Chapter 01

Solution

CONTENT

1. INTRODUCTION:

➢ A solution is a homogeneous mixture of two or more substances which are chemically non-reacting. We come across many types of solutions in our daily life. e.g., solid-liquid, liquid-liquid, gas-gas. In this chapter we will learn several properties of solutions and their applications.

⇒ **Some Important Terms : –**

Solution :	A homogeneous mixture of two or more substances is known as solution.
Solute :	The substance present in smaller amount in a solution is called solute.
Solvent :	The substance present in larger amount in a solution is called solvent.
Binary solutions:	Those solutions which contain two components are called binary solutions, e.g., salt solution, benzene and toluene.
Ternary solutions:	Those solutions which contain three components are called ternary solutions, e.g., ethanol + water + acetic acid.
Aqueous solution :	When solute is dissolved in water, it is called aqueous solution, e.g., sugar solution, ethanol in water.
Non-aqueous solution :	When solute is dissolved in solvent other than water, it is called non-aqueous solution, e.g., iodine dissolved in alcohol (Tincture of iodine).
Miscible liquids :	Those liquids which mix with each other and form homogeneous mixture are called miscible liquids.
Immiscible liquids :	Those liquids which do not mix with each other are called immiscible liquids.
Alloys :	Solid solutions of the two or more metals are called alloys. One of them can be a non-metal also.

Types of Solutions:

Table 1

S.No.	Solute	Solvent	Types of Solutions	Examples
Solid Solutions				
1	Solid	Solid	Solid in solid	All alloys like brass, bronze, an alloy of copper and gold, etc.
2	Liquid	Solid	Liquid in solid	Amalgam of mercury with Na, $CuSO_4.5H_2O$. $FeSO_4.7H_2O$
3	Gas	Solid	Gas in solid	Solution of H_2 in Pd, dissolved gases in minerals.
Liquid Solutions				
4	Solid	Liquid	Solid in liquid	Sugar solution, salt solution, I_2 in CCl_4
5	Liquid	Liquid	Liquid in liquid	Benzene in toluene, alcohol in water.
6	Gas	Liquid	Gas in liquid	CO_2 in water, NH_3 in water etc.
Gaseous Solutions				
7	Solid	Gas	Solid in gas	Iodine vapours in air, camphor vapours in N_2.

8	Liquid	Gas	Liquid in gas	Water vapours in air, $CHCl_3$ vapours in N_2.
9	Gas	Gas	Gas in gas	Air ($O_2 + N_2$)

The concentration of a solution can be expressed by different concentration terms which are described as follows.

(a) Dilute Solution

A solution in which relatively a small amount of solute is dissolved in large amount of solvent is called a dilute solution.

(b) Concentrated solution

A solution in which relatively a large amount of the solute is present is called a concentrated solution.

PROPERTIES OF A SOLUTION:

(i) A solution is uniform throughout, so it has uniform properties such as density, refractive index etc.

(ii) Size of solute particles in a solution is the less than 10^{-7}- 10^{-8} cm is known as true solutions.

(iii) The components of a solution cannot be easily separated by physical methods.

(iv) The properties of a solution are the properties of its components. i.e. the components do not lose their properties when they form a solution.

(v) The composition of a solution is not definite but can vary within certain limits.

(vi) Certain properties of solution such as density, viscosity, surface tension, boiling point, freezing point etc. vary with the composition of the solution.

2. CONCENTRATION TERMS:

(i) MOLARITY (M):

➢ The number of moles of solute present in one litre solution is called its molarity (M).

- $$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{volume of solution (L)}} = \frac{n}{V_{(L)}}$$

(ii) 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.

$$= \frac{\text{Number of gram equivalents of solute}}{\text{volume of solution in litre (L)}} = \frac{\text{Mass of solute (g)}}{\text{Equivalent mass} \times \text{Volume of solution (L)}}$$

(iii) MOLALITY (m):

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

- $$\text{Molality of a solution} = \frac{\text{Number of moles of solute}}{\text{Amount of solvent (kg)}} = \frac{\text{Number of moles of solute} \times 1000}{\text{Amount of solvent (g)}}$$

(iv) FORMALITY (F) :

➢ It is the number of formula mass in grams present per litre of solution. Formality is generally used for solutions of ionic compounds.

- $$\text{Formality} = \frac{\text{Mass of solute (g)}}{\text{Formula mass of solute (g)} \times \text{Volume of solution (L)}}$$

(v) Strength of a Solution (S):

➢ The mass of solute in g dissolved in 1L solution is known as its strength in gL^{-1}.

- $$S = \frac{\text{Mass of solute (g)}}{\text{volume of solution (L)}}$$
- S = Molarity of solution × Molar mass of solute.
- S = Normality of solution × Equivalent mass of solute.

(vi) CONCENTRATION IN TERMS OF PERCENTAGE

(a) PERCENTAGE BY MASS (w/W):

➢ Mass of solute in (g) present in given mass of solution (g) ; is called mass fraction of the solute.

- Thus, $\text{mass fraction} = \dfrac{w}{w+W}$
- Where 'w' grams of solute is dissolved in W grams of solvent.
- $\text{Mass}\,\% = \dfrac{\text{Mass of solute (g)}\times 100}{\text{Mass of solution (g)}} = \dfrac{w\times 100}{w+W}$
- Mass % is independent of temperature.

(b) PERCENT BY VOLUME (v/V):

➢ This method is used for solutions of liquid in a liquid. The volume of liquid (solute) in ml dissolved in given volume of solution in ml is called volume fraction.

- $\text{Volume fraction} = \dfrac{\text{Volume of liquid solute (mL)}}{\text{volume of solution (mL)}}$
- $\text{Volume}\,\% = \dfrac{\text{Volume of solute}\times 100}{\text{Volume of solution}} = \dfrac{v}{v+V}\times 100$

$$\begin{bmatrix} v = \text{volume of solute in ml} \\ V = \text{volume of solvent in ml} \end{bmatrix}$$

(c) PERCENT BY STRENGTH/ PERCENTAGE MASS BY VOLUME (w/V):

- $\%\left(\dfrac{w}{V}\right) = \dfrac{\text{Mass of solute (g)}\times 100}{\text{Volume of solution (ml)}} = \dfrac{w\times 100}{V}$ $\quad\begin{bmatrix} w = \text{weight of solute in g} \\ V = \text{volume of solution in ml} \end{bmatrix}$

Example.1 The density of a solution containing 13% by mass of sulphuric acid is 1.09 g/ml. Calculate the molarity of the solution

(1) 1.445 M (2) 14.45 M (3) 144.5 M (4) 0.1455 M

Solution. (1) Volume of 100 gram of the solution = $\dfrac{100}{d} = \dfrac{100}{1.09}$ mL = $\dfrac{100}{1.09\times 1000}$ litre = $\dfrac{1}{1.09\times 10}$ litre

Number of moles of H_2SO_4 in 100 gram of the solution = $\dfrac{13}{98}$

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

Example.2 Calculate the molarity of pure water (d = 1gm/ml)

(1) 555 M (2) 5.55 M (3) 55.5 M (4) none

Solution. (3) Consider 1000 mL of water

Mass of 1000 mL of water = 1000 × 1 = 1000 gram

Number of moles of water = $\dfrac{1000}{18} = 55.5$

$$\text{Molarity} = \frac{\text{No. of moles of water}}{\text{Volume in litre}} = \frac{55.5}{1} = 55.5\text{ M}$$

Example.3 The molarity of 20% (w/w) solution of sulphuric acid is 2.55 M. The density of the solution is

(1) 1.25 g cm^{-3} (2) 0.125 g l^{-1} (3) 2.55 g cm^{-3} (4) unpredictable

Solution. (1) Volume of 100 g of solution = $\dfrac{100}{d}$ ml

$$\therefore M = \frac{20\times d\times 1000}{100\times 98} \text{ or } d = \frac{2.55\times 100\times 98}{20\times 1000} = 1.249 \approx 1.25$$

Example.4 15 gram of methyl alcohol is dissolved in 35 gram of water. What is the mass percentage of methyl alcohol in solution ?

(1) 30% (2) 50% (3) 70% (4) 75%

Solution. (1) Total mass of solution = (15 + 35) gram = 50 gram

$$\text{Mass percentage of methyl alcohol} = \frac{\text{Mass of methyl alcohol}}{\text{Mass of solution}} \times 100 = \frac{15}{50} \times 100 = 30\%$$

(vii) PARTS PER MILLION (ppm):

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

- ppm of substance (by mass) = $\dfrac{\text{Mass of solute in gms} \times 10^6}{\text{Mass of solution(g)}}$
- ppm (by volume) = $\dfrac{\text{Volume of solute} \times 10^6}{\text{volume of solution}}$
- $\text{ppm}\left(\dfrac{w}{V}\right) = \dfrac{\text{mass of solute(g)}}{\text{volume of solution(mL)}} \times 10^6$

(viii) MOLE FRACTION:

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

- Mole fraction of solute $X_B = \dfrac{\text{moles of solute(n)}}{\text{mole of solute(n)+moles of solvent (N)}}$
- Mole fraction of solvent $X_A = \dfrac{\text{moles of solvent(N)}}{\text{mole of solute(n)+moles of solvent (N)}}$

$$\boxed{X_A + X_B = 1}$$

$$\boxed{\frac{X_A}{X_B} = \frac{n_A}{n_B}}$$

(xi) RELATION BETWEEN MOLARITY AND NORMALITY:

➢ S = Molarity × Molar mass of solute and S = Normality × Equivalent mass of solute.

So we can write

- Molarity × Molar mass of solute = Normality × Equivalent weight of solute.
- $\text{Normality} = \dfrac{\text{Molarity} \times \text{Molar mass of solute}}{\text{Equivalent mass of solute}} = \dfrac{\text{Molarity} \times \text{Molar mass of solute}}{\text{(Molar mass of solute/valency factor)}}$
- Normality = Molarity × Valency factor
- N = M × n factor

(x) RELATION BETWEEN MOLALITY (m) AND MOLE FRACTION:

- $\dfrac{x_B}{x_A} = \dfrac{n_B}{n_A} = \dfrac{n_B \times M_A \times 1000}{w_A \times 1000}$
- $\dfrac{x_B}{x_A} = \dfrac{\text{molality} \times M_A}{1000}$
- $\dfrac{x_B}{1 - x_B} = \dfrac{\text{molality} \times M_A}{1000}$: If $x_B <<< 1$ for very dilute $x_B = \dfrac{\text{molality} \times M_A}{1000}$

(xi) RELATION BETWEEN MOLALITY (m) AND MOLARITY (M):

- $m = \dfrac{M \times 1000}{(d \times 1000) - (M \times M_B)}$
- d = density of solution

- M_B = molecular weight of solute

(xii) VOLUME STRENGTH OF H_2O_2 SOLUTION:

➢ Volume of O_2(L) produced by decomposition of unit volume solution of H_2O_2 at NTP/STP; is called volume strength.

➢ **Relationship between volume strength of H_2O_2 and Molarity/Normality/(g/L)/%(w/V)**

- Let volume strength of H_2O_2 solution be 'X' V, it means 1L solution of H_2O_2, can produce 'X' L of O_2 at NTP.

$$\begin{array}{ll} 2H_2O_2 \longrightarrow 2H_2O + O_2(g) \\ 2\text{ mol} \qquad\qquad\qquad 1\text{ mol} \end{array}$$

∵ 1 mole O_2 can be produced by = 2 mole H_2O_2 solution

∴ $\frac{X}{22.4}$ mole of O_2 can be produced by = $\frac{2X}{22.4}$ mole H_2O_2 solution

$$= \frac{2X}{22.4} \text{ mole of } H_2O_2 \text{ solution}$$

(a) Molarity = $\frac{\text{number of moles of solute}}{\text{volume of solution(L)}} = \frac{2X}{22.4} = \frac{X}{11.2}$

Hence $\boxed{M = \frac{X}{11.2}}$

(b) Normality = molarity × valence factor = $\frac{X}{11.2} \times 2 = \frac{X}{5.6}$

Hence $\boxed{N = \frac{X}{5.6}}$

(c) Strength (g/L): S = N × E

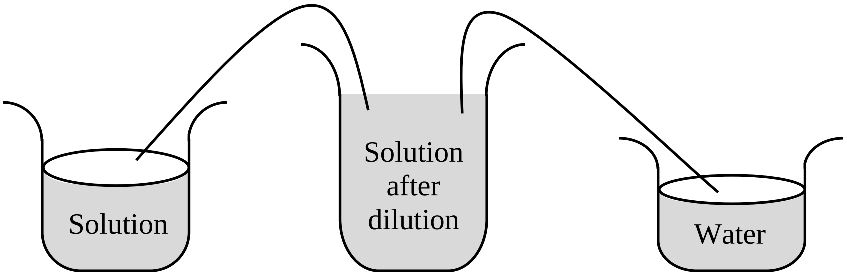
Hence $\boxed{S = \frac{X}{5.6} \times 17}$ g/ L

(d) $\boxed{\%\left(\frac{w}{V}\right) = \frac{X}{5.6} \times \frac{17}{10}}$

CONCEPTS OF DILUTION:

➢ The term dilution means addition of a solvent in a solution, where following remains unchanged after dilution and before dilution

- amount of solute (w_B)
- moles of solute (M × V)
- Number of gram equivalent of solute (N × V)



Moles = M_1V_1
g. eq. = N_1V_1

Moles = M_2V_2
g. eq. = N_2V_2
$V_2 = V_1 + V_{H_2O}$
$$\boxed{\begin{matrix} N_1V_1 = N_2V_2 \\ M_1V_1 = M_2V_2 \end{matrix}}$$

Volume = V_{H_2O}

Volume = $\mathbf{V_{H_2O}}$

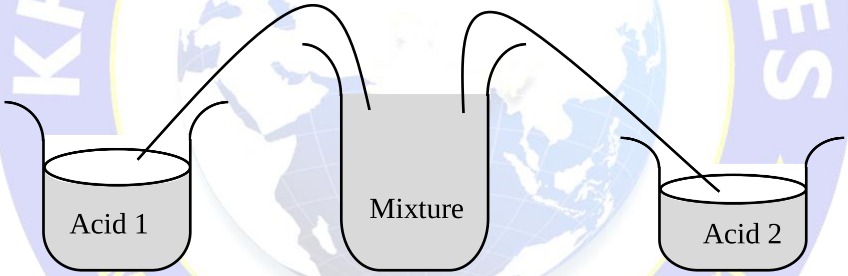
Condition of dilution:

$$\boxed{\begin{matrix} M_1V_1 = M_2V_2 \\ N_1V_1 = N_2V_2 \end{matrix}}$$

CONCEPTS OF MIXING OF SOLUTIONS

- **Case I: When acid-acid or base-base are mixed.**

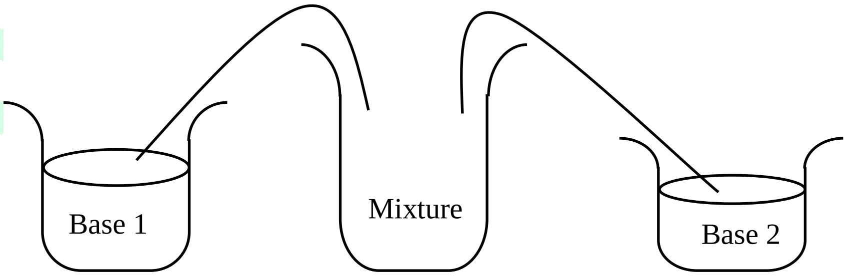
$$N_R = \frac{N_1V_1 + N_2V_2 + N_3V_3 + \ldots}{V_1 + V_2 + V_3 + \ldots}$$



N_1V_1

N V
$N \times V = N_1V_1 + N_2V_2$
$V = V_1 + V_2$

N_2V_2



N_1V_1

N V
$N \times V = N_1V_1 + N_2V_2$
$V = V_1 + V_2$

N_2V_2

- **Case II: Concept of neutralisation** (when acid-base are mixed) then neutralisation will occur.

(i) Complete neutralisation

$$\boxed{N_AV_A = N_BV_B}\begin{pmatrix} A \rightarrow \text{Acid} \\ B \rightarrow \text{Base} \end{pmatrix}; \left[N_R = \frac{N_AV_A}{V_A + V_B}\right]$$ where N_R is the normality of salt.

(ii) Incomplete neutralisation

If $N_A\,V_A > N_B\,V_B$

Then, $N_R = \dfrac{N_A V_A - N_B V_B}{V_A + V_B}$

If $N_B V_B > N_A V_A$

Then, $N_R = \dfrac{N_B V_B - N_A V_A}{V_A + V_B}$

SPOT LIGHT

- ➢ If the density of solution is approximately 1g/cc then Molality > Molarity
- ➢ ppm unit is used to represent concentration of very dilute solutions like pollutants in environment and salts present in sea water.
- ➢ Those concentration terms which involves volume of any component are temperature dependent.
- ➢ Molarity, normality, formality, % by volume, % w/V, are temperature dependent.
- ➢ Molality, % w/W, mole fraction are temperature independent.

Note : All volume related concentration terms are temperature dependent.

Example.5 Two solutions of a substance (non-electrolyte) are mixed in the following manner. 480 ml of 1.5 M first solution + 520 mL of 1.2 M second solution. What is the molarity of the final mixture?

(1) 1.50 M (2) 1.20 M (3) 2.70 M (4) 1.344 M

Solution. (4) Total millimoles of solute

$= 480 \times 1.5 + 520 \times 1.2 = 720 + 624 = 1344.$

Total volume = 480 + 520 = 1000.

Molarity of the final mixture = (1344)/(1000)

= 1.34 MM.

Example.6 The molality of a urea solution in which 0.0100 g of urea, $[(NH_2)_2CO]$ is added to 0.3000 dm^3 of water at STP is:

(1) 0.555 m (2) 5.55×10^{-4} m (3) 33.3 m (4) 3.33×10^{-2} m

Solution. (2) Molality $= \dfrac{\text{moles of solute}}{\text{water}(\text{kg})}$

Moles of urea $= \dfrac{0.010}{60}$ mol

Water at STP $\left(d = 1\dfrac{g}{cm^3} = 1kg/dm^3\right)$

$= 0.3\ dm^3 = 0.3$ kg

$\therefore$ Molality $= \dfrac{0.010}{60 \times 0.3} = 5.555 \times 10^{-4}$ m.

3. SOLUBILITY

- ➢ Maximum amount of solute which can be dissolved in a specified amount of solvent at constant temperature is solubility. Solubility is affected by nature of solute and solvent as well as by temperature and pressure.

(a) Solubility of Solid in 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.

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

- Solubility of solids is affected by temperature and pressure according to Le-Chatlier's principle. If dissolution is exothermic then solubility decreases with increase in temperature and if endothermic then solubility increases with increase in temperature.
- Solubility of solids is not affected by pressure significantly since solids are highly incompressible.

(b) 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 affected by pressure and temperature.
- Increasing pressure increases solubility and increase in temperature decreases solubility of gases in liquid.
- During dissolution of gas pressure of gas decrease and dissolution of gas is exothermic in nature.

HENRY'S LAW

➢ It can be stated at constant temperature 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.

or

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

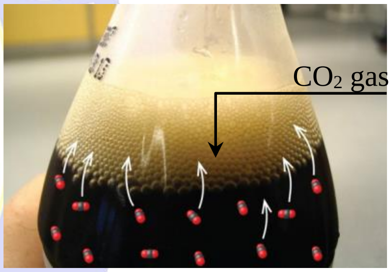
or

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

$P = K_HX$ K_H = Henry's Constant

➢ Henry's Constant is not a universal constant. It depends on nature of gas and temperature. K_H increases with increase in temperature therefore solubility of gas decreases.

APPLICATION OF HENRY'S LAW



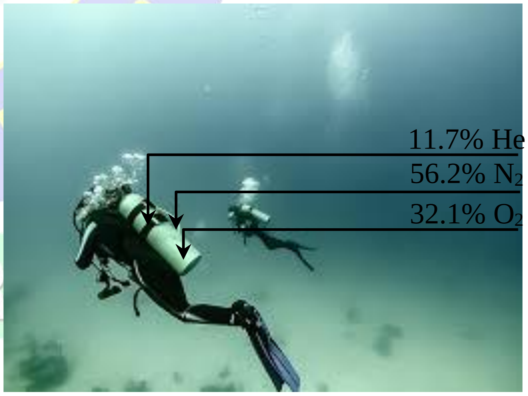
Soft Drink Bottle

1. Soft drink bottles are sealed at high pressure, to increase the solubility of CO_2 in the soft drink.
2. At high altitude, partial pressure of oxygen is low, it leads to low concentration of oxygen in blood of people living there.

- Low concentration of oxygen develops anoxia, i.e. unable to think and act properly.

3. When scuba divers go deep in the sea, solubility of atmospheric gases increases in blood.

- When the divers come up, there is release of dissolved gases and it leads to the formation of bubbles of nitrogen in our blood capillaries and hence there is painful sensation called bends.
- To avoid bends; the tanks of scuba divers are filled with 11.7% He, 56.2% N_2 and 32.1% oxygen.
  - (i) Gases are less soluble in aqueous solutions of electrolytes than in pure water. It is called salting out effect.
  - (ii) Non-electrolytes such as sugar if present in a solution also reduce the solubility of gases in water.



Scuba Divers

4. VAPOUR PRESSURE OF A PURE LIQUID OR PURE SOLID

(1) Vapour pressure of a pure liquid: *The pressure exerted by the vapours over the liquid surface at equilibrium is called vapour pressure.* It increases with the increase in temperature.

- **Note:** Volatile solids (like Iodine) also evaporate and have a vapour pressure at any given temperature, just like liquids.

(2) Vapour pressure of solution: *The pressure exerted by the vapours of solvent 'A' and solute 'B' in equilibrium with the liquid phase is called the vapour pressure of solution.*

(3) **Definition of vapour pressure:** The partial pressure of vapours in equilibrium with pure solid or pure liquid at a given temperature.

- At equilibrium, rate of evaporation = rate of condensation

  e.g. $H_2O(l) \rightleftharpoons H_2O(g)$,

  $K_p = p^{eq}_{H_2O,g}$

- Hence V.P is equilibrium constant (K_P) of the process, liquid $\rightleftharpoons$ vapours.

(4) Since vapour pressure is an equilibrium constant. so it's value is dependent only on temperature.

- **Factors affecting vapour pressure of liquid**

  (a) **Nature of liquid:** The value of a liquid's vapour pressure depends on the magnitude of the intermolecular forces in the liquid. The smaller the intermolecular forces, higher the vapour pressure because loosely held molecules escape more easily into vapour phase.

  (b) **Temperature of the given liquid :** At higher temperature, more molecules from the liquid have enough KE to escape from the surface of the liquid. That will increase the saturated vapour pressure.

  liquid $\rightleftharpoons$ vapours. ΔH is +ve

  - Vapourization (liquid to vapour) is always 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 that increasing the temperature increases the amount of vapour present, and so increases the saturated vapour pressure.
  - The dependence of vapour pressure with temperature is given by **Clausius-Clapeyron equation.**
  - $\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$, where ΔH_v = molar enthalpy of vapourisation of the given liquid,

  p_2 = vapour pressure of the liquid at T_2 and p_1 = vapour pressure of the liquid at T_1.

  (c) Vapour pressure of a liquid does not depend on :

  (i) the amount of liquid taken **(ii)** surface area of the liquid

  (iii) volume or shape of the container

(5) **Partial vapour pressure:** *The pressure of vapours of a component 'A' over a solution of 'A' and 'B' is called partial vapour pressure of component A.* It is denoted by p_A.

(6) **Partial pressure of vapours**: If vapours of a liquid are present in a gaseous mixture then,

- Partial pressure of vapours of the liquid = $\frac{\text{Pressure of vapours}}{\text{Total pressure}}$

➢ **Saturation:** A gas or gaseous mixture is said to be saturated with the vapours of a liquid if the partial pressure of the liquid vapours is equal to its (saturated) vapour pressure.

(7) (a) Saturated (Equilibrium) Vapour pressure of water, at a given temperature, is called aqueous tension.

- The value of aqueous tension is different at different temperature.

(b) Relative Humidity (R.H.) = $\frac{\text{Partial pressure of water vapour at given temperature}}{\text{Vapour pressure of water at the same temperature}} \times 100\%$

(8) **Saturated vapour pressure and boiling point:**

➢ A liquid boils when its saturated vapour pressure becomes equal to the external pressure on the liquid. When that happens, it enables bubbles of vapour to form throughout the liquid. If the external pressure is higher than the saturated vapour pressure, these bubbles are prevented from forming, and we just get evaporation at the surface of the liquid.

* $P_{ext} > P_{sat} \Rightarrow$ evaporation * $P_{ext} = P_{sat} \Rightarrow$ Boiling

- If the liquid is in an open container and exposed to normal atmospheric pressure, the liquid boils when its saturated vapour pressure becomes equal to 1 atmosphere. This happens with water when the temperature reaches 100°C. But at different pressures, water will boil at different temperatures. For example, at the top of Mount Everest the pressure is so low that water will boil at about 70°C.
  (a) Boiling point : The boiling point is the temperature at which the vapour pressure of a liquid is equal to the external pressure.
  (b) At boiling temperature, vapour pressure of the pure liquid i.e. $P° = P_{ext}$
  (c) At normal boiling point, vapour pressure of the pure liquid i.e. P° = 1atm

(9) Saturated vapour pressure and solids: Sublimation

- Solids can also loose particles from their surface to form a vapour, except that in this case we call the effect sublimation rather than evaporation. Sublimation is the direct change from solid to vapour without going through the liquid stage.
- The forces of attraction in many solids are too high to allow much loss of particles from the surface. However, there are some solids which easily form vapours.
- Naphthalene (used in "moth balls") has quite a strong smell. Molecules must be breaking away from the surface as a vapour, because otherwise we wouldn't be able to smell it.
- Solid carbon dioxide never forms a liquid at atmospheric pressure and always converts directly from solid to vapour. That's why it is known as dry ice.

(10) If partial pressure of vapours of a liquid is increased beyond the saturated (equilibrium) vapour pressure value (P°), its vapours begin to condense till their partial pressure becomes equal to the saturated vapur pressure.

(11) If the partial pressure of vapour is less than v.p. of liquid, the liquid (if present) will vaporize till
(a) its v.p. is attained or (b) the liquid completely gets vaporized

(12) If a volatile solid/ liquid is brought in contact with a gas (or vaccuum), vapours of that solid/ liquid occupy the gas phase till the gas phase becomes saturated with that solid /liquid vapours.

Example.7 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water. The vapour pressure of water for this aqueous solution at 100° C is

(1) 7.60 Torr (2) 76.00 Torr (3) 752.40 Torr (4) 759.00 Torr

Solution. (3) Relative lowering or vapour pressure is equal to mole fraction of glucose $\frac{P° - P}{P°}$ = mole fraction of glucose …(i)

moles of glucose = $\frac{18}{180} = 0.1$

moles of water = $\frac{178.2}{18} = 9.9$

mole fraction of glucose = $\frac{0.1}{0.1+9.9} = 0.01$

Substituting in equation (i) we get.

$$\frac{760 - P}{760} = 0.01$$

On solving we get,

P = 725.40 torr

Example.8 A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be

(1) 350 (2) 300 (3) 700 (4) 360

Solution. (1) From Raoult's law, we have

$$P_T = P_A^0 X_A + P_B^0 X_B \qquad \begin{pmatrix} A - \text{ethylalcohol} \\ B - \text{propylalcohol} \end{pmatrix}$$

$X_A + X_B = 1$

$0.6 + X_B = 1$

$X_B = 0.4$

Now, $290 = 0.6\ P_A^\circ + 200\ (0.4)$

$290 - 80 = 0.6\,P_A^\circ$

$$P_A^0 = \frac{210}{0.6}$$

$P_A^0 = 350$ mm

Example.9 The vapour pressure of water at 20°C is 17.5 mm Hg. If 18 g of glucose ($C_6H_{12}O_6$) is added to 178.2 g of water at 20°C, the vapour pressure of the resulting solution will be

(1) 17.675 mm Hg (2) 15.750 mm Hg (3) 16.500 mm Hg (4) 17.325 mm Hg

Solution. (4) In solution containing nonvolatile solute, pressure is directly proportional to its mole fraction.

$P_{Solution}$ = Vapour pressure of its pure component × mole fractiopn in solution.

$\therefore\ P_{Sol} = P^\circ X_{Solvent}$

Let A be the solute and B the solvent

$$\therefore\ X_B = \frac{n_B}{n_A + n_B} = \frac{\frac{178.2}{18}}{\frac{18}{18} + \frac{178.2}{18}}$$

$$X_B = \frac{9.9}{10} = 0.99$$

Now, $P_{solution} = P^\circ X_{solvent} = 17.5 \times 0.99$

$P_{solution} = 17.32$

Example.10 On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25.0 of heptane and 35 g of octane will be (molar mass of heptane = 100 g mol^{-1} and of octane = 114 g mol^{-1}):

(1) 144.5 kPa (2) 72.0 kPa (3) 36.1 kPa (4) 96.2 kPa

Solution. (2) Mole fraction of Heptane

$$= \frac{25/100}{\frac{25}{100} + \frac{35}{114}} = \frac{0.25}{0.557} = 0.45$$

$X_{Heptane} = 0.45$

$\therefore$ Mole fraction of octane = 1 – 0.45 = 0.55 = X_{octane}

Total pressure = $\sum X_i P_i^0$

$P_t = (105 \times 0.45) + (45 \times 0.55)$ kPa

$P_t = 72.0$ kPa

RAOULT'S LAW

(a) **For liquid – liquid system:** For a solution of volatile liquids the partial vapour pressure of any component at constant temperature is equal to vapour pressure of pure component multiplied by mole fraction of that component in the solution.

	Liquid (B)	**Liquid (A)**
Vapour pressure in pure state	$P_B{}^0$	$P_A{}^0$
Partial vapour pressure	P_B	P_A
Mole fraction in solution	X_B	X_A
Moles	n_B moles	n_A moles
Mass	W_B gm	W_A gm
Molar mass	M_B	M_A

$P_A \propto X_A$ so $P_A = P_A^0 X_A$ ...(i)

$P_B \propto X_B$ so $P_B = P_B^0 X_B$ ....(ii)

- At constant temperature partial vapour pressure of component is directly proportional to mole fraction of component in solution.

DALTON'S LAW:

➢ Partial pressure of gas = mole fraction × total pressure of gas

$P_A = Y_A P_T$

$P_B = Y_B P_T$

$P_A + P_B = P_T$

$$\boxed{\begin{array}{l} X_A P_A^0 = Y_A P_T \\ X_B P_B^0 = Y_B P_T \end{array}}$$

Y_A and Y_B are mole fraction in vapour phase (Where $P_T = P_S$)
X_A and X_B gives mole fraction in liquid phase.

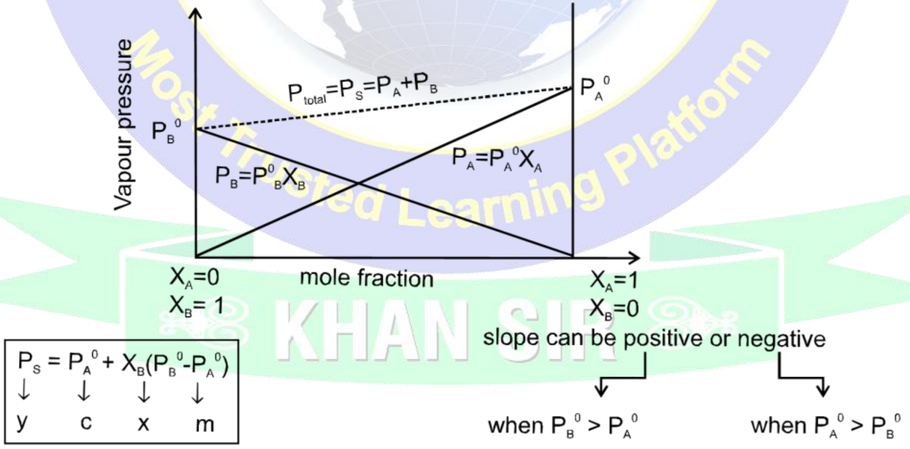
➢ **According to Dalton's law given below:**

- $P_{total} = P_A + P_B + ...$

For 2 components

$\boxed{P_s = X_A P_A^0 + X_B P_B^0}$; $X_A + X_B = 1$

$P_S = (1 - X_B)\, P_A{}^0 + X_B\, P_B{}^0$ $P_S = P_A{}^0 - X_B P_A{}^0 + X_B P_B{}^0$ $P_S = P_A{}^0 + X_B(P_B{}^0 - P_A{}^0)$



(b) **For solid–liquid system:** non-volatile solute (B) and volatile solvent (A)

$P_B^0 = 0$

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

$P_S = X_A P_A^0$ $\boxed{P_S = \frac{n_A}{n_A + n_B} P_A^0}$ $P_A{}^0$ = VP of liq. A constant temperature so $P_s \propto X_A$

➢ For solution of non-volatile solute: At constant temperature vapour pressure of solution containing non-volatile solute is proportional to mole fraction of solvent.

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

$$X_A + X_B = 1 \;\; ; P_S = (1 - X_B)P_A^0 \qquad ; P_S = P_A^0 - X_B P_A^0$$

$$X_B P_A^0 = P_A^0 - P_S \qquad ; \frac{P_A^0 - P_S}{P_A^0} = X_B = \frac{n_B}{n_B + n_A}$$

($P_A^0 - P_S = \Delta P$, lowering of vapour pressure)

$\frac{P_A^0 - P_S}{P_A^0}$ = relative lowering of vapour pressure.

➢ When a non-volatile solute is added to a volatile liquid its vapour pressure decrease because less number of solvent particles present in solution at surface. (as compare to pure solvent)

∴ less vapour is formed and vapour pressure of solution decreases

$$\frac{P_A^0}{P_A^0 - P_S} = \frac{n_B + n_A}{n_B} ; \frac{P_A^0}{P_A^0 - P_S} = 1 + \frac{n_A}{n_B} ; \frac{P_A^0 - P_A^0 + P_S}{P_A^0 - P_S} = \frac{n_A}{n_B} ; \frac{P_S}{P_A^0 - P_S} = \frac{n_A}{n_B} \boxed{\frac{P_A^0 - P_S}{P_S} = \frac{n_B}{n_A}} ; \Delta P \propto \frac{n_B}{n_A}$$

Example.11 Benzene and toluene form nearly ideal solutions. At 20°C, the vapour pressure of benzene is 75 torr and that of toluene is 22 torr. The partial vapour pressure of benzene at 20°C for a solution containing 78 g of benzene and 46 g of toluene in torr is -

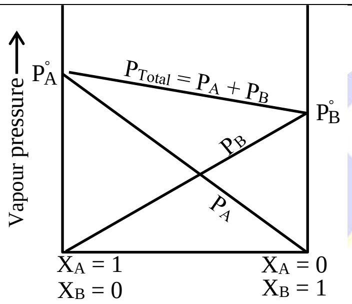
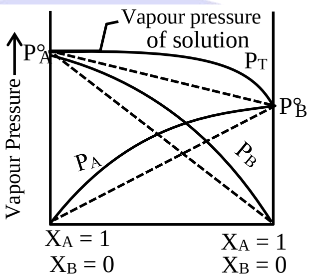
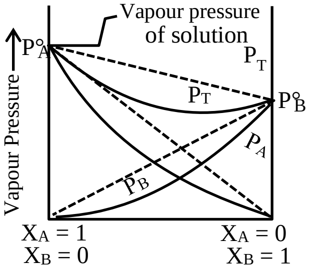
(1) 25 (2) 50 (3) 53.5 (4) 37.5

Solution. (2) According to Raoult's law-

$$P_B = P_B^0 \times X_B = 75 \times \frac{\frac{78}{78}}{\frac{78}{78} \times \frac{46}{92}} = 75 \times \frac{1}{1 + 0.5} = 50 \text{ Torr}$$

IDEAL AND NON-IDEAL SOLUTIONS

IDEAL SOLUTION (mixture of two liquids A and B)	**Non-ideal Solution**	
	Positive deviation from Raoult's Law	**Negative deviation from Raoult's Law**
1. A solution which obeys Raoult's law exactly at all concentrations and at all temperatures is called an ideal solution.	Those solutions which do not obey Raoult's law are called non-ideal solutions.	Those solutions which do not obey Raoult's law are called non-ideal solutions.
2. A-A interaction = B - B interaction = A - B interaction. There should be no chemical reaction between liquid A and liquid B.	In these solutions A-B interaction are less than A-A and B-B molecular interaction. $P_A > P_A^0 X_A$; $P_B > P_B^0 X_B$	In these solutions A-B interaction are stronger than A-A and B-B molecular interactions. $P_A < P_A^0 X_A$; $P_B < P_B^0 X_B$
3. Volume change on mixing should be zero. $\Delta V_{mix} = 0$	$\Delta V_{mix} > 0$; volume increase after dissolution.	$\Delta V_{mix} < 0$; volume decreases during dissolution.
4. Heat change on mixing should be zero. $\Delta H_{mix} = 0$ (Heat is neither absorbed nor evolved)	$\Delta H_{mix} > 0$; endothermic dissolution ; heat is absorbed.	$\Delta H_{mix} < 0$; exothermic dissolution ; heat is evolved.
5. observed VP = calculated VP	The total vapour pressure of the solution will be greater than the corresponding vapour pressure expected in case of an ideal solution of same composition, i.e. $P_{total} > (P_A^0 X_A + P_B^0 X_B)$	Total vapour pressure is less than sum of individual vapour pressure. $P_{total} < (P_A^0 X_A + P_B^0 X_B)$
6. observed BP = calculated BP	$(B.P.)_{th} > (B.P.)_{exp}$	$(B.P.)_{th} < (B.P.)_{exp}$

7. $\Delta S_{mix} > 0$	$(\Delta S)_{mix}$ = +ve,	$(\Delta S)_{mix}$ = +ve,
8. $\Delta G < 0$	ΔG = –ve	ΔG = –ve
9. **Examples :** (i) Benzene and toluene (ii) CCl_4 and $SiCl_4$ (iii) n-hexane and n-heptane (iv) C_2H_5Br and C_2H_5Cl (v) PhCl and PhBr (vi) n-butylchloride and n-butylbromide	**Examples :** (i) Ethanol and cyclohexane (ii) Ethanol and Water (iii) Ethanol and Acetone (iv) Methanol and H_2O (v) CCl_4 and Benzene (vi) CCl_4 and Toluene (vii) CCl_4 and $CHCl_3$ (viii) CCl_4 and Methanol (ix) Benzene and Acetone	**Examples:** (i) $CHCl_3$ and CH_3COOH (ii) $CHCl_3$ and C_6H_6 (iii) $CHCl_3$ and $C_2H_5OC_2H_5$ (iv) $CHCl_3$ and HNO_3 (v) $CHCl_3$ and CH_3COOH (vi) H_2O and HCl (vii) H_2O and HNO_3 (viii) CH_3COOH and CH_3OH
		

Example.12 Which of the following liquid pairs shows a positive deviation from Raoult's law?

(1) Water-hydrochloric acid (2) Benzene-methanol

(3) Water-nitric acid (4) Acetone-chloroform

Solution. (2) Benzene-methanol attraction are weaker than that of benzene – benzene and methanol – methanol attraction. So, benzene liquid pair shows a positive deviation from Raoult's law.

Example.13 A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the following statements is correct regarding the behaviour of the solution?

(1) The solution is non-ideal, showing –ve deviation from Raoult's law

(2) n-heptane shows +ve deviation while ethanol shows –ve deviation from Raoult's law

(3) The solution formed is an ideal solution.

(4) The solution is non-ideal, showing +ve deviation from Raoult's law

Solution. (4) n-Heptane and ethanol show positive deviation from Raoult's law, the forces of attraction between n-heptane and ethanol will be less than their individual molecules. They form a non-ideal solution.

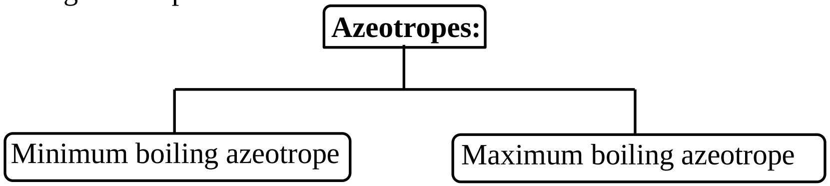
AZEOTROPIC MIXTURE:

- Some liquids on mixing, form azeotropes which are binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature.
- Components form azeotrope can't be separated by fractional distillation but can be separated by azeotropic distillation.
- Solutions showing Positive deviation form minimum boiling azeotrope and solutions showing negative deviation form maximum boiling azeotrope.

There are two types of azeotropes:

(a) Minimum boiling azeotrope

(b) Maximum boiling azeotrope



Minimum Boiling azeotrope	Maximum Boiling azeotrope

(a)	The solutions which show a large positive deviation from Raoult's law from minimum boiling azeotrope at a specific composition.	(i)	The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition.
(b)	For example, ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95.57% w/W ethanol.	(ii)	Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393.5K.

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

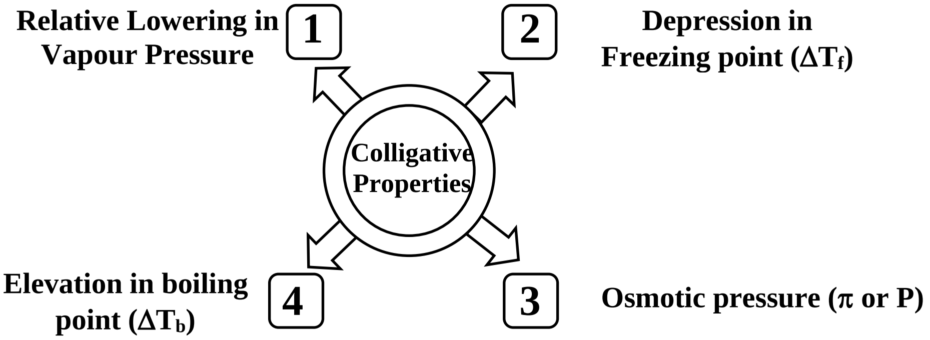
SPOT LIGHT

- ➢ Those gases which can react with solvent do not follow Henry's Law. e.g. NH_3 in water.
- ➢ Raoult's law is special case of Henry's Law.
- ➢ ΔS is positive and ΔG is negative for ideal as well as non ideal solutions.

5. COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS (CP):

➢ Those physical properties of a solution which depends upon the relative number of particles of solute and do not depend on nature of solute particles; are called colligative properties.

- CP $\propto$ Number of solute particles.
  - $\propto$ Number of molecules (In the solution of non-electrolyte)
  - $\propto$ Number of ions (In the solution of electrolytes)
  - $\propto$ Number of moles of solute
  - $\propto$ Mole fraction of solute



➢ **The following four properties are (CP):**

(a) Relative lowering in vapour pressure (b) Elevation in boiling point (ΔT_b)

(c) Depression in freezing point (ΔT_f) (d) Osmotic pressure (π or P)

(a) Relative Lowering in Vapour Pressure:

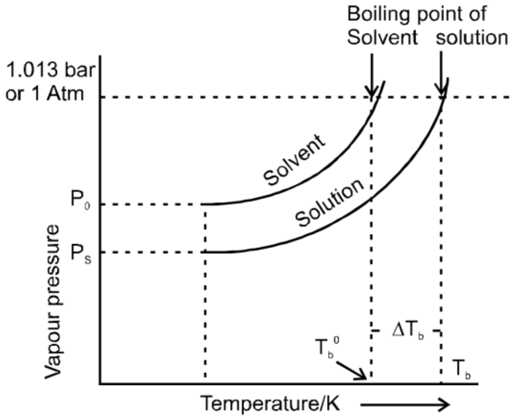
➢ When a nonvolatile solute is dissolved in a pure solvent, the vapour pressure of the solvent is lowered i.e. the vapour pressure of a solution is always lower than that of pure solvent, (due to lesser solvent molecules per unit surface area).

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

- According the Raoult's law:
- Relative lowering of vapour pressure $= \dfrac{P_A^0 - P_S}{P_A^0} = \dfrac{n_B}{n_A + n_B}$
- For a dilute solution $n_B << n_A$ $\therefore$ $\dfrac{P_A^0 - P_S}{P_A^0} \approx \dfrac{n_B}{n_A}$ So $\Delta P \propto \dfrac{n_B}{n_A}$

➢ Relative lowering depends upon relative number of solute particles. Therefore, it is called colligative properties.

(b) Elevation in Boiling Point:



The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.

- ➢ The boiling point of a liquid is that temperature at which its vapour pressure becomes equal to atmospheric pressure.
- ➢ When a non-volatile solute is dissolved in a pure solvent, its vapour pressure is decreased and boiling point increases. The difference of boiling points of the solution and pure solvent is called elevation in boiling point. (ΔT_b)
- ➢ If T^0_b 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 $\Delta T_b = T_b - T_b^0$
- ➢ The elevation in boiling point (ΔT_b) is directly proportional to lowering of vapour pressure of the solution i.e.

$\Delta T_b \propto (P^\circ - P_S)$ from graph and

$$\Delta T_b \propto \Delta P \propto \frac{n_B}{n_A}$$

$$\therefore \quad \Delta T_b \ \mu \ \frac{n_B}{n_A} = \frac{W_B M_A}{M_B W_A} \text{ for a solvent } P^0 \& \ M_A = \text{constant}$$

$$\therefore \quad \Delta T_b \ \mu \ \frac{W_B}{M_B W_A} \quad \text{or} \quad \Delta T_b = \frac{K W_B}{M_B W_A}$$

- where K = elevation constant

if $\frac{W_B}{M_B}$ = 1 mole and W_A = 1 g

then ΔT_b = K (Elevation constant or molecular elevation constant)

If $\frac{W_B}{M_B}$ = 1 and W_A = 1000 gram; Then $\Delta T_b = K_b$(molal elevation constant)

$$\therefore \quad \frac{K}{1000} = K_b \text{ (molal elevation constant or Ebullioscopic constant)}$$

$$\Delta T_b = \frac{K_b \times W_B \times 1000}{M_B \times W_A}$$

ΔT_b = Molality × K_b

$\therefore \quad \Delta T_b \propto$ molality

- Hence elevation in boiling point (ΔT_b) is a colligative property.

➢ K_b only depends on nature of solvent which can be explained by thermodynamic relation.

$$\boxed{K_b = \frac{R\left(T_b^0\right)^2}{1000 L_V} = \frac{M_A R\left(T_b^0\right)^2}{1000 \Delta H_{vap}}}$$

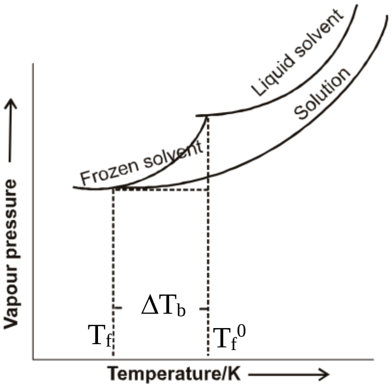
- Where T_b = Boiling point of solvent.
  M_A = Molar mass of solvent.
  ΔH_{vap} = Enthalpy of vapourisation per mole of solvent
  L_v = latent heat of vapourisation per gram of solvent

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

Solvent	B.P. (°C)	Molal elevation constant (K_b)
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

(c) Depression in freezing point:



- The freezing point of a liquid is that temperature at which the 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 is dissolved in a pure solvent the vapour pressure of the solvent is lowered.
- If T_f^o is the freezing point of pure solvent and T_f is freezing point of solution then, $T_f < T_f^o$
- The difference in the freezing point of pure solvent and solution is called depression of freezing point (ΔT_f)

$$\Delta T_f = T_f^{\,0} - T_f$$

The depression in freezing point is directly proportional to lowering in vapour pressure (ΔP)

$$\Delta T_f \propto \Delta P \propto \frac{n_B}{n_A}\ ;\ \Delta T_f \propto \frac{n_B}{n_A}$$

so $\boxed{\Delta T_f = K_f \times \text{molality}}$

- K_f = molal depression constant or Cryoscopic constant.
- K_f only depends on nature of solvent which can be explained by thermodynamic relation

$$\boxed{K_f = \frac{R\left(T_f^0\right)^2}{1000L_f} = \frac{R\left(T_f^0\right)^2 M_A}{1000\Delta H_f}}$$

Where T_f° = Freezing point of solvent

M_A = Molar mass of solvent.

ΔH_f = Enthalpy of fusion per mole of solvent

L_f= latent heat of fusion per gram of solvent

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

Solvent	F.P. (°C)	Molal depression constant (K_f)
Water	0.0	1.86
Ethyl alcohol	-114.6	1.99
Chloroform	-63.5	4.79
Carbon tetra chloride	-22.8	31.80
Benzene	5.5	5.12
Camphor	179.0	39.70

Example :14 A solution of urea in water has boiling point of 100.15° C. Calculate the freezing point of the same solution if K_f and K_b for water are 1.87 K kg mol^{-1} and 0.52 K kg mol^{-1} respectively.

(1) –0.52°C (2) –0.60°C (3) –0.62°C (4) –0.54°C

Solution. (4) $\Delta T_b = (100.15 - 100) = 0.15°$ C

We know that, $\Delta T_b = \text{molality} \times K_b$

$$\text{Molality} = \frac{\Delta T_b}{K_b} = \frac{0.15}{0.52} = 0.2884$$

$\Delta T_f = \text{molality} \times K_f = 0.2884 \times 1.87 = 0.54°$ C

Thus, the freezing point of the solution = – 0.54° C

Example.15 Equimolar solutions in the same solvent have

(1) Same freezing point but different boiling point

(2) Same boiling point but different freezing point
(3) Different boiling and different freezing point
(4) Same boiling and same freezing points

Solution. (4) The elevation in the boiling point and the depression in the freezing point are colligative properties and depend on the number of solute particles.

Equimolar solutions of non-electrolytes have the same number of solute particles.

Hence, equimolar solutions of two non-electrolytes in the same solvent have the same boiling point and same freezing point.

Example.16 Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at – 6°C will be:

(K_f for water = 1.86 K kg mol^{-1}, and molar mass of ethylene glycol = 62 g mol^{-1})

(1) 400.00 g (2) 304.60 g (3) 804.32 g (4) 204.30 g

Solution. (3) $\Delta T_f = k_f.m = 0 - (-6) = 1.86\ m$

$m = \frac{6}{1.86}$ i.e., $= \frac{6}{1.86}$ mole in 1 kg.

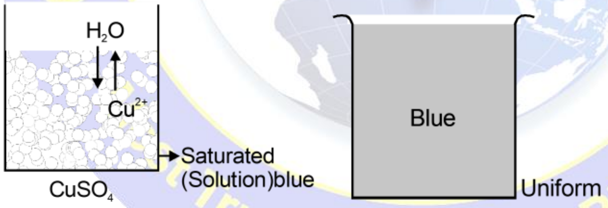
$\therefore \frac{6}{1.86} \times 4$ mole i 4 kg.

$Wt = \frac{6}{1.86} \times 4 \times 62 = 804.32$ gram

OSMOSIS AND OSMOTIC PRESSURE

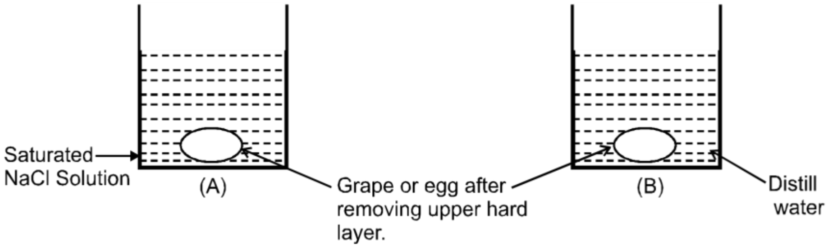
- **Diffusion:** Spontaneous flow of particles from high concentration region to lower concentration region is known as diffusion.

Example.



- **Osmosis:** The spontaneous flow of solvent particles from solvent side to solution side or from solution of low concentration side to solution of high concentration side through a semipermeable membrane (SPM) is known as osmosis.
- **Semipermeable Membrane(SPM):** A membrane which allows only solvent particles to move across it.
  (a) Natural : Semi permeable membrane
  Animal/plant cell membrane formed just below the outer skins.
  (b) Artificial membranes also:
  Copper ferrocyanide. $Cu_2[Fe(CN)_6]$ & Silicate of Ni, Fe, Co can act as SPM.

Example.

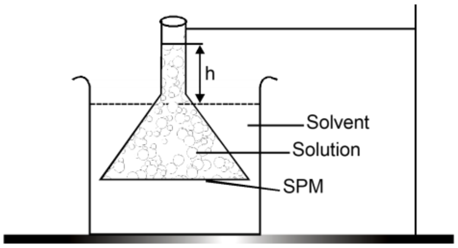


- **Conclusion:** After some time in (A) grape or egg will shrink and in (B) grape or egg will swell.

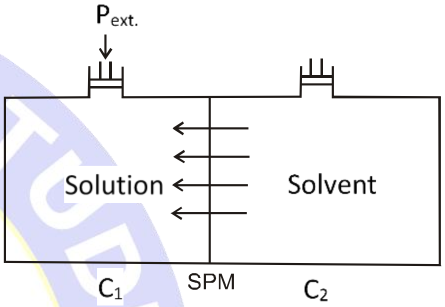
e.g. (i) A raw mango placed in concentrated salt solution loses water & shrivel into pickle.

(ii) People taking lot of salt, experience water retention in tissue cells. This results in puffiness or swelling called edema.

➢ **The phenomenon of osmosis :**



- A solution inside the bulb is separated from pure solvent in the beaker by a semipermeable membrane, Net passage of solvent from the beaker through the membrane occurs, and the liquid in the tube rises until equilibrium is reached.
- At equilibrium, the osmotic pressure exerted by the column liquid in the tube is sufficient to prevent further net passage of solvent.



➢ Although the passage of solvent through the membrane takes place in both direction, passage from the pure solvent side to the solution side is more favoured and occurs faster. As a result , the amount of liquid on the pure solvent side decreases, the amount of liquid on the solution side increases, and the concentration of the solution decreases.

➢ **Osmotic Pressure:** The equilibrium hydrostatic pressure developed by solution column when it is separated from solvent by semipermeable membrane is called O.P. of the solution.

$\pi = \rho gh$; ρ = density of solution.

g = acceleration due to gravity ; h = eq. height

1 atm = 1.013×10^5 N/m^2

➢ **Definition:**

- The external pressure which must be applied on solution side to stop the process of osmosis is called osmotic pressure of the solution.
- If two solutions of concentration C_1 and C_2 are kept separated by SPM, and $C_1 > C_2$ then particle movement take place from lower to higher concentration. So, extra pressure is applied on higher concentration side to stop osmosis. And $P_{ext.} = (\pi_1 - \pi_2)$

➢ **Reverse Osmosis:** If the pressure applied on the solution side is more than osmotic pressure of the solution then the solvent particles will move from solution to solvent side. This process is known as reverse osmosis.

➢ **Berkeley Hartley device/method** uses the above pressure to measure osmotic pressure.
e.g. used in desalination of sea-water.

➢ **Vant – Hoff Formula** (For calculation of osmotic pressure)

- $\pi \propto$ concentration (molarity)

$\propto T$

$\pi = CST$

S = ideal solution constant

= 8.314 J mol^{-1} K^{-1}

= R (ideal gas) constant

$\pi = CRT = \frac{n}{V} RT$ (just like ideal gas equation) π = atm.

$$\left\{\begin{array}{l} C - \text{mol/lit.} \\ R - 0.082 \text{ lit.atm. mol}^{-1} K^{-1} \\ T - \text{kelvin} \end{array}\right.$$

- In ideal solution solute particles can be assumed to be moving randomly without any interactions.

∴ C = total concentration of all types of particles.

$= C_1 + C_2 + C_3 + s.................$

$$= \frac{(n_1 + n_2 + n_3 + ...)}{V}$$

Type of solutions :

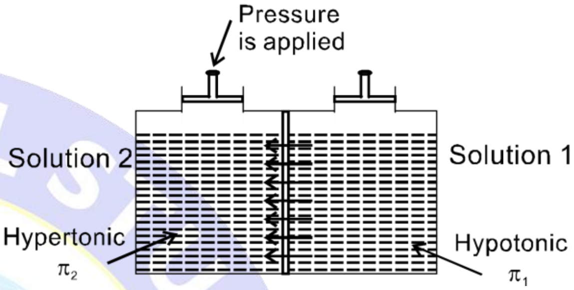
(a) **Isotonic solution:** Two solutions having same osmotic pressure are consider as isotonic solution.
$\pi_1 = \pi_2$ (at same temperature)

(b) **Hypotonic & Hypertonic solutions:** If two solutions 1 and 2 are such that $\pi_2 > \pi_1$, then solution 2 is called hypertonic solution and solution 1 is called hypotonic solution.

➢ **Conclusion :** Pressure is applied on the hypertonic solution to stop the flow of solvent particles, this pressure become equal to $(\pi_2 - \pi_1)$ and if hypotonic solution is replaced by pure solvent then pressure becomes equal to π_2.

➢ **Note: Osmotic pressure of very dilute solutions is also quite significant. So, its measurement in lab is very easy.**

➢ **Plasmolysis:** *When the cell is placed in solution having osmotic pressure greater than that of the cell sap, water passes out of the cell due to osmosis. Consequently, cell material shrinks gradually. The gradual shrinking of the cell material is called plasmolysis.*



Example.17 Which one of the following statement is False?

(1) Raoult's law states that the vapour pressure of a component over a solution is proportional to its mole fraction

(2) The osmotic pressure (π) of a solution is given by the equation π = MRT where M is the molarity of the solution

(3) The correct order of osmotic pressure for 0.01M aqueous solution of each compound is $BaCl_2 > KCl > CH_3COOH >$ Sucrose

(4) Two sucrose solutions of same molality prepared in different solvent will have the same freezing point depression

Solution. (4) The extent of depression in freezing point varies with the number of solute particles for a fixed solvent only and it is a characteristics feature of the nature of solvent also. So, for two different solvents the extent of depression may vary even if number of solute particles be dissolved.

Example.18 A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm^{-3}, molar mass of the substance will be

(1) 90.0 g mol^{-1} (2) 115.0 g mol^{-1} (3) 105.0 g mol^{-1} (4) 210.0 g mol^{-1}

Solution. (4) Since the solutions are isotonic, the concentration of the substance = Concentration of urea

$$\therefore \quad \frac{5.25}{M} = \frac{1.5}{60}$$

($\therefore$ 100 g solution = 100 ml as d = 1 g/ml and 1 L = 1000 ml)

$$M = \frac{52.5 \times 60}{15} = 210 \text{ g/mol}$$

Example.19 A 5% solution of cane sugar (molar mass 342) is isotonic with 1% of a solution of an unknown solute. The molar mass of unknown solute in g/mol is:

(1) 136.2 (2) 171.2 (3) 68.4 (4) 34.2

Solution. (3) Molar conc. of can sugar,

$$= \frac{5}{342} \times \frac{1000}{100} = \frac{50}{342}$$

Molar conc. of solution,

$$X = \frac{1}{M} \times \frac{1000}{100} = \frac{10}{M}$$

$$\frac{10}{M} = \frac{50}{342} \qquad \Rightarrow M = 68.4$$

SPOT LIGHT

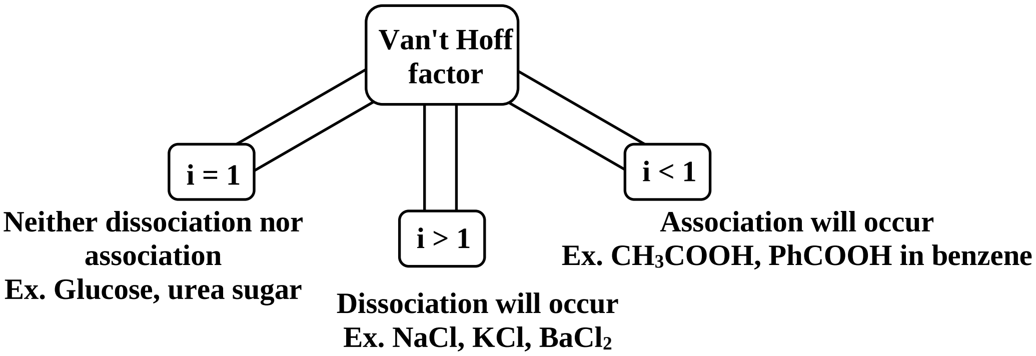
- (i) $\frac{\Delta P}{P^0} \approx \frac{n}{N} \Rightarrow \Delta P = \frac{wM}{mW} \times P^0$ (ii) $\Delta T_b = \left(\frac{w \times 1000}{m \times W}\right) K_b$

  (iii) $\Delta T_f = \left(\frac{w \times 1000}{m \times W}\right) K_f$ (iv) $\pi = CRT$
- Best method to determine molecular weight of biomolecules like protein and polymers is osmotic pressure.
- Because in this colligative property there is no temperature change is involved so there is no chance of change in nature of biomolecule.
- In other methods changes are very less and it is difficult to measure very small changes accurately.
- But osmotic pressure can be easily measured at room temperature at which biomolecules remain in original state.
- 0.91 % $\left(\frac{W}{V}\right)$ NaCl solution is isotonic with blood.
- Intravenous injections need to be isotonic with blood to prevent damage to RBC.
- Magnitude of osmotic pressure is independent with the nature of solvent.
- Berkley Hartley's method and Funnel experiment (p = hdg) are used to determine osmotic pressure.
- Ostwalds process is used to determine elevation in boiling point.
- Camphor is the best solvent for determination of molar mass of solute by using depression in freezing point since its K_f is very high.

6. 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 Factor (i):** Tells about relationship between normal colligative properties and abnormal colligative properties.
- $$i = \frac{\text{number of particles after dissoication or association}}{\text{number of particles before dissoication or association}} = \frac{\text{observed colligative properties}}{\text{calculated colligative properties}}$$

  $$= \frac{\text{calculated molecular mass}}{\text{observed molecular mass}}$$
- If i = 1 Neither dissociation nor association : Example. Glucose, urea, sugar
- If i > 1 Dissociation will occur : Example. NaCl, KCl, $BaCl_2$
- If i < 1 Association will occur : Example. CH_3COOH, PhCOOH in benzene



Neither dissociation nor association
Ex. Glucose, urea sugar

Dissociation will occur
Ex. NaCl, KCl, $BaCl_2$

Association will occur
Ex. CH_3COOH, PhCOOH in benzene

Case-I:

DISSOCIATION OF SOLUTE:

- Molecules of electrolytes undergo ionization or dissociation in polar solvents to give two or more particles in solution.
- This dissociation results in an increase in the total number of particles, and therefore the value of colligative properties of such solutions will be higher.
- As the colligative properties are inversely related to molecular weight, so the molecular weight of ionizable solute will be less than the theoretical value.
- Number of solute particles in solution increases.
- observed/experimental C.P. > calculated C.P. (normal)
- observed/experimental Molecular weight of of solute < calculated (normal) molecular weight of solute.

$$\therefore \quad \text{C.P.} \propto \frac{1}{\text{molecular weight of solute}}$$

- Calculation of 'i': Let solute be A_xB_y (electrolyte)

$\mathbf{A_xB_y \rightarrow xA^{y+} + yB^{x-}}$; x + y = n (total number of ions)

Initially	1 mol	0	0
After dissociation	$(1-\alpha)$	$x\alpha$	$y\alpha$

Total number of solute particles $= 1 - \alpha + x\,\alpha + y\,\alpha$

$= 1 - \alpha + (x + y)\alpha$

$= 1 - \alpha + n\,\alpha$

- Observed colligative property is proportional to observed number of solute particles $(1 - \alpha + n\alpha)$

$$i = \frac{\text{number of particles after dissociation}}{\text{number of particles before dissociation}} = \frac{1-\alpha+n\alpha}{1}$$

$$\boxed{i = 1 - \alpha + n\alpha} \qquad \alpha = \frac{(i-1)}{(n-1)}$$

where α is the degree of dissociation

- For strong electrolytes

if α = 1 or 100% then i = n

Example. NaCl ⇒ i = 2; for α = 100%

K_2SO_4 ⇒ i = 3 α= 100%

Example. $K_4[Fe(CN)_6]$ ⇒ i = 5 for α = 100%

For α ⇒50% $i = 1 + (n-1)\alpha$

i = 3

- Observed C.P. = i (normal C.P.)

Case II:

Association of solute:

- The formation of a bigger molecule by the union of two, three or more solute molecules is called association As a result, the total number of particles in solution becomes less than the number of molecules initially dissolved in the solution and hence the colligative properties will have lower value.
- As the molar mass of solute is inversely proportional to the colligative properties, so the molar mass of solute will be greater than theoretical value.
- Number of solute particles in solution decreases.
- observed/experimental C.P. < calculated C.P.
- observed/experimental molecular weight of solute > normal molecular weight of solute.

$$\therefore \quad \text{C.P.} \propto \frac{1}{\text{molecular weight of solute}}\ ;\ i < 1 \text{ for association.}$$

- Calculation of 'i'

$$\begin{array}{llcl} & \mathbf{nA} & \longrightarrow & \mathbf{[A]_n} \\ \text{Initially} & 1 & \longrightarrow & 0 \\ \text{After association} & (1-\alpha) & \longrightarrow & \dfrac{\alpha}{n} \end{array}$$

$$\text{Total number of solute particles } = 1-\alpha+\frac{\alpha}{n}$$

- Observed C.P. ∝ observed number of solute particles
- Van't hoff factor (i) $= \dfrac{\text{number of particles after association}}{\text{number of particles before association}}\ ;\ I = \dfrac{1-\alpha+\dfrac{\alpha}{n}}{1}$

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

α – degree of association

n – number of solute particles which are associated.

- if α = 100% or 1 or α is not specified $\boxed{i = \dfrac{1}{n}}$

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

Example.20 If α is the degree of dissociation of Na_2SO_4, the Vant of Hoff's factor (i) used for calculating the molecular mass is

(1) 1 – α (2) 1 + α (3) 1 – 2 α (4) 1+2 α

Solution. (4)

$Na_2SO_4 \longrightarrow 2Na^+ + SO_4^{2-}$ = ions = n

i = 1 – α + nα n = no. of ions dissociation

i = 1 – α + 3α

i = 1 + 2α

Example.21 The degree of dissociation (α) of a weak electrolyte, A_xB_y is related to Van't Hoff factor (i) by the expression:

(1) $\alpha = \dfrac{x+y-1}{i-1}$ (2) $\alpha = \dfrac{x+y+1}{i-1}$ (3) $\alpha = \dfrac{i-1}{(x+y-1)}$ (4) $\alpha = \dfrac{i-1}{(x+y+1)}$

Solution. (3)

$$\underset{1-\alpha}{A_xB_y} \rightarrow \underset{x\alpha}{xA^{y+}} + \underset{y\alpha}{yB^{x-}}$$

$i = 1 - \alpha + x\alpha + y\alpha = 1 + \alpha(x + y - 1)$

$$\therefore \quad \alpha = \frac{i-1}{(x+y-1)}$$

Example.22 If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f), when 0.01 mol of sodium sulphate is dissolved in 1 kg of water, is (K_f = 1.86 K kg mol^{-1}):

(1) 0.0186 K (2) 0.0372 K (3) 0.0558 K (4) 0.0744 K

Solution. (3) $Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-}$

Van't Hoff factor (i) for N_2SO_4 = 3

$\Delta T_f = i \times K_f \times m = 3 \times 1.86 \times 0.01$

$$\left[\therefore m = \frac{0.1\text{mol}}{1\text{Kg}} = 0.1\,\text{mol Kg}^{-1}\right] = 0.0558\text{ K}$$

Example.23 x g of non-electrolytic compound (molar mass = 200) is dissolved in 1.0 litre of 0.05 M NaCl solution. The osmotic pressure of this solution is found to be 4.92 atm at 27° C. Calculate the value of ‘x’. Assume complete dissociation of NaCl and ideal behaviour of this solution.

(1) 16.52 gm (2) 24.032 gm (3) 19.959 gm (4) 12.35 gm

Solution. (3)

(i) For NaCl : $\pi = iCRT = 2 \times 0.05 \times 0.0821 \times 300 = 2.463$ atm

(ii) For unknown compound, $\pi = CRT = \dfrac{x}{200} \times 0.0821 \times 300 = 0.01231 \times$ atm

Total osmotic pressure $\pi = \pi_1 + \pi_2$

$4.92 = 2.463 + 0.1231\,x$

$x = 19.959$ g

SPOT LIGHT

(i) Variation of vapour pressure with temperature (Clausius -Clapeyron equation)

$$\log_{10}\left(\frac{P_2}{P_1}\right)=\frac{\Delta H_{vap}}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

P_1 = vapour pressure at T_1
P_2 = vapour pressure at T_2
ΔH = Enthalpy of vaporation per mole

(ii) Anti-freeze solutions:

- Water is used in radiators of cars and other automobiles. In cold countries where the atmospheric temperature becomes less than zero degree, the water in the radiators would freeze.
- Anti-freeze solutions are useful under these conditions when the vehicles are used in the regions of sub-zero temperature so that the water does not freeze in radiators.
- Such solutions are made by dissolving ethylene glycol in water.
- Freezing point can be lowered to the desired extent by varying the concentration of ethylene glycol.
- Glycerol can also be used as anti-freeze.

(iii) Freezing mixture:

- It is a mixture of ice and common salt (NaCl). It is used in the making of ice-cream and in that laboratories to create low temperatures.
- With the help of this mixture, a temperature as low as -33°C (240 K) can be achieved.
- **Note:** Ebulloscopic and cryoscopic methods are effective when:
  - (i) Solutions are dilute. Solutions obey Raoult's law.
  - (ii) The solute is non-volatile.
  - (iii) There is not association or dissociation of solute molecules in the solution.
  - (iv) Solute does not form a solid solution with solvent in frozen state, i.e., only solvent separates in solid state on freezing the solution.
  - (v) Equimolal quantities of different substances dissolved in the same quantity of solvent bring out the same depression in freezing point of the solvent under identical conditions.

SOLUTIONS

Concentration Terms

Mass Percentage:
Mass% of the solution

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

Parts per million =

$$\frac{\text{Mass of component}}{\text{Total mass of solution}} \times 10^6$$

Molarity:
Molarity (M) =

$$\frac{\text{moles of solute}}{\text{Volume of solution (mL)}} \times 1000$$

Molality:
Molality (m) =

$$\frac{\text{moles of solute}}{\text{Mass of solvent in grams}} \times 1000$$

Mole Fraction:

$$\text{Mole Fraction of a component} = \frac{\text{No. of moles of the component}}{\text{Total no. of moles of all component}}$$

Normality:

$$\text{Normality (N)} = \frac{\text{No. of gram equivalent of solute}}{\text{Volume of solution in mL}} \times 1000$$

Formality:

$$\text{Formality (F)} = \frac{\text{No. of formula Unit of solute}}{\text{Volume of solution in litre}}$$

Abnormal molar mass and Van't Hoff factors:

$$i = \frac{\text{Observed value of colligative property}}{\text{Normal value of colligative property}}$$

$$= \frac{\text{Calculated molecular mass}}{\text{Observed molecular mass}}$$

For solute undergoing association: $a = (1 - i)\frac{n}{n - 1}$; $i < 1$

For solute undergoing dissociation :

$$\frac{P^\circ - P_s}{P^\circ} = ix_2;\ \Delta T_b = iK_b\, m,\ \Delta T_f = iK_f\, m;\ \pi = iCRT$$

Laws

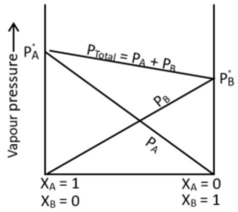
Henry's Law: The law states that "the mole fraction of a gas dissolved per unit volume of the solvent at constant temperature is directly proportional to the pressure (p) the gas in equilibrium with the solution." $\boxed{p = K_H X}$

Raoult's Law: The Law states that "at a given temperature, for a solution of volatile liquids, the partial vapour pressure of each component in solution is equal to the product of the vapour pressure of pure component and its mole fraction".

$$\boxed{P_S = P_A^\circ X_A + P_B^\circ X_B}$$

Types of Solution

Ideal Solutions: A solution which obeys Raoult's law exactly at all concentrations and at all temperatures is called an ideal solution.

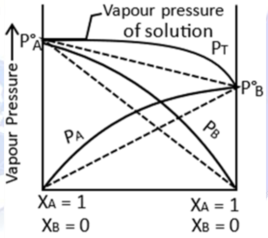


Examples :
(i) Benzene and toluene
(ii) CCl_4 and $SiCl_4$

Non-Ideal Solutions showing +ve deviations:

$P_A > P_A^\circ X_A$

$P_B > P_B^\circ X_B$

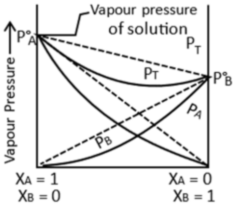


Examples :
(i) Ethanol and cyclohexane
(ii) Ethanol and Water

Non-Ideal Solutions Showing –ve deviations:

$P_A < P_A^\circ X_A$

$P_B < P_B^\circ X_B$



Examples:
(i) $CHCl_3$ and CH_3COOH
(ii) $CHCl_3$ and C_6H_6

Colligative Properties

Relative lowering in vapour pressure:
The relative lowering in vapour pressure of an ideal solution containing the non-volatile solute is equal to the mole fraction of the solute (X_B) at a given temperature.

$$\boxed{\frac{P_A^\circ - P_A}{P_A^\circ} = P_A}$$

Elevation in boiling point:
Elevation in boiling point (i.e. ΔT_b) is directly proportional to the molality (m) of the solute in solution.
$\Delta T_b \propto m$

$$\boxed{\Delta T_b = K_b m}$$

Where,
K_b = molal boiling point elevation constant.

Depression in freezing point:
Depression in freezing point (i.e. ΔT_f) is directly proportional to the molal concentration of solute (m).
$\Delta T_f \propto m$

$$\boxed{\Delta T_f = K_f m}$$

Where,
K_f = molal freezing point depression constant.

Osmotic Pressure:
At any temperature, the osmotic pressure (π) of a solution is proportional to the molar concentration (C) of the solute and absolute temperature.

$$\boxed{\pi = CRT}$$

Where, R = universal gas constant.

◆