01 Liquid Solution

Solution :

When two or more chemically non-reacting substances are mixed and form homogeneous mixture, it is called solution.

When the solution is composed of only two chemical substances, it is termed a binary solution, similarly, it is called ternary and quaternary if it is composed of three and four components respectively.

Solution = solute + solvent

Solute : Generally the component present in lesser amount than other component in solution is called solute.

Solvent : Generally, the component present in greater amount is called the solvent. Physical state of solution is determined by solvent.

Types of solution :

S. No.	Solvent	Solute	Examples
1.	Gas	Gas	Mixture of gases, eg. air.
2.	Gas	Liquid	Water vapour in air, mist, $CHCl_3(\ell) + N_2(g)$
3.	Gas	Solid	Smoke, camphor (s) + $N_2(g)$.
4.	Liquid	Gas	CO_2 gas dissolve in water (aerated drink), soda water.
5.	Liquid	Liquid	Mixture of miscible liquids e.g. alcohol in water.
6.	Liquid	Solid	Salt in water, sugar in water.
7.	Solid	Gas	hydrogen over palladium.
8.	Solid	Liquid	Mercury in zinc, mercury in gold i.e. all amalgams.
9.	Solid	Solid	Alloys e.g. copper in gold. zinc in copper.

Various concentration terms :

Mass percentage :

It may be defined as the number of parts of mass of solute per hundred parts by mass of solution.

$$\% \text{ by mass} = \%\left(\frac{w}{W}\right) : = \frac{\text{wt. of solute}}{\text{wt. of solution}} \times 100$$

[X % by mass means 100 gm solution contains X gm solute; $\therefore$ (100 – X) gm solvent]

Mass-volume percentage (W/V %) :

It may be defined as the mass of solute present in 100 cm^3 of solution. For example, if 100 cm^3 of solution contains 5 g of sodium hydroxide, then the mass-volume percentage will be 5% NaOH solution.

$$\% \left(\frac{w}{V}\right) = \frac{\text{wt. of solute (in gm)}}{\text{volume of solution (in mL)}} \times 100$$

$\left[X\ \%\left(\frac{w}{V}\right) \text{ means 100 ml solution contains X gm of solute}\right]$

Volume Percent :

It can be represented as % v/v or % volume and used to prepare such solutions in which both components are in liquids state. It is the number of parts of by volume of solute per hundred parts by volume of solution. Therefore,

$$\% = \left(\frac{v}{V}\right) = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100$$

Parts per million (ppm) :

This method is used for expressing the concentration of very dilute solutions such as hardness of water, air pollution etc.

$$\text{ppm of substance} = \frac{\text{Mass of solute} \times 10^6}{\text{Mass of solution}}$$

$$= \frac{\text{Volume of solute} \times 10^6}{\text{volume of solution}}$$

Mole fraction :

The ratio of the number of moles of one component to the total number of all the components present in the solution, is called the mole fraction of that component.

Mole fraction of solute (χ_A) is given by $\chi_A = \frac{n_A}{n_A + n_B} = \frac{n_A}{\Sigma n}$

Mole fraction of solvent (χ_B) is given by $\chi_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{\Sigma n}$

Where n_A is moles of solute of A & n_B is moles of solvent of B.

For binary solution of A & B $\chi_A + \chi_B = 1$

Molarity (Molar concentration) :

It is defined as the number of moles of the solute dissolved in per litre of the solution, i.e.,

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in } \ell)} = \frac{w_A}{m_A \times V} = \frac{c(gm/\ell)}{m_A} = \frac{\%\frac{W}{W} \times d \times 10}{m_A}$$

where let w_A g of the solute of molecular mass m_A be dissolved in V litre of solution, d = density of solution in g/mL.

Molarity of dilute solution :

Before dilution After dilution

moles of solute = moles of solute

$M_1V_1 = M_2V_2$

Molarity of mixing :

Let there be three samples of solution (containing same solvent and solute) with their molarity M_1, M_2, M_3 and volumes V_1, V_2, V_3 respectively. These solutions are mixed; molarity of mixed solution may be given as :

$M_1V_1 + M_2V_2 + M_3V_3 = M_R(V_1 + V_2 + V_3)$

where, M_R = Resultant molarity

$V_1 + V_2 + V_3$ = Resultant volume after mixing

Note :

Molarity is dependent on volume; therefore, it depends on temperature.]

1M	Molar solution, i.e., molarity is 1
0.5 M or M/2	Semimolar
0.1 M or M/10	Decimolar
0.01 M or M/100	Centimolar
0.001 M or M/1000	Millimolar

Relation between molarity 'M' and mole fraction :

Let M be the molarity of solution, and χ_A, χ_B be mole fractions of solvent and solute, respectively.

Suppose n_A and n_B moles of solvent and solute are mixed to form solution.

Mass of solution = $n_A m_A + n_B m_B$ ... (i)

where m_A and m_B are molar masses of solvent and solute, respectively.

Volume of solution = $\frac{\text{Mass}}{\text{Density}} = \frac{(n_A m_A + n_B m_B)}{d}$

Molarity = Number of moles of solute × $\frac{1000}{\text{Volume of solution}}$

$M = n_B \times \frac{1000 \times d}{(n_A m_A + n_B m_B)}$

Dividing both numerator and denominator by $(n_A + n_B)$,

$$M = \left\{\frac{n_B}{n_A + n_B}\right\} \times \frac{1000 \times d}{\frac{n_A}{n_A + n_B} \times m_A + \frac{n_B}{n_A + n_B} \times m_B}$$

$$M = \frac{x_B \times 1000 \times d}{x_A m_A + x_B m_B}$$

Molality (m) :

The number of moles or gram-mole of solute dissolve in 1000 gram of the solvent is called molality of the solution.

Molality of a solution = $\frac{\text{Number of moles of solute}}{\text{Mass of solvent in kg.}} = \frac{\text{Number of moles of solute} \times 1000}{\text{Mass of solvent in grams.}}$

* It is independent of temperature.

Relation between molality and molarity :

$$\frac{\text{Molarity}}{\text{Molality}} = \frac{\text{Moles of solute}}{\text{volume of solution}} \times \frac{\text{mass of solvent (kg)}}{\text{moles of solute}} = \frac{\text{mass of solvent(kg)}}{\text{volume of solution (in litre)}}$$

$$= \frac{\text{mass of solvent(in grams)}}{\text{volume of solution (in mL)}} = \frac{W}{V}$$

Let the density of the solution = d g. mL^{-1}

Mass of solution = V × d

Mass of solute = number of moles × molecular mass of solute = n × m_A

Mass of solvent(W) = mass of solution – mass of solute

= (V × d) – (n × m_A)

Thus $\frac{\text{Molarity}}{\text{Molality}} = \frac{(V \times d) - (n \times m_A)}{V}$

Molality (m) = $\frac{\text{molarity} \times V}{(V \times d) - (n \times m_A)} = \frac{\text{molarity}}{d - \left(\frac{n}{V} \times m_A\right)}$

$m = \frac{\text{molarity}}{d - \left(\frac{\text{molarity} \times m_A}{1000}\right)} = \frac{M \times 1000}{1000d - m.m_A}$

Normality (N) :

The number of equivalents or gram equivalents of solute dissolved in one litre of the solution is known as normality (N) of the solution.

Normality (N) = $\frac{\text{Number of gram equivalents of solute}}{\text{volume of solution in litre}} = \frac{\text{weight of solute in gram}}{\text{equivalent weight} \times \text{volume of solution (litre)}}$

$= \frac{\text{strength of solution in gram / litre}}{\text{Equivalent weight of solute}}$

Equivalent weight of a substance is that weight which reacts with or displaces one gram of hydrogen, 8 grams of oxygen or 35.5 grams of chlorine.

Solutions are expressed as : 1N, $\frac{N}{2}, \frac{N}{10}, \frac{N}{100}, \frac{N}{1000}$, etc.

1N = Normal = One gram equivalent of the solute per litre of solution $\Rightarrow$ Normality is 1

$\frac{N}{2}$ = Seminormal = 0.5 g equivalent of the solute per litre of solution $\Rightarrow$ Normality is 0.5

$\frac{N}{10}$ = Decinormal = 0.1g equivalent of the solute per litre of solution $\Rightarrow$ Normality is 0.1

$\frac{N}{100}$ = Centinormal = 0.01g equivalent of the solute per litre of solution $\Rightarrow$ Normality is 0.01

$\frac{N}{1000}$ = Millinormal = 0.001g equivalent of the solute per litre of solution $\Rightarrow$ Normality is 0.001

Relation between molarity and normality :

Number of equivalents = (Number of moles × Valency factor)

So, we can write

Molarity × Molecular weight of solute = Normality × equivalent weight of solute.

Normality = $\frac{\text{molarity} \times \text{molecular weight of solute}}{\text{equivalent weight of solute}} = \frac{\text{molarity} \times \text{molecular weight of solute}}{(\text{molecular weight of solute/valency factor})}$

Normality = molarity × valency factor

N = M × n {n = Valency factor}

Strength (S grams/litre**) :**

The numbers of grams of solute dissolved in one litre solution is known as its strength in grams per litre.

S = $\frac{\text{wt. of solute in grams} \times 1000}{\text{volume of solution in mL}}$ = Molarity of solution × molecular wt. of solute.

S = Normality of solution × equivalent weight of solute.

Illustration 1:

If 0.4 gm of NaOH is present in 80 ml of solution. What is the molarity and normality [M.wt. of NaOH = 40]

Solution:

$$\text{Molarity} = \frac{\text{wt. of solute} \times 1000}{\text{M.Wt. of solute} \times \text{volume of solution (mL)}} = \frac{0.4}{40 \times 80} \times 1000 = 0.125 \text{ M} = 0.125 \text{ N}$$

Illustration 2:

The normality of 1.5M H_3PO_4 is –

Solution:

Basicity of H_3PO_4 is 3

$$N = M \times n = 4.5 \text{ N} \qquad (n \rightarrow \text{n - factor})$$

Illustration 3:

How much volume of 10M HCl should be diluted with water to prepare 2.00 L of 5M HCl ?

Solution:

In dilution the following equation is applicable :

$$M_1V_1 = M_2V_2$$

$$10 \times V_1 = 5 \times 2.00$$

$$V_1 = \frac{5 \times 2.00}{10} = 1.00 \text{ L}$$

Illustration 4:

Find out the weight of H_2SO_4 in 150 mL, $\frac{N}{7}$ H_2SO_4.

Solution:

wt. in gram = eq. wt × N × volume

$$= 49 \times \frac{1}{7} \times \frac{150}{1000} = \frac{21}{20} = 1.05 \text{ g}$$

Illustration 5:

Find out the molarity of 1 litre of 93% H_2SO_4 and its density is 1.84.

Solution:

$$\text{Molarity} = \frac{\text{Wt. in g} \times \text{density} \times 1000}{\text{molecular wt.} \times 100} = \frac{93 \times 1.84 \times 1000}{98 \times 100} = 17.46 \text{ M}$$

Illustration 6:

A 100 cm^3 solution is prepared by dissolving 2g of NaOH in water. Calculate the normality of the solution.

Solution:

$$2 \text{ g NaOH} = \frac{2}{40} \text{ g. eq.} = \frac{1}{20} \text{ g eq.}$$

$$N = \frac{\frac{1}{20}}{100} \times 1000 = \frac{1}{20} = 0.5 \text{ N}$$

Illustration 7:

Find the percentage by weight and weight fraction of aspirin in the solution prepared by dissolving 3.65 g of aspirin in 25.08 g of water.

Solution:

weight of solution = 3.65 + 25.08 = 28.73 g

weight fraction = $\frac{3.65}{28.73}$ = 0.127

weight percent = 0.127 × 100 = 12.7%

Illustration 8:

A solution was prepared by adding 125 cm^3 of isopropyl alcohol to water until the volume of the solution was 175 cm^3. Find the volume fraction and volume percent of isopropyl alcohol in the solution.

Solution:

volume of solute = 125 cm^3

volume of solution = 175 cm^3

$\therefore$ volume fraction = $\frac{125}{175}$ = 0.714

and volume percent = $\frac{125}{175}\times 100$ = 71.4%

Illustration 9:

The density of a solution containing 13% by mass of sulphuric acid is 1.09 g/mL. Calculate the molarity and normality of the solution.

Solution:

Volume of 100 g of the solution = $= \frac{100}{d} = \frac{100}{1.09}$ mL $= \frac{100}{1.09\times 1000}$ litre $= \frac{1}{1.09\times 10}$ litre

Number of moles of H_2SO_4 in 100 g of the solution = $\frac{13}{98}$

Molarity = $\frac{\text{No. of moles of } H_2SO_4}{\text{Volume of solution. in litre}} = \frac{13}{98}\times\frac{1.09\times 10}{1}$ = 1.445 M

Note :

In solving such numerical, the following formula can be applied :

Molarity = $\frac{\%\text{ strength of solution}\times\text{density of solution}\times 10}{\text{Mol. mass}}$

Similarly,

Normality = $\frac{\%\text{ strength of solution}\times\text{density of solution}\times 10}{\text{Eq. mass}}$

We know that,

Normality = Molarity × n = 1.445 × 2 $\left[n = \frac{\text{Mol. mass}}{\text{Eq. mass}} = \frac{98}{49} = 2\right]$ = 2.89 N

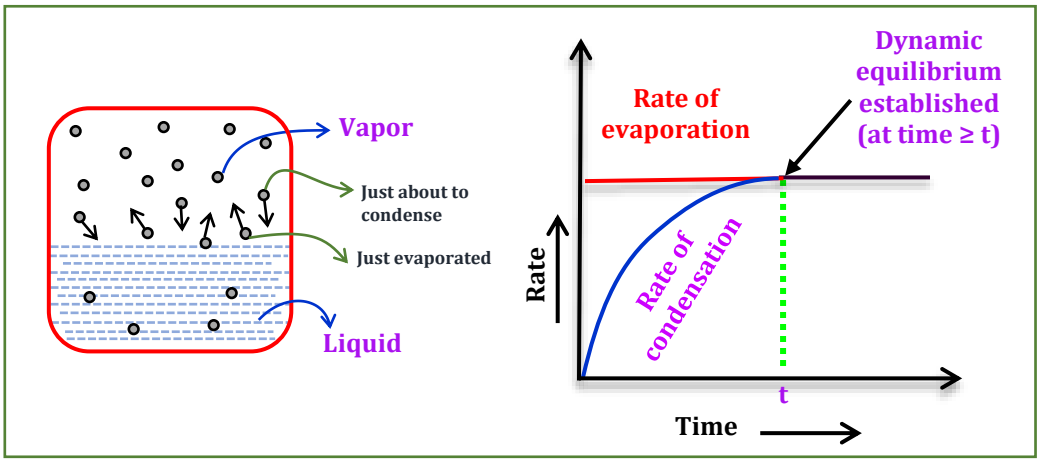
Vapour pressure :

The Evaporation of a Liquid in a Closed Container

When a liquid is taken in a closed vessel at constant temperature, then there are two process which takes place.

(i) evaporation (ii) condensation

In the constant evaporation from the surface particles continue to break away from the surface of the liquid. As the gaseous particles bounce around, some of them will hit the surface of the liquid again, and will be trapped there. This is called condensation. The rate of condensation increases with time, but rate of evaporation remains constant. There will rapidly be an equilibrium set up in which the number of particles leaving the surface is exactly balanced by the number re-joining it.



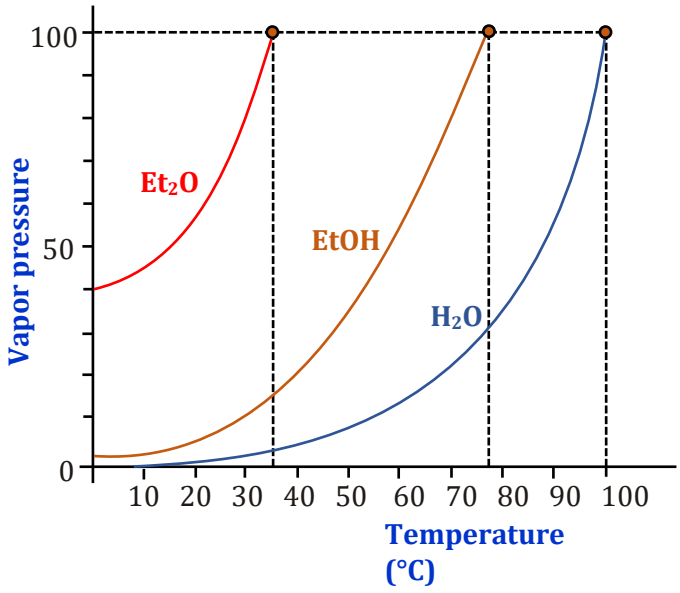
This pressure at equilibrium is called the **saturated vapour pressure** (also known as **saturation vapour pressure**).

Effect of Temperature on vapour pressure

When the space above the liquid is saturated with vapour particles, the equilibrium occurring on the surface of the liquid is :

$$\text{liquid} \rightleftharpoons \text{vapour}, \quad \Delta H > 0$$

The forward change (liquid to vapour) is endothermic. It needs heat to convert the liquid into the vapour. According to Le Chatelier, increasing the temperature of a system in a dynamic equilibrium favours the endothermic change. That means increasing the temperature increase the amount of vapour present, and so increases the saturated vapour pressure.



Effect of nature : Vapour pressure $\propto \dfrac{1}{\text{Inter molecular attraction force(I.M.A.F.)}}$

Solubility :

Maximum amount of solute which can be dissolved in a specified amount of solvent at constant temperature is solubility. Solubility is effected by

1. nature of solute and solvent
2. temperature and
3. pressure

Solubility of solid in a liquid :

Polar solutes are soluble in polar solvent and non-polar solutes are soluble in non-polar solvent due to similar intermolecular forces.

When solid solutes are dissolved in solvent than following equilibrium exits.

Solute + Solvent $\underset{\text{Crystallization}}{\overset{\text{Dissolution}}{\rightleftharpoons}}$ Solution. ; ΔH may be positive or negative

Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a saturated solution. An unsaturated solution is one in which more solute can be dissolved at the same temperature. The solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent.

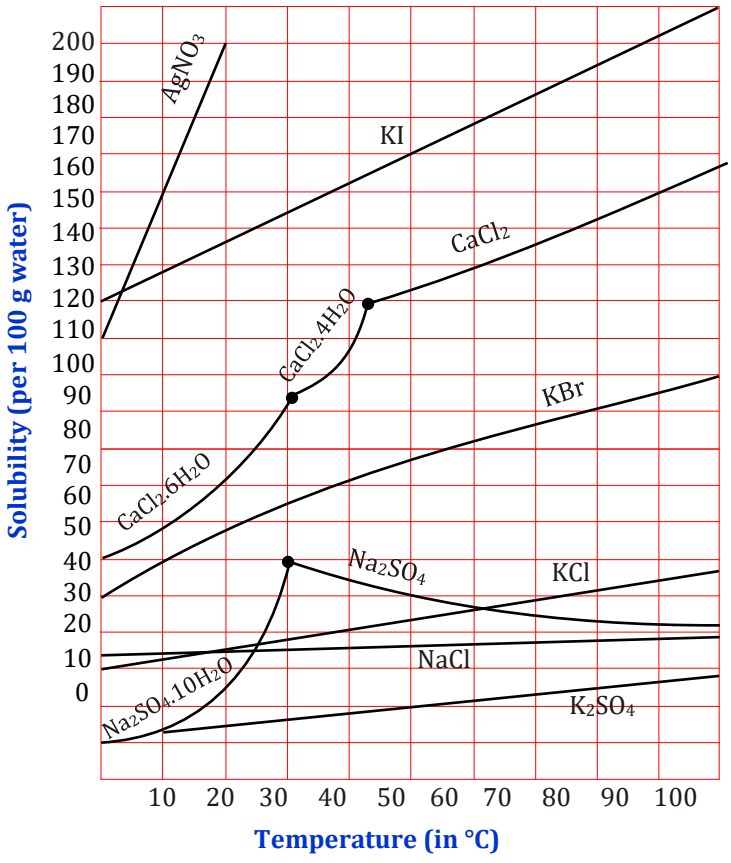
Effect of temperature :

The solubility of a solid in a liquid is significantly affected by temperature changes, obeying **Le Chateliers Principle**. In general, if in a nearly saturated solution, the dissolution process is endothermic ($\Delta_{sol}H > 0$), the solubility should increase with rise in temperature and if it is exothermic ($\Delta_{sol}H < 0$) the solubility should decrease. These trends are also observed experimentally.

Effect of pressure:

Pressure does not have any significant effect on solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

Solubility curves of some compounds :



Solubility of gases in liquid :

Certain gases are highly soluble in water like NH_3, HCl etc. and certain gases are less soluble in water like O_2, N_2, He etc. Solubility of gases is highly effected by pressure and temperature. Increasing pressure increases solubility. Increase in temperature decreases solubility since dissolution of any gas in any liquid is exothermic in nature.

Henry' Law :

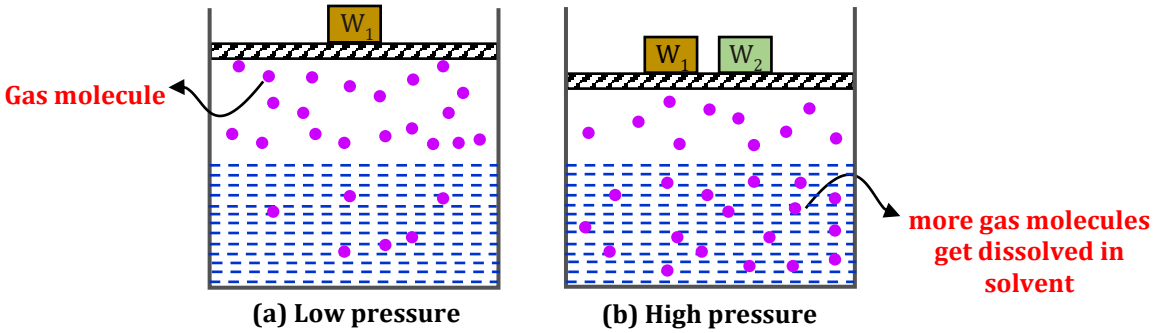
Mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.

or

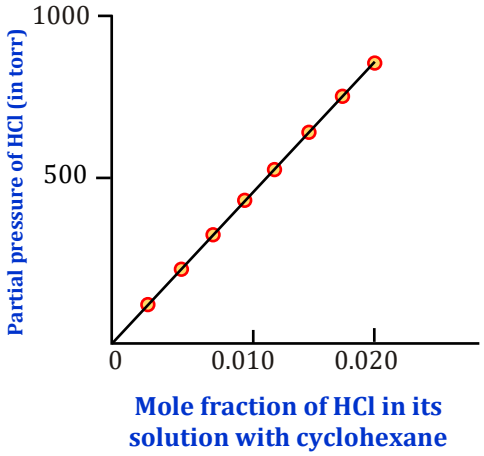
The partial pressure of the gas in vapour phase (P) is proportional to the mole fraction of the gas (x) in the solution.

$\mathbf{P = K_H X}$ K_H = Henry's Constant

Henry's Constant depends on nature of gas and temperature. K_H increases with increases in temperature therefore high K_H means low solubility.



Effect of pressure on the solubility of a gas. The concentration of dissolved gas is proportional to the pressure on the gas above the solution.



Experimental results for the solubility of HCl gas in cyclohexane at 293 K.
The slope of the line is the Henry's constant (K_H)

The solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

Effect of temperature :

Solubility of gases in liquids decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. Dissolution process involves dynamic equilibrium and thus must follow Le Chatelier's Principle. As dissolution is an exothermic process, the solubility should decrease with increase of temperature

Henry' law application :

(1) To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

(2) Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life. To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

(3) At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

Values of Henry's Law Constant for Some Selected Gases in Water

Gas	Temperature/K	K_H /kbar
He	293	144.97
H_2	293	69.16
N_2	293	76.48
N_2	303	88.84
O_2	293	34.86
O_2	303	46.82
Argon	298	40.3
CO_2	298	1.67
Formaldehyde	298	1.83×10^{-5}
Methane	298	0.413
Vinyl chloride	298	0.611

Illustration 10:

If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 kbar.

Solution:

The solubility of gas is related to the mole fraction in aqueous solution.

The mole fraction of the gas in the solution is calculated by applying

Henry's law. Thus :

$$\chi(\text{Nitrogen}) = \frac{P(\text{nitrogen})}{K_H} = \frac{0.98\ \text{bar}}{76,480\ \text{bar}} = 1.29 \times 10^{-5}$$

As 1 litre of water contains 55.5 mol of it, therefore if n represents number of moles of N_2 in solution,

$$\chi \text{ (Nitrogen)} = \frac{n\,\text{mol}}{n\,\text{mol} + 55.5\,\text{mol}} = \frac{n}{55.5} = 1.29 \times 10^{-5}$$

(n in denominator is neglected as it is < < 55.5)

Thus $n = 1.29 \times 10^{-5} \times 55.5$ mol $= 7.16 \times 10^{-4}$ mol $= 0.716 \times 10^{-3}$ mol $= 0.716$ m mol

Illustration 11:

Henry's law constant for the molality of methane in benzene at 298 K is 4.27×10^5 mm Hg. Calculate the mole fraction of methane in benzene at 298 K under 760 mm Hg.

Solution:

Here, $P = 760$ mm Hg

$k_H = 4.27 \times 10^5$ mm Hg

According to Henry's law,

$$p = k_H \chi$$

$$\Rightarrow \quad \chi = \frac{P}{k_H} = \frac{760\,\text{mm Hg}}{4.27 \times 10^5\,\text{mm Hg}} = 177.99 \times 10^{-5} = 178 \times 10^{-5} \text{ (approximately)}$$

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

Illustration 12:

The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% and 79% by volume at 298 K. The water is in equilibrium with air at a pressure of 10 atm. At 298 K, if the Henry's law constants for oxygen and nitrogen are 3.30×10^7 mm and 6.51×10^7 mm respectively. Calculate the composition of these gases in water.

Solution:

Percentage of oxygen (O_2) in air = 20%

Percentage of nitrogen (N_2) in air = 79%

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

Partial pressure of oxygen, $P_{O_2} = \frac{20}{100} \times 7600\,\text{mm Hg} = 1520$ mm Hg

Partial pressure of nitrogen, $P_{N_2} = \frac{79}{100} \times 7600\,\text{mm Hg} = 6004$ mm of Hg

Now, according to Henry's law :

$$P = K_H \chi$$

For oxygen :

$$P_{O_2} = K_H . \chi_{O_2}$$

$$\Rightarrow \quad \chi_{O_2} = \frac{P_{O_2}}{K_H} = \frac{1520 \text{ mm of Hg}}{3.30 \times 10^7\,\text{mm of Hg}} = 4.61 \times 10^{-5}$$

For nitrogen,

$$P_{N_2} = K_H . \chi_{N_2}$$

$$\Rightarrow \quad \chi_{N_2} = \frac{P_{N_1}}{K_H} = \frac{6004 \text{ mm Hg}}{6.51 \times 10^7 \text{ mm Hg}} = 9.22 \times 10^{-5}$$

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

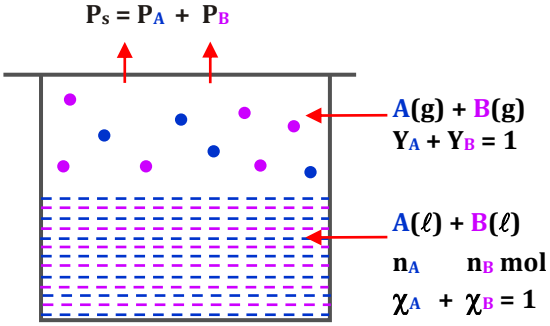
Vapour pressure of liquid solution :

Raoult's law :

The partial pressure of any volatile constituents of a solution at a constant temperature is equal to the vapour pressure of pure constituents multiplied by the mole fraction of that constituent in the solution, at equilibrium.

Vapour pressure of liquid – liquid solution :

Let P_A and P_B be the partial vapour pressures of two constituents A and B in solution and P_A^0 and P_B^0 the vapour pressures in pure state respectively.



Thus, according Raoult's law

$$P_A = \frac{n_A}{n_A + n_B} P_A^0 = \chi_A P_A^0 \quad ...(1)$$

and $$P_B = \frac{n_B}{n_A + n_B} P_B^0 = \chi_B P_B^0 \quad ...(2)$$

If total pressure be P_S, then

$P_S = P_A + P_B = \chi_A P_A^0 + \chi_B P_B^0$

$P_S = \chi_A P_A^0 + (1 - \chi_A) P_B^0$ $[\because \chi_A + \chi_B = 1]$

$P_S = \chi_A P_A^0 - \chi_A P_B^0 + P_B^0$

$P_S = \chi_A [P_A^0 - P_B^0] + P_B^0$

Relation between Dalton's Law and Raoult's Law :

The composition of the vapour in equilibrium with the solution can be calculated applying Dalton's law of partial pressures. Let the mole fraction of A and B in vapours be Y_A and Y_B respectively.

$P_A = Y_A P_S = \chi_A P_A^0$ ...(1)

$P_B = Y_B P_S = \chi_B P_B^0$ ...(2)

Now, $\chi_A = \frac{\gamma_A \cdot P_S}{P_A^0}$ and $\chi_B = \frac{\gamma_B \cdot P_S}{P_B^0}$

As, $\chi_A + \chi_B = 1$, $\frac{\gamma_A \cdot P_S}{P_A^0} + \frac{\gamma_B \cdot P_S}{P_B^0} = 1$

$\therefore \quad \frac{1}{P_S} = \frac{\gamma_A}{P_A^0} + \frac{\gamma_B}{P_B^0}$

Hence, the total vapour pressure of solution may be calculated from liquid composition at equilibrium as

$$P_S = \chi_A \cdot P_A^0 + \chi_B \cdot P_B^0$$

and from vapour composition at equilibrium at

$$\frac{1}{P_S} = \frac{\gamma_A}{P_A^0} + \frac{\gamma_B}{P_B^0}$$

Comparison between liquid and vapour composition :

$$\frac{\gamma_A}{\gamma_B}=\frac{P_A/P_S}{P_B/P_S}=\frac{P_A}{P_B}=\frac{\chi_A\cdot P_A^0}{\chi_B\cdot P_B^0}$$

If A is more volatile than B $\left(P_A^0>P_B^0\right)$, then $\frac{\gamma_A}{\gamma_B}>\frac{\chi_A}{\chi_B}$

It means that the mole-fraction of A is vapour form is relatively greater than that in liquid form, relative to B. Hence, in any ideal solution, vapour is always more richer in the more volatile component, relative to liquid.

Raoult's law as a special case of Henry's law :

From Raoult's law, the vapour pressure of volatile component in the solution is $P = P^0.\chi$.

In the solution of gas in liquid, one component is so volatile that it exist as gas and its pressure is given by Henry's law as $P = K_H.\chi$

In both laws, the partial pressure of volatile component is directly proportional to its mole-fraction in solution. Only the proportionality constant K_H differs from P^0. Hence, Raoult's law becomes a special case of Henry's law in which K_H becomes P^0.

Vapour pressure of solution of solids in liquid :

Let us assume A = non-volatile solid & B = volatile liquid

According to Raoult's law –

$\because$ $P_s = \chi_A P_A^0 + \chi_B P_B^0$

for A, $P_A^0 = 0$

$\therefore$ $P_s = \chi_B P_B^0$ ...(5)

Let $P_B^0 = P^0$ = Vapour pressure of pure state of solvent.

here χ_B is mole fraction of solvent

$$P_S=\frac{n_B}{n_A+n_B}\,P^0 \qquad ...(6)$$

$$P_S\propto\frac{n_B}{n_A+n_B}$$ i.e. vapour pressure of solution $\propto$ mole fraction of solvent

$\Rightarrow$ $P_S = \chi_B P_B^0 \Rightarrow P_S = (1-\chi_A)\,P_B^0$

$\Rightarrow$ $P_S = P_B^0 - \chi_A\,P_B^0$

$\Rightarrow$ $\frac{P_B^0-P_S}{P_B^0}=X_A$

or $\frac{P^0-P_S}{P^0}=\chi_A$ ...(7)

$$\boxed{\frac{P^0-P_S}{P^0}=\frac{n_A}{n_A+n_B}} \qquad ...(8)$$

or $\frac{P^0}{P^0-P_S}=\frac{n_A+n_B}{n_A}$

or $\frac{P^0}{P^0-P_S}=1+\frac{n_B}{n_A}$ or $\frac{P^0}{P^0-P_S}-1=\frac{n_B}{n_A}$

$$\frac{P_S}{P^0 - P_S} = \frac{n_B}{n_A}$$

$$\boxed{\frac{P^0 - P_S}{P_S} = \frac{n_A}{n_B} = \frac{w_A . m_B}{m_A . w_B}} \quad ...(9)$$

Ideal and non-ideal solutions :

The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions.

Table : Comparison between Ideal and Non-ideal solutions

Ideal solutions	Non-ideal solutions	
	+ve deviation from Raoult's law	– deviation from Raoult's law
1. Obeys Raoult's law at every concentration.	Do not obey Raoult's law.	Do not obey Raoult's law.
2. $\Delta H_{mix} = 0$; Neither heat is evolved nor absorbed during dissolution.	$\Delta H_{mix} > 0$. Endothermic dissolution; heat is absorbed.	$\Delta H_{mix} < 0$; exothermic dissolution heat is evolved.
3. $\Delta V_{mix} = 0$; total volume of solution is equal to sum of volumes of the components.	$\Delta V_{mix} > 0$. Volume is increased after dissolution.	$\Delta V_{mix} < 0$; volume is decreased during dissolution.
4. $P = p_A + p_B = p_A^0\chi_A + p_B^0\chi_B$ i.e., $P_A = p_A^0\chi_A ; p_B = p_B^0\chi_B$	$P_A > p_A^0\chi_A$; $p_B > p_B^0\chi_B$ $\therefore (P_A + p_B) > (p_A^0\chi_A + p_B^0\chi_B)$	$P_A < p_A^0\chi_A$; $p_B < p_B^0\chi_B$ $\therefore (P_A + p_B) < (p_A^0\chi_A + p_B^0\chi_B)$
5. A — A, A — B, B — B interactions should nearly be same, i.e., 'A' and 'B' are identical in shape, size and character.	A — B, attraction force should be weaker than A — A and B — B attractive forces. 'A' and 'B' have different shape, size and character.	A — B, attraction force should be greater than A — A and B — B attractive forces. 'A' and 'B' have different shape, size and character.
6. Escaping tendency of 'A' and components 'B' should be same in pure liquids and in the solution.	'A' and 'B' escape easily showing high vapour pressure than the expected value.	Escaping tendency of both A and B is lowered showing lower vapour pressure than expected ideally.
Example : dilute solutions ; benzene + toluene ; n-hexane + n-heptane ; chlorobenzene + bromobenzene ; ethyl bromide + ethyl iodide ; n-butyl chloride + n-butyl bromide $CCl_4 + SiCl_4$; $C_2H_4Br_2 + C_2H_4Cl_2$ $C_2H_5Br + C_2H_5Cl$	**Example :** acetone + ethanol ; acetone + CS_2 ; water + methanol ; water + ethanol ; $CCl_4 + CHCl_3$; CCl_4 + toluene ; acetone + benzene $CCl_4 + CH_3OH$; cyclohexane + ethanol	**Example :** acetone + aniline ; acetone + chloroform ; $CH_3OH + CH_3COOH$; $H_2O + HNO_3$; water + HCl ; acetic acid + pyridine ; $HNO_3 + CHCl_3$

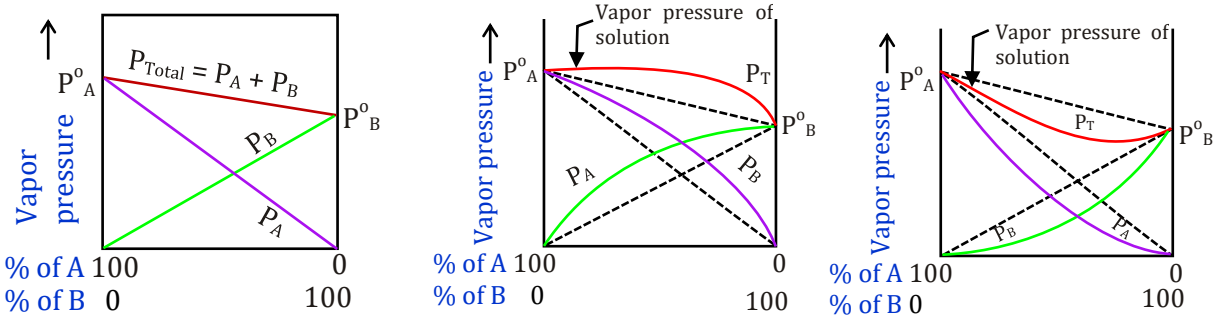


Illustration 13:

1 mole heptane (V.P. = 92 mm of Hg) is mixed with 4 mole Octane (V.P. = 31 mm of Hg), form an ideal solution. Find out the vapour pressure of solution.

Solution:

Total mole = 1 + 4 = 5

Mole fraction of heptane = $\chi_A = 1/5$

Mole fraction of octane = $\chi_B = 4/5$

$P_S = \chi_A P_A^0 + \chi_B P_B^0 = \frac{1}{5}\times 92 + \frac{4}{5}\times 31 = 43.2$ mm of Hg.

Illustration 14:

At 88°C, benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will be boil at 88°C at 1 atm pressure, benzene – toluene form an ideal solution.

Solution:

P_S = 760 torr, because solution boils at 88°C

$\therefore \quad 760 = 900\, x + 360\,(1 - \chi)$

$\chi = 0.74$ where 'x' is mole fraction C_6H_6.

Illustration 15:

The vapour pressure of benzene at 90°C is 1020 torr. A solution of 5 g of a solute in 58.5 g benzene has vapour pressure 990 torr. What is the molecular weight of solute ?

Solution:

$$\frac{P^0 - P_S}{P_S} = \frac{w \times M}{m \times W} \Rightarrow \frac{1020 - 990}{990} = \frac{5 \times 78}{m \times 58.5} \Rightarrow m = 220$$

Illustration 16:

Two liquids A and B form an ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 mole of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states.

Solution:

Let the vapour pressure of pure A be = P_A^0 ; and the vapour pressure of pure B be = P_B^0.

Total vapour pressure of solution (1 mole A + 3 mole B)

= $\chi_A . P_A^0 + \chi_B . P_B^0$ [χ_A is mole fraction of A and χ_B is mole fraction of B]

$550 = \frac{1}{4}P_A^0 + \frac{3}{4}P_B^0$ or $2200 = P_A^0 + 3P_B^0$ ...(i)

Total vapour pressure of solution (1 mole A + 4 mole B) = $\frac{1}{5}P_A^0 + \frac{4}{5}P_B^0$

$560 = \frac{1}{5}P_A^0 + \frac{4}{5}P_B^0$

$2800 = P_A^0 + P_B^0$ ...(ii)

Solving equations. (i) and (ii)

P_B^0 = 600 mm of Hg = vapour pressure of pure B

P_A^0 = 400 mm of Hg = vapour pressure of pure A

Illustration 17:

Liquids 'A' and 'B' form an ideal solution. Calculate the vapour pressure of solution having 40 mole-percent of A in the vapour at equilibrium. $\left(P_A^0 = 80\text{cm Hg},\ P_B^0 = 30\text{cm Hg}\right)$

Solution:

$$\frac{1}{P_{total}} = \frac{\gamma_A}{P_A^0} + \frac{\gamma_B}{P_B^0} = \frac{0.4}{80} + \frac{0.6}{30} = \frac{1}{40}$$

P_{total} = 40 cm Hg

Illustration 18:

Liquids 'A' and 'B' form an ideal solution. Calculate the molar-fraction of 'A' in vapour form above the liquid solution containing 25 mole-percent of 'A' at equilibrium $\left(P_A^0 = 0.2\text{atm},\ P_B^0 = 0.5\text{atm}\right)$

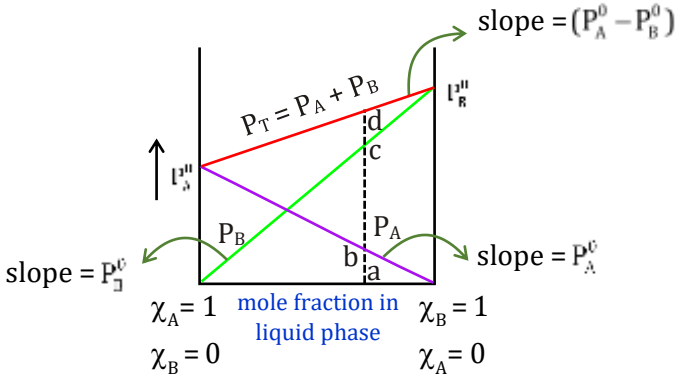
Solution:

$$\gamma_A = \frac{P_A}{P_{total}} = \frac{\chi_A \cdot P_A^0}{\chi_A \cdot P_A^0 + X_B \cdot P_B^0} = \frac{0.25 \times 0.2}{0.25 \times 0.2 + 0.75 \times 0.5} = \frac{2}{17}$$

Graphs for ideal binary solution of liquid A & liquid B :

(Assume $P_A^0 < P_B^0$)

I. Vapour pressure v/s liquid composition :



$P_A = \chi_A P_A^0 = (1 - \chi_B)P_A^0$

$P_A = P_A^0 - \chi_B P_A^0$

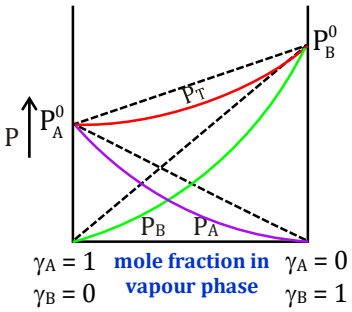
$P_B = \chi_B P_B^0$

$P_T = \chi_A P_A^0 - \chi_B P_B^0 = (1-\chi_B)P_A^0 + \chi_B P_B^0$

$\therefore \quad P_T = P_A^0 + \chi_B (P_B^0 - P_A^0)$

As $P_T = P_A + P_B$, ad = ab + ac

II. Vapour pressure V/s vapour composition

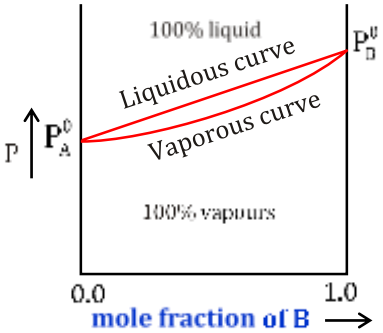


$$\frac{1}{P_T} = \frac{\gamma_A}{P_A^0} + \frac{\gamma_B}{P_B^0}$$

$$\frac{1}{P_T} = \frac{1}{P_A^0} + \gamma_B\left(\frac{1}{P_B^0} - \frac{1}{P_A^0}\right) \; ; \quad \frac{1}{y} = c + mx \,,$$

Graph will not be a straight line.

III. Vapour pressure V/s composition :



(i) The V.P. of ideal solution always lie in between the V.P. of pure components.

(ii) Below vaporous curve, the system will by 100% vapour & above liquidous and curve, 100% liquid. Both the physical states exists only in between the curves.

(iii) At any composition, the physical state of system may be changed by changing the pressure.

(iv) At any pressure in between P_A^0 and P_B^0, the physical state of system may be changed by changing the composition.

Boiling point :

Boiling point of a liquid is the temperature at which the vapour pressure of the liquid become equal to the atmospheric pressure.

Illustration 19:

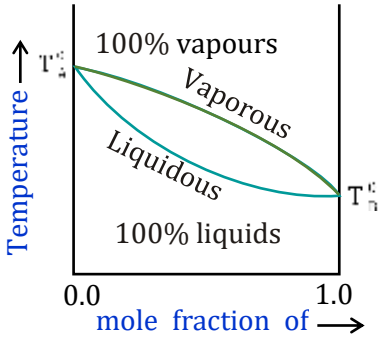
Liquid 'A' and 'B' form an ideal solution. At 27°C, the vapour pressure of pure liquids 'A' and 'B' are 0.6 atm and 1.2 atm, respectively. What the composition of liquid solution boiling at 27°C?

Solution:

$P_T = \chi_A \cdot P_A^0 + \chi_B \cdot P_B^0$

or $1 = \chi_A \times 0.6 + (1-\chi_A) \times 1.2 \quad \Rightarrow \quad \chi_A = \frac{1}{3}$

Boiling point curves for ideal binary solution :



(i) The boiling point of ideal solution always lie in between the boiling points of pure liquids.

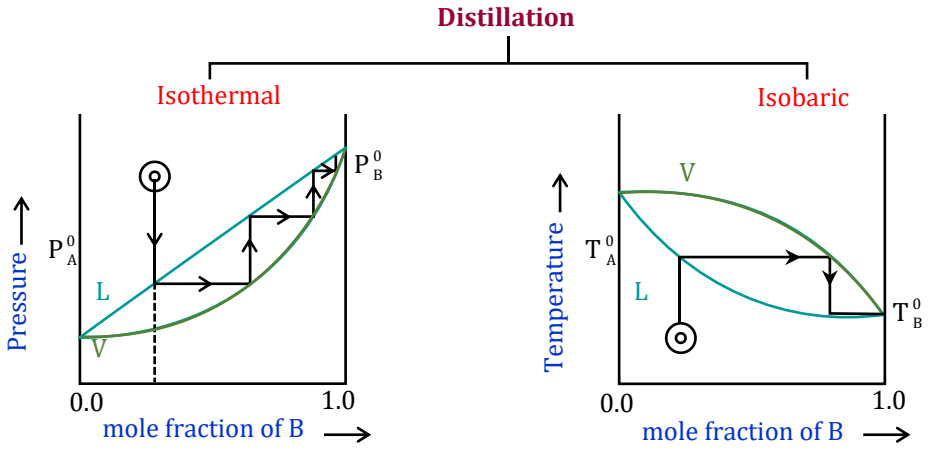
(ii) Below liquidus curve, the system in 100% liquid and above vapours curve, the system is 100% vapour. Both the physical states exists only in between the curves.

(iii) At any composition, the physical state of system may be changed by changing the temperature.

(iv) At any temperature in between T_A^0 and T_B^0, the physical state of system may be changed by changing the composition.

Distillation :

It is the method of seperation of liquids by converting them into vapours (boiling).

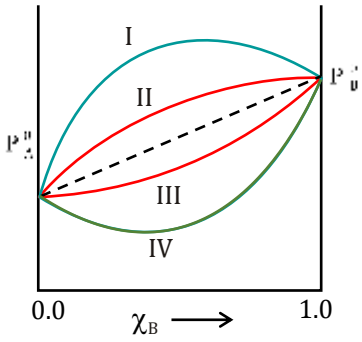


(i) The separation of liquid by distillation occurs because at any T or P, the composition of distillate or condensate is different than the composition of original liquid.

(ii) With the elimination of vapour above the liquid, the boiling point of residual liquid increases.

(iii) The boiling point of distillate is less than that of original liquid.

Graphs for Non-ideal solutions and azeotropic mixture :



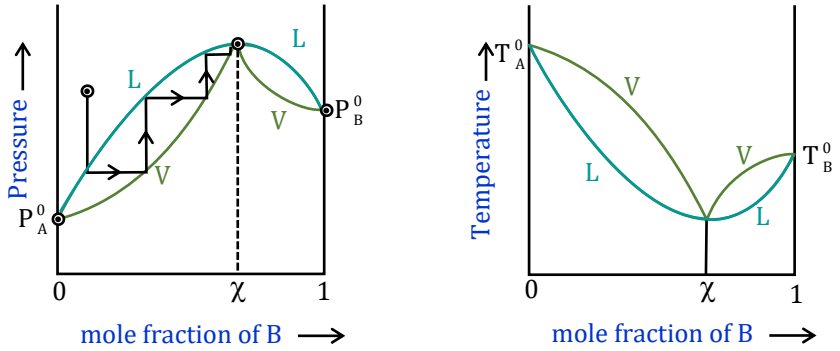
(I) Large positive deviation : $(V.P.)_{solution} > P_B^0$ at some composition

(II) Small positive deviation : $P_A^0 < (V.P.)_{solution} < P_B^0$

(III) Small negative deviation : $P_A^0 < (V.P.)_{solution} < P_B^0$

(IV) Large negative deviation : $(V.P.)_{solution} < P_A^0$ at some composition

Large positive deviation (Minimum boiling azeotrope) :



The solution of large positive deviation cannot be separated by distillation because at composition 'χ', the liquid & vapour composition becomes identical.

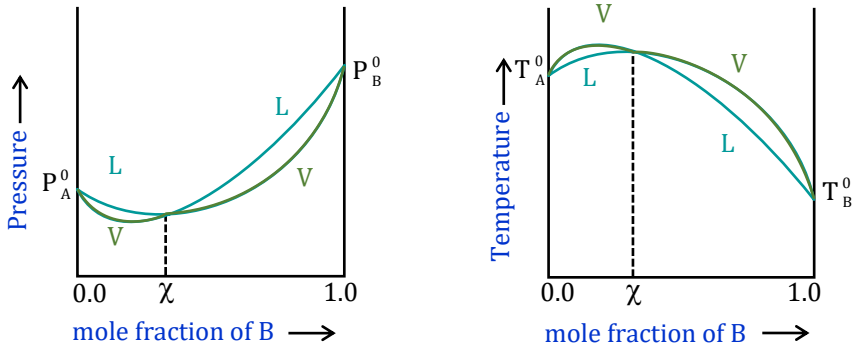
Such solution which cannot be separated by distillation are called **azeotropic mixture or constant boiling solution.**

At any composition less than χ, traces of pure A may be obtained but not pure B. Similarly, at composition greater than χ, traces of pure B may be obtained but not pure A.

Minimum Boiling Point Azeotropic

Mixture	% Composition of azeotrope	Boiling point (pressure = 1 atm)
1. Water-Ethanol	96 Ethanol	78.15° C
2. Pyridine-Water	57.00 Pyridine	92.60° C
3. Ethanol-Benzene	32.4 Ethanol	67.80° C
4. Acetic acid-Toluene	28.0 Acetic acid	105.40° C

Large negative deviation (Maximum boiling azeotrope) :



Maximum Boiling Point Azeotropic

Mixture	% Composition of azeotrope	Boiling point (pressure = 1 atm)
1. Nitric acid-Water	68% Nitric acid	125.5° C
2. Acetic acid-Pyridine	65% Pyridine	139.0° C
3. Chloroform-Acetone	80% Chloroform	65.0° C
4. Hydrogen chloride-Water	79.8% Water	108.6° C

Note :

Azeotrope is not formed in ideal solution or solution of small deviations.

Illustration 20:

Liquids 'A' and 'B' form an ideal solution. At 80°C, P_A^0 = 0.4 bar and P_B^0 = 0.4 bar. All the vapour above the liquid solution containing equal moles of both the liquids at equilibrium is collected in another empty vessel and condensed. Now, the condensate is heated to 80°C and all the vapours above the liquid solution at equilibrium is again collected in another empty vessel and condensed. What is the mole-fraction of 'B' is new condensate ?

Solution:

For the first condensate,

$$\frac{n_B'}{n_A'}=\frac{\chi_B'}{\chi_A'}=\frac{\gamma_B}{\gamma_A}=\frac{\chi_B}{\chi_A}\cdot\frac{P_A^0}{P_B^0}=\frac{n_B}{n_A}\times\frac{P_B^0}{P_A^0}$$

For second condensate,

$$\frac{n_B''}{n_A''}=\frac{\chi_B''}{\chi_A''}=\frac{\gamma_B'}{\gamma_A'}=\frac{\chi_B'\cdot P_B^0}{\chi_A'\cdot P_A^0}=\frac{n_B}{n_A}\times\left(\frac{P_B^0}{P_A^0}\right)^2=\frac{x}{x}\times\left(\frac{0.8}{0.4}\right)^2=\frac{4}{1}$$

$\therefore$ Mole fraction of $B=\frac{4}{5}=0.8$

Note :

For multi-step condensation at constant temperature,

$$\boxed{\frac{n_B^f}{n_A^f}=\frac{n_B^i}{n_B^i}\cdot\left(\frac{P_B^0}{P_A^0}\right)^n}$$ n : number of steps

Illustration 21:

Liquid A & B form an ideal solution. In a cylinder piston arrangement, 2 moles of vapours of liquid A & 3 moles of vapours of liquid B are taken at 0.3 atm., P_A^0 = 0.4 atm, P_B^0 = 0.6 atm.

(i) Predict whether vapours will condense or not ?

(ii) If the vapours are compressed slowly & isothermally, at what pressure Ist drop of liquid will form ?

(iii) If the initial volume of vapours was 10L, at what volume Ist drop of liquid will form ?

(iv) What is the composition of Ist drop of liquid formed ?

(v) If the vapours are further compressed slowly & isothermally, at what P almost complete condensation will occur ?

(vi) What is the composition of last traces of vapours remained ?

(vii) What is the composition of system at 0.58 atm ?

(viii) What is the composition of system at 0.51 atm ? Also calculate moles of A & B in liquid & vapour form.

(ix) At what P, half of the total amount of vapours will condense ?

Solution:

(i) $\frac{1}{P_T}=\frac{\gamma_A}{P_A^0}+\frac{\gamma_B}{P_B^0}=\frac{2/5}{0.4}+\frac{3/5}{0.6} \Rightarrow P_{total}$ = 0.5 atm > 0.3 atm

$\therefore$ 100% gas, no condensation

(ii) 0.5 atm.

(iii) $P_iV_i = P_fV_f$

$$V_f = \frac{0.3\times10}{0.5} = 6L$$

(iv) $P_{total} = \chi_A \cdot P_A^0 + \chi_B \cdot P_B^0$

or $0.5 = \chi_A \times 0.4 + (1 - \chi_A) \times 0.6 \Rightarrow \chi_A = 0.5$

(v) $P_T = 0.4 \times 0.4 + 0.6 \times 0.6 = 0.52$ atm

Note :

For a pure liquid, there is a fixed P(V.P.) below & above which, the system will be 100% gas & 100% liquid, respectively but for a solution, a pressure range exist in which both physical states will be present.

(vi) $Y_A = \frac{\chi_A \cdot P_A^0}{P_{total}} = \frac{0.4\times0.4}{0.52} = \frac{4}{13}$

(vii) 100% liquid, A = 2mole and B = 3 mole

(viii) $P_{total} = \chi_A P_A^0 + \chi_B P_B^0$

$0.51 \times \chi_A \times (0.4) + (1 - \chi_A) \times 0.6$ &

$\chi_A = 0.45$

$Y_A = \frac{\chi_A P_A^0}{P_{total}} = \frac{0.45\times0.4}{0.51} = 0.35$

A = 2 mol
B = 3 mol

Liquid	Vapor
A = x mol	A = (2 – x)
B = y mol	B = (3 – y)

$$\chi_A = \frac{9}{20} = \frac{x}{x+y} \text{ and } \gamma_A = \frac{18}{51} = \frac{2-x}{(2-x)+(3-y)}$$

$\therefore$ x = 1.09 ; y = 1.33

(ix)

A = 2 mol
B = 3 mol

Liquid = 2.5 mole	Vapor = 2.5 mole
A = z mole	A = (2 – z) mole
B = (2.5 – z) mole	B = (0.5 – z) mole

$$P_T = \frac{z}{2.5} \times 0.4 + \frac{2.5-z}{2.5} \times 0.6$$

$$\frac{2-z}{2.5} = \frac{z \times 0.4}{2.5 \times P_T}$$

On solving, z = 1.12, P_T = 0.5104 atm

Colligative properties :

Properties of a solution which depends on the number of solute particles irrespective of their nature, relative to the total number of particles present in solution are called colligative properties.

The following properties are colligative properties of solution :

(i) Relative lowering of vapour pressure.

(ii) Elevation in boiling point.

(iii) Depression in freezing point.

(iv) Osmotic pressure.

Lowering of vapour pressure :

When a non-volatile solute 'A' is dissolved in a pure solvent 'B', the vapour pressure of the solvent is lowered i.e. the vapour pressure of a solution is always lower than that of pure solvent, because the escaping tendency of solvent molecules decreases.

If at a certain temperature P° is the vapour pressure of pure solvent, and P_s is the vapour pressure of solution then

Lowering of vapour pressure = P° – P_s

Relative lowering of vapour pressure = $\frac{P^0 - P_s}{P^0}$

from equation (8)

$$\frac{P^0 - P_S}{P^0} = \frac{\Delta P}{P^0} = \frac{n_A}{n_A + n_B} = \chi_A$$

For a very dilute solution $n_A << n_B$

so $$\frac{P^0 - P_S}{P^0} = \frac{n_A}{n_B} = \frac{w_A}{m_A} \times \frac{m_B}{w_B}$$

Illustration 22:

Calculate the vapour pressure lowering caused by addition of 50 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.

Solution:

According to Raoult's law,

$$\frac{P_0 - P_s}{P_0} = \frac{n}{n+N} \text{ or } \Delta P = \frac{n}{n+N}.P_0$$

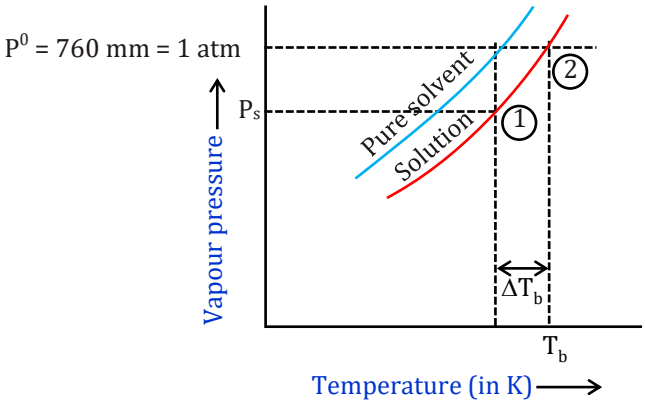
Given : $n = \frac{50}{342} = 0.146$; $N = \frac{500}{18} = 27.78$ and $p_0 = 23.8$ mmHg

Substituting the values in the above equation,

$$\Delta P = \frac{0.146}{0.146+27.78} \times 23.8 = 0.124 \text{ mm Hg}$$

Elevation in boiling point (Ebullioscopy) :

$\text{solvent}(\ell) \rightleftharpoons \text{solvent}(g)$



The vapour pressure curve for solution lies below curve for pure solvent.
ΔT_b denotes the elevation of boiling point of a solution.

When a non-volatile solute A is dissolved in a pure solvent B, its vapour pressure decreases and hence the boiling point increases. The difference ΔT_b of boiling points of the solution and pure solvent is called elevation in boiling point.

If is the boiling point of pure solvent and T_b is the boiling point of the solution then, $T_b > T_b^0$

and the elevation in boiling point $\Delta T_b = T_b - T_b^0$

Experiments have shown that for dilute solutions, the elevation of boiling point (ΔT_b) is directly proportional to the molal concentration of the solute in a solution. Thus

$\Delta T_b \propto m$

or $\Delta T_b = K_b.m$

where K_b = boiling point elevation constant or molal elevation constant or ebulioscopic constant.

Molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_b = \frac{RT^{\circ 2}_b.M}{1000\Delta H_{vap}} = \frac{RT^{\circ 2}_b}{1000 L_{vap}}$$

Where, R is molar gas constant = 2 cal/mol–K, M = molar mass of solvent

T_b is the boiling point of the pure solvent (in K)

and ΔH_{vap} is molar enthalpy of vaporisation of pure solvent (unit cal/mole or J/mole)

L_{vap} is latent heat of vaporisation in cal/g or J/g.

For water $K_b = \frac{2\times(373)^2}{1000\times540} = 0.515$ = K-kg/mol

The molal elevation constant for some common solvents are given in the following table

Solvent	B.P. (°C)	Molal elevation constant
Water	100.0	0.52
Acetone	56.0	1.70
Chloroform	61.2	3.63
Carbon tetrachloride	76.8	5.03
Benzene	80.0	2.53
Ethyl alcohol	78.4	1.20

Illustration 23:

0.15 g of a substance dissolved in 15 g of solvent boiled at a temperature higher by 0.216°C than that of the pure solvent. What is the molecular weight of the substance. [K_b for solvent = 2.16 K-kg/mol]

Solution:

Given : K_b = 2.16°C, w = 0.15 g, ΔT_b = 0.216°C, W = 15 g

ΔT_b = molality × K_b

$$\Delta T_b = \frac{w}{m\times W}\times1000\times K_b$$

$$0.216 = \frac{0.15}{m\times15}\times1000\times2.16$$

$$m = \frac{0.15\times1000\times2.16}{0.216\times15} = 100$$

Illustration 24:

The rise in boiling point of a solution containing 1.8 g glucose in 100 g of a solvent is 0.1°C. The molal elevation constant of the liquid is :–

Solution:

ΔT_b= 0.1°C, m = 180, W = 100, w = 1.8

$$K_b = \frac{\Delta T_b\times m\times W}{1000\times w} = \frac{180\times0.1\times100}{1000\times1.8} = 1.0$$

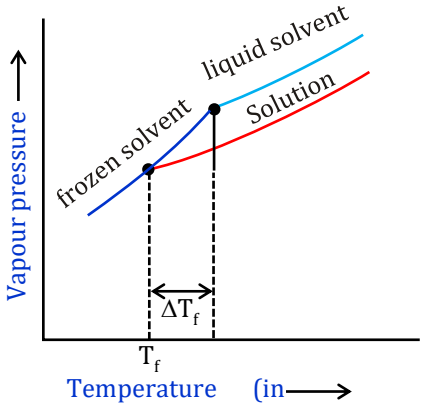
Depression in freezing point (Cryoscopy) :

The freezing point of a liquid is that temperature at which the liquid and its solid state exist in equilibrium with each other. It may also be defined as the temperature at which the liquid and solid states of a substance have the same vapour pressure.

When a non-volatile non-electrolyte is dissolved in a pure solvent, the vapour pressure of the solvent is lowered and it became equal to that of solid solvent at lower temperature.

If T_f^0 is the freezing point of pure solvent and (T_f) is the freezing point of its solution then,

$$T_f < T_f^0$$



The difference in the freezing point of pure solvent and solution is the depression of freezing point (ΔT_f)

Thus, $T_f^0 - T_f = \Delta T_f$

Similar to elevation in boiling point, depression in freezing point for dilute solution is directly proportional to its molality,

$\Delta T_f \propto m$

or $\Delta T_f = K_f.m$

where K_f is called freezing point depression constant or molal depression constant or cryoscopic constant. K_f is characteristic of a particular solvent and can be calculated from the thermodynamical relationship

$$K_f = \frac{R \cdot T_f^{0^2} \cdot M}{1000 \cdot \Delta H_{fus}} = \frac{RT^{\circ 2}_f}{1000 L_{fus}}$$

where, T_f^0 is the freezing point of pure solvent in (Kelvin) and ΔH_{fus} is the molar enthalpy of fusion pure solvent (unit cal/mol or J/mol).

L_{fus} is latent heat of fusion (unit cal/g or J/g)

For water,

$$K_f = \frac{0.002 \times (273)^2}{80} = 1.86 \text{ K-kg/mol}$$

The molal depression constant for some common solvents are given in the following table

Solvent	F.P.(°C)	Molal depression solvents
Water	0.0	1.86
Ethyl alcohol	– 114.6	1.99
Chloroform	– 63.5	4.79
Carbon tetrachloride	– 22.8	31.8
Benzene	5.5	5.12
Camphor	179.0	39.70

Illustration 25:

If freezing point of a solution prepared from 1.25 g of a non-electrolyte and 20 g of water is 271.9 K, the molar mas of the solute will be – (K_f of water = 1.86 K-kg/mol)

Solution:

Given, $T_f = 271.9$ K

$w = 1.25$ g $W = 20$ g $K_f = 1.86$

$\Delta T_f = T_f^0 - T_f = 273 - 271.9 = 1.1$ K

ΔT_f = molality × K_f

$$\Rightarrow \Delta T_f = \frac{w}{m \times W} \times 1000 \times K_f$$

$$\text{or } m = \frac{w \times 1000 \times K_f}{\Delta T_f \times W} = \frac{1.25 \times 1000 \times 1.86}{1.1 \times 20} = 105.68 \text{ mol/kg}$$

Illustration 26:

Molal depression constant for water is 1.86. What is freezing point of a 0.05 molal solution of a non-electrolyte in water ?

(K_f of water = 1.86 K-kg/mol)

Solution:

ΔT_f = molality × K_f

= 0.05 × 1.86 = 0.093°C

T_f = – 0.093 = 0 – 0.093

T_f = – 0.093°C

Illustration 27:

2m aqueous urea solution is cooled to –7.44°C. Calculate the mass percent of water present in solution, which will separate as ice, (K_f of water = 1.86 K-kg/mol)

Solution:

Let the initial mass of water in the solution = 1kg

$\therefore$ Moles of solute = 2

Now, $\Delta T_f = K_f.m = K_f . \frac{n_{solute}}{Kg_{solvent}}$ or $7.44 = 1.86 \times \frac{2}{Kg_{solvent}}$

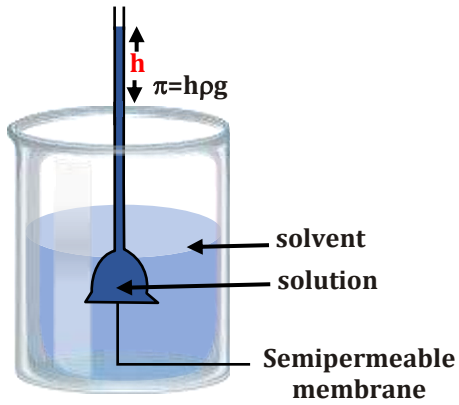
$\therefore$ $Kg_{solvent}$ left in the solution = 0.5

$\therefore$ Mass percent of water separated as ice = $\frac{0.5}{1} \times 100 = 50\%$

Osmosis and osmotic pressure :

Osmosis :

Osmosis is defined as the spontaneous flow of solvent molecules through semipermeable membrane from a pure solvent to solution.



Level of solution rises in the funnel due to osmosis of solvent

Semi-permeable membrane (SPM) :

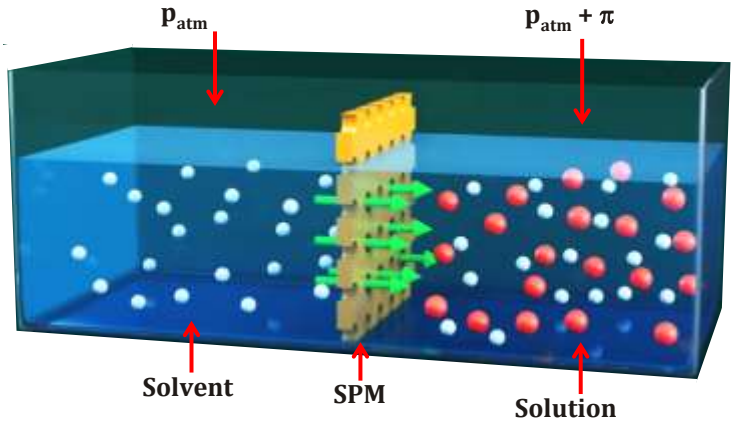
There are the membranes (substances) which allow selective movement of particles across them. For a solution of solid solute in a liquid solvent, ideal SPM allow free movement of solvent particles across it, but not solute particles. These membranes contain a network of submicroscopic holes or pores through which small solvent molecules may pass but not the bigger solute particle.

Osmotic presssure (π) :

It is the pressure which should be applied on the solution to just prevent osmosis or the hydrostatic pressure built up on the solution which just stops the osmosis.

osmotic pressure = hydrostatic pressure

$\pi = \rho gh$



The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis

Van't Hoff laws :

(i) The osmotic pressure (π) of a solution is directly proportional to its molar concentration(C), when the temperature is kept constant. (Van't Hoff-Boyle's law)

thus $\pi \propto C$ (when temperature is constant)

(ii) Concentration remaining same, the osmotic pressure of a dilute solution is directly proportional to its absolute temperature (T). (Van't Hoff-Charle's law)

$\pi \propto T$ (when C is constant)

Combining the two laws, i.e., when concentration and temperature both are changing, the osmotic pressure will be given by :

$\pi \propto C.T$ or $\pi = CRT$

Where R = Universal gas constant.

Isotonic or iso-osmotic solution :

Solutions which have the same osmotic pressures at a given temperature are called isotonic or iso-osmotic solutions.

When isotonic solutions are separated by semipermeable membrane, no osmosis occurs between them. For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) sodium chloride solution, called normal saline solution and it is safe to inject intravenously. On the other hand, if we place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cells and they would shrink. Such a solution is called **hypertonic**. If the salt concentration is less than 0.9% (mass/volume), the solution is said to be **hypotonic**. In this case, water will flow into the cells if placed in this solution and they would swell.

Illustration 28:

A cane sugar solution has an osmotic pressure of 2.46 atm at 300 K. What is the strength of the solution.

Solution:

$$\pi = CRT \text{ or } C = \frac{\pi}{RT} = \frac{2.46}{300 \times 0.0821} = 0.1\,M$$

Illustration 29:

A solution containing 8.6 g urea in one litre was found to be isotonic with 0.5% (wt./vol.) solution of an organic, non-volatile solution. The molecular weight of latter is

Solution:

Solutions are isotonic

so $\pi_1 = \pi_2$

$$\frac{n_1}{V_1}RT = \frac{n_2}{V_2}RT \qquad \{R \text{ \& } T \text{ are constant}\}$$

so, $\frac{n_1}{V_1} = \frac{n_2}{V_2}$

or $\left(\frac{w_1}{m_1 \times v_1}\right)_{urea} = \left(\frac{w_2}{m_2 \times v_2}\right)_{organic}$

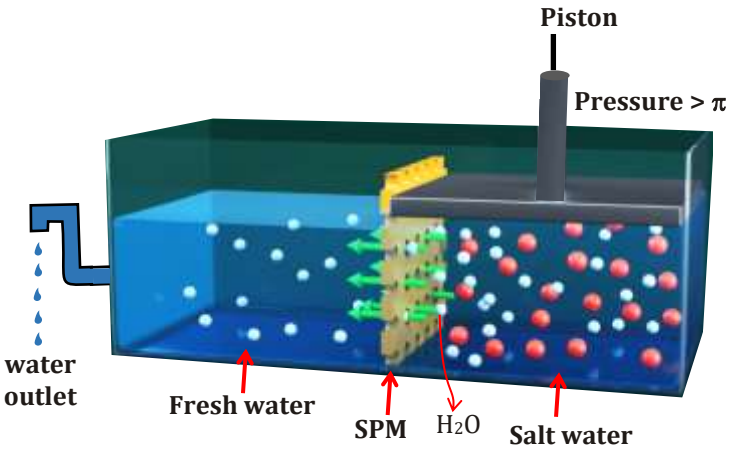
or $\frac{8.6}{60 \times 1000} = \frac{0.5}{m_2 \times 100}$

$m_2 = 34.89$ gm/mol

Reverse Osmosis and water purification :

If external pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, i.e., in reverse direction of the ordinary osmosis.

Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.



Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

Abnormal colligative properties :

It has been observed that difference in the observed and calculated molecular masses of solute is due to association or dissociation of solute molecules in solution. It results in a change in the number of particles in solution.

Van't Hoff in 1880, introduced a factor, called Van't Hoff factor (i). The factor 'i' is defined as

$$i = \frac{\text{observed colligative property}}{\text{Calculated colligative property}} = \frac{\text{Normal molecular mass}}{\text{observed molecular mass.}}$$

$$= \frac{\text{total number of particles after dissociation / association}}{\text{Number of particles initially taken}}$$

In case of association of solute particles in solution, the observed molecular weight of solute being more than the normal, the value of factor 'i' is less than unity (i.e. $i < 1$), while for dissociation the value of i is greater than unity (i.e. $i > 1$), because the observed molecular weight has lesser value than normal molecular weight.

Values of Van't Hoff factor, I, at Various Concentrations for NaCl, KCl, $MgSO_4$ and K_2SO_4

Salt	*Values of i			Van't Hoff factor I for complete dissociation of solute
	0.1 m	0.1 m	0.001 m	
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
$MgSO_4$	1.21	1.53	1.82	2.00
K_2SO_4	2.32	2.70	2.84	3.00

Calculation of 'i' in case of dissociation

	A_xB_y	$\longrightarrow$	$x\,A^{y\oplus}$	+	$yB^{x\ominus}$
Initial mol	1		0		0
after dissociation	$1-\alpha$		$x\alpha$		$y\alpha$

Total no. of solute particles = $1 - \alpha + x\alpha + y\alpha = 1 - \alpha + \alpha(x + y)$

or $i = 1 - \alpha + n\alpha$ [where $x + y = n$ (total ions.)]

or $i = 1 + \alpha(n - 1)$

For strong electrolytes : $\alpha = 1$ or 100%, so i = n (total no. of ions)

$NaCl \rightarrow Na^{\oplus} + Cl^{\ominus}$ (i = 2)

$K_2SO_4 \rightarrow 2K^{\oplus} + SO_4^{2\ominus}$ (i = 3)

For complex compound

$K_4[Fe(CN)_6] \rightarrow 4K^{\oplus} + [Fe(CN)_6]^{4\ominus}$

$\Rightarrow n = 5$

S.No.	Solute type	Example	Ionisation	No. of particles in the solution from 1 mole solute (n)	Van't Hoff factor ('i')	Abnormal molecular mass
1.	Non-electrolyte	Urea, sucrose, glucose, fructose	–	1	1	m_{normal}
2.	Binary electrolyte AB type	NaCl, KCl, HCl, CH_3COOH, NH_4OH, NaOH etc.	$AB \rightleftharpoons A^{\oplus} + B^{\ominus}$ $1-\alpha \quad \alpha \quad \alpha$	2	$1 + \alpha$	$\frac{m_{normal}}{1+\alpha}$
3.	Ternary electrolyte AB_2 type or A_2B type	$CaCl_2$, $BaCl_2$, H_2SO_4, $K_2[PtCl_6]$	$AB_2 \rightleftharpoons A^{2\oplus} + 2B^{\ominus}$ $1-\alpha \quad \alpha \quad 2\alpha$ $A_2B \rightleftharpoons 2A^{\oplus} + B^{\ominus}$ $1-\alpha \quad 2\alpha \quad \alpha$	3 3	$1 + 2\alpha$ $1 + 2\alpha$	$\frac{m_{normal}}{1+2\alpha}$ $\frac{m_{normal}}{1+2\alpha}$

4.	Quanternary electrolyte AB_3 or A_3B type	$AlCl_3$, $K_3[Fe(CN)_6]$	$AB_3 \rightleftharpoons A^{3\oplus} + 3B^{\ominus}$ $1-\alpha \quad \alpha \quad 3\alpha$ $A_3B \rightleftharpoons 3A^{\oplus} + B^{3\ominus}$ $1-\alpha \quad 3\alpha \quad \alpha$	4 4	$1+3\alpha$ $1+3\alpha$	$\frac{m_{normal}}{1+3\alpha}$ $\frac{m_{normal}}{1+3\alpha}$
5.	General electrolyte AB_{n-1}	One mole of solute giving 'n' ions in the solution	$AB_{n-1} \rightleftharpoons A^{\oplus(n-1)} + (n-1)B^{\ominus}$ $1-\alpha \quad \alpha \quad (n-1)\alpha$	n	$1+(n-1)\alpha$	$\frac{m_{normal}}{[1+(n-1)\alpha]}$

Calculation of 'i' in case of association :

	nA	$\longrightarrow$	$(A)_n$
Initial mol	1		0
after dissociation	$1-\alpha$		α/n

$$i = \frac{1-\alpha+\frac{\alpha}{n}}{n}, \alpha = \text{degree of association}$$

$$i = 1 + \alpha\left(\frac{1}{n}-1\right)$$

Illustration 30:

Determine the amount of $CaCl_2$ (i = 2.47) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27°C.

Solution:

We know that,

$$\pi = i\frac{n}{V}RT \Rightarrow \pi = i\frac{w}{MV}RT \Rightarrow w = \frac{\pi MV}{iRT} = \frac{0.75\times111\times2.5}{2.47\times0.0821\times300} = 3.42\ g$$

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

Illustration 31:

19.5 g of CH_2FCOOH is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.0°C. Calculate the Van't Hoff factor and dissociation constant of fluoro-acetic acid.

Solution:

It is given that :

$w_1 = 500\ g$

$w_2 = 19.5\ g$

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

$\Delta T_f = 1\ K$

We know that :

$$M_2 = \frac{K_f\times w_2\times1000}{\Delta T_f\times w_1} = \frac{1.86\,K\,kg\,mol^{-1}\times19.5g\times1000g\,kg^{-1}}{500g\times1K} = 72.54\ mol^{-1}$$

Therefore, observed molar mass of CH_2FCOOH, $(M_2)_{obs} = 72.54$ mol

The calculated molar mass of CH_2FCOOH is :

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

Therefore, Van't Hoff factor, $i = \frac{(M_2)_{cal}}{(M_2)_{obs}} = \frac{78\,g\,mol^{-1}}{72.54\,g\,mol^{-1}} = 1.0753$

Let α be the degree of dissociation of CH_2FCOOH

	$CH_2FCOOH \rightleftharpoons$	$CH_2FCOO^{\ominus}$ +	$H^{\oplus}$	
Initial conc.	C mol L^{-1}	0	0	
At equilibrium	C (1 – α)	Cα	Cα	Total = C (1 + α)

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

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

$= 1.0753 - 1 = 0.0753$

Now, the value of K_a is given as :

$K_a = \frac{[CH_2FCOO^{\ominus}][H^{\oplus}]}{[CH_2FCOOH]} = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$

Taking the volume of the solution as 500 mL. We have the concentration :

$C = \frac{19.5\times1000}{78\times500} M = 0.5\ M$

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

$= \frac{0.5\times(0.0753)^2}{1-0.0753} = \frac{0.5\times0.00567}{0.9247} = 0.00307$ (approximately) $= 3.07 \times 10^{-3}$

Illustration 32:

Which of the following solutions will exhibit highest boiling point?

(A) 0.01 M Na_2SO_4 (B) 0.01 M KNO_3 (C) 0.015 M urea (D) 0.015 M glucose

Ans. (A)

Solution:

$\Delta T = i \times K_b \times m$

$i \times m$ of Na_2SO_4 is highest, hence its boiling point will also be highest.

Na_2SO_4 $i \times m = 3 \times 0.01 = 0.03$

KNO_3 $i \times m = 2 \times 0.01 = 0.02$

Urea $i \times m = 1 \times 0.015 = 0.015$

Glucose $i \times m = 1 \times 0.015 = 0.015$

Illustration 33:

Mixture of volatile components A and B has total vapour pressure (in torr) :

$P = 254 - 119\ x_A$

Where χ_A is mol fraction of A in mixture.

Hence P_A^0 and P_B^0 are (in torr)

(A) 254, 119 (B) 119, 254 (C) 135, 254 (D) 154, 119

Ans. (C)

Solution:

when $\chi_A = 0, \chi_B = 1$

$\therefore \quad P = P_B^0$

$\therefore \quad P_B^0 = 254,$

when $\chi_A = 1, \chi_B = 0$

$\therefore \quad P_A^0 = P = 254 - 119 = 135$

Illustration 34:

Heptane and octane form ideal solution. At 373 K, the vapour pressures of the two liquids are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure, in bar, of a mixture of 25g of heptane and 35 g of octane ?

Solution:

(A) Heptane C_7H_{16} $\quad m_A = 100$

(B) Octane C_8H_{18} $\quad m_B = 114$

$$n_A = \frac{w_A}{m_A} = \frac{25}{100} = 0.25; \qquad n_B = \frac{35}{114} = 0.3$$

$$x_A = \frac{0.25}{0.25+0.30} = 0.45 \qquad x_B = \frac{0.3}{0.25+0.30} = 0.55$$

$= 0.45$

$p = p_A^0 x_A + p_B^0 x_B$

$= 105.2 \times 0.45 + 46.8 \times 0.55$

$= 47.34 + 25.74 = 73.08$ kPa

Advanced Level Illustrations

Illustration 1:

A certain substance 'A' tetramerises in water to the extent of 80%. A solution of 2.5 g of A in 100 g of water lowers the freezing point by 0.3°C. The molar mass of A is :

(A) 122 (B) 31 (C) 244 (D) 62

Ans. (D)

Solution:

$$\alpha = \frac{1-i}{1-\frac{1}{n}}$$

$$0.8 = \frac{1-i}{1-\frac{1}{n}}; i = 0.4$$

$$\Delta T = i \times K_f \times m$$

$$0.3 = 0.4 \times 1.86 \times \frac{w_B \times 1000}{m_B \times w_A}$$

$$0.3 = 0.4 \times 1.86 \times \frac{2.5 \times 1000}{m_B \times 100}$$

$$m_B = 62$$

Illustration 2:

What is the osmotic pressure of 12 % w/v solution of cane sugar (mol. wt. 342) at 17°C.

Solution:

12 g. sugar is dissolved in 100 mL

thus 342 g. sugar is dissolved in 8 litres

Now, $\pi V = ST$ $\{\because n = 1\}$

$$\pi = \frac{ST}{V} = \frac{0.0821 \times 290}{2.85} = 8.35 \text{ atm}$$

Illustration 3:

The freezing point depression of 0.001 m $K_x[Fe(CN)_6]$ is 7.10×10^{-3} K. Determine the value of x. Given, $K_f = 1.86$ K kg mol^{-1} for water.

Solution:

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

$$7.10 \times 10^{-3} = i \times 1.86 \times 0.001$$

$$i = 3.817$$

$$\alpha = \frac{i-1}{n-1}$$

$$1 = \frac{3.817-1}{(x+1)-1}$$

$$x = 2.817 \approx 3$$

$\therefore$ Molecular formula of the compound is $K_3[Fe(CN)_6]$.

Illustration 4:

Match the boiling point with K_b for x, y and z, if molecular weight of x, y and z are same. **[JEE 2003]**

	b.pt.	**K_b**
x	100	0.68
y	27	0.53
z	253	0.98

Solution:

$K_b(x) = 0.68$, $K_b(y) = 0.53$, $K_b(z) = 0.98$

Illustration 5:

During depression of freezing point in a solution, the following are in equilibrium **[JEE 2003]**

(A) liquid solvent-solid solvent (B) liquid solvent-solid solute

(C) liquid solute-solid solute (D) liquid solute-solid solvent

Ans. (A)

Solution:

Equilibrium exists between liquid solvent & solid solvent.

Illustration 6:

A 0.004 M solution of Na_2SO_4 is isotonic with a 0.010 M solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is **[JEE 2004]**

(A) 25% (B) 50% (C) 75% (D) 85%

Ans. (C)

Solution:

$\pi_{Na_2So_4} = \pi_{g10C^\circ}$

$i \times 0.004 = 0.010$

$i = 2.5 = 1 + 2\alpha \Rightarrow \alpha = 0.75$ or 75%