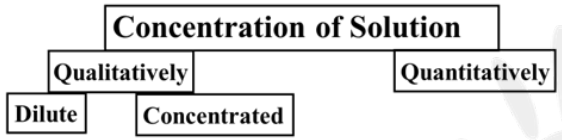
Solution

It is the homogeneous mixture of two or more component.

The substance which dissolves other substance is Solvent & the substance which is dissolved is Solute, independent of their quantity.

If both are soluble in each other then the substance present in larger amount by mole is Solvent.

A Solvent may exist in any state.



Percentage by Weight (w/w %)

Percentage by Volume (v/v %)

Weight by Volume (w/v %)

Mole fraction (X)

Molality

Molarity

Normality

Solubility

Maximum amount of Solute which can be dissolved in a specified amount of Solvent at constant temperature is called Solubility.

MIND MAP

Liquid Solution

1. Nature of Solute and Solvent.

2.Temperature.

3.Pressure.

Solubility of a 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 then following equilibrium exists.

$$\text{Solute} + \text{Solvent} \underset{\text{Crystallization}}{\overset{\text{Dissolution}}{\rightleftharpoons}} \text{Solution}$$

Effect of Temperature

The Solubility of a solid in a liquid is significantly affected by temperature changes.

This being dynamic equilibrium, must follow Le Chatelier's Principle.

($\Delta_{sol}H > 0$), the Solubility should increase with rise in temperature.

($\Delta_{sol}H < 0$) the solubility will decrease with rise in temperature.

Effect of Pressure

Pressure does not have any significant effect on Solubility of solid in liquid.

It is so because solid and liquid are highly incompressible and practically remain unaffected by changes in pressure.

Solubility of a Gas in a Liquid

Certain gases are highly soluble in water like NH_3, HCl etc.

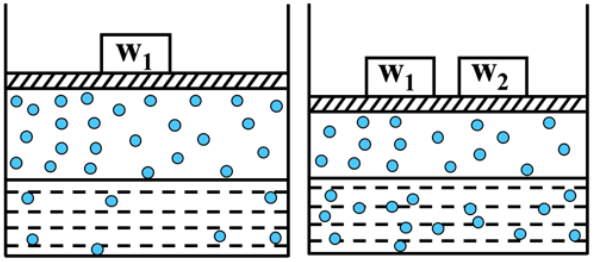
Certain gases are less soluble in water like O_2, N_2, He etc.

Solubility of gases is highly effected by pressure and temperature.

Effect of Pressure

Pressure has a significant effect on Solubility of gas in a liquid.

Increasing pressure increases Solubility.



(a) Low pressure (b) High pressure

Henry's Law

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

$P \propto X$

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

$P = K_H.X$

K_H = Henry's Constant

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.

Henry's Constant depends on nature of gas and temperature.

Now, according to Henry's law

$P = K_H.X$

For oxygen

$P_{O_2} = K_H . X_{O_2}$

Effect of Temperature

Solubility of gases in liquid decreases with rise in temperature.

MIND MAP

Liquid Solution

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 will decrease with increase of temperature.

K_H increases with increase in temperature therefore high K_H means low solubility.

Vapour Pressure of Liquid - Liquid Solutions

Let us consider a binary Solution of two volatile liquids and denote the two components as 1 and 2.

When taken in a closed vessel both the components would evaporate and eventually an equilibrium would be established between the vapour phase and the liquid phase.

Vapour Pressure of Liquid - Liquid Solutions

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When taken in a closed vessel both the components would evaporate and eventually an equilibrium would be established between the vapour phase and the liquid phase.

Let the total vapour pressure at this stage be P_{total} and P_1 and P_2 be the partial vapour pressures of the two components 1 and 2 respectively.

These partial pressures are related to the mole fraction x_1 and x_2 of the two component of 1 and 2 respectively.

The French Chemist, Francois Marte Raoult (1886) gave the quantitative relationship between them.

Raoult's Law

According to this 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.

(i) For liquid – liquid Solution

Let a mixture (Solution) be prepared by mixing n_A moles of liquid A and n_B moles of liquid B.

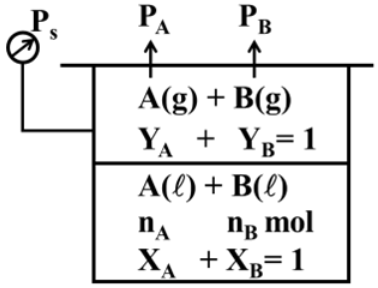
Let P_A and P_B be the partial pressures of two constituents A and B in solution and P_A^0 and P_B^0 the vapour pressures in pure state respectivity.

Thus, according to Raoult's law

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

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

If total pressure is P_S, then



$$P_s = P_A + P_B$$

$$= \frac{n_A}{n_A + n_B} P_A^0 + \frac{n_B}{n_A + n_B} P_B^0$$

$$= X_A P_A^0 + X_B P_B^0$$

MIND MAP

Liquid Solution

$$P_s = X_A P_A^0 + (1 - X_A) P_B^0$$

$$[\because \ X_A + X_B = 1]$$

$$P_s = X_A P_A^0 - X_A P_B^0 + P_B^0$$

$$P_s = X_A \left[P_A^0 - P_B^0\right] + P_B^0$$

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.

Let P_A and P_B be the partial pressure of vapours A and B respectively and total pressure P_S.

$$P_A = Y_A P_s \quad .....(1)$$

$$P_B = Y_B P_s \quad .....(2)$$

$$P_A = X_A P_A^0 \quad .....(3)$$

$$P_B = X_B P_B^0 \quad .....(4)$$

Equating eqs. (i) and (iii),

$$Y_A P_s = X_A P_A^0$$

$$\text{or } Y_A = \frac{X_A P_A^0}{P_S} = \frac{P_A}{P_S}$$

Similarly, equating eq. (ii) and (iv)

$$Y_B = \frac{X_B P_B^0}{P_S} = \frac{P_B}{P_S}$$

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

(ii) For Solid – liquid Solution

Let us assume A = Non volatile solid

B = Volatile liquid

According to Raoult's law –

$\because \ P_s = X_A P_A^0 + X_B P_B^0$

for A, $P_A^0 = 0$

$\therefore \ P_s = X_B P_B^0 \quad \because (5)$

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

here X_B is mole fraction of Solvent

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

$$P_S \propto \frac{n_B}{n_A + n_B}$$

i.e. Vapour pressure of Solution ∝ mole fraction of Solvent

$$\Rightarrow P_s = X_B P_B^0$$

$$\Rightarrow P_s = (1 - X_A) P_B^0$$

$$\Rightarrow P_s = P_B^0 - X_A P_B^0$$

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

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

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

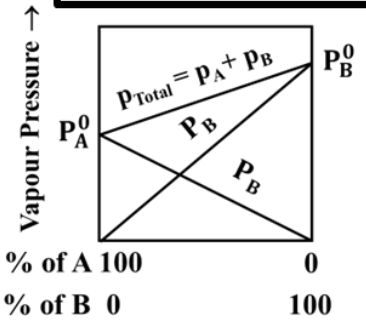
$$\text{or } \frac{P^0}{P^0 - P_S} = \frac{n_A + n_B}{n_A}$$

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

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

MIND MAP

Liquid Solution



Ideal and Non ideal Solutions

Comparison between Ideal and Non-ideal Solutions

Ideal Solutions	Non-ideal Solutions	
	+ve deviation from Raoult's law	–ve deviation from Raoult's law
Escaping tendency of 'A' and '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 components A and B is lowered showing lower vapour pressure than expected ideally.

Ideal Solutions	Non-ideal Solutions	
	+ve deviation from Raoult's law	–ve deviation from Raoult's law
$\Delta H_{mix} = 0$; 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.

Ideal Solutions	Non-Ideal Solutions	
	+ve deviation from Raoult's law	–ve deviation from Raoult's law
Obeys Raoult's law at every concentration	Do not obey Raoult's law.	Do not obey Raoult's law.

Ideal Solutions	Non-Ideal Solutions	
	+ve deviation from Raoult's law	–ve deviation from Raoult's law
A — A, A — B, B — B interactions should 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.	A – B, attraction force should be greater than A – A and B – B attractive forces. 'A' and 'B' have different shape.

Ideal Solutions	Non-ideal Solutions	
	+ve deviation from Raoult's law	–ve deviation from Raoult's law
$\Delta V_{mix} = 0$; total volume of Solution is equal to sum of volume of the components.	$\Delta V_{mix} > 0$; Volume is increased after dissolution.	$\Delta V_{mix} < 0$; volume is decreased during dissolution.

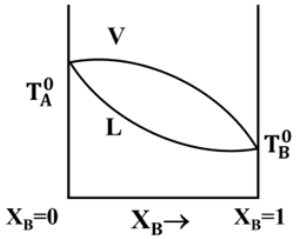
Ideal Solutions	Non-ideal Solutions	
	+ve deviation from Raoult's law	–ve deviation from Raoult's law
$P = p_A + p_B = p_A^0X_A + p_B^0X_B$	$P_A + P_B > p_A^0X_A + p_B^0X_B$	$P_A + P_B < p_A^0X_A + p_B^0X_B$

Ideal	+ve Deviation	-ve Deviation
Dilute solutions	Acetone + Ethanol	Phenol + Aniline
Benzene + Toluene	Acetone + CS_2	Acetone + Chloroform

MIND MAP

Liquid Solution

Vapour Liquid Equilibrium diagram

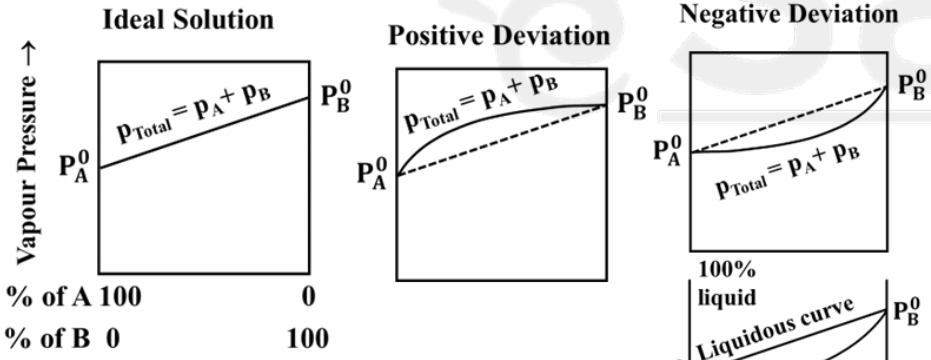


Distillation

It is the method of separation of liquid by converting them into vapours (boiling).

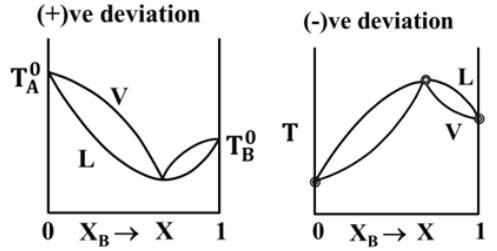
With the elimination of vapour above the liquid the boiling point of residual liquid increases.

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



Vapour Liquid Equilibrium Diagram

Graph for Non-Ideal Solution



Konowaloff's Rule

In ideal or non-ideal solution the vapour is always more rich in the component addition of which in liquid increases the vapour pressure of solution.

Azeotropic Mixtures

Binary mixtures that have same compostion in liquid and vapour phase and boil at a constant temperature and can be distilled unchanged in composition are known as Azeotropic mixture or simply Azeotropes.

Thus Azeotropes behave as pure liquid.

Note

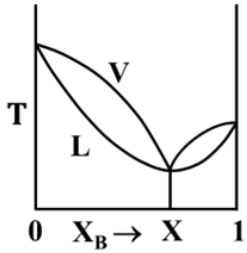
Azeotrope is always formed only in large (+)ve or (–)ve deviation.

Type of Azeotropic mixtures

There are two types of Azeotropes called as minimum boiling Azeotropes and maximum boiling Azeotropes respectively.

(i) Minimum boiling Azeotropic mixtures

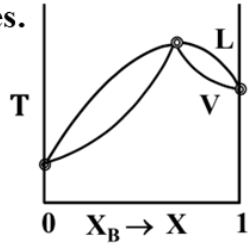
The non-ideal binary Solutions which show positive deviation from Raoult's law form minimum boiling Azeotropes at a constant composition.



Mixture	% Composition of Azeotrope	Boiling Point (Pressure = 1 atm)
1. Water-Ethanol	96 Ethanol	78.15°C

(ii) Maximum boiling Azeotropic mixtures

The non-ideal Solution which show negative deviation from Raoult's law form maximum boiling Azeotropes.



Maximum boiling point Azeotropes

Mixture	% Composition of Azeotrope	Boiling Point (Pressure = 1 atm)
1. Nitric acid-Water	68 Nitric acid	125.5°C

MIND MAP

Liquid Solution

Colligative Properties

Those properties of a dilute solution which depends upon the relative number of solute particles in a given volume of the solution or the mole fraction of the solute are called Colligative Properties.

The following four properties are colligative properties of solution-

Relative lowering of vapour pressure

Elevation in boiling point

Depression in freezing point

Osmotic pressure

Coll. prop. $\propto$ No. of particles/molecules/ions

$\propto$ No. of moles of solute

$\propto$ Mole fraction of solute

$\propto$ 1/mol. wt. of solute

(I) 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.

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^0 is the vapour pressure of pure Solvent, and P_s is the vapour pressure of Solution then

Lowering of vapour pressure = P^0-P_s

Relative lowering of vapour pressure

$$= \frac{P^0 - P_s}{P^0}$$

from equation

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

for a more dilute solution $n_A << n_B$

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

[Only for very dilute solutions]

Measurement of Relative Lowering in Vapour Pressure

(Ostwald and Walker Method)

It consists of two sets of bulbs.

The first set of three bulbs is filled with solution to half of their capacity and second set of another three bulbs is filled with the pure solvent.

The bulbs of Solution and pure Solvent are kept in a thermostat maintained at a constant temperature.

The air takes up an amount of vapours proportional to the vapour pressure of the solution first.

Then it takes up more amount of vapours from the solvent which is proportional to the difference in the vapour pressure of the solvent and the vapour pressure of solution i.e., $p^0 - p_s$.

The two sets of bulbs are weighed again.

The guard tubes are also weighed.

Loss in mass in the solution bulbs $\propto P_s$

Loss in mass in the solvent bulbs $\propto (P^0 - P_s)$.

$\propto p_0$

Total loss in both sets of bulbs $\propto$ $[P_s + (P_0 - P_s)]$

Total loss in mass of both sets of bulbs is equal to gain in mass of guard tubes.

$$\frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Total loss in mass in both sets of bulbs}}$$

$$= \frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}}$$

We know from Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{w_A/m_A}{w_A/m_A + w_B/m_B}$$

MIND MAP

Liquid Solution

$$\therefore \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of gaurd tubes}}$$

$$= \frac{w_A/m_A}{w_A/m_A + w_B/m_B}$$

The above relationship is used for calculation of molecular masses of non-volatile solutes.

For very dilute solutions, the following relationship can be applied

$$\frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of gaurd tubes}}$$

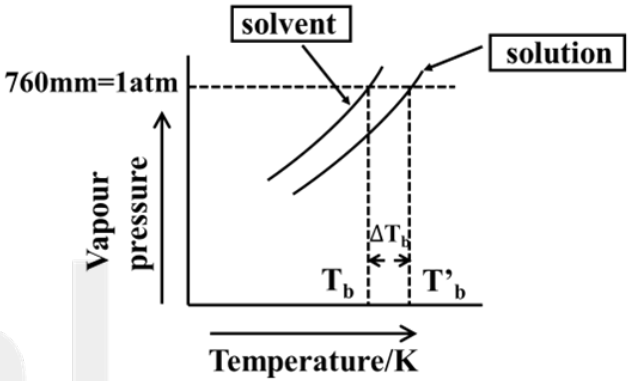
$$= \frac{w_A m_B}{w_B m_A}$$

When a non-volatile solute A is dissolved in a pure solvent B, its vapour pressure is decreased.

The difference ΔT_b of boiling points of the solution and pure solvent is called elevation in boiling point.

(ii) Elevation in boiling point (Ebullioscopy)

The normal boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atmospheric pressure. i.e. 760 mm of Hg.



The vapour pressure curve for solution lies below curve for pure solvent.

ΔT_b denotes the elevation of boiling point of a solution.

If T_b is the boiling point of pure solvent and T_b' is the boiling point of the solution then, $T_b' > T_b$.

The elevation in boiling point.

$\Delta T_b = T'_b - T_b$

The elevation in boiling point (ΔT_b) is directly proportional to lowering of vapour pressure of the solution i.e. $\Delta T_b \propto P^o - P_s$.

for a Solvent P^0 & m_B = const.

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

Where K = elevation constant

If $\frac{w}{m} = 1$

W = 100 grams

$$\therefore \Delta T_b = \frac{K}{100}$$

K' = molecular elevation constant

$\therefore$ K = 100 K'

$$\Delta T_b = \frac{100K' \times w}{m \times W}$$

If $\frac{w}{m} = 1$

W = 1000 grams

$$\therefore \Delta T_b = \frac{K}{1000} = K_b$$

(K_b = molal elevation constant or Ebulloscopic constant)

MIND MAP

Liquid Solution

K_b is defined as the elevation in boiling point produced when 1 mole of solute is dissolved in 1000 g of the solvent.

$\therefore \Delta T_b$ = molality × K_b

The elevation in boiling point of solution of non-electrolyte is proportional to its molality and equimolal solution of all the substances in the same solvent will show equal elevation in boiling points.

These are known as Raoult's laws of elevation of boiling point.

These are known as Raoult's laws of elevation of boiling point.

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

$$K_b = \frac{RT_b^2}{1000\ L_v}$$

Where, R is molar gas constant = 2 cal/mol^{-K}

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

L_v the latent heat of vaporisation of pure solvent in calories per gram = ΔH_{vap} (Cal/mol)/$M_{solvent}$ (g/mol)

For water

$$K_b = \frac{2 \times (373)^2}{1000 \times 540}$$

$$= 0.515K - Kg\ /\ mol$$

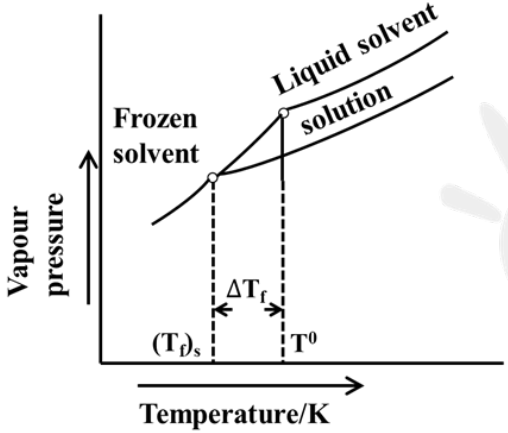
The molal elevation constant for some common solvents are given in the following table

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

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 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.

If T_o is the freezing point of pure solvent and $(T_f)_s$ is the freezing point of its solution then, $(T_f)_s < T_o$

MIND MAP

Liquid Solution

The difference in the freezing point of pure solvent and solution is the depression of freezing point (ΔT_f) Thus, $T_o - (T_f)_s = \Delta T_f$.

Depression in freezing point is directly proportional to the lowering of vapour pressure of solution.

$$\Delta T_f \propto P^0 - P_s$$

From Raoult's law for dilute solution

$$\frac{P^0 - P_S}{P^0} = \frac{w_A}{m_A} \cdot \frac{m_B}{w_B}$$

$$\text{or } P^0 - P_S = \frac{w_A}{m_A} \cdot \frac{m_B}{w_B} \cdot P^0$$

For the pure Solvent, P^0 and m_B are constant. therefore

$$P^0 - P_S \propto \frac{w_A}{m_A w_B}$$

$$\text{or } \Delta P \propto \frac{w_A}{m_A w_B} \propto \Delta T$$

$$\Delta T_f = K \frac{w_A}{m_A w_B}$$

Where K is a constant, called depression constant.

$$\text{If } \frac{w_A}{m_A} = 1 \quad w_B = 100 \text{ g}$$

$$\text{then } \Delta T_f = \frac{K}{100} = K'$$

K' is called molecular depression constant.

$$\text{Thus } \Delta T_f = \frac{100K' \times w_A}{m_A \times w_B}$$

$$\text{If } \frac{w_A}{m_A} = 1 \quad w_B = 1000 \text{ g}$$

$$\Delta T_f = \frac{K}{1000} = K_f$$

K_f is defined as the depression of freezing point produced when 1 mole of solute is dissolved in 1000 g of the solvent.

$$\text{or } \Delta T_f = \frac{1000 K_f \times w_A}{m_A \times w_B}$$

$$\text{or } \Delta T_f = \text{molality} \times K_f$$

$$K_f = \frac{RT_f^2}{1000\,L} = \frac{0.002\,T_f^2}{L_f}$$

Where, T_f is the freezing point of solvent in absolute scale and Lf the latent heat of fusion in calories per gram of the solvent.

For water,

$$K_f = \frac{0.002 \times (273)^2}{80}$$

= 1.86 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 tetra chloride	– 22.8	31.8
Benzene	5.5	5.12
Camphor	179.0	39.70

MIND MAP

Liquid Solution

Osmosis and Osmotic Pressure

Osmosis

Osmosis is defined as the spontaneous flow of solvent molecules through semi permeable membrane from its high concentration to its low concentration.

Osmotic presssure (π)

Osmotic pressure = hydrostatic pressure

$\pi = h\rho g$

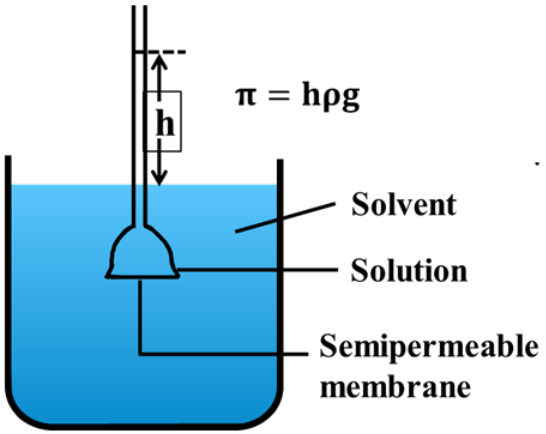
The hydrostatic pressure developed as a result of Osmosis is a measure of Osmotic pressure of the Solution.

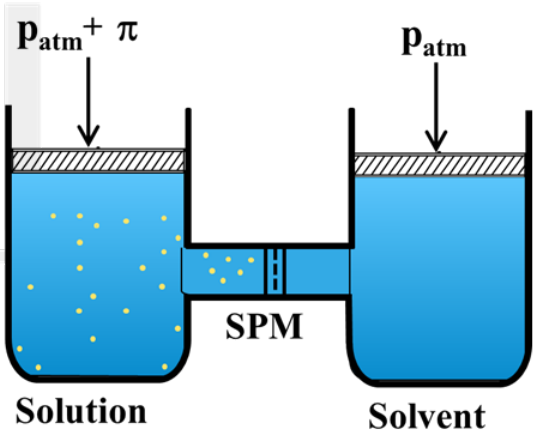
The hydrostatic pressure built up on the solution which just stops the Osmosis.

h = increase in level in the tube of unit cross section

ρ = density of solution

g = acceleration due to gravity





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