SOLUTIONS & COLLIGATIVE PROPERTIES

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.

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.*

2. **Types of Solutions :**

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.

3. **Concentration Terms :**

% Concentration

Mass percentage : *It is the amount of solute in grams dissolved per 100 g of solution.* e.g., 10% solution of sodium chloride means 10 g of solid sodium chloride present in 100 g of solution.

$$\textbf{\% w/w} = \frac{\text{weight of solute (g)}}{\text{weight of solution (g)}} \times 100$$

Ex. 10% w/w urea solution = 10 g of urea is present in 100 g of solution.
= 10 g of urea is present in 90 g of water.

Mass by volume percentage (% w/v) : *It is defined as mass of solute dissolved per 100 ml of solution.* It is commonly used in medicine and pharmacy.

% wt/vol. (w/v)

% w/v = wt. of solute/100 mL of solution

$$\% \text{ w/v} = \frac{\text{gram of solutes}}{\text{volume of solution in mL}} \times 100$$

Ex. 10% (w/v) urea solution. = 10 g of urea is present in 100 mL of solution.

But not 10 g of urea present in 90 ml of water
for dilute solution : volume solution = volume solvent.

Volume percentage (% v/v) : *It is defined as volume of a solute dissolved per 100 ml of solution.*

% v/v = $\dfrac{\text{volume of solute}}{\text{volume of solution}} \times 100$

Strength of solution in g/L : Weight of solute (in gram) per litre (1000 mL) of solution.

Ex. 10% (w/v) sucrose solution, then specify its concentration in g/L
100 mL .... 10 g
1000 mL .... $\dfrac{10}{100} \times 1000$ = 100 g/L

Solved Examples

Example-1 : If we have 6% w/w urea solution with density 1.060 g/mL, then calculate its strength in g/L ?

Solution : 6 g urea is present in 100 g solution.

6 g in $\dfrac{100}{1.060}$ mL

$\dfrac{100}{1.060}$ mL $\longrightarrow$ 6 g.

1000 mL = × 1.060 × 1000 = 10.6 × 6 = 63.6

Molarity (M) : *It is expressed as the number of moles of solute per litre of solution.*

Molarity = No. of moles of solute per litre of solution.

Let n = No. of moles of solute ; N = No. of moles of solvent ; V = volume of solution

$$M = \frac{n}{V(\text{in L})} = \left(\frac{W}{M}\right) \times \frac{1000}{V(\text{in mL})}$$

no. of moles of solute = molarity x volume (in L)
no. of m. moles of solute = molarity x volume (in mL)

If V_1 mL of C_1 molarity solution is mixed with V_2 mL of C_2 molarity solution (same substance or solute)

$$C_f (V_1+V_2) = C_1V_1 + C_2V_2$$

$C_f = \left[\dfrac{C_1V_1 + C_2V_2}{V_1 + V_2}\right] = \dfrac{\text{Total moles}}{\text{Total volume}}$ where C_f = molarity of final solution

Molality (m) : *It is defined as number of moles of solute per 1000 g or 1 kg of solvent.*

Molality = No. of moles of solute per kg(1000 g) of solvent.

Let w gram of solute (Molar mass = Mg/mole) is dissolved in 'W' gram of solvent.

molality = $\left(\dfrac{w}{M}\right) \times \dfrac{1000}{W(g)}$; molality = $\dfrac{\text{moles} \times 1000}{W(g)\text{of solvent}}$

Molality not depends on temperature.

Solved Examples

Example-2 : If 20 ml of 0.5 M Na_2SO_4 is mixed with 50 ml of 0.2 M H_2SO_4 & 30 ml of 0.4 M $Al_2(SO_4)_3$ solution. Calculate [Na^+], [H^+], [SO_4^{2-}], [Al^{3+}]. [Assuming 100% dissociation]

Solution : Molarity = $\frac{\text{moles}}{\text{volume}} \Rightarrow$ 10 m. moles of Na_2SO_4 $\Rightarrow$ 20 m. moles of Na^+

(i) $[Na^+] = \frac{20}{100} = 0.2$ M

(ii) $[H^+]$ = ?

10 m. moles H_2SO_4

20 m. moles H^+

$[H^+] = \frac{20}{100} = 0.2$ M

(iii) $[SO_4^{2-}] = \frac{10+10+36}{100} = \frac{56}{100} = 0.56$ M

(iv) $[Al^{3+}] = \frac{24}{100} = 0.24$ M

Example-3 : **(a)** Derive a relationship between molality & molarity of a solution in which w g of solute of molar mass M g/mol is dissolved in W g solvent & density of resulting solution = 'd' g/ml.

(b) Calculate molality of 1.2 M H_2SO_4 solution? If its ρ = 1.4 g/mL

Solution : **(a)** Say 1 L solution taken,

mass of 1 lit solution = (1000 d) g

moles of solute = (molarity)

mass of solute = (molarity) x m

mass of solvent = W = 1000 d – (molarity) × m

$\therefore$ molality = $\frac{(\text{molarity}) \times 1000}{1000\ \ d\ \ -\text{molarity} \times \text{M.Wt}}$ [Where no.of moles of solute = molarity]

(b) Molality = $\frac{1.2 \times 1000}{1000 \times 1.4 - \ 1.2 \times 98}$ **= 0.936**

Normality : *It is defined as number of gram equivalents of solute dissolved per litre of solution.*

No. of equivalents per litre of solution = $\frac{\text{no. of equivalents of solute}}{\text{volume of solution (in L)}}$ = n-factor molarity

No. of equivalents = normality × volume (in L)

Equivalent mass = $\frac{\text{Molar mass}}{n-\text{factor}}$

No. of equivalent = $\frac{\text{Mass of the species}}{\text{equivalent mass}} = \frac{\text{Mass of the species}}{\frac{\text{Molar mass}}{n-\text{factor}}}$

'n' - factor

(i) For oxidizing/reducing agents : no. of e^- involved in oxidation/reduction half reaction per mole of oxidising agent /reducing agent.

e.g. : $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + H_2O$ n- factor = 5

(ii) For acid/ base reactions : no. of H^+ ions displaced/ OH^- ions displaced per mole of acid/ base.
e.g. : NaOH n - factor = 1 H_2SO_4 n - factor = 2

(iii) For salt : n = Total charge on cations.

$$\left.\begin{array}{c} n = \text{Total charge on cations.} \\ \text{or} \\ \text{total charge on anions} \end{array}\right\} \text{Simple salts}$$

e.g. : $Al_2(SO_4)_3$ n - factor = charge on the cation = 2 x 3 = 6

Mole-fraction (x) : *It is the ratio of number of moles of a particular component to the total number of moles of all the components.* e.g., mole-fraction of component A, $x_A = \frac{n_A}{n_A + n_B}$, where n_A is the number of moles of component 'A' and n_B is the number of moles of component 'B'.

For binary mixture.

$$X_{solute} = \frac{\text{moles of solute}}{\text{total moles in solutions}} = \frac{n}{n+N} \ ; \ X_{Solvent} = \frac{\text{moles of solvent}}{\text{Total moles in solutions}} = \frac{N}{n+N}$$

$X_{solute} + X_{Solvent} = 1$

Parts per million (ppm) : *The number of parts of solute present in 1 million parts of solution are called its ppm.* When a solute is present in small quantities (very minute amounts), it is easier to express the concentration in parts per million.

(a) $\text{ppm (w/w)} = \frac{\text{wt. of solute (in g)}}{\text{wt. of solution (in g)}} \times 10^6$

(b) $\text{ppm (w/v)} = \frac{\text{wt. of solute (in g)}}{\text{vol. of solution (in mL)}} \times 10^6$

(c) $\text{ppm (moles/moles)} = \frac{\text{moles of solute}}{\text{moles of solution}} \times 10^6$

Table : 1

Name	Units	Advantage	Disadvantages
Molarity (M)	$\frac{\text{mol solute}}{\text{L solution}}$	Useful in stoichiometry; measure by volume	Temperature-dependent; must know density to find solvent mass
Mole fraction (x)	None	Temperature-independent; useful in special applications	Measure by mass ; must know density to convert to molarity
Mass %	%	Temperature-independent; useful for small amounts	Measure by mass ; must know density to convert to molarity
Molality (m)	$\frac{\text{mol solute}}{\text{kg solvent}}$	Temperature-independent useful in special applications	Measure by mass ; must know density to convert to molarity

Note : All volume related concentration terms are temperature dependent.

Solved Examples

Example-4 : If we have 10 molal urea solution, Calculate mole fraction of urea in this solution & also calculate % w/w of urea (MW = 60).

Solution : 10 moles urea in 1000 g of water

$$X_{urea} = \frac{10}{10 + \frac{1000}{18}} = \frac{10}{65.55} = 0.1526$$

% w/w weight of urea = $\frac{10\times 60}{10\times 60+1000}$ x 100 = 37.5%

*** Note :** For dil. aq. solution molality molarity, as d ≈ 1 g/mL

$$\text{molality} = \frac{\text{molarity} \quad \times 1000}{1000\times d-\text{molarity}\times m}$$

Example-5 : Calculate molarity of $CaCO_3$(aq.) solution which has concentration of $CaCO_3$ = 200 ppm.

Solution : 200 g of $CaCO_3$ in 10^6 g of water.

$\frac{200}{100}=2$ moles of $CaCO_3$ in 10^3 liters of water. (density =1g/mL)

So molarity = $\frac{2}{10^3}$ = 2 × 10^{-3} M.

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4. Colligative properties & constitutional properties :

- **Constitutional Properties :** Properties which are dependent on nature of particles are constitutional properties like electrical conductance.

- **Colligative properties :** The properties of the solution which are dependent only on the total no. of particles relative to solvent/solution or total concentration of particles in the solution and are not dependent on the nature of particle i.e. shape, size, neutral /charge etc. of the particles.

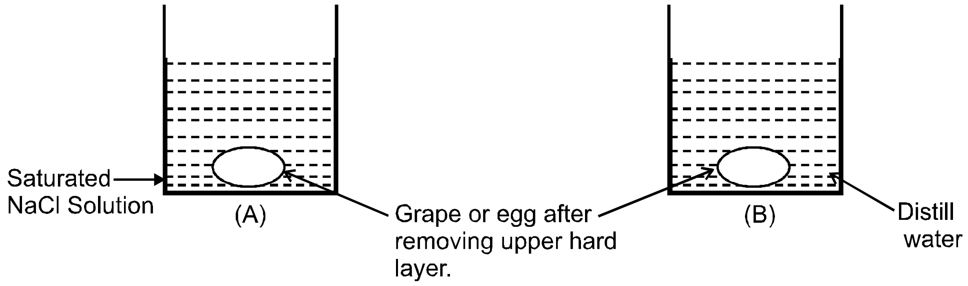
There are 4 colligative properties of solution :

- ❍ Osmotic pressure
- ❍ Relative lowering in vapour pressure $\left(\frac{\Delta P}{P}\right)$
- ❍ Elevation in b.p. (ΔT_b)
- ❍ Depression in freezing pt. (ΔT_f)

(i) Osmosis & Osmotic pressure :

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.

Ex.



Figure

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.

Biological Importance of Osmosis

The cell walls of plants and animals are semipermeable in nature and thus are responsible for the osmosis. When a cell comes in contact with water a tendency of flow of water into the cell is developed. The pressure developed inside the cell due to the inflow of water is called turgor.

If the cell comes in contact with a concentrated solution, cell would shrink, which is called plasmolysis. Cell walls are able to permit the flow of selected ions and molecules also along with water.

Various processes taking place due to osmosis are :

(a) Absorption of water from soil through the cell walls of roots.

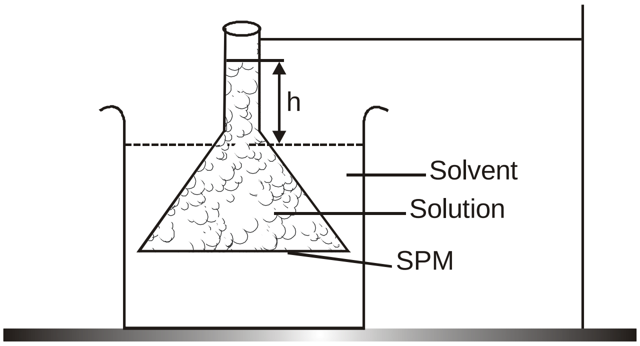
(b) Movement of water from roots to the upper parts of plants & trees.

(c) Various types of locomotion in plants like stretching of leaves, opening of flowers, etc., are also based on osmosis.

(d) Germination is also caused due to osmosis as water moves into the seeds through cell walls.

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 memberane occurs, and the liquid in the tube rises untill 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.

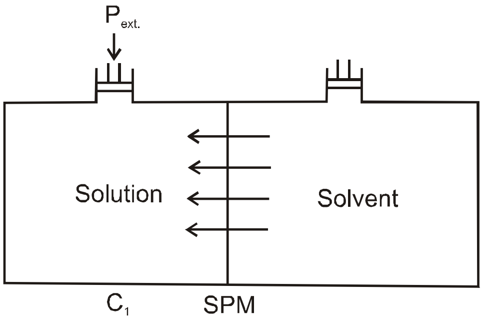


Osmotic Pressure : The equilibrium hydrostatic pressure developed by solution column when it is seperated from solvent by semipermeable membrane is called O.P. of the solution.

$\pi = \rho g h$; ρ = density of soln.

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.

Berkely : Hartely 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 π = atm.
  = 8.314 J mol^{-1} K^{-1} (exp value)
  = R (ideal gas) constant
  $\pi = CRT = \frac{n}{V}RT$ (just like ideal gas equation)

C – mol/lit.
R – 0.082 lit.atm. $mol^{-1}K^{-1}$
T – kelvin

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

$\therefore$ C = total concentration of all types of particles.

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

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

Solved Examples

Example-6 : If V_1 mL of C_1 solution + V_2 mL of C_2 solution are mixed together then calculate final concentration of solution and final osmotic pressure. If initial osmotic pressure of two solutions are π_1 and π_2 respectively ?

Solution : $C_f = \frac{C_1V_1 + C_2V_2}{V_1 + V_2}$

$\pi_1 = C_1RT,\ C_1 = \left(\frac{\pi_1}{RT}\right)$; $\pi_2 = C_2RT,\ C_2 = \left(\frac{\pi_2}{RT}\right)$

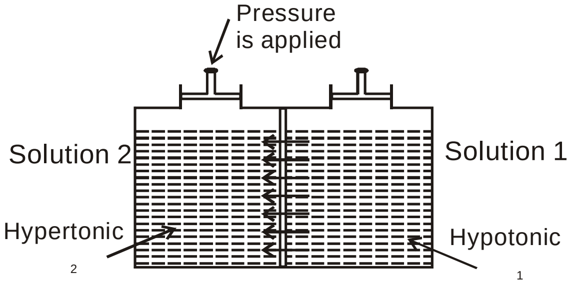
$\pi = \left(\frac{C_1V_1 + C_2V_2}{V_1 + V_2}\right)RT$; $\pi = \left(\frac{\pi_1V_1 + \pi_2V_2}{V_1 + V_2}\right)$

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 2 is called hypertonic solution and 1 is called hypotonic solution.



Figure

Conclusion : Pressure is applied on the hypertonic solution to stop the flow of solvent partices, 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.*

- **Abnormal Colligative Properties : [Vant–Hoff correction :]**
  - For electrolytic solutes the number of particles would be different from the number of particles actually added, due to dissociation or association of solute.
  - The actual extent of dissociation/association can be expressed with a correction factor known as vant Haff factor (i).

Vant–Hoff factor : $i = \dfrac{\text{moles of particles in solution after dissociation/association}}{\text{moles of solute dissolved}}$

- If solute gets associated or dissociated in solution then experimental / observed / actual value of colligative property will be different from theoretically predicted value so it is also known as **abnormal colligative property.**
- This abnormality can be calculated in terms of Vant-Hoff factor.

$$i = \frac{\text{exp/observed/actual/abnormal value of colligative property}}{\text{Theoretical value of colligative property}}$$

$$= \frac{\text{exp./observed no. of particles or concentration}}{\text{Theoretical no. of particles or concentration}} = \frac{\text{(Theoretical molar mass of substance)}}{\text{(Experimental molar mass of the substance)}}$$

$i > 1$ dissociation

$i < 1$ association

$$i = \frac{\pi_{\text{exp.}}}{\pi_{\text{theor.}}}$$

- **Modified formula** $\therefore \pi = i\text{CRT}$

$$\pi = (i_1C_1 + i_2C_2 + i_3C_3.....)\ RT$$

Case - I : Electrolyte dissociates

Relation between i & α (degree of dissociation) :

Let the electrolyte be A_xB_y

$$\begin{array}{llll} & A_xB_y\ (aq.) \longrightarrow & xA^{y+} & +\ yB^{x-} \\ t = 0 & C & 0 & 0 \\ t_{eq} & C(1-\alpha) & xC\alpha & yC\alpha \end{array}$$

Net concentration = $C - C\alpha + xC\,\alpha + yC\alpha = C\,[1 + (x+y-1)\,\alpha] = C\,[1 + (n-1)\,\alpha]$.

$n = x + y$

= no. of particles in which 1 molecule of electrolyte dissociates

$$i = \frac{C\ [1+(n-1)\alpha]}{C}$$

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

e.g. NaCl (100% ionised), i = 2. ; $BaCl_2$ (100% ionised), i = 3. ; $K_4[Fe(CN)_6]$ (75% ionised), i = 4.

Case - II : Electrolyte associates

Relation between degree of association β & i.

$$\begin{array}{lll} & nA \longrightarrow & A_n. \\ t = 0 & C & 0 \end{array}$$

t_{eq} $\quad C\,(1-\beta) \quad \frac{C\beta}{n}$

Net concentration = $C - C\beta + \frac{C\beta}{n} = C\left[1 + \left(\frac{1}{n}-1\right)\beta\right]$

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

if dimerise n = 2 ; trimerise n = 3 ; tetramerise n = 4.

e.g. CH_3COOH 100% dimerise in benzene, i = $\frac{1}{2}$; C_6H_5COOH 100% dimerise in benzene, i = $\frac{1}{2}$

Solved Examples

***Example*.7** Calculate π of a solutions having 0.1 M NaCl & 0.2 M Na_2SO_4 and 0.5 HA (weak acid which is 20% dissociation solutions at 300 K)

Sol. $\pi = (0.2 + 0.6)\,RT + i_3\, C_3\, RT$

$i_3 = 1+(1).2 = 1.2$

$\Rightarrow [0.8 + 0.6]\,RT = (1.4 \times 0.083 \times 300) = 1.162 \times 30 = 34.86$ atm

***Example*.8** If 0.04 M Na_2SO_4 solutions at 300 K is found to be isotonic with 0.05 M NaCl (100 % disscociation) solutions calculate degree of disscociation of sodium sulphate.

Sol. $i\, C_1\, RT = i_2\, C_2\, RT$

$[1+(2)\,\alpha]\, 0.042 = 2 \times \frac{0.05}{2}$

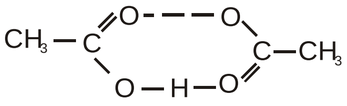
$1 + 2\,\alpha = \frac{5}{2} - 1$

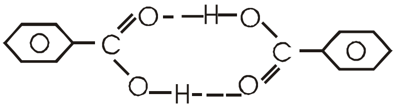
$2\,\alpha = \frac{3}{2}$

$\alpha = \frac{3}{4} \times 100 = 75\ \%.$

***Example*.9** If 6 gm of CH_3 COOH is dissolved in benzene to make 1 litre at 300 K π of solutions is found to be 1.64 atm. If it is known that CH_3COOH in benzene forms a dimer.

Sol.





Calculate degree of association of acetic acid in benzene

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

$1.64 = 0.0823 \times 300 \times \left[1 + \left(\frac{1}{n}-1\right)\beta\right] \Rightarrow \quad 1.64 = 0.0823 \times 300\ \left[1 - \frac{\beta}{2}\right] 0.1$

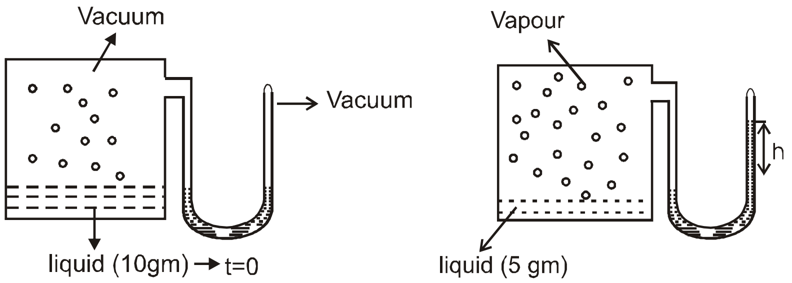
$\frac{1.64}{00.823 \times 30} = \frac{2\text{-}\beta}{2} \Rightarrow \quad \frac{1.64}{2.46} = \frac{2\text{-}\beta}{2} \Rightarrow \quad 4 = 6 - 3\beta$

$3\beta = 2 \Rightarrow \quad \beta = \frac{2}{3}$

(ii) Relative lowering in vapour pressure (RLVP) :

- **Vapour Pressure :**

The conversion of a liquid to a vapour takes place in a
visible way when the liquid boils, it takes place under all conditions.
say 5 gm liquid left at t_{eq}



At eq. : the rate of evaporation = rate of condense

$H_2O(\ell) \rightleftharpoons H_2O(g)$

$K_p = P_{H_2O(g)}$ eq.

∴ finally

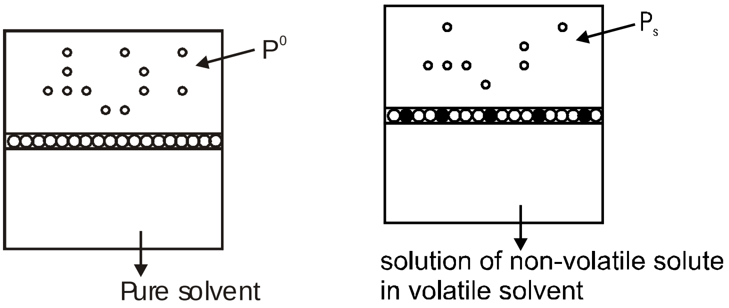
- The pressure exerted by vapours of the liquid when equilibrium is established between vapours & its liquid. is known as vapour pressure.
- Vapour pressure is an equilibrium constant (K_P) of the reaction.

  liquid $\rightleftharpoons$ vapours.
- Since vapour pressure is an equilibrium constant so its value is dependent only on temperature for a particular liquid
- It does not depends on the amount of liquid taken or surface area of the liquid or on volume or shape of the container. It is a characteristic constant for a given liquid.

- **Vapour Pressure of a solution**

  Vapour Pressure of a solutions of a non volatile solute (solid solute) is always found to be less than the vapour pressure of pure solvent .

Reason : Some of the solute molecules will occupy some surface area of the solutions so tendency of the solvent particles to go into the vapour phase is slightly decreased hence $P^o > P_S$, where P^o is vapour pressure of pure solvent and P_S is vapour pressure of the solution.



Lowering in VP = $P^o - P_S = \Delta P$

and Relative lowering in Vapour Pressure = $\frac{\Delta P}{P^0}$

Raoult's law (For non–volatile solutes): The vapour pressure of a solution of a non-volatile solute is equal to the vapour pressure of the pure solvent at that temperature multiplied by its mole fraction.

OR Relative Lowering in Vapour Pressure = mole fraction of the non volatile solute in solution.

$$P_S = x_{solvent}P^0 = (1 - x_{solute})P^0$$

$$\text{RLVP} = \frac{P^0 - P_s}{P^0} = x_{Solute} = \frac{n}{n + N}$$

where n = number of moles of non-volatile solute and N = number of moles of solvent in the solution.

$$\frac{P^0}{P^0\text{-}P_s} = \frac{n+N}{n} = 1+\frac{N}{n}$$

$$\frac{N}{n} = \frac{P^0\text{-}P_s}{P^0} - 1 = \frac{P_s}{P^0\text{-}P_s}$$

$$\frac{P^0\text{-}P_s}{P_s} = \frac{n}{N}$$

$$\frac{P^0\text{-}P_s}{P_s} = \frac{w}{m} \times \frac{M}{W} = \frac{w}{m} \times \frac{M}{W} \times \frac{1000}{1000} = \frac{w}{m} \times \frac{1000}{W} \times \frac{M}{1000}$$

$$\frac{P^0\text{-}P_s}{P_s} \mathbf{= (molality) \times} \frac{M}{1000}$$

where w and W = mass of non-volatile solute and volatile solvent respectively
m and M = molar mass of non-volatile solute and volatile solvent respectively

If solute gets associated or dissociated ; $\frac{P^0\text{-}P_s}{P_s} = \frac{i.n}{N}$ that is $\frac{P^0\text{-}P_s}{P_s} = i \times (\text{molality}) \times \frac{M}{1000}$

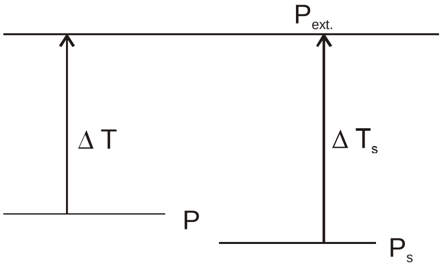
(iii) Elevation in Boiling point (ΔT_b)

- **Boiling point of a Liquid :** The temprature at which vapour pressure of a liquid becomes equal to the external pressure present at the surface of the liquid is called b.p of liquid at that pressure.

- **Normal boiling point :** The temperature at which boiling ocuurs when the external pressure is exactly 1 atm is called the normal boiling point of the liquid. (T_b)

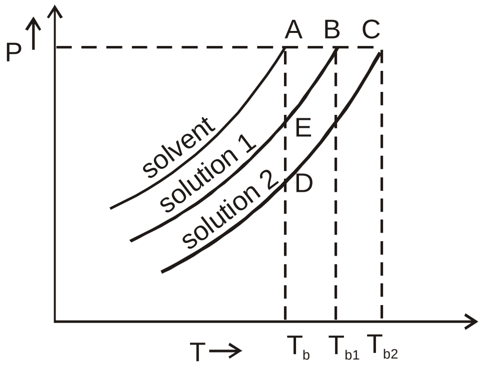
Boiling pt of any solution :

- Since V.P. of solution is smaller then V.P. of pure solvent at any temperature hence to make it equal to $P_{ext.}$ we have to increase the temp. of solution by greater amount in comparision to pure solvent.



$\Delta H_{\text{vapour of solvent}} = \Delta H_{\text{vapour solution}}$

Graphical :



Using Raoult's law : $\frac{\Delta P}{P} = \frac{n}{n+N}.\ P$ or $\Delta P = \frac{w/m}{W/M}.P$

$\Rightarrow \quad \Delta T_b \ \alpha \ \frac{w}{m}.\frac{M}{W}.P = \left(\frac{w}{m}\times\frac{1000}{W}\right)\left(\frac{M}{1000}.\ P\right)$; $\Delta T_b = K_b \times$ molality

- K_b is dependent on property of solvent and known as molal elevation constant of solvent
- It is also known as ebullioscopic constant.
- K_b = elevation in boiling point of 1 molal solution.
- **Units :** $\frac{\Delta T_b}{\text{molality}} = \frac{K}{\text{mol/kg}}$ = K kg mol^{-1}

Using thermodynamics : $K_b = \frac{RT_b^{\,2}}{1000 \times L_{vap}}$

∴ L_{vap} – is latent heat of vapourization in cal/g or J/g

R = 2 cal mol^{-1} K^{-1} or 8.314 J mol^{-1} K^{-1}. ; T_b = b.p. of liquid (in kelvin)
K_b = K kg mol^{-1}

- Also $K_b = \frac{RT_b^{\,2}\ M}{1000 \times \Delta H_{vap}}$ Here : ΔH_{vap} = molar enthalpy of vaporisation in cal/mole of J/mole

M ⇒ mole wt. of solvent

$L_{vap} = \left(\frac{\Delta H_{vap}}{M}\right)$

- If solute gets associated/dissociated : $\Delta T_b = i \times K_b \times$ molality

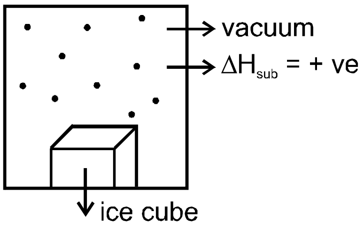
Solved Examples

***Example*.10** Calculate K_b of water if L_{vap} = 540 Cal/gm T_b = 100ºC

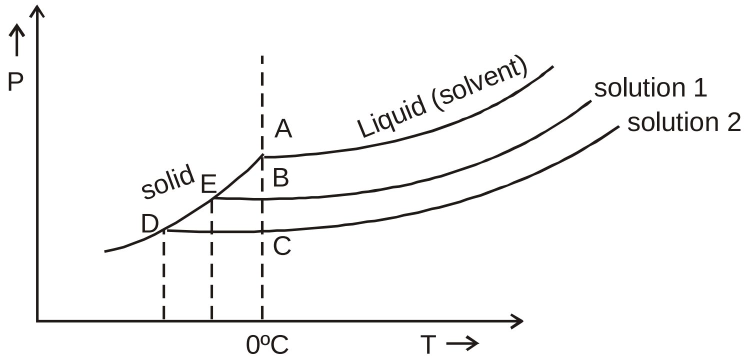
Sol. $K_b = \frac{2 \times 373 \times 373}{1000 \times 540}$ = 0.52 K kg mol^{-1}

(iv) Depression in freezing pt (ΔT_f)

Freezing point : Temperature at which vapour pressure of solid becomes equal to v.p of liquid is called freezing point of liquid or melting point of solid.



$\Delta H_{sub} > \Delta H_{vap.}$



- For - dil. solutions BE & CD can be assumed to be straight lines.

  ∴ using similar triangles

  $\Delta T_f \propto \Delta P$

  ∴ $\Delta T_f = K_f$. Molality
- K_f = molal depression constant = cryoscopic constant

  $K_f = \dfrac{RT_f^2}{1000 \times L_{fusion}} = \dfrac{RT_f^2\ M}{1000 \times \Delta H_{fusion}}$
- for water T_f = 273 K & L_{Fusion} = 80 cal / gm

  $K_f = \dfrac{2 \times 273 \times 273}{1000 \times 80} = 1.86 \text{ K kg mol}^{-1}$
- At freezing point or below it only solvent molecules will freeze not solute molecules (solid will be of pure solvent)

Solved Examples

***Example*.11** A 0.01 molal solution of ammonia freezes at – 0.02ºC. Calculate the van't Hoff factor, i and the percentage dissociation of ammonia in water. $(K_{f(H_2O)}) = 1.86$ deg molal^{-1}.

Sol. Experimental $\Delta T = 0.02^o$

Theoretical $\Delta T = 1.86 \times 0.01 = 0.0186^o$

i = van't Hoff factor = $\dfrac{0.02}{0.0186} = 1.075$

Degree of dissociation , $\alpha = \dfrac{i-1}{v-1}$ (v = no. of species formed on dissociation)

$= \dfrac{0.075}{2-1} = 0.075$

% dissociation = 7.5. **Ans.** 1.075, 7.5.

Example-12 : Van't Hoff factors of aqueous solutions of X, Y, Z are 1.8, 0.8 and 2.5. Hence, their (assume equal concentrations in all three cases)

(A) b.p. : X < Y < Z (B) f. p. Z < X < Y
(C) osmotic pressure : X = Y = Z (D) v. p. : Y < X < Z

Solution : As van't Hoff factor increases RLVP increases i.e., V.P. decreases y > x > z
Elevation in b.p. increases i.e., b.p. increases y < x < z
Depresion in f.p increases i.e., f.p decreases y > x > z
Osmotic pressure increases so y < x < z. **Ans. (B)**

Example-13 : A 0.001 molal solution of a complex reprsented as $Pt(NH_3)_4Cl_4$ in water had a freezing point depression of 0.0054ºC. Given K_f for H_2O = 1.86 molality^{-1}. Assuming 100% ionisation of the complex, write the ionisation nature and formula of complex.

Solution : Let n atoms of Cl be the acting as ligand. Then formula of complex and its ionisation is :

$$\begin{array}{lcl} [Pt(NH_3)_4Cl_n]Cl_{(4-n)} \longrightarrow & [Pt(NH_3)_4Cl_n]^{+(4-n)} & + \ (4-n)\ Cl^- \\ \quad 1 & 0 & \quad 0 \\ \quad 0 & 1 & \quad (4-n) \end{array}$$

Thus particles after dissocation = 4 – n + 1 = 5 – n
and therefore, van't Hoff factor (i) = 5 – n
Now $\Delta T_f = K'_f \times \text{molality} \times \text{van't Hoff factor}$
$0.0054 = 1.86 \times 0.001 \times (5 - n)$
$\therefore$ $n = 2.1 \approx 2$ (integer value)
Thus complex and its ionisation is :

$$[Pt(NH_3)_4Cl_2]Cl_2 \longrightarrow [Pt(NH_3)_4Cl_2]^{2+} + 2Cl^-$$

Example-14 : Depression of freezing point of 0.01 molal aq. CH_3COOH solution is 0.02046°. 1 molal urea solution freezes at – 1.86°C. Assuming molality equal to molarity, pH of CH_3COOH solution is :
(A) 2 (B) 3 (C) 3.2 (D) 4.2

Solution : For urea

$$\Delta T_f = k_f \times m \qquad \text{or} \qquad k_f = \frac{\Delta T_f}{m} = \frac{1.86}{1} = 1.86$$

Now for CH_3COOH
$\Delta T_f = i\, k_f\, m$
so $i = \ = 1.1$
Now $i = 1 + \alpha$
so $\alpha = 1.1 - 1 = 0.1$

$$\begin{array}{lcccc} \text{Now} & CH_3COOH & \rightleftharpoons \ CH_3COO^- & + & H^+ \\ & C & 0 & & 0 \\ & C - C\alpha & C\alpha & & C\alpha \end{array}$$

$[H^+] = C\alpha = 0.01 \times 0.1 = 0.001$

so pH = 3. **Ans. (B)**

5. SOLUTIONS CONTAINING

$$\begin{Bmatrix} \text{VOLATILE} & \text{SOLVENT} \\ \text{VOLATILE} & \text{SOLUTE} \end{Bmatrix} \begin{array}{l} \text{Liq . solution} \\ \text{Liq . solution} \end{array}$$

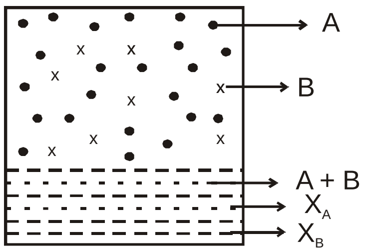
Mixture of 2 volatile liquids
Raoult's law (for volatile Liq. Mixture)

Statement of Raoult's law (for volatile liq. mixture): In solution of volatile liquids, the partial vapour pressure of each component is directly proportional to its mole fraction.

$p_A \propto x_A \qquad \Rightarrow \qquad p_A = x_A P_A^o$

p_A = Partial vapour pressure of component A
x_A = Mole fraction of component 'A' in solution.
P_A^o = Vapour pressure of pure component 'A' at given temperature

Derivation of total pressure over solution using Raoult's law and Dalton's law:
Let A, B be to two volatite liquids in a closed container as shown.

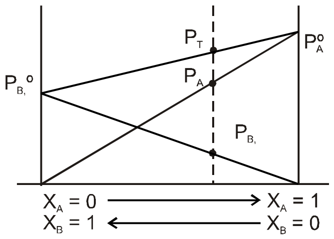


$p_A = x_A P_A^o$
Similarly, for liquid B we have,
$p_B = x_B P_B^o$
Total pressure over the solution P_T, according to Dalton's law is
$P_T = p_A + p_B = x_A P_A^0 + x_B P_B^0$

Determining composition of vapour phase:
Let, y_A = mole fraction of A in vapour phase above the solution and
y_B = mole fraction of B in vapour phase above the solution
Now, we have, $p_A = y_A P_T$ .....Dalton's law of partial pressure for a gaseous mixture
$p_A = x_A P_A^o$ ....Raoult's law
Thus, $p_A = y_A P_T = x_A P_A^o$
Also, $p_B = y_B P_T = x_B P_B^o$

$$x_A + x_B = 1 = \frac{y_A P_T}{P_A^0} + \frac{y_b P_T}{P_B^0} \; ; \qquad \text{Thus, } \frac{1}{P_T} = \frac{y_A}{P_A^0} + \frac{y_B}{P_B^0}$$

Graphical Representation of Raoult's Law:



$p_A = x_A P_A^o$ & $p_B = x_B P_B^o$

$P_T = x_A P_A^o + x_B P_B^o$

$P_T = (P_A^o - P_B^o)\, x_A + P_B^0$

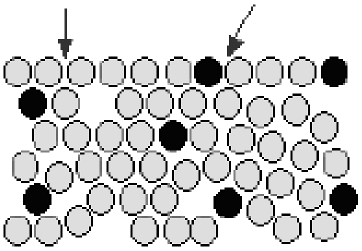
$P_T = (P_B^o - P_A^o)\, x_B + P_A^0$

This represents equation of straight line. P_T v.s. x

Note: If $P_A^o > P_B^o$, A is more volatile than B. B.P. of A < B.P. of B.

Limitations of Raoult's Law: Raoult's Law only works for ideal solutions. Very dilute solutions obey Raoult's Law to a reasonable approximation.

(6) **Ideal Solutions :** Those solutions which obey Raoult's law over the entire range of conc. are called ideal solutions. When the forces of attraction between A—A, B—B is similar to A—B, then A and B will form ideal solution.



In an ideal solution, the forces between the solvent molecules

.... are exactly the same as those between solvent and solvent and solute.

Thatmeans that it takes the same amount of energy for solvent molecules to break away from the surface in either case.

Properties of ideal solution :

(i) Raoult's law is obeyed

(ii) $\Delta H_{mix} = 0$, i.e., there should not be enthalpy change when components of ideal solutions are mixed.

(iii) $\Delta V_{mix} = 0$, (1L + 1L = 2L) i.e., there should not be change in volume on mixing. e.g.; n-hexane and n-heptane; ethyl bromide and ethyl iodide; benzene and toluene; chlorobenzene and bromobenzene form ideal solutions.

(iii) $\Delta S_{mix} = +ve$ **(iv)** $\Delta G_{mix} = -ve$

(7) Non-Ideal Solutions :

Those solutions which do not obey Raoult's over the entire range of concentration are called non-ideal solutions.

When the forces of attraction between A—A, B—B is different from A—B then 'A' and 'B' form non-ideal solutions. For these solutions :

(i) Raoult's law is not obeyed. (ii) $\Delta H_{mix} \neq 0$; (iii) $\Delta V_{mix} \neq 0$.

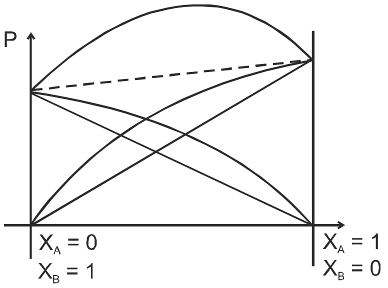
Types of Non-Ideal Solutions : Non-ideal solution can be two types.

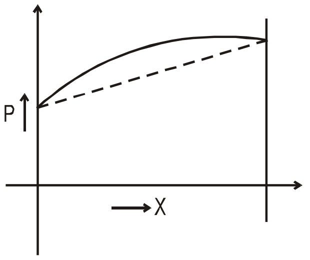
- ❍ Non ideal solutions showing positive deviation
- ❍ Non ideal solutions showing negative deviation

	Positive deviation solution		Negative deviation solution
(i)	$P_T > \left(X_A P_A^0 + X_B P_B^0\right)$	(i)	$P_T < X_A P_A^0 + X_B P_B^0$
(ii)	The inter molecular interaction is weaker as interaction found in any one of the pure components.	(ii)	The inter molecular interaction is more than the interaction found in any of the pure components
	A............A B............B molecular interaction is Stronger than A.............B		A............B molecular interaction is more than A............A B............B
(iii)	There is increase in volume on mixing and absorption of heat.	(iii)	There is decrease in volume on mixing and evolution of heat takes place on mixing
	ΔV_{mix} = positive ΔH_{mix} = positive		$\Delta V_{mix} = -ve$ $\Delta H_{mix} = -ive$
	$\Delta S_{mix} = +ive$ $\Delta G_{mix} = -ive$		$\Delta S_{mix} = +ive$ $\Delta G_{mix} = -ive$
Ex.	$H_2O + CH_3OH$, C_2H_5OH + Hexane C_2H_5OH + Cyclohexane, $CHCl_3 + CCl_4$	Ex.	$H_2O + HCOOH$, $H_2O + CH_3COOH$ $H_2O + HNO_3$, $CHCl_3 + CH_3OCH_3$

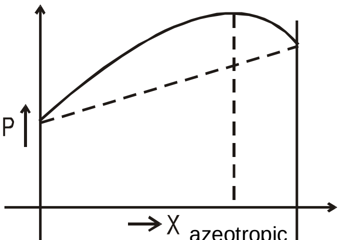
$CHCl_3 + CCl_4$:
dipole dipole interaction becomes weak

$P^0_A > P^0_B$

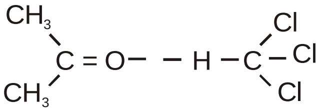




Azeo tropic mixture

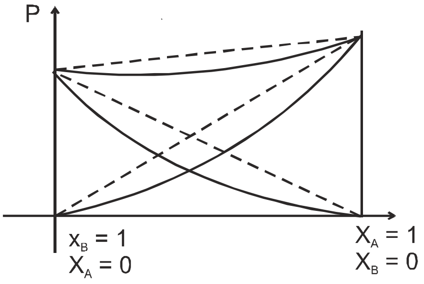


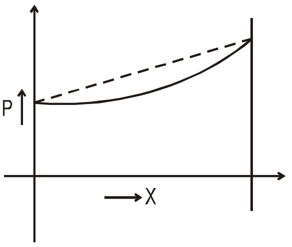
azeotropic
(constant boiling mix/Composition)
→ Minimum boiling azeotropic mix.



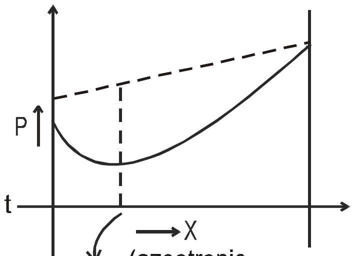
CH_3 $\diagdown$ $C=O - - H - C(Cl)_3$ with second CH_3

$P^0_A > P^0_B$





Azeo tropic mixture



(azeotropic
composition) max.
boiling azeotropic mix

(8) **Azeotropic Mixtures :** Very large deviations from ideality lead to a special class of mixtures known as azeotropes, azeotropic mixtures, or constant-boiling mixtures.

Azeotropes : Liquid mixtures which distill over without changes in composition are called constant boiling mixtures or Azeotropes or Azeotropic mixtures.

A boiling liquid mixture at the azeotropic composition produces a vapour of exactly the same composition, and the liquid does not change its composition as it evaporates. Two types of azeotropes are known.

- **Minimum Boiling Azeotropes :** *Non-ideal solutions showing large positive deviation from Raoult's law form minimum boiling azeotropes which boil at temperature lower than boiling point of its components 'A' and 'B',* e.g., water and benzene, chloroform and methanol.
- **Maximum Boiling Azeotropes :** *Non-ideal solutions showing large negative deviation from Raoult's law form maximum boiling azeotropes which boil at temperature higher than the boiling point of its components A and B respectively,* e.g., a mixture of HCl and H_2O containing 20.2% HCl by weight boils at 108.5ºC higher than either pure HCI (– 85°C) or water (100°C).

(9) **Solubility of gases in liquids :**

Factors Affecting Solubility of Gas In Liquid :

(i) Nature of gas (ii) Nature of liquid (iii) Temperature (iv) Pressure

- **Henry's Law (effect of pressure on solubility of gases in liquids) :**
  Statement : The solubility of a gas in a liquid at a given temperature is directly proportional to its partial pressure at which it is dissolved.

Let x = Mole fraction of unreacted gas in solution at a given temperature as a measure of its solubility.

p = Partial pressure of gas in equilibrium with the solution.

By Henry's law: $x \propto p$ or $p \propto x$

That is; $p = K_H x$ or $x = \frac{p}{K_H}$, where K_H = Henry's law constant.

Characteristics of Henry's Law constant (K_H).

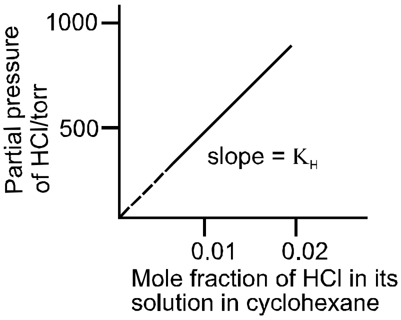
(i) Unit same as those of pressure: torr or bar.

(ii) Different gases have different value of K_H for the same solvent.

(iii) The K_H value of a gas is different in different solvents and it increase with the increase in temperature.

(iv) Higher the value of K_H of a gas, lower will be its solubility. Since, $x = \frac{p}{K_H}$.

Plot of p Vs x is a straight line passing through the origin with slope equal to K_H .



Plot of p Vs x for solution of HCl in cyclohexane.

Note : If a mixture of gases is brought in contact with solvent each constituent gas dissolves in proportion to its partial pressure. It means Henry's law applies to each gas independent of the pressure of other gas.

Effect of temperature : Solubility of gases in liquids decreases with rise in temperature.

Explanation : 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. We have learnt that dissolution process involves dynamic equilibrium and thus must follow Le Chatelier's principle. As dissolution of gases in liquids is an exothermic process, the solubility should decrease with increase of temperature.

Note : K_H values for both N_2 and O_2 increase with increase of temperature indicating that the solubility of gases increases with decrease of temperature. It is due to this reason that aquatic spcies are more comfortable in cold water rather than warm water.

- **Applications of Henry's law :** It has several applications in biological and industrial phenomena.
  (i) To increase the solubility of CO_2 in soft drinks and soda water the bottle is sealed under high pressure.
  (ii) Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmosphere gases in blood. When the divers come towards surface, the pressure is gradually decreased. 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).

(iii) 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**.

Solved Examples

***Example*.15** 1 mole heptane (V.P. = 92 mm of Hg) is mixed with 4 mol. Octane (V.P. = 31 mm of Hg), from an ideal solution. Find out the vapour pressure of solution.

Sol. total mole = 1 + 4 = 5

Mole fraction of heptane = $X_A = 1/5$

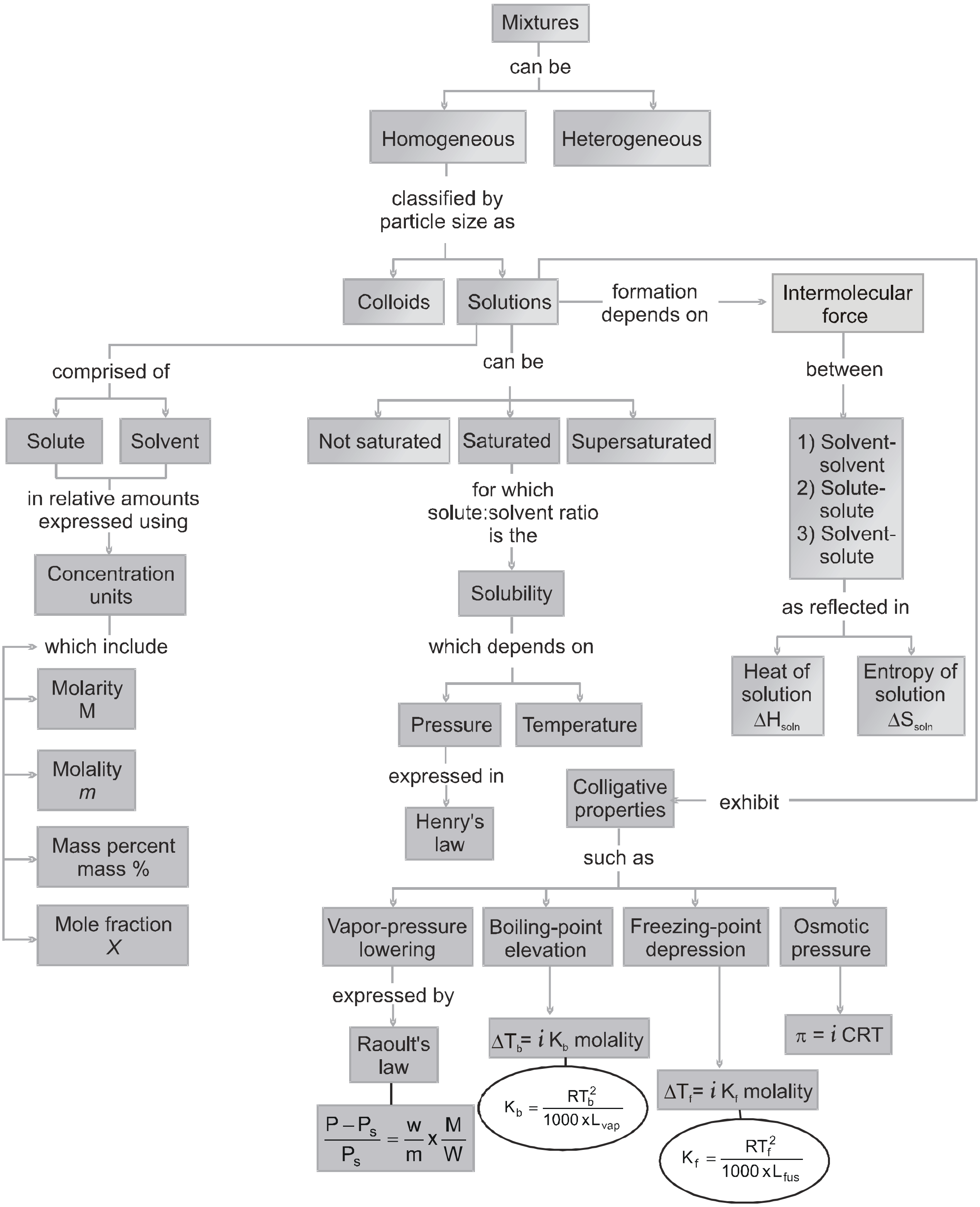
Mole fraction of octane = $X_B = 4/5$

$P_S = X_A P_A^0 + X_B P_B^0 = \frac{1}{5} \times 92 + \frac{4}{5} \times 31 = 43.2$ mm og Hg

***Example*.16** The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what shall be the partial pressure of the gas ?

Ans. 0.762 bar

Summary


Mixtures
can be
Homogeneous
Heterogeneous
classified by particle size as
Colloids
Solutions
formation depends on
Intermolecular force
between
1) Solvent-solvent
2) Solute-solute
3) Solvent-solute
as reflected in
Heat of solution ΔH_{soln}
Entropy of solution ΔS_{soln}
comprised of
Solute
Solvent
in relative amounts expressed using
Concentration units
which include
Molarity M
Molality *m*
Mass percent mass %
Mole fraction *X*
can be
Not saturated
Saturated
Supersaturated
for which solute:solvent ratio is the
Solubility
which depends on
Pressure
Temperature
expressed in
Henry's law
Colligative properties
exhibit
such as
Vapor-pressure lowering
Boiling-point elevation
Freezing-point depression
Osmotic pressure
expressed by
Raoult's law
$\frac{P-P_s}{P_s}=\frac{w}{m}\times\frac{M}{W}$
$\Delta T_b = i\,K_b$ molality
$K_b=\frac{RT_b^2}{1000\times L_{vap}}$
$\Delta T_f = i\,K_f$ molality
$K_f=\frac{RT_f^2}{1000\times L_{fus}}$
$\pi = i\,CRT$

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. A 6.90 M solution of KOH in water has 30% by weight of KOH. Calculate density of solution.

Sol. Let V = 1 lt , then moles of solute = 6.9

wt of solute = 6.9 × 56 gm

So wt. of solution = $6.9 \times 56 \times \frac{100}{30}$ gm

So density = $6.9 \times 56 \times \frac{100}{30} \times \frac{1}{1}$ = 1288 gm/ lt **Ans.**

2. 10 ml of sulphuric acid solution (sp. gr. = 1.84) contains 98% by weight of pure acid. Calculate the volume of 2.5 M NaOH solution required to just neutralize the acid.

Sol. Wt of solute = $10 \times 1.84 \times \frac{98}{100}$ gm

So moles of solute = $\frac{18.4}{98} \times \frac{98}{100} = 0.184$

So $0.184 = M \times \frac{Vml}{1000}$

So Vml = 147.2 **Ans.**

3. The density of 3M solution of $Na_2S_2O_3$ is 1.25 g mL^{-1}. Calculate.

(a) the % by weight of $Na_2S_2O_3$

(b) mole fraction of $Na_2S_2O_3$

Ans. (a) 37.92 (b) 0.065

4. Calculate Molality of aqueous urea solution which has $X_{urea} = 0.2$

Sol. $\frac{n}{n+N} = 0.2$

0.2 moles of urea in 0.8 moles water $\Rightarrow \frac{0.2}{0.8 \times 18} \times 1000 = \frac{250}{18} = \frac{125}{9}$ m **Ans.**

5. If 10 gm of an unknown substance (non-electrolyic) is dissolved to make 500 mL of soln then OP at 300 K is observed to be 1.23 atm find m.wt. ?

Sol. π = CRT so $1.23 = \frac{10/M}{.5} \times 0.082 \times 300$, so M 400 gm/mol **Ans.**

6. If 6 gm of urea, 18 gm glucose & 34.2 gm sucrose is dissolved to make 500 mL of a soln at 300 K calculate π

Sol. $p = \left(\frac{6/60 + 18/180 + 34.2/342}{0.5}\right) \times 0.082 \times 300 = 14.76$ atm **Ans.**

7. If 200 ml of 0.2 M $BaCl_2$ solutions is mixed with 500 ml of 0.1 M Na_2SO_4 solutions. Calculate π of resulting solutions.

Ans. π = 6.685 atm.

Sol. $C_{net} = \frac{C_1V_1 + C_2V_2}{V_1 + V_2}$ Now $\pi = C_{net}$ RT

8. 1 Lit. of aq. solution of urea having density = 1.060 gm/mL is found to have $\Delta T_b = 0.5^oC$, If temp. of this solution increase to 101.5ºC then calculate amount of water which must have gone is vapour state upto this pt. given $K_b = 0.5$ K kg mol^{-1} for water

Ans. $W_{water} = \frac{1000}{3}$ gm. = 666.67 gm

9. Find the molality of a solution containing a non-volatile solute if the vapour pressure is 2% below the vapour pressure of pure water.

Ans. Given, If P° = 100 than P_S = 98

Now, $\frac{P^\circ - P_S}{P_S} = \frac{w \times M}{m \times W} = \left(\frac{w}{m \times W} \times 1000\right) \frac{M}{1000}$

$\left(\frac{100-98}{98}\right)$ = molality $\times \frac{18}{1000}$

$\therefore$ molality = $\frac{2}{98} \times \frac{1000}{18}$ = 1.133

10. An aqueous solution of 2 percent non-volatile solute exerts a pressure of 1.004 bar at the boiling point of the solvent. What is the molecular mass of the solute ?

Ans. Given P_s = 1.004 bar, P° = 1.013 bar (at boiling point P = P = 1.013 bar.)

Note : 2 % solution should be reported in terms of w/W and not simply 2%

From Raoult's law : $\frac{P' - P_s}{P_s} = \frac{w \times M}{m \times W}$

$$\frac{1.013 - 1.004}{1.004} = \frac{2 \times 18}{m \times 98}$$

m = 41 g mol^{-1}

11. The vapour pressure of water is 12.3 kPa at 300 K. Calculate vapour pressure of 1 molal solution of a solute in it.

Ans. 1 molal = 1000 g solvent contains 1 mole of solute, moles of solvent = $\frac{1000}{18}$

$\therefore$ n = 1

$\therefore P_s = \frac{N}{n+N} P^\circ$

$\therefore P_s$ = 12.08 kPa

12. Calculate the mass of a non-volatile solute (molecular mass 40) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%

Ans. $\frac{P^\circ - P_s}{P_s} = \frac{n}{N} = \frac{wM}{m \times W}$ (Given m = 40, w = 114g, M_{octane} = 114)

$\frac{100-80}{80} = \frac{w \times 114}{40 \times 114}$

w = 10 g

Note : By $\frac{P^\circ - P_s}{P^\circ} = \frac{n}{N}$ (only for dilute solution, the answer comes 8 g)