_{\mathrm{A}}^{\mathrm{o}}=100 \mathrm{mmHg}$
V. P. of pure $B \quad p_{B}^{o}=150 \mathrm{mmHg}$

Distillate of vapours of a solution containing 2 moles $A$ and 3 moles $B$ will have total vapour pressure, approximately, on condensation
(A) 135 mm
(B) 130 mm
(C) 140 mm
(D) 145 mm
Q. 161 mole benzene $\left(\mathrm{P}^{0}=42 \mathrm{~mm}\right)$ and 2 moles toluene $\left(\mathrm{P}^{\mathrm{o}}=36 \mathrm{~mm}\right)$ will have
(A) total vapour pressure 38 mm
(B) mole fraction of vapours of benzene above liquid mixture is $7 / 19$
(C) ideal behaviour
(D) all of the above
Q. 17 At a given temperature, the vapour pressure of pure $A$ and $B$ is 108 and 36 torr respectively. What will be the mole fraction of $B$ in the vapour phase which is in equilibrium with a solution containing equimole fraction of A and B , under ideal behaviour conditions?
(A) 0.25
(B) 0.33
(C) 0.50
(D) 0.60
Q. 18 A solution of benzene ( $\mathrm{p}^{\mathrm{o}}=120$ torr) and toluene ( $\mathrm{p}^{\mathrm{o}}=80$ torr) has 2.0 mol of each component. At equilibrium the mol fraction of toluene in vapour phase is -
(A) 0.50
(B) 0.25
(C) 0.60
(D) 0.40
Q. 19 Liquids A and B form an ideal solution and the former has stronger intermolecular forces. If $\mathrm{X}_{\mathrm{A}}$ and $\mathrm{X}_{\mathrm{A}}^{\prime}$ are the mole fractions of A in the solution and vapour in equilibrium, then -
(A) $\frac{X_{A}^{\prime}}{X_{A}}=1$
(B) $\frac{\mathrm{X}_{\mathrm{A}}^{\prime}}{\mathrm{X}_{\mathrm{A}}}>1$
(C) $\frac{\mathrm{X}_{\mathrm{A}}^{\prime}}{\mathrm{X}_{\mathrm{A}}}<1$
(D) $\mathrm{X}_{\mathrm{A}}^{\prime}+\mathrm{X}_{\mathrm{A}}=1$
Q. 20 Mole fraction of a liquid $A$ in an ideal mixture with another liquid $b$ is $X_{A}$. If $X_{A}^{\prime}$ is the mole fraction of component A in the vapour in equilibrium, the total pressure of the liquid mixture is $\left(\mathrm{P}_{\mathrm{A}}^{\mathrm{o}}=\right.$ vapour pressure of pure $\mathrm{A} ; \mathrm{P}_{\mathrm{B}}^{\mathrm{o}}=$ vapour pressure of pure B$)$
(A) $\mathrm{P}^{\mathrm{o}} \mathrm{A} \frac{\mathrm{X}_{\mathrm{A}}^{\prime}}{\mathrm{X}_{\mathrm{A}}}$
(B) $\frac{\mathrm{P}_{\mathrm{A}}^{o} \mathrm{X}_{\mathrm{A}}}{\mathrm{X}_{\mathrm{A}}^{\prime}}$
(C) $\frac{\mathrm{P}_{\mathrm{B}}{ }_{\mathrm{B}} \mathrm{X}_{\mathrm{A}}^{\prime}}{\mathrm{X}_{\mathrm{A}}}$
(D) $\frac{\mathrm{P}_{\mathrm{B}}^{o} \mathrm{X}_{\mathrm{A}}}{\mathrm{X}_{\mathrm{A}}^{\prime}}$
Q. 21 Two liquids A and B have $\mathrm{P}_{\mathrm{A}}^{\mathbf{o}}: \mathrm{P}_{\mathrm{B}}^{\mathrm{o}}=1: 3$ at a certain temperature. If the mole fraction ratio of $x_{A}: x_{B}=1: 3$, the mole fraction of $A$ in vapour in equilibrium with the solution at a given temperature is-
(A) 0.1
(B) 0.2
(C) 0.5
(D) 1.0
Q.22 At a certain temperature pure liquid $A$ and liquid $B$ have vapour pressures 10 torr and 37 torr respectively. For a certain ideal solution of $A$ and $B$, the vapour in equilibrium with the liquid has the components $A$ and B in the partial pressure ratio $\mathrm{P}_{\mathrm{A}}: \mathrm{P}_{\mathrm{B}}=1: 7$. What is the mole fraction of A in the solution?
(A) 0.346
(B) 0.654
(C) 0.5
(D) none of these
Q. 23 Mole fraction of the toluene in the vapour phase which is in equilibrium with a solution of benzene ( $\mathrm{p}^{\mathrm{o}}=120$ ) and toluene ( $\mathrm{p}^{\mathrm{o}}=80$ ) having 2.0 moles of each, is -
Q. 24 The vapour pressure of pure liquid A at 300 K is 575 torr and that of pure liquid B is 390 torr. These two compounds form ideal liquid and gaseous mixtures. The mole fraction of A in the vapour phase is 0.35 . Then :
(i) The total pressure of the mixture is
(A) 526 torr
(B) 965 torr
(C) 440 torr
(D) 715 torr
(ii) composition of the liquid mixture is -
(A) $\mathrm{A}=27 \%, \mathrm{~B}=73 \%$
(B) $\mathrm{A}=57 \%, \mathrm{~B}=43 \%$
(C) $\mathrm{A}=33 \%$. $\mathrm{B}=67 \%$
(D) $\mathrm{A}=30 \%, \mathrm{~B}=70 \%$
Q. 2564 gm of methanol \& 46 gm of ethanol forms in an ideal solution at 350 K . If the vapour pressure of methanol and ethanol at 350 K are $8.1 \times 10^{4}$ and $4.5 \times 10^{4} \mathrm{~N} \mathrm{~m}^{-2}$ respectively, then mole fraction of methanol in vapour phase is -
(A) 0.62
(B) 0.22
(C) 0.80
(D) 0.78
Q. 26 Two liquids A and B forms an ideal solution at temperature T. When the total vapour pressure above the solution is 400 torr, the mole fraction of A in the vapour phase is 0.40 and in the liquid phase 0.75 . The vapour pressure of pure A and B respectively are -
(A) 165.54 torr , 772.00 torr
(B) 240.24 torr , 840.00 torr
(C) 213.33 torr, 960.00 torr
(D) 312.15 torr , 865.00 torr
Q. 27 Vapour pressure of a mixture of benzene and toluene is given by $\mathrm{P}=179 \mathrm{x}_{\mathrm{B}}+92$ where $\mathrm{x}_{\mathrm{B}}$ is mole fraction of benzene. Determine :
(i) vapour pressure of the solution obtained by mixing 936 gm of benzene and 736 gm of toluene
(A) 199.4 mm
(B) 271 mm
(C) 280 mm
(D) 289 mm
(ii) If vapours are removed and condensed into liquid then what will be the ratio of mole fraction of
(A) 2.8
(B) 1.5
(C) 3.5
(D) 4.5
(iii) This condensed liquid again brought to the same temperature then what will be the mole fraction
(A) 0.07
(B) 0.93
(C) 0.65
(D) 0.45
Q. 28 Benzene and toluene from nearly ideal solutions. If at $27^{\circ} \mathrm{C}$ the vapour pressures of pure toluene and pure benzene are 32.06 mm and 103.01 mm respectively, the vapour pressure of a solution containing 0.60 mole fraction of toluene, is -
(A) 60.44 mm
(B) 30.22 mm
(C) 120.12 mm
(D) 76.52 mm
Q. 29 An aqueous solution containing $28 \%$ by mass of a liquid A (mol. mass $=140$ ) has a vapour pressure of 160 mm at $37^{\circ} \mathrm{C}$. The vapour pressure of water at $37^{\circ} \mathrm{C}$ is 150 mm , then the pressure of pure liquid A , is -
(A) 180.22 mm
(B) 300.32 mm
(C) 360.15 mm
(D) 276.55 mm
Q. 30 The vapour pressure of ethyl alcohol and methyl alcohol are 45 mm and 90 mm . An ideal solution is formed at the same temperature by mixing 60 g of $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$ with 40 g of $\mathrm{CH}_{3} \mathrm{OH}$. Total vapour pressure of the solution is approximately -
(A) 70 mm
(B) 35 mm
(C) 105 mm
(D) 140 mm

## Type of Solution

## (i) Ideal Solution

An ideal solution may be defined as the one which obeys Raoult's law over all concentration ranges at a given temperature. The total vapour pressure of an ideal solution containing liquids A and B is given by the following equation.

$$
\mathrm{P}=\mathrm{P}_{\mathrm{A}}+\mathrm{P}_{\mathrm{B}}=\mathrm{P}_{\mathrm{A}}^{0} \mathrm{X}_{\mathrm{A}}+\mathrm{P}_{\mathrm{B}}^{0} \mathrm{X}_{\mathrm{B}}
$$

In an ideal solution of two components A and B , all attractive forces between A and B molecules or between $A$ and $A$ molecules or between $B$ and $B$ molecules ( $A-B, A-A$ and $B-B$ ) must be identical so that the escaping tendency of an $A$ or $B$ molecule is independent of whether it is surrounded by A molecules, B, molecules or varying proportions of A and B molecules. The escaping tendency of pure liquid $A$ in solution remains the same. Similarly the escaping tendency of B remains the same. Liquids form ideal solution only when they have nearly same molecular size and related constitution so that they have similar molecular environment in the pure state as well as in solution. A perfect ideal solution is rare but many liquids form nearly ideal solution. Liquid heptane and hexane form an ideal solution because the interaction between a hexane molecule and another hexane molecule is the same as the interaction between two heptane molecules other examples of ideal solutions are:
benzene + toluene, chlorobenzene + bromobenzene; ethyl bromde + ethyl iodide; $\quad n$-butyl chloride +n -butyl bromide ethyl alcohol + methyl alcohol

Conditions for Forming Ideal Solution: Two liquids on mixing form an ideal solution only when 1. both have similar structures and polarity so that they have similar molecular environment.
2. both have similar molecular sizes.
3. both have identical intermolecular forces.

## Characteristics Of Ideal Solution:

Mixing of two substances results in an ideal solution only when:

1. They obey Raoult's Law
2. $\Delta \mathrm{H}_{\text {mixing }}=0 \Rightarrow$ that is no heat is absorbed or released during dissolution
3. $\Delta \mathrm{V}_{\text {mixing }}=0 \Rightarrow$ that is the total volume of the solution is equal to the sum of the volume of the pure liquids mixed to form the solution.

## Graphical Representation of Vapour Pressure of Ideal Solutions:

Figure shows the relationship between partial vapour pressure and mole fraction of an ideal solution at constant temperature.


Note : Components of ideal solution can be saperated in pure form by fractional distillation

## (ii) Non-Ideal Solutions

Solutions which do not obey Raoult's law over all concentration ranges at constant temperature are called non-ideal solutions.

## Characteristic of nonideal solution

(i) $\quad \mathrm{P}_{\mathrm{A}} \neq \mathrm{P}_{\mathrm{A}}^{0} \mathrm{X}_{\mathrm{A}}+\mathrm{P}_{\mathrm{B}} \neq \mathrm{P}_{\mathrm{B}}^{0} \mathrm{X}_{\mathrm{B}}, \mathrm{P} \neq \mathrm{P}_{\mathrm{A}}^{\mathrm{o}} \mathrm{X}_{\mathrm{A}}+\mathrm{P}_{\mathrm{B}}^{\mathrm{o}} \mathrm{X}_{\mathrm{B}}$
(ii) $\Delta \mathrm{V}_{\text {mix }} \neq 0$,
(iii) $\Delta \mathrm{H}_{\text {mix }} \neq 0$

## Types of Non-Ideal Solutions

1. Non ideal solutions showing +ve deviation
2. Non ideal solutions showing -ve deviation.

## 1. Non ideal solutions showing +ve deviation

## Condition for forming non-ideal solution showing +ve deviation from Raoult's law.

Tow liquids A and B on mixing form this type of solution when

1. A-B attractive force should be weaker than $A-A$ and $B-B$ attractive forces.
2. ' $A$ ' and ' $B$ ' have different shape, size and charater.
3. ' A ' and ' B ' escape easily showing higher vapour pressure than the expected value.

## Characteristic of non-ideal solution showing +ve deviation

1. Do not obey Raoult's law
2. $\Delta \mathrm{H}_{\text {mix }}>0$. (endothermic dissolution heat is absorbed.)
3. $\Delta \mathrm{V} \mathrm{mix}>0$. (Volume is increased after dissolution)
4. $\quad \mathrm{p}_{\mathrm{A}}>\mathrm{p}_{\mathrm{A}}^{0} \mathrm{X}_{\mathrm{A}} ; \mathrm{p}_{\mathrm{B}}>\mathrm{p}_{\mathrm{B}}^{\mathrm{o}} \mathrm{X}_{\mathrm{B}}, \quad \therefore \mathrm{p}_{\mathrm{A}}+\mathrm{p}_{\mathrm{B}}>\mathrm{p}_{\mathrm{A}}^{\mathrm{o}} \mathrm{X}_{\mathrm{A}}+\mathrm{p}_{\mathrm{B}}^{\mathrm{o}} \mathrm{X}_{\mathrm{B}}$

## Example :

$\begin{array}{llc}\text { acetone }+ \text { ethanol } & \text { acetone }+\mathrm{CS}_{2} ; & \text { water }+ \text { methanol; } \\ \text { water + ethanol; } & \mathrm{CCl}_{4}+\text { toluene; } & \mathrm{CCl}_{4}+\mathrm{CHCl}_{3} ; \\ \text { acetone }+ \text { benzene; } & \mathrm{CCl}_{4}+\mathrm{CH}_{3} \mathrm{OH} ; & \text { cyclohexane }+ \text { ethanol }\end{array}$

## Graphical representation of vapour of non-ideal solution showing +ve deviation



## 2. Non ideal solutions showing -ve deviation.

Condition for forming non-ideal solution showing +ve deviation from Raoult's law.
Two liquids A and B on mixing form this type of solution when

1. A-B attractive force should be greater than $\mathrm{A}-\mathrm{A}$ and $\mathrm{B}-\mathrm{B}$ attractive forces.
2. ' A ' and ' B ' have different shape, size and character
3.Escaping tendency of both components ' A ' and ' B ' is lowered showing lower vapour pressure than expected ideally.

## Characteristic of non-ideal solution showing +ve deviation

1. Do not obey Raoult's law.
2. $\Delta \mathrm{H}_{\text {mix }}<0$. (Exothermic dissolution; heat is evolved.)
3. $\Delta \mathrm{Vmix}<0$. (Volume is decreased during dissoluton)
4. $\quad \mathrm{p}_{\mathrm{A}}<\mathrm{P}_{\mathrm{A}}{ }^{0} \mathrm{X}_{\mathrm{A}} ; \mathrm{p}_{\mathrm{B}}<\mathrm{p}_{\mathrm{B}}{ }^{0} \mathrm{X}_{\mathrm{B}}, \quad \therefore \mathrm{p}_{\mathrm{A}}+\mathrm{p}_{\mathrm{B}}<\mathrm{p}_{\mathrm{A}}^{0} \mathrm{X}_{\mathrm{A}}+\mathrm{p}_{\mathrm{B}}^{0} \mathrm{X}_{\mathrm{B}}$

## Example

$$
\begin{array}{ll}
\text { acetone }+ \text { aniline; } & \mathrm{CH}_{3} \mathrm{OH}+\mathrm{CH}_{3} \mathrm{COOH} ; \\
\text { chlorofrom }+ \text { diethyl ether, } \\
\text { chloroform }+ \text { benzene } & \text { acetic acid }+ \text { pyridine; }
\end{array}
$$

water +HCl


Graphical representation of vapour of non-ideal solution showing +ve deviation

(iii) Azeotropes

The non-ideal solution showing large deviations from Raoult's law can not be purified by distillation. A solution at certain composition which continues to boil at constant temperature without change in the composition of the solution and its vapour is called an AZEOTROPE or constant boiling mixture. Azeotropes are of two types:

1. Azeotropes with Max. vapour pressure and Min. BP : When liquid in a solution do not have great chemical affinity for each other (+ve deviation from ideality) their higher escape tendencies increase the vapour pressure much more than expected on the basis of Raoult's law. In many cases, the deviations are so extreme as to lead to a maximum in the curve. The point of maximum vapour pressure means that the bp at this composition will be minimum and constant.

## Example of Minimum Boiling Azeotrope

## Components

| A | B | Mass\% of B | A | B | Azeoterope |
| :--- | :---: | :---: | :--- | :--- | :--- |
| $\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$ | 95.57 | 373 | 351.3 | 351.10 |
| $\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{OH}$ | 71.69 | 373 | 370.0 | 350.72 |
| $\mathrm{CHCl}_{3}$ | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$ | 67.00 | 334 | 351.3 | 332.30 |

2. Azeotropes with Min. vapour pressure and Max. bp : When liquids in solution form chemical bonds (-ve deviation from ideality), their escape tendencies and hence the vapour pressure decreases than expected on the basis of Raoult's law. In many cases, the maximum in the temperature composition curve is obtained. The point of minimum vapour pressure in the curve means that the bp of this composition will be max. and constant.

## Examples of Max. Boiling Azeotrope

## Components

| A | B | Mass\% of B | A | B | Azeoterope |
| :--- | :--- | :---: | :---: | ---: | :--- |
| $\mathrm{H}_{2} \mathrm{O}$ | HCl | 20.3 | 373 | 188 | 383 |
| $\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{HNO}_{3}$ | 58.0 | 373 | 359 | 393.5 |
| $\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{HClO}_{4}$ | 71.6 | 373 | 383 | 476 |

Completely Immiscible Liquids : When they are distilled, they distil in the ratio of their vapor pressure at that temperature. e.g. When $A$ and $B$ are distilled wt ratio $\frac{w_{B}}{w_{A}}$ is given as $\frac{w_{B}}{w_{A}}=\frac{P_{B}^{\circ} \cdot M_{B}}{P_{A}^{\circ} \cdot M_{A}}$

Completely Miscibile Liquids. They can be handled by Raoult's Law i.e.

$$
\mathbf{y}_{\mathbf{i}} \mathbf{P}=\mathbf{x}_{\mathbf{i}} \mathbf{P}_{\mathbf{i}}^{\mathbf{0}}
$$

where $\mathrm{P}=$ Total pressure of vapors in equilibrium with the liquid solution,
$\mathrm{P}_{\mathrm{i}}{ }^{0}=$ vapor pressure of component $i$ in pure state
$y_{i}=$ mole fraction of ith component in vapor state, $\mathrm{x}_{\mathrm{i}}=$ mole fraction of $\mathrm{i}^{\text {th }}$ component in liquid state
This most fundamental expression may be arranged in many useful forms. e.g. for binary solutions :
or

$$
\begin{aligned}
& \mathbf{P}=\mathbf{x}_{1}\left(\mathbf{P}_{1}{ }^{0}-\mathbf{P}_{2}{ }^{0}\right)+\mathbf{P}_{\mathbf{2}}{ }^{0} \\
& \mathbf{1} / \mathbf{P}=\mathbf{1} / \mathbf{P}_{\mathbf{2}}{ }^{0}+\mathbf{y}_{\mathbf{1}}\left(\mathbf{1} / \mathbf{P}_{\mathbf{1}}{ }^{0}-\mathbf{1} / \mathbf{P}_{\mathbf{2}}{ }^{\mathbf{0}}\right)
\end{aligned}
$$

Note : Vapor pressure of an ideal solution is always between $\mathrm{P}_{1}{ }^{0}$ and $\mathrm{P}_{2}{ }^{0}$ (Curve1 in Fig. 1 and 2)
Bubble Point. When the first bubble of vapor appears in liquid solution.
Dew Point. When the first drop of liquid condenses from a mixture of vapors. OR when the last drop of liquid remains and rest of the liquid is completely vaporised.

## Colligative Properties

The property of a solution which depends upon the fraction of solute particles and solvent particles and not upon the chemical nature of solute is called a colligative property. Greater the no. of particles of solute in solution, greater is the extent to which colligative property is affected.

## Type of colligative properties

(i) Lowering of vapour pressure
(ii) Elevation of Boiling point
(iii) Depression of Freezing point
(iv) Osmotic Pressure

Factors that Affect the Colligative Property: The no. of solute particles in solution. To be more accurate, the colligative property depends upon the fraction of solute and solvent particles in solution.
(1) Nature of the solvent
(2) Independent of the nature of the solute
(3) Extent of association and dissociation of solute particles in solution.
(i) Lowering of Vapour Pressure: Vapour pressure lowering of a solution has already been explained under Raoult' Law. It was derived that the relative lowering of vapour pressure is given by the equation
$\frac{\mathrm{P}_{\mathrm{A}}^{\mathrm{o}}-\mathrm{P}_{\mathrm{A}}}{\mathrm{P}_{\mathrm{A}}^{\mathrm{o}}}=\mathrm{X}_{\mathrm{B}}=\frac{\mathrm{n}_{\mathrm{B}}}{\mathrm{n}_{\mathrm{A}}+\mathrm{n}_{\mathrm{B}}}$
(ii) Elevation of Boiling Point: The boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. When the atmospheric pressure is 1 atm , boiling point is called the normal boiling point.


Plot of variation of vapour pressure elevation of boiling point
The vapour pressure of a liquid decreases when a non-volatile solute is dissolved in it. The decreased vapour-pressure means that the solution would have to be heated to a higher temperature so that its vapour pressure becomes equal to the atmospheric pressure. In other words, the boiling point of the solution $T_{b}$ is higher than the boiling point of the pure solvent $T_{b}{ }^{0}$. The difference $T_{b}^{s}-T_{b}{ }^{0}$ is called the boiling point elevation and denoted by $\Delta T_{b}$.
$\Delta T_{b}=T_{b}-T_{b}{ }^{0}$
It is found that the elevation of boiling point is directly proportional to the number of moles of the solute in a given amount of the solvent ( m ).

$$
\begin{equation*}
\Delta \mathrm{T} \propto \mathrm{~m} \quad \Rightarrow \quad \Delta \mathbf{T}_{\mathrm{b}}=\mathbf{K}_{\mathrm{b}} \cdot \mathbf{m} \tag{2}
\end{equation*}
$$

where m is the molality of the solution and $\mathrm{K}_{\mathrm{b}}$ is a constant for a given solvent known as boiling-point elevation constant or molal boiling point elevation constant or ebullioscopic constant of solution.
Molal Elevation Constant or Ebullioscopic Constant: When molality of the solution is 1m, ( 1 mole of the solute is dissolved in 1 kg of the solvent) the above equation reduces to
$\Delta \mathrm{T}_{\mathrm{b}}=\mathrm{K}_{\mathrm{b}} \times 1 \mathrm{~m}=\mathrm{K}_{\mathrm{b}}$
This indicates that molal elevation constant of a liquid $\left(\mathrm{K}_{\mathrm{b}}\right)$ is equal to elevation of boiling point when molality of the solution is 1 m . the unit of $\mathrm{K}_{\mathrm{b}}$ is $\mathrm{Km}^{-1} . \mathrm{K}(\mathrm{mol} / \mathrm{kg})^{-1}=\mathrm{K} \mathrm{kg} \mathrm{mol}^{-1}$.

## Determination of $K_{b}$ of solvent :

$K_{b}=\frac{R_{b}^{2}}{1000 L_{v}}$
where $R$ is molar gas constant, $T_{b}$ is the boiling point of the solvent on Kelvin scale and $L_{v}$ the latent heat of vaporization of solvent in calories per gram.
For water $\quad \mathrm{K}_{\mathrm{b}}=\frac{2 \times(373)^{2}}{1000 \times 540}=0.515 \mathrm{~K}-\mathrm{kg} / \mathrm{mol}$
Example:. Estimate the boiling point of a solution of 25.0 g of urea $\mathrm{NH}_{2} \mathrm{CONH}_{2}$ plus 25.0 g of thiourea $\mathrm{NH}_{2} \mathrm{CSNH}_{2}$ in 500 g of chloroform, $\mathrm{CHCl}_{3}$. The boiling point of pure chloroform is $61.2^{\circ} \mathrm{C}, \mathrm{K}_{b}$ of chloroform $=3.63 \mathrm{Km}^{-1}$.
Solution: $\quad$ Moles of urea $=\frac{\text { Mass of urea }}{\text { Molecular mass of urea }}=\frac{25.0 \mathrm{~g}}{60 \mathrm{~g} / \mathrm{mol}}=0.42 \mathrm{~mol}$
Moles of thiourea $=\frac{25.0}{76 \mathrm{~g} / \mathrm{mol}}=0.33 \mathrm{~mol} \quad \therefore$ Total moles of solute $=0.42+0.33=075$
Molality, $\mathrm{m}=\frac{\text { Moles of solute }}{\text { Mass of solvent in } \mathrm{kg}}=\frac{0.75 \mathrm{~mol}}{(500 \mathrm{~g} / 1000 \mathrm{~g}) \mathrm{kg}}=1.50 \mathrm{~m}$
$\Delta \mathrm{T}_{\mathrm{b}}=\mathrm{T}_{\mathrm{b}}-\mathrm{T}_{\mathrm{b}}^{0}=\mathrm{K}_{\mathrm{b}} \cdot \mathrm{m}=3.63 \times 1.50=5.44 \mathrm{~K}=5.445^{\circ} \mathrm{C}$
$\mathrm{T}_{\mathrm{b}}=5.445^{\circ} \mathrm{C}+\mathrm{T}_{\mathrm{b}}{ }^{\circ} \quad=5.445^{\circ} \mathrm{C}+61.2^{\circ} \mathrm{C}=66.645^{\circ} \mathrm{C}$
(iii) Depression in Freezing Point: The freezing point of a liquid is the temperature at which it begins to freeze and the crystallized solid and liquid are in equilibrium. At freezing point, the vapour pressure of the solid is equal to the vapour pressure of the liquid. When a dilute solution is cooled to freezing point, it is assumed that crystals of pure solvent always separate out first.


Plot of variation of vapour pressure of a solution with temperature and depression in freezing point.

The vapour pressure of a liquid decreases when a non-volatile solute is dissolved in it. Therefore, a solid-liquid equilibrium exists only at a temperature lower than the freezing point of the pure solvent. In other words, for a solid to have the same vapour pressure as that of the solution, the freezing point should lower down. If $T_{f}^{0}$ is the freezing point of the pure solvent and $T_{f}$ that of the solution, the difference $T_{f}^{0}-T_{f}$ is called the freezing point depression and denoted by $\Delta T_{s}$

$$
\begin{equation*}
\Delta T_{s}=T_{f}^{0}-T_{f} \tag{1}
\end{equation*}
$$

It is found that the depression in freezing point is directly proportional to the number of moles of the solute in a solute given amount of the solvent.

$$
\begin{equation*}
\Delta \mathbf{T}_{\mathrm{f}}=\mathbf{K}_{\mathrm{f}} \cdot \mathbf{m} \tag{2}
\end{equation*}
$$

where m is the molality of the solution and $\mathrm{K}_{\mathrm{f}}$ is a constant for a given solvent known as molal depression constant or cryoscopic constant.

Molal Depression Constant or Cryoscopic Constant: When molality of the solution is 1 m , ( 1 mole of the solute is dissolved in 1 kg of the solvent) the above equation reduces to $\Delta \mathrm{T}_{\mathrm{f}}=\mathrm{K}_{\mathrm{f}} \times 1 \mathrm{~m}=\mathrm{K}_{\mathrm{f}}$
This indicates that molal depression constant of a liquid $\left(\mathrm{K}_{\mathrm{f}}\right)$ is equal to depression of freezing point when molality of the solution is 1 m . the unit of $\mathrm{K}_{\mathrm{f}}$ is $\mathrm{Km}^{-1} . \mathrm{K}(\mathrm{mol} / \mathrm{kg})^{-1}=\mathrm{K} \mathrm{kg} \mathrm{mol}{ }^{-1}$.

## Determination of $\mathrm{K}_{\mathrm{f}}$ of solvent

$\mathrm{K}_{\mathrm{f}}$ is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$
\begin{equation*}
K_{f}=\frac{R_{f}^{2}}{1000 L_{f}} \tag{3}
\end{equation*}
$$

where $T_{f}$ is the freezing point of solvent in absolute scale and $L_{f}$ the latent heat of fusion in calories per gram of the solvent. For water,
$\mathrm{K}_{\mathrm{f}}=\frac{0.002 \times(273)^{2}}{80}=1.86 \mathrm{~K}-\mathrm{kg} / \mathrm{mole}$
Example: What is the percent by mass of iodine needed to reduce the freezing point of benzene to $3.5^{\circ} \mathrm{C}$ ? The freezing point and cryoscopic constant of pure benzene are $5.5^{\circ} \mathrm{C}$ and $5.12 \mathrm{~K} / \mathrm{m}$ respectively.
Solution: $\quad \Delta \mathrm{T}_{\mathrm{f}}=\mathrm{T}_{\mathrm{f}}^{0}-\mathrm{T}_{\mathrm{f}}=\mathrm{K}_{\mathrm{f}} . \mathrm{m}$
$5.5^{\circ} \mathrm{C}-3.5^{\circ} \mathrm{C}=5.12 \times \mathrm{m}$
$\mathrm{m}=\frac{2}{5.12}=0.39 \mathrm{molal}$
$\therefore$ Mass of iodine needed for 1000 g of benzene $=\mathrm{m} \times$ molecular mass of iodine $\mathrm{I}_{2}$ $=0.39 \mathrm{~mol} / \mathrm{kg} \times 254 \mathrm{~g} / \mathrm{mol}=99.06 \mathrm{~g} / \mathrm{kg}$
$\therefore 1000 \mathrm{~g}+99.06 \mathrm{~g}$ solution contains $99.06 \mathrm{~g} \mathrm{I}_{2}$
100 g solution contains $\frac{99.06 \mathrm{~g} \times 100}{1099.06 \mathrm{~g}}=9.01 \%$

## Practice Problems III

Q. 1 A solution containing $0.52 \mathrm{~g} \mathrm{of}_{10} \mathrm{H}_{8}$ in $\mathrm{CCl}_{4}$ produced an elevation in boiling point by $0.402^{\circ} \mathrm{C}$. On the other hand a solution of 0.62 g of an unknown solute dissolved in same amount of $\mathrm{CCl}_{4}$ produced an elevation by $0.65^{\circ} \mathrm{C}$. Molecular weight of solute is -
(A) 85.53
(B) 181.51
(C) 94.38
(D) 160.62
Q. 20.65 g naphthalene $\left(\mathrm{C}_{10} \mathrm{H}_{8}\right)$ was dissolved in 100 g methyl acetate. Elevation of b . pt of methyl acetate solution was $0.103^{\circ} \mathrm{C}$. If b. pt. of pure methyl acetate is $57^{\circ} \mathrm{C}$, its molar heat of vaporisation will be -
(A) $8.96 \mathrm{kcal} \mathrm{mol}^{-1}$
(B) $7.946 \mathrm{kcal} \mathrm{mol}^{-1}$
(C) $6.24 \mathrm{kcal} \mathrm{mol}^{-1}$
(D) $15.65 \mathrm{kcal} \mathrm{mol}^{-1}$
Q.3 When 174.5 mg of octa atomic sulphur is added to 78 g of bromine, the boiling point of bromine is [Given $\mathrm{K}_{\mathrm{b}}$ for $\mathrm{Br}_{2}$ is $5.2 \mathrm{~K} \mathrm{~mol}^{-1} \mathrm{~kg}$ and b . pt. of $\mathrm{Br}_{2}$ is 332.15 K ]
(A) 415.23 K
(B) 330 K
(C) 220.92 K
(D) 332.19 K
Q. 44.00 g of substance A, dissolved in $100 \mathrm{~g} \mathrm{H}_{2} \mathrm{O}$ depressed the f. pt. of water by $0.1^{\circ} \mathrm{C}$. While 4 g of another substance B , depressed the f. pt. by $0.2{ }^{\circ} \mathrm{C}$. What is the relation between molecular weights of the two substance -
(A) $M_{A}=4 M_{B}$
(B) $M_{A}=M_{B}$
(C) $\mathrm{M}_{\mathrm{A}}=0.5 \mathrm{M}_{\mathrm{B}}$
(D) $\mathrm{M}_{\mathrm{A}}=2 \mathrm{M}_{\mathrm{B}}$
Q. 5 An aqueous solution containing $5 \%$ by weight of urea and $10 \%$ by weight of glucose. Freezing point of solution is [ $\mathrm{K}_{\mathrm{f}}$ for $\mathrm{H}_{2} \mathrm{O}$ is $1.86 \mathrm{~K} \mathrm{~mol}^{-1} \mathrm{~kg}$ ]
(A) $3.04^{\circ} \mathrm{C}$
(B) $-3.04^{\circ} \mathrm{C}$
(C) $-5.96^{\circ} \mathrm{C}$
(D) $5.96^{\circ} \mathrm{C}$
Q. 6 The amount of ice that will separate out from a solution containing 25 g of ethylene glycol in 100 g of water and is cooled to $-10^{\circ} \mathrm{C}$, will be -
[ Given : $\mathrm{K}_{\mathrm{f}}$ for $\mathrm{H}_{2} \mathrm{O}=1.86 \mathrm{~K} \mathrm{~mol}^{-1} \mathrm{~kg}$ ]
(A) 50.0 g
(B) 25.0 g
(C) 12.5 gm
(D) 30.0 gm
Q. 7 It has been found that minimum temperature recorded in a hill station is $-10^{\circ} \mathrm{C}$. The amount of glycerine to be added to $40 \mathrm{dm}^{3}$ water used in car radiator, so that it does not freeze, is - [ $\Delta \mathrm{H}_{\text {fusion }}$ $=6.01 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ]
(A) 39.78 kg
(B) 22.45 kg
(C) 19.89 kg
(D) 42.66 kg
Q. 8 In winter, the normal temperature in Kullu valley was found to be $-11^{\circ} \mathrm{C}$. Is a $28 \%$ (by mass) aqueous solution of ethylene glycol suitable for a car radiator? $\mathrm{K}_{\mathrm{f}}$ for water $=1.86 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}$.
(A) Yes
(B) No
(C) can't predict
Q. 9 The temperature at which ice will begin to separate from a mixture of 20 mass percent of glycol $\left(\mathrm{C}_{2} \mathrm{H}_{6} \mathrm{O}_{2}\right)$ in water, is -
[ $\mathrm{K}_{\mathrm{f}}($ water $)=1.86 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}$ ]
(A) 280.5 K
(B) 265.5 K
(C) 276.5 K
(D) 269.5 K
Q. 10 The amount of urea to be dissolved in 500 ml of water $\left(\mathrm{K}_{\mathrm{f}}=18.6 \mathrm{~K} \mathrm{~mol}^{-1} 100 \mathrm{~g}\right.$ solvent $)$ to produce a depression of $0.186^{\circ} \mathrm{C}$ in freezing point is -
(A) 0.3 gm
(B) 3 gm
(C) 6 gm
(D) 9 gm
Q. 11 The molal boiling point constant of water is $0.53^{\circ} \mathrm{C}$. When 2 mole of glucose are dissolved in 4000 gm of water, the solution will boil at -
(A) $100.53^{\circ} \mathrm{C}$
(B) $101.06^{\circ} \mathrm{C}$
(C) $100.265^{\circ} \mathrm{C}$
(D) $99.47^{\circ} \mathrm{C}$
Q. 12 The boiling point of an aqueous solution of a non-volatile solute is $100.15^{\circ} \mathrm{C}$. What is the freezing point of an aqueous solution obtained by diluting the above solution with an equal volume of water?
[ $\mathrm{K}_{\mathrm{b}}$ and $\mathrm{K}_{\mathrm{f}}$ for water are 0.512 and $1.86 \mathrm{~K} \mathrm{molality}^{-1}$ ]
(A) $-0.544^{\circ} \mathrm{C}$
(B) $-0.512^{\circ} \mathrm{C}$
(C) $-0.272^{\circ} \mathrm{C}$
(D) $-1.86^{\circ} \mathrm{C}$
Q. 13 The freezing point of a solution prepared from 1.25 gm of non-electrolyte and 20 gm of water is 271.9 K . If molar depression constant is $1.86 \mathrm{~K} \mathrm{molality}^{-1}$. Then molar mass of the solute will be
(A) 105.68
(B) 106.7
(C) 115.3
(D) 93.9
Q. 14 Elevation in $b$. p of a solution of non-electrolyte in $\mathrm{CCl}_{4}$ is 0.60 . What is depression in f. p. for the same solution ? $\mathrm{K}_{\mathrm{f}}\left(\mathrm{CCl}_{4}\right)=30.00 \mathrm{~kg} \mathrm{~mol}^{-1} \mathrm{~K} ; \mathrm{K}_{\mathrm{b}}\left(\mathrm{CCl}_{4}\right)=5.02 \mathrm{~kg} \mathrm{~mol}^{-1} \mathrm{~K}$.
(A) $0^{\circ}$
(B) $5.39^{\circ}$
(C) $3.59^{\circ}$
(D) $2.49^{\circ}$
Q.15 A solution of a non-volatile solute in water has a boiling point of 375.3 K . The vapour pressure of water above this solution at 338 K is -
[Given $p_{0}($ water $)=0.2467$ atm at $338 \mathrm{~K}^{2}$ and $\mathrm{K}_{\mathrm{b}}$ for water $=0.52 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}$ ]
(A) 0.18 atm
(B) 0.23 atm
(C) 0.34 atm
(D) 0.42 atm
Q. 16 Elevation in boiling point of an aqueous urea solution is $0.52^{\circ} .\left(\mathrm{K}_{\mathrm{b}}=0.52 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}\right)$. Hence mole fraction of urea in this solution is -
(A) 0.982
(B) 0.0567
(C) 0.943
(D) 0.018
Q. 17 Density of 1 M solution of a non-electrolyte $\mathrm{C}_{6} \mathrm{H}_{12} \mathrm{O}_{6}$ is $1.18 \mathrm{~g} / \mathrm{mL}^{2}$. If $\mathrm{K}_{\mathrm{f}}\left(\mathrm{H}_{2} \mathrm{O}\right)$ is $1.86 \mathrm{~K} \mathrm{~mol}^{-1}$ kg , solution freezes at -
(A) $1.58^{\circ} \mathrm{C}$
(B) $-1.86^{\circ} \mathrm{C}$
(C) $-3.16^{\circ} \mathrm{C}$
(D) $1.86^{\circ} \mathrm{C}$
Q. 18 When a solution containing mg of urea in 1 kg of water is cooled to $-.372^{\circ} \mathrm{C}, 200 \mathrm{~g}$ of ice is separated. If $\mathrm{K}_{\mathrm{f}}$ for water is $1.86 \mathrm{~K} \mathrm{~kg} \mathrm{~mol}^{-1}, \mathrm{w}$ is -
(A) 4.8 g
(B) 12.0 g
(C) 9.6 g
(D) 6.0 g
Q. 19 Relative decrease in V. P. of an aqueous glucose dilute solution is found to be 0.018 . Hence, elevation in boiling point is : (it is given 1 molal aq. urea solution boils at $100.54^{\circ} \mathrm{C}$ at 1 atm . pressure)
(A) $0.018^{\circ}$
(B) $0.18^{\circ}$
(C) $0.54^{\circ}$
(D) $0.03^{\circ}$
Q. 20 Glucose is added to 1 litre water to such an extent that $\Delta T_{f} / K_{f}$ becomes equal to $1 / 1000$, the weight of glucose added is
(A) 180 gm
(B) 18 gm
(C) 1.8 gm
(D) 0.18 gm

## Answer Key

1. Practice Problem I
2. (A)
3. (C)
4. (A)
5. (B)
6. (C)
7. (B)
8. (A)
9. (A)
10. (B)
11. (A)
12. (A)
13. (C)
14. (C)
15. (B)
16. (C)
17. (B)
18. (B)
19. (A)
20. (A)

## 2. Practice Problem II

| 1. (B) | 2. (C) | 3. (C) | 4. (D) | 5. (B) | 6. (B) | 7. (C) |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 8. (C) | 9. (B) | 10. (A) | 11. (B) | 12. (C) | 13. (i) (A) | (ii) (D) |
| 14. (C) | 15. (A) | 16. (D) | 17. (A) | 18. (D) | 19. (C) | 20. (B) |
| 21. (A) | 22. (A) | 23. (D) | 24. (A) | 25. (D) | 26. (C) |  |
| 27. (i) (A) | (ii) (D) | (iii) (B) | 28. (A) | 29. (C) | 30. (A) |  |

## 3. Practice Problem III

| 1. (C) | 2. (B) | 3. (D) | 4. (D) | 5. (B) | 6. (B) | 7. (C) |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 8. (A) | 9. (B) | 10. (B) | 11. (C) | 12. (A) | 13. (A) | 14. (C) |
| 15. (B) | 16. (D) | 17. (B) | 18. (C) | 19. (C) | 20. (D) |  |

