Ch-2 → Solution

Mixture

1. Homogenious
Ex⇒ Solution
Particle size:- Less than 1nm

2. Hetrogeneous
Ex⇒ Colloids (1-1000 nm)
Suspension more than 1000 nm

Solution:- Solution is a homogeneous mixture of two or more components.

Binary solution :- A solution which contain two component is called binary solution.

Solute and Solvent
A component of solution which is present in large amount is called solvent and other component is called solute.

Aqueous solution:- A solution in which water is present as a solvent is called aqueous solution.

Types of solution

There are 3 types of solution:-

S.No.	Solute	Solvent	Types of solution	Examples
1	Solid	Solid	Solid solution	Alloys
2	Liquid	Solid	Solid solution	Amalgum of Hg in Na
3	Gas	Solid	Solid solution	H_2 gas in Pd
4	Solid	liquid	liquid solution	Sugar in water.

5.	liquid	Liquid	Liquid solution	Alcohol in water
6.	Gas	Liquid	Liquid solution	O_2 in water
7.	Solid	Gas	Gas solution	Camphor in air
8.	Liquid	Gas	Gas solution	Water vapour in air
9.	Gas	Gas	Gas solution	Air

Some important symbols and units

Solvent + Solute = Solution

'1' or 'A' '2' or 'B' S

* Mass or amount or weight (w) ⇒ $w_1 + w_2 = w_S$

Unit of mass = g or kg

1 kg = 1000 g and 1 g = 1000 mg

* Volume (V) ⇒ $V_1 + V_2 \neq V_S$

Unit of volume = ml or litre

1 ml = 1 cc = 1 cm^3

1 litre = 1 dm^3

1 litre = 1000 ml

1 m^3 = 1000 litres

* Density (d) = density = $\frac{\text{Mass}}{\text{Vollume}}$

$\boxed{d_1 = \frac{w_1}{V_1}}$ or $\boxed{d_2 = \frac{w_2}{V_2}}$ or $\boxed{d_S = \frac{w_S}{V_S}}$

Unit of density ⇒ $g\,ml^{-1} = kg\,L^{-1}$

Molar mass or molecular mass

M_1 = Molar mass of solvent

M_2 = Molar mass of solute

* Atomic mass of some elements:-
[H=1 , C=12 , O=16 , N=14 , Na=23 , Mg=24 , P=31
S=32 , Cl=35.5 , Ca=40 , Br=80 , I=127 , K=39]
Unit of molar mass ⇒ u = g mol^{-1}

* No. of moles(n) = $\frac{\text{Mass(gram)}}{\text{Molar mass}}$

$\boxed{n_1 = \frac{W_1}{M_1}}$ or $\boxed{n_2 = \frac{W_2}{M_2}}$ or $\boxed{n_s = n_1 + n_2}$

Expression of Concentration of Solution

Conc. of solution express in the fallowing terms:

Molarity (M):- It may be defined as the no. of moles of solute present in 1 litre of solution.

$$M = \frac{n_2}{V_s \text{ (in litre)}}$$

$$M = \frac{W_2 \text{ (in gram)}}{M_2 \times V_s \text{ (in litre)}} \qquad \left(\because n_2 = \frac{W_2}{M_2} \right)$$

Unit of molarity ⇒ mol L^{-1}

* 2.5 M H_2SO_4 solution means ⇒ n_2 = 2.5 moles and V_s = 1 litre

$$n_2 = \frac{W_2}{M_2}$$
$$W_2 = n_2 \times M_2$$
$$W_2 = 2.5 \times 98 = 245$$

$$W_s = V_s \times d_s =$$
$$W_1 = W_s - W_2 =$$
$$n_1 = \frac{W_1}{M_1} =$$

* Semi-molar ⇒ M = 1/2
deci molar ⇒ M = 1/10
Centi molar ⇒ M = 1/100
Millimolar ⇒ M = 1/1000

Molality (m):- It may be defined as no. of moles of solute present in 1 kg of solvent.

$$m = \frac{n_2}{W_1 (\text{in kg})}$$

Unit of Molality = mol kg^{-1}

* 2.5 m H_2SO_4 solution means

$n_2 = 2.5$ moles

$W_1 = 1$ kg

$n_2 = \frac{w_2}{M_2}$

$W_s = W_1 + W_2$

$V_s = \frac{W_s}{d_s}$

$W_2 = n_2 \times M_2$

$n_1 = \frac{W_1}{M_1}$

Mole fraction (x)

Mole fraction of a component is the fraction obtain by dividing no. of moles of that component by the total no. of moles of all the component present in the solution.

If in a solution, n_1 and n_2 are the no. of moles of solvent and solute respectively, Then,

Mole fraction of solute $(x_2) = \frac{n_2}{n_1 + n_2}$

Mole fraction of solvent $(x_1) = \frac{n_1}{n_1 + n_2}$

* For binary solution, $\boxed{x_1 + x_2 = 1}$

* For 3 component solution, $\boxed{x_1 + x_2 + x_3 = 1}$

where $\boxed{x_1 = \frac{n_1}{n_1 + n_2 + n_3}}$

Hints:- (a) If mole fraction is given and molality is find? Then suppose the mass of solvent = 1Kg

$W_1 = 1$ kg

$n_1 = \frac{W_1}{M_1} = \frac{1000\,g}{✓} = ✓$

$$x_2 = \frac{n_2}{n_1+n_2}$$

$$n_2 = \checkmark$$

$$m = \frac{n_2}{W_1} = \frac{\checkmark}{1kg} = \checkmark$$

(b) If mole fraction is given and molarity is find, Then, suppose the volume of solution = 1 litre which is equal to volume of solvent.

$$W_1 = V_1 \times d_1 = \checkmark$$

$$n_1 = \frac{W_1}{M_1} = \checkmark$$

$$x_2 = \frac{n_2}{n_1+n_2}$$

$$\checkmark = \frac{n_2}{\checkmark + n_2}$$

$$n_2 = \checkmark$$

$$M = \frac{n_2}{V_S \text{ (in litre)}} = \frac{\checkmark}{1 \text{ litre}} = \checkmark$$

Formality (F):-

In case of ionic compound, molarity is known as formality.

Strength (S):-

Strength of a solution is defined as the mass of solute in gram present in 1 litre of solution.

$$S = \frac{W_2(g)}{V_S(\text{In litre})}$$

Unit of strength = $g L^{-1}$

Hints (a) Strength = $15 g L^{-1}$ means

$$W_2 = 15$$

$n_2 = \frac{W_2}{M_2}$

$V_s = 1$ litre

$W_s = V_s \times d_s = ✓$

$W_1 = W_s - W_2$

$n_1 = \frac{W_1}{M_1} = ✓$

(b) Relation with Molality(M):-

$$\boxed{S = M \times M_2}$$

(c) Relation with Normality(N):-

$$\boxed{S = N \times E_2}$$

Where E_2 = Equivalent weight of solute.

Percentage

(a) Percentage by mass:- Percentage by mass means the mass of solute in grams present in 100 gram of solution.

Mass % solute $= \frac{W_2(g)}{W_s(g)} \times 100$

Hints:- 20% HNO_3 solution by mass (or by wt or w/w):-

$W_2 = 20 g$ $\quad W_s = 100 g$ $\quad W_1 = W_s - W_2 = ✓$

$n_2 = \frac{W_2}{M_2} = ✓$ $\quad V_s = \frac{W_s}{d_s}$ ✓ $\quad n_1 = \frac{W_1}{M_1}$

(b) Percentage by volume:- Percentage by volume means volume of solute in ml present in 100 ml of solution.

Volume % solute $= \frac{V_2(ml)}{V_{(s)}(ml)} \times 100$

Hints:- 20 % HNO_3 solution by volume (or V/V) means:-

$V_2 = 20 ml$ $\quad V_s = 100 ml$ $\quad V_1 = V_s - V_2$

$W_2 = V_2 \times d_2$ $\quad W_s = V_s \times d_s = ✓$ $\quad W_1 = V_1 \times d_1$

$W_2 = ✓$

$n_2 = \frac{W_2}{M_2}$ $W_1 = W_S - W_2 = \checkmark$

$n_1 = \frac{W_1}{M_1} = \checkmark$

(c) <u>Percentage mass by volume</u> :- Percentage ~~by~~ mass by volume means the mass of solute in gram present in 100 ml of solution.

(Mass by Volume) % solute = $\frac{W_2(g)}{V_S(ml)} \times 100$

<u>Hints</u>:- 20 % HNO_3 solution by (W/V) means

$W_2 = 20g$ $V_S = 100\ ml$

$n_2 = \frac{W_2}{M_2} = \checkmark$ $W_S = V_S \times d_S = \checkmark$

$W_1 = W_S - W_2 = \checkmark$

$n_1 = \frac{W_1}{M_1} = \checkmark$

<u>ppm (Parts per million parts)</u> :- For very dilute solution, the concentration of solute is expressed in ppm. It is defined as the mass of solute present in one million parts by mass of the solution.

ppm (solute by mass) = $\frac{W_2(g)}{W_S(g)} \times 10^6$

<u>Hints</u>:- 15 ppm HNO_3 solution by mass:-

$W_2 = 15g$, $W_S = 10^6 g$ $W_1 = W_S - W_2$

$n_2 = \frac{W_2}{M_2} = \checkmark$, $V_S = \frac{W_S}{d_S} = \checkmark$ $W_1 = 10^6 - 15$

$W_1 \simeq 10^6 g$

$n_1 = \frac{W_1}{M_1} = \checkmark$

<u>Problem</u>

1. Why is molality preffered over molarity to express the concentration of solution?

Ans. Molality is preffered over molarity. This is because molality involves mass, which does not depend upon temperature.

2. What is the effect of temperature on molarity?

Ans2. With increase in temperature, volume of the solution increase. As a result, molarity of solution decrease.

3. Which aq. solution has higher concentration, 1 molar or 1 molal solutions of the same solute?

Ans3. In aqueous solution, 1 molar is more conc. than 1 molal. This is because 1 molal aq. solution means 1 mole of solute in 1 kg of solvent or 1 litre of solvent (because $d = 1\,kg\,L^{-1}$). A molar aqueous solution means 1 mole of solute in 1 litre of solution, which contain less than 1 litre of solvent because solute is also presented in them.

1. Calculate the mole fraction of a solute of 2.5m aq. solut

2.5 m aq. solution of solute means-

$n_2 = 2.5$ moles $W_1 = 1\,kg$

$$n_1 = \frac{W_1}{M_1} = \frac{1000}{18} = 55.55 \text{ moles}$$

$$x_2 = \frac{n_2}{n_1+n_2} = \frac{2.5}{55.5+2.5} = \frac{2.5}{58.05} = 0.043$$

2. The mole fraction of water is 0.85 in the solution of sulphuric acid. Calculate the molality of sulphuric acid solution.

$x_1 = 0.85$

$$\frac{n_1}{n_1+n_2} = 0.85$$

Let $w_1 = 1\,kg$

Now, $0.85\,n_1 + 0.85\,n_2 = n_1$

$n_2 = 0.15\,n_1$

Now, $n_1 = \frac{W_1}{M_1} = \frac{1000}{18}$

~~$m = \frac{n_2}{W_1}$~~

$n_2 = \frac{0.15 \times 1000}{18} = \frac{150}{18}$

$m = \frac{150}{18 \times 1} = 9.83$

2. Calculate the molality and mole fraction of solute in aq. solution containing 3g of Urea (NH_2CONH_2) M. M = 60 per 250g of water.

$m = \frac{n_2}{W_1}$

250 g of water = 3g of Urea
1 kg of water = 12g of Urea

Let $W_1 = 1000g = 1\,kg$

$M_2 = \frac{W_2}{M_2} = \frac{3 \times 4}{60} = \frac{1}{5} = 0.2$

$m = 0.2$

$x_2 = \frac{n_2}{n_1 + n_2}$

$n_1 = \frac{W_1}{M_1} = \frac{1000}{18} = 55.55$

$x_2 = \frac{0.2}{0.2 + 55.55} = 0.0036$

3. Calculate the molarity and molality of 20% aq. solution of ethanol by volume. Density of solution $0.96\,g\,ml^{-1}$.

20 ml of ethanol is present in 100 ml solution

$V_2 = 20\,ml$

$$d_s = \frac{W_s}{V_s}$$

$W_s = d_s \times V_s$

$= 0.96 \times 100$

$= 96g.$

~~$W_1 = n_1 \times M_1$ $W_s - W_2$ = g.~~

~~Now $W_1 = \frac{1000 \times 18}{18}$~~

$V_1 = V_s - V_2 = 80 ml$

$W_1 = d_s \times V_s$

$= 1 \times 80 = 80g.$

$W_2 = W_s - W_1 = 16g.$

$n_2 = \frac{W_2}{M_2} = \frac{16}{46}$

Molarity $= \frac{n_2}{V_s} = \frac{16}{46 \times 0.1} = \frac{16}{4.6} = 3.48 \text{ mol } L^{-1}$

Molality $= \frac{n_2}{W_1} = \frac{16}{80 \times 46 \times 10^{-3}} = 4.35 \text{ mol kg}^{-1}$

4. A 10 cm^3 ~~[illegible]~~ sample of a solution was found to have 5 mg of urea on analysis. Calculate the molarity of the solution.

$V_s = 10 cm^3$, $W_2 = 5mg$

$M_2 = 60 g/mol$

$$M = \frac{W_2}{M_2 (V_s)} = \frac{5 \times 10^{-3}}{60 \times 10 \times 10^{-3}} = \frac{1}{120}$$

$M = 0.0083 \text{ mol } L^{-1}$

5. The conc. of sulphuric acid is 18 M. The solution has a density of 1.84 g/ml. What is the mole fraction and mass % of sulphuric acid in the solution.

$n_2 = 18$ and $V_s = 1000 ml$

$W_2 = n_2 \times M_2$

$= 18 \times 98$

$= 1764 g$

$W_s = V_s \times d_s$

$= 1.84 \times 1000$ ~~×[illegible]~~

$= 1840 g.$

W_1 $= W_s - W_2$

$=$ ~~1764~~ $1840 - 1764$

$=$ ~~1580~~ 76

$n_1 = \frac{W_1}{M_1} = \frac{76}{18} =$ ~~87.7~~ 4.2

$x_2 = \frac{n_2}{n_1+n_2} = \frac{18}{18+4.2} = \frac{18}{22.2} = 0.81$

Mass % $= \frac{W_2}{W_s} \times 1000 = \frac{1764}{1840} \times 100 = 95.87\%$

Equivalent mass(E):-

Equivalent mass of an element is the mass of an element which combines with ~~or~~ displace 1.008g of hydrogen or 8 g of oxygen or 35.5g of chlorine.

Equivalent mass (E) = $\frac{\text{Atomic mass or molecular mass(M)}}{\text{Valency factor}(x)}$

Value of valency factor ⇒

(i) For element, x = valency.

(ii) For ions, x = total charge on ions.

(iii) For acids, x = no. of H^+ ions produced

(iv) For base, x = no. of OH^- ions produced

(v) For salt, x = total positive or negative charge

(vi) For redox reaction, x = total no. of electrons loss or gain by one molecule.

Problems

1. Calculate the equivalent weight of :-

(i) Carbon $\Rightarrow E = \frac{12}{4} = 3$

(ii) H_2SO_4 $\Rightarrow E = \frac{98}{2} = 49$

(iii) $NaHCO_3$ $\Rightarrow E = \frac{84}{1} = 84$

(iv) SO_4^{2-} $\Rightarrow E = \frac{96}{2} = 48$

(v) NaOH $\Rightarrow E = \frac{40}{1} = 40$

(vi) $Al_2(SO_4)_3$ $\Rightarrow E = \frac{342}{6} = 57$

2. A 100 cm^3 solution of Na_2CO_3 (MM. 106) is prepared by dissolving 8.653g of the salt in water. The density of solution is 1.0816 g/ml. Calculate the molality and Molality of solution.

$V_s = 100$, $W_2 = 8.653g$

$d_s = 1.0816$

$$\left[W_1 = W_s - W_1 = 108.16 - 8.653 = 99.5079 \right]$$

$d_s = \frac{W_s}{V_s} \Rightarrow W_s = d_s \times V_s$

$= 1.0816 \times 100$

$= 108.16\ g. = 108.16 \times 10^{-3}$

$n_2 = \frac{W_2}{M_2} = \frac{8.653}{106} = 0.081$

$\text{Molality} = \frac{n_2}{W_1} = \frac{0.081}{99.5079} \times 10^3 = 0.820$ mol kg

$\text{Molarity} = \frac{n_2}{V_s} = \frac{0.081}{100} \times 10^3 = 0.81 M$

No. of gram equivalent of solute = $\frac{W_2 (\text{in gram})}{E_2}$

Normality (N)

Normality of a solution may be defined as the no. of gram equivalent present in 1 litre of solution.

$$N = \frac{W_2 (\text{in gram})}{E_2 \times V_S (\text{in litre})}$$

Unit = Gram eq. L^{-1}

Hints:- (a) Relation between N and M (Molarity) :- $\boxed{N = n \times M}$
where n is valency factor.

(b) If reactants react with each other and form product then they have the same value of gram equivalent.

Ex→ $A + 2B \rightarrow C + 3D$

no. of gram equivalent of A = no. of gram eq. of B = no. of gram eq. of C = no. of gram eq. of D

(c) no. of gram equivalent = $\frac{W(g)}{E} = N \times V (\text{in litre})$

(d) no. of milli equivalent = $\frac{W(g) \times 10^{-3}}{E} = N \times V (\text{in ml})$

(e) Dilution equation or Normality equation or Molarity equation

$$\underset{(\text{Before dilution})}{N_1 V_1} = \underset{(\text{after dilution})}{N_2 V_2}$$

$$\underset{(\text{Before dilution})}{M_1 V_1} = \underset{(\text{after dilution})}{M_2 V_2}$$

* Volume of adding water = $V_2 - V_1$

(f) Mixing of solution

(i) By mixing of same nature solutions:-

$$N_1 V_1 + N_2 V_2 + \ldots\ldots = N_S V_S$$

or $M_1 V_1 + M_2 V_2 + \ldots\ldots = M_S V_S$

(ii) By mixing of different nature solutions.

$$N_1V_1 - N_2V_2 = N_SV_S$$

or $x_1M_1V_1 - x_2N_2V_2 = x_1M_SV_S$

(g) * In case of balance chemical equation, normality equation :- $\frac{M_1V_1}{x_1} = \frac{M_2V_2}{x_2}$

where x_1 and x_2 are cofficient of reactant in balance equation.

* In case of unbalanced chemical equation, narmality equation ⇒

$$x_1M_1V_1 = x_2M_2V_2$$

where x_1 and x_2 are valency factor of reactant.

1 20 ml of 10M HCl solution are diluted with distilled water to form 1 litre of the solution. What is the molarity of the diluted solution.

From dilution equation,

$$M_1V_1 = M_2V_2$$

$$\cancel{1}0 \times 2\cancel{0} = M_2 \times 10\cancel{0}\cancel{0}$$

$$M_2 = 0.2 \text{ molL}^{-1}$$

2 A 6.9M solution of KOH in water contains 30% by mass of KOH. Calculate the density of KOH solution (MM. of KOH = 56g/mol).

$d_S = ?$ $\therefore d_S = W_S$

Let mass of KOH = 30

and let the V_S = 1 litre then $n_2 = 6.9$

$W_2 = n_2 \times M_2 = 6.9 \times 56 = 386.4$

$$M = \frac{W_2}{M_2 \times V_S \text{ (in litre)}}$$

$$6.9 = \frac{30}{56 \times V_S}$$

$$V_S = \frac{30}{6.9 \times 56} = \frac{30000}{6.9 \times 56} \text{ ml}$$

$$d_S = \frac{W_S}{V_S} = \frac{100 \times 56 \times 6.9}{30000} = 1.288 \text{ g ml}^{-1}$$

3. The mole fraction of benzene in a solution in Toluene is 0.5. Calculate the mass % of benzene in the solution (M.M of benzene = 78 and M.M of Toluene = 92)

$x_B = 0.5$

$$x_B = \frac{n_B}{n_B + n_T}$$

Let $W_S = 100$ g and $W_2 = x$ g and $W_1 = (100 - x)$ g

$$n_1 = \frac{W_1}{M_1} = \frac{100 - x}{92} \text{ and } n_2 = \frac{W_2}{M_2} = \frac{x}{78}$$

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{\frac{x}{78}}{\frac{100 - x}{92} + \frac{x}{78}} = \frac{92x}{7800 + 14x} = 0.5 \Rightarrow x = 45.9$$

$$\frac{W_2}{W_S} \times 100 = \frac{45.9}{100} \times 100 = 45.9 \text{ g.}$$

4. Calculate the volume of 80% H_2SO_4 solution ($d_s = 1.8$ g/ml) required to prepare 1 litre of 20% H_2SO_4 solution (density = 1.25 g/ml)

Here, $W_2 = 80$ g and $W_S = 100$ g

$$V_S = \frac{W_S}{d_S} = \frac{100}{1.8} = 55.5$$

~~In other case, $W_2 =$~~

For 80% H_2SO_4 solution by mass :-

$W_2 = 80g$, $W_s = 100g$, $d_s = 1.8 g ml^{-1}$

$V_s = \frac{W_s}{d_s} = \frac{100}{1.8} ml = \frac{100}{1.8 \times 1000}$ litre $= \frac{1}{18}$ litre

$M = \frac{W_2(g)}{M_2 \times V_s} = \frac{80 \times 18}{98 \times 1} = 14.69$

For 20% H_2SO_4 solution by mass :-

$W_2 = 20g$, $W_s = 100g$, $d_s = 1.25 g ml^{-1}$

$V_s = \frac{100}{1.25} ml = \frac{1}{12.5}$ litre

$M = \frac{20 \times 12.5}{98 \times 1} = 2.55$

From molarity equation,

$M_1 V_1 = M_2 V_2$

(80% H_2SO_4 soln) (20% H_2SO_4 soln)

~~80×18~~ $14.69 \times V_1 = 2.55$

$V_1 = 0.173$ l

$V_1 = 173$ ml

5. Calculate the no. of moles of methanol in 5 litre of its 2m solution. ($d_s = 0.981$ kg/l and M.M=32g/

2m solution:- 2moles in 1000g of solvent.

$W_2 = n_2 \times M_2 = 2 \times 32 = 64g$

So total mass of solution = 64+1000 = 1064g.

~~Given~~ So 1064 g of solution contain = 2 moles.

Now no of moles in 5 litre of solution:-

$W_s = V_s \times d_s = 5 \times 0.981 = 4.905 kg$

$W_s = 4905 g$

So 1 g of solution contain $= \frac{2}{1064}$ mols

Hence, 4905g of solution contain $= \frac{2 \times 4905}{1064} = 9.22$ mole

6 20% mass by volume and 30% mass by volume H_2SO_4 solution mixed together in 1:2 of volume. The final volume of the solution is 1 litre. Find out the conc. of resulting solution in terms of mass by volume.

Suppose the volume of first solution is V ml and Volume of second solution is mixture = 2V ml

Given $V + 2V = 1$ litre

$$3V = 1000$$

$$V = \frac{1000}{3} \text{ ml}$$

For Ist solution:- $W_2 = 20g$, $V_s = 100ml$

Because 100 ml of solution contain = 20g of solute

$\therefore \frac{1000}{3}$ ml of solution contain $= \frac{20}{1\cancel{00}} \times \frac{10\cancel{00}}{3} = \frac{200}{3}g$

For IInd solution:- $W_2 = 30g$, $V_s = 100ml$

100 ml of solution contain = 30g of solute

$2 \times \frac{1000}{3}$ ml of solution $= \frac{\overset{2}{\cancel{30}}}{1\cancel{00}} \times \frac{2 \times 10\cancel{00}}{\cancel{3}} = 200g$

Total mass of solute $= 200 + \frac{200}{3} = \frac{800}{3}$

$$\% \text{ of solute } (w/v) = \frac{W_2}{V_s} \times 100 = \frac{800}{3 \times 1000} \times 100$$

$$= 26.67\%$$

Solid in liquid Solution

Solubility:- The solubility of a solid in liquid at a particular temperature is defined as the maximum amount of solid in gram which can dissolve in 100 g of liquid to form the saturated solution at that temperature.

Factors affecting solubility of solid in liquid and liquid (solvent)

1. Nature of solid (solute) and liquid (solvent)
According to like dissolves dissolves like concept, polar compound like NaCl is highly soluble in polar solvent like water and insoluble in nonpolar solvent like benzene; CCl_4, ether etc.

2. Temperature
In case of some solids, like KCl, $NaCl$, KNO_3, $NaNO_3$ etc solubility increase with increase in temperature this is because the process of dissolution is endotherm

In case of some solid, like lithium carbonate $(Li_2CO_3$ $Ce(SO_4)_2$, $Na_2CO_3.H_2O$ etc, solubility decrease with increase in temperature, this is because the process of dissolution is exothermic

In case of some solid like $Na_2SO_4.10H_2O$, $CaCl_2.6H_2O$ e solubility first increase and then decrease this is because these substance change their form with temperature.

The temperature at which one form of substanc change into another form is called transition temperature.

In case of $Na_2SO_4.10H_2O$, transition temperature i

$$Na_2SO_4.10H_2O \underset{\text{below } 32.9°C}{\overset{\text{above } 32.9°C}{\rightleftharpoons}} Na_2SO_4$$

* 3. Pressure
Pressure has no effect (very low effect) on the solubility of a solid in a liquid because solids are highly incompressible.

Gas in liquid solution

The factors affecting the solubility of gas in liquid are as follows:-

1. **Nature of gas and liquid.**

Gases like NH_3, HCl, etc are more soluble in water this is because they have high critical temperature. Gases like oxygen, CO_2 etc are less soluble in water because they have low value of crital temperature.

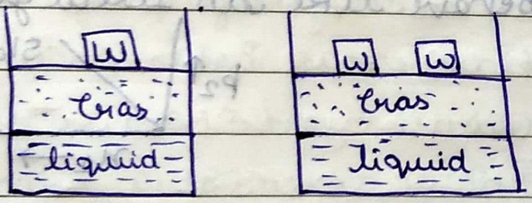
2. **Temperature**

With increase in temperature, solubility of gas in liquid decrease this is because this process is exothermic

*3. **Pressure**

The solubility of gas in liquid increase with increase in pressure of gas.

Quantitevely, the effect of pressure on the solubility of a gas in a liquid was studied by Henry and is called Henry's law.



(a) (b)

At a constant temperature, the solubility of a gas in liquid is directly proportional to the pressure of a gas.

i.e $m \propto p$

$m = K_H p$

where m = mass of gas dissolved in liquid

p = pressure of gas in equillibrium with liquid.

K_H = proportionality constant called Henry's constant whose value depends upon nature of the gas, nature of the liquid and temperature.

** The value of K_H increase with increase in temperature. With increase in value of K_H, solubility of gas decrease.

Modified Henry Law

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

i.e. $p_2 \propto x_2$

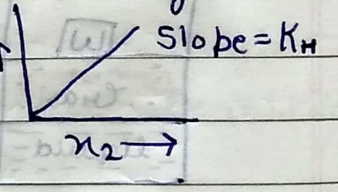
$p_2 = K_H x_2$

where p_2 = partial pressure of the gas in vapour phase

x_2 = mole fraction of the gas in solution.

Limitation of Henry's Law

1. The gas should not undergo compound formation with the liquid.
2. The gas should behave like an Ideal gas.



Application of Henry's Law

1. To increase the solubility of gas in soft drinks, soda water, the bottle are sealed under high pressure.
2. At high altitudes, the partial pressure of oxygen is less than at the ground level as a result, there is low conc. of oxygen in blood and tissue of people living at high altitudes. Therefore, they feel weakness and are unable to think properly.

3. Deep sea divers(or Scuba divers) depend upon compress air for their oxygen supply. According to Henry's law, solubility of gases increase with pressure both nitrogen and oxygen gas will dissolve in blood. Oxygen is used up for metabolic, but due to high pressure and greater solubility, nitrogen gas will remain dissolve and form bubbles when the divers comes to the atmospheric pressure. These bubbles affects nerve impulse and give rise to a diseases and called Bend. To avoid bend, the cylinder used by the divers are filled with air diluted Helium, which is less soluble in blood.

Formula for numericals

1. $p_2 = K_H \times x_2$ [unit of K_H = Unit of pressure (Pascal)]
2. $M = K_H p_2$ [Unit of K_H = unit of M/p];
3. $m = K_H p$ [Unit of K_H = Unit of m/p]

Hints:-(a) Always use formula on the basis of unit of K_H.
For finding K_H, used $p_2 = K_H \times x_2$
(b) Always used same unit:-
1 atm = 1.013 bar = 1.013×10^5 Pa or Nm^{-2} = 760 mm Hg or torr
1 bar = 0.987 atm = 10^5 Pa = 760 mm Hg.
(c) Partial pressure of vapour phase (p_2) = mole fraction in vapour × P(total)
(d) Mole fraction of gas in solution (x_2) = $\frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1}$.

1 At what partial pressure, oxygen will have a solubility of 0.052 g L^{-1} in water at 298 K. Henry's constant for oxygen in water at 298 K is 34.86 K bar. Assume the density of solution to be same as that of

the solvent.

$p_2 = ?$ $K_H = 34.86$ K bar

Solubility of oxygen = 0.05 g L^{-1} means–

$W_2 = 0.05g$, $V_s = 1$ litre

$n_2 = \frac{W_2}{M_2} = \frac{0.05}{32} = 0.0015$ moles

$W_s = V_s \times d_s$

$= 1000ml \times 1 = 1000 g$

$W_1 = W_s - W_2$

$= 1000 - 0.05 = 1000$

$n_1 = \frac{W_1}{M_1} = \frac{1000}{18} = 55.55.$

$x_2 = \frac{n_2}{n_1+n_2} = \frac{0.0015}{55.55 - 0.0015} = 2.81 \times 10^{-5}$

From Henry's law,

$p_2 = K_H \times x_2 = 34.86 \times 10^3 \times 2.81 \times 10^{-5}$

$= 0.97$ bar

2. Henry's law constant for O_2 dissolived in water is 4.34×10^4 ~~bar~~ atm at 25°C. If the partial pressure of oxygen in air is 0.2 atm. Calculate the conc in mol L^{-1} of dissolved oxygen in water at 25°C.

$M = ?$ $K_H = 4.34 \times 10^4$ atm , $p_2 = 0.2$ (given)

From Henry law:-

$p_2 = K_H \times x_2$

$\frac{0.20}{4.34 \times 10^4} = x_2$

$x_2 = 4.6 \times 10^{-6}$

$x_2 = \frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1}$

For 1 litre of water, $n_1 = \frac{1000}{18} = 55.55$ moles

$4.6\times10^{-6} = \frac{n_2}{55.5}$

$n_2 = 2.55\times10^{-4}$ moles

molarity $= \frac{n_2}{V_s} = \frac{2.55\times10^{-4}}{1} = 2.55\times10^{-4}\ \text{mol}\,L^{-1}$

3. The mole fraction of Helium in a saturated solution at 20°C is 1.2×10^{-6}. Find the pressure of helium. Given K_H 144.97 kg bar.

$p_2 = K_H \times x_2$

$p_2 = 144.97\times10^{3} \times 1.2\times10^{-6}$

$= 0.14497\times10^{6} \times 1.2\times10^{-6}$

$= 0.174$ bar.

~~M=~~

4 Calculate the solubility of hydrogen in water at 25°C. If its partial pressure is 1 bar and Henry's constant for hydrogen is 71.18 K bar.

From Henry's law

$p_2 = K_H \times x_2$

$1 = 71.18 \times x_2 \times 10^{3}$

$x_2 = \frac{1}{71.18\times10^{3}} = 0.014\times10^{-3} = 1.4\times10^{-5}$

5 What conc. of nitrogen should be present in a glass of water at room temperature. Assume a temperature of 25°C, a total pressure of 1 atm and moll fraction of nitrogen in air is 0.78. (K_H for nitrogen $= 8.42\times10^{-7}$ M/mmHg)

$M = K_H p_2$

$p_2 =$ ~~$K_H \times x_2$~~ mole fraction × p-total

~~$p_2 = 8.42\times10^{-7} \times 0.78$~~ $0.78\times1 = 0.78$ atm

~~Now, $M = 8.42\times10^{-7}$~~ $p_2 = 0.78 \times 760$ mm Hg

~~$p_2 =$~~

Volatile→ Substance which convert into vapours
Non-Volatile→ Substance which cannot be converted into vapours.

From Henry's law,

$$M = K_H p_2$$

$$M = 8.42 \times 10^{-7} \times 0.78 \times 760$$

$$M = 4.99 \times 10^{-4} \text{ mol}L^{-1}.$$

Vapour pressure of liquid

Vapour pressure of a liquid is the pressure exerted by the vapours in equilibrium with liquid at a particular temperature.

Factors affecting vapour pressure of a liquid

Nature of liquid:- Weaker are the intermolecular force among the molecules of liquid, greater is the vapour pressure of the liquid. Lower the boiling point of a liquid, weaker are the intermolecular force and hence greater is the vapour pressure.

Temperature:- Higher the temperature, greater is the vapour pressure. This is because with increase in temperature, K.E of the molecules increase and hence more molecules leave the surface of liquid and come into vapour pressure.

* Adding of non-volatile solute:- Vapour pressure of a liquid decrease by adding a non-volatile solute. This is because some of the solute particle occupy the position of liquid molecules on its surface. Therefore, surface area of liquid decrease.

Liquid - Liquid solution

* Raoult's law for volatile liquid solution

For a solution of volatile liquid, partial vapour pressure of each component is directly proportional to its mole fraction.

For liquid 1:-

$p_1 \propto x_1$

$p_1 = p_1^\circ x_1 \rightarrow ①$

where p_1 = partial vapour pressure

p_1° = Vapour pressure of pure liquid 1.

x_1 = mole fraction of liquid 1 in solution

Similiarly for liquid 2

$p_2 = p_2^\circ x_2 \rightarrow ②$

According to Dalton's law of partial pressure, the total pressure over the solution phase in the container will be the sum of the partial pressure of the component of the solution.

$\therefore p_{Total} = p_1 + p_2$

$p_{Total} = p_1^\circ x_1 + p_2^\circ x_2$ (From eq. 1 and 2)

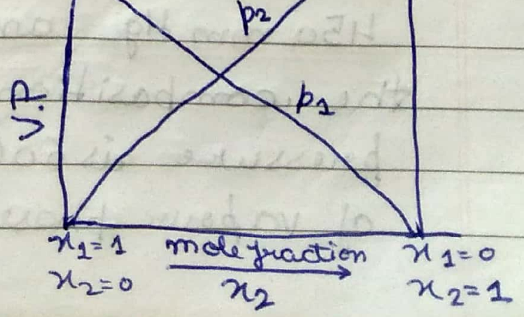
$p_{Total} = p_1^\circ(1 - x_2) + p_2^\circ x_2$ ($\because x_1 = 1 - x_2$)

$p_{Total} = p_1^\circ + x_2(p_2^\circ - p_1^\circ)$

The following conclusion can be drawn from equation:-

1. Total vapour pressure of the solution can be related to the mole fraction of any one component.
2. Total vapour pressure of the solution shows variation linearly with the mole fraction of liquid.

$p_{Total} = p_1^\circ + x_2(p_2^\circ - p_1^\circ)$



Formula for numericals of Ideal solution or two liquid solⁿ

1. $p_1 = p_1^\circ x_1$

$p_2 = p_2^\circ x_2$

$p_{Total} = p_1 + p_2$

or

$p_{Total} = p_1^\circ + x_2(p_2^\circ - p_1^\circ)$

2 Mole fraction of liquid 1 in vapour phase $(y_1) = \frac{p_1}{p_{Total}} = \frac{p_1^\circ x_1}{p_{Total}}$

Mole fraction of liquid 2 in vapour phase $(y_2) = \frac{p_2}{p_{Total}} = \frac{p_2^\circ x_2}{p_{Total}}$

$$\boxed{y_1 + y_2 = 1}$$

where p_1° = vapour pressure of pure liquid 1
p_2° = vapour pressure of pure liquid 2
p_1 = partial pressure of liquid 1
p_2 = partial pressure of liquid 2
p_{Total} = Total vapour pressure of solution
x_1 = mole fraction of liquid (1) in solution
x_2 = mole fraction of liquid (2) in solution

Hints:- (a) Use any unit of vapour pressure
(b) for finding the composition of liquid mixture find x_1 and x_2.
(c) for finding the composition of vapour phase, find y_1 and y_2

Problem

1. The vapour pressure of pure liquid A and B are 450 mm Hg and 700 mm Hg at 350 K. Calculate the composition of liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of vapour phase.

From Raoult's law,

$$p_{Total} = p_1^\circ + x_2(p_2^\circ - p_1^\circ)$$

$$600 = 450 + x_2(700-450)$$

$$\frac{\overset{3}{\cancel{150}}}{\underset{5}{\cancel{250}}} = x_2$$

$$x_2 = 0.6$$

$$x_1 = 1 - x_2 = 0.4$$

$$y_1 = \frac{p_1}{p_{Total}} = \frac{p_1^\circ x_1}{p_{Total}} = \frac{450\times 0.4}{600} = 0.3$$

$$y_2 = \frac{p_2}{p_{Total}} = \frac{p_2^\circ x_2}{p_{Total}} = \frac{700\times 0.\cancel{6}}{\cancel{600}} = 0.7$$

2 Vapour pressure of chloroform and dichloromethane at 298 K are 200 mm Hg and 415 mm Hg respectively.

(i) Calculate the vapour pressure of the solution prepared by mixing 25.5 g of chloroform and 40 g of dichloromethane.

(ii) Calculate the mole fraction of each component in vapour phase (M.M of chloroform 119.5 g and dichloromethane 18 g)

(i) $n_2 = \frac{W_2}{M_2} = \frac{25.5}{119.5} = 0.213$

$n_1 = \frac{W_1}{M_1} = \frac{40}{85} = 0.470$

$x_2 = \frac{n_2}{n_1+n_2} = \frac{0.213}{0.213+0.470} = \frac{0.470}{0.683} = 0.688$

$$p_{Total} = p_1^\circ + x_2(p_2^\circ - p_1^\circ)$$

$$= 200 + 0.688(415-200)$$

$$= 200 + \cancel{66.865}\ 147.9$$

$$= \cancel{266.865}\ 347.9 \text{ mm Hg}$$

(ii) $y_1 = \frac{p_1^\circ x_1}{p_{Total}} = \frac{200 \times 0.311}{347.9} = 0.178$

$y_2 = 1 - 0.178 = 0.822.$

3. Two liquids A^2 and B^1 on mixing form ideal solution. Their vapour pressure in the pure state are 200 and 100 torr respectively. What will be mole fraction of liquid B in the vapour phase in equillibrium with equimolar solution of the two.

$x_B = 0.5$

Then ~~p_B~~ $p_{Total} = p_1^\circ + x_2(p_2^\circ - p_1^\circ)$

$= 100 + 0.5(200 - 100)$

$= 100 + 50 = 150$

$y_1 = \frac{p_B^\circ x_B}{p_{Total}} = \frac{200 \times 0.5}{150} = \frac{\cancel{50}}{\cancel{150}} = \frac{1}{3} = 0.33$

4. Ethylene $\overset{2}{\text{dibromide}}$ and $\overset{1}{\text{1-2}}$, dibromo propane form a series of ideal solution at 85°C, vapour pressure of these liquid are $\overset{2}{173}$ and $\overset{1}{127}$ torr respectively. What would be the mole fraction of ethylene dibromide in a solution at 85°C in equillibrium with 1:1 molar mixture in the vapour.

$y_1 = 0.5$ and $y_2 = 0.5$

$p_{Total} = p_1^\circ + x_2(p_2^\circ - p_1^\circ)$

$p_{Total} = 127 + x_2(173 - 127)$

$p_{Total} = 127 + 46x_2$

$y_2 = \frac{p_2^\circ x_2}{p_{Total}}$

$0.5 = \frac{173 \times x_2}{127 + 46x_2}$

$63.5 + 23x_2 = 173x_2$

$63.5 = 150x_2$

$$x_2 = \frac{63.5}{150} = 0.42$$

5. Two liquids X and Y on mixing farm ideal solution. At 30°C, vapour pressure of solution containing 3 moles of X and 1 mole of Y is 550 mmHg. But when 4 mole of X and 1 moll of Y are mixed, vapour pressure of the solution is 560 mmHg. What would be the vapour pressure of pure X and Y at this temperature.

far 3 mole of X and 1 mole of Y.

$$p_{Total} = p_1^\circ + x_2(p_2^\circ - p_1^\circ)$$

$$550 = p_1^\circ + 0.25(p_2^\circ - p_1^\circ)$$

$$550 = 0.25\,p_2^\circ + 0.75\,p_1^\circ \times 4 \rightarrow (i) \Rightarrow 2200 = p_2^\circ + 3p_1^\circ$$

For 4 mole of X and 1 mole of Y,

$$560 = p_1^\circ + 0.20(p_2^\circ - p_1^\circ)$$

$$560 = 0.80\,p_1^\circ + 0.20\,p_2^\circ \times 5$$

$$2800 = p_2^\circ + 4p_1^\circ \rightarrow (ii)$$

On subtracting, we get

$$600 = p_1^\circ$$

$$\text{and } p_2^\circ = 400,$$

6. Benzyne and Toluene farm ideal solution. At a certain temp., vapour pressure of pure benzene and Toluene is $\overset{2}{150}$ and 50 mm Hg. Calculate Vapour pressure of solution containing equal weights of two. (Benzene - 78 and Toluene 92)

Let W be the weight of both.

$$n_1 = \frac{W}{92} \quad \text{and } n_2 = \frac{W}{78}$$

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{\frac{W}{78}}{\frac{W}{92} + \frac{W}{78}} = \frac{\cancel{\frac{W}{78}}}{\frac{170\cancel{W}}{92 \times \cancel{78}}} = \frac{92}{170}$$

$$p_{Total} = 50 + \frac{92}{170}(150 - 50) = 50 + \frac{920\cancel{0}}{17\cancel{0}} = 104.1 \text{ Ans}$$

Raoult's law

According to Raoult's law, for any volatile component of the solution, $p_2 \propto x_2$

$$\boxed{p_2 = p_2^\circ x_2}$$

i.e partial Vapour pressure of the volatile component, (solvent or solute) is directly proportional to the mole fraction of that component in the solution.

If gas is the solute and liquid is the solvent, then according to Henry's law, $p_2 = K_H x_2$

i.e partial ~~vap~~ pressure of the volatile component (gas) is directly proportional to the mole fraction of that component (gas) in the solution.

Therefore, Raoult's law and Henry's law become identical except that their proportionality constant are different.

Thus, Raoult's law become a special case of Henry's law, in which K_H becomes equal to p_i°

Ideal Solution

The solution which obey Rault's law over the entire range of concentration are known as ideal solution. Ex ① n-Hexane or n-heptane

② Benzene and Toluene

Hint→ Liquid containing same functional group form ideal solution.

Explaination for Ideal Solution

The magnitude of interaction among the molecules of liquid A and B in solution is same then that of A-A interaction or

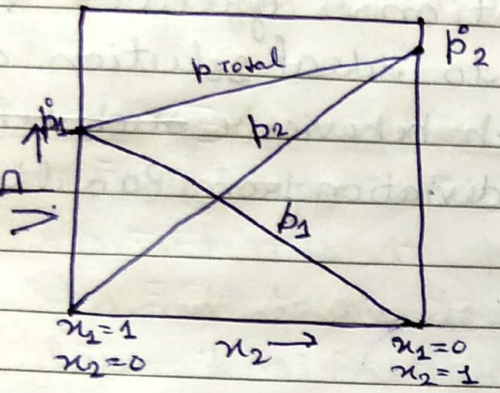
B - B interaction

Characteristics of Ideal solution

1 $p_1 = p^\circ_1 x_1$, $p_2 = p^\circ_2 x_2$ and $p_{Total} = p_1 + p_2$

2 $\Delta_{mix}V = 0$ i.e. there will be no change in volume on mixing the two liquids.

3. $\Delta_{mix}H = 0$ i.e there will be no change in enthalpy.



Non-ideal Solution

A solution which does not obey Raoult's law is called non-ideal solution.

Ex→ ① H_2O and C_6H_6

② CH_3OH and CH_3Cl

~~Charac~~ Explaination for Non-ideal solution

The magnitude of interaction among the molecules of liquid A and liquid B in solution is different than that of A-A interaction or B-B interaction.

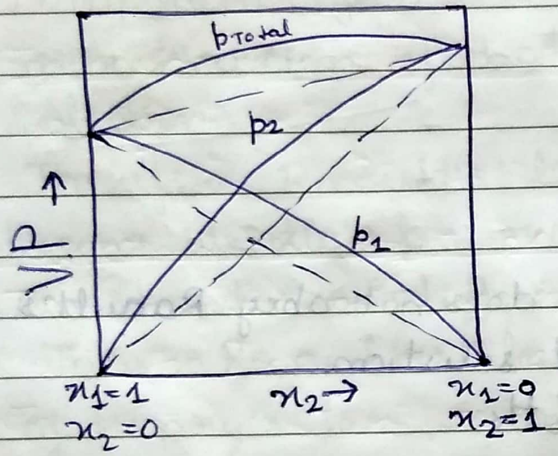
Characteristics of Non-ideal solution

1. $p_1 \neq p^\circ_1 x_1$ and $p_2 \neq p^\circ_2 x_2$
2. $\Delta_{mix}V \neq 0$
3. $\Delta_{mix}H \neq 0$

There are 2 types of Non-ideal solution:-

1. Positive deviation from Raoult's law

When a liquid A is added to another liquid B, sometime the partial pressure of liquid A is found to be more than expected on the basis of Raoult's law. A similiar effect is observed for liquid B. The total vapour pressure of the solution is greater than that corresponding to ideal solution of the same composition such behaviour ~~such behaviour~~ of both is called positive deviation from Raoult's law.



Explaination for positive deviation from Raoult's law

The interaction among the molecules of liquid A and B in solution is weaker than that of interaction A-A and B--B.

Characterstics

1. $p_1 > p_1^\circ x_1$,
   $p_2 > p_2^\circ x_2$

and $p_{Total} > p_1^\circ x_1 + p_2^\circ x_2$

2. $\Delta_{mix} V > 0$ i.e volume of solution increase.
3. $\Delta_{mix} H > 0$ i.e endothermic process and solution becomes cool.

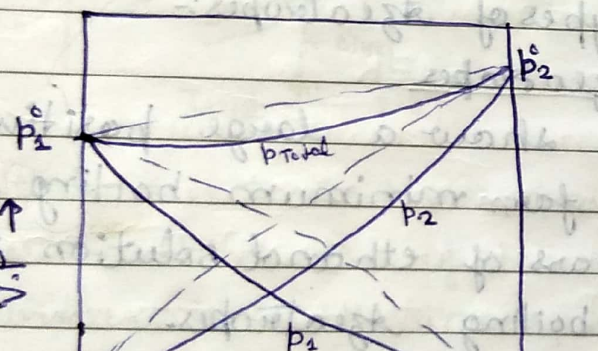
Example of positive deviation from Raoult's law

1. $H_2O + C_6H_6$
2. $H_2O + C_2H_5OH$
3. $H_2O + CH_3OH$
4. $CCl_4 + C_6H_6$
5. $C_2H_5OH + C_6H_6$

Hints (a) Water with other (Except HCl, HNO_3, H_2SO_4)
(b) Hydrogen bonded liquid with other.

2. Negative Deviation from Raoult's law

When a liquid A is added to another liquid B, sometimes the partial pressure of liquid A is found to be less than expected from Raoult's law. A similiar effect is observed for liquid B. The total vapour pressure of the solution is less, than that corresponding to ideal solution of the same composition such behaviour of solution is known as negative deviation from Raoult's law.



Explaination for negative deviation from Raoult's law

The interaction among the molecules of liquid A and B in solution is stronger than that of A--A interaction and B--B interaction.

Characteristics of negative deviation from Raoult's law

1. $p_1 < p_1^\circ x_1$,
   $p_2 < p_2^\circ x_2$
   and $p_{Total} < p_1^\circ x_1 + p_2^\circ x_2$
2. $\Delta_{mix} V < 0$ i.e. volume of solution decrease
3. $\Delta_{mix} H < 0$ i.e exothermic process and solution become warm

Examples of negative deviation

1. $H_2O + HCl$
2. $H_2O + HNO_3$
3. $H_2O + H_2SO_4$
4. Acetone + chloroform
5. Acetone + Aniline
6. $CHCl_3 + C_6H_6$

Hints :- 1. If hydrogen bond is formed after mixing of liquid.

Azeatropes or Azeatropic mixture or constant boiling mixture

The liquid mixture having a definate composition and boiling like a pure liquid is called azeatropes.

There are two types of Azeatropes:-

Minimum boiling Azeotropes

The solution which show a large positive deviation from Raoult's law form minimum boiling Azeotropes.

For ex→ 95.4% by mass of ethanol solution in water form minimum boiling Azeatropes.

Maximum boiling Azeatropes

The solution which show a large negative deviation from Raoult's law form maximum boiling Azeatropes at a specific composition.

For ex→ 68% by mass HNO_3 solution in water form maximum boling Azeatropes.

Colligative properties

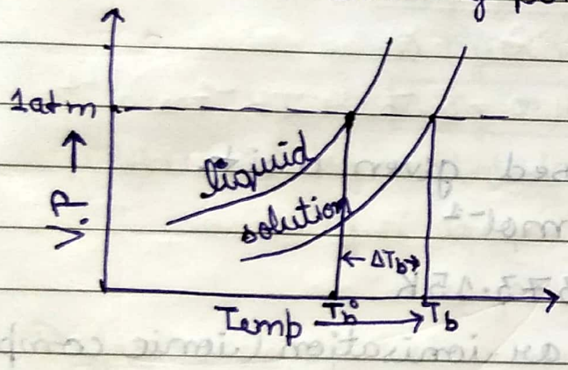
Thase properties of solution which depend only on the no. of particles of solute dissolve in a definite amount of solvent and donot depend on the nature of solute are called colligative properties.

Some important colligative properties:-

1. Elevation of boiling point
2. Depression of freezing point
3. Osmotic pressure
4. Relative lowering in vapour pressure.

Elevation of boiling point.

The temperature at which vapour pressure of the liquid becomes equal to the atmospheric pressure is called boiling point of the liquid.



We know that the vapour pressure of the solution is lower than that of pure solvent and vapour pressure increase with increase in temperature. Hence the solution has to be heated more to make the vapour pressure equal to atmospheric pressure. Therefore, the boiling point of solution is always higher than that of original solvent.

Experimentally, for very dilute solution, elevation in boiling point is directly proportional to molality of the solution, i.e.

$$\boxed{\Delta T_b \propto m}$$

$\Delta T_b = K_b m$

Where ΔT_b = Elevation in boiling point
m = molality of the solution
K_b = molal elevation constant or
Ebullioscopic constant.

Define K_b

If $m = 1$ molal then $\Delta T_b = K_b$
Molal elevation constant may be defined as elevation in boiling point, when the molality of solution is unity.

Formula for numericals

$$\Delta T_b = T_b - T_b^\circ$$

T_b → B.P of solution
T_b° → B.P of liquid

$$m = \frac{W_2 (g)}{M_2 \times W_1 (kg)}$$

(a) ΔT_b, T_b°, T_b → Always used given unit.

(b) For water, $K_b = 0.52\ K\ Kg\ mol^{-1}$
$T_b^\circ = 100^\circ c$ or $373.15 K$

(c) In case of dissociation or ionisation (ionic compounds like KCl, NaCl, K_2SO_4 etc, coordination compounds $K_4[Fe(CN)_6]$, organic acid (RCOOH) in water) and for association (Dimer, trimer, tetramer) use Van't Hoff factor (i)

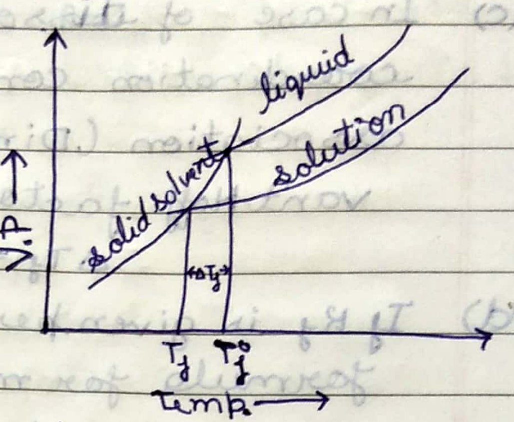
$$\boxed{\Delta T_b = i K_b \times m}$$

(d) If K_b is given in per 100 gram then use the following formula of molality.

$$m = \frac{W_2 (g) \times 100}{M_2 \times W_1 (g)}$$

Depression in freezing point

Freezing point of liquid is the temperature at which vapour pressure of the liquid and solid phases becomes equal.



We know that the vapour pressure of the solution is less than that of the pure solvent. Freezing point is the temperature at which the vapour pressure of liquid and the solid phase are equal.

Therefore, for the solution, this will lower occur at lower temperature. Experimentally, for dilute solution, depression in freezing point is directly proportional to the molality of the solution, i.e.

$$\Delta T_f \propto m$$

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

where K_f = Molal depression constant or Cryascopic constant.
ΔT_f = Depression in freezing point

Define K_f

If $m = 1$ molal then $\Delta T_f = K_f$

Molal depression constant may be defined as depression in freezing point, when the molality of solution is unity.

Formula for numericals

$\Delta T_f = K_f m$

where $\Delta T_f = \underset{\text{F.p of solvent}}{T_f^{\circ}} - \underset{\text{F.p of solution}}{T_f}$

$$m = \frac{W_2 \text{ (in gram)}}{M_2 \times W_1 \text{ (in kg)}}$$

Hints - (a) $\Delta T_f \neq T_f^{\circ}$, $T_f \Rightarrow$ used given unit.

(b) For water $K_f = 1.86\ K\ Kg\ mol^{-1}$

$T_f^{\circ} = 0^{\circ}C$ or 273 K

(c) In case of dissociation or Ionisation (Ionic compound, coordination compound, organic acid in water) or association (Dimer, tetramer, trimer) used vant Hoff factor (i)

$$\Delta T_f = i K_f m$$

(d) If K_f is given per 100gm, use the following formula for molality.

$$m = \frac{W_2(g) \times 100}{M_2 \times W_1(g)}$$

(e) $$K_b = \frac{R(T_b^{\circ})^2}{1000 L_v} = \frac{M_1 R (T_b^{\circ})^2}{1000 \Delta_{vap} H}$$

$$K_f = \frac{R(T_f^{\circ})^2}{1000 L_f} = \frac{M_1 R (T_f^{\circ})^2}{1000 \Delta_{fus} H}$$

R = Gas constant and $R = 8.314\ JK^{-1} mol^{-1}$

M_1 = Molar mass of solvent or liquid.

L_v = Latent heat of vapourisation

L_f = Latent heat of fusion.

$\Delta_{vap} H$ - Enthalpy of vapourisation

$\Delta_{fus} H$ = Enthalpy of fusion

X **Osmotic Pressure**

Formula for Numericals

Osmosis and Osmotic pressure

If semi-permiable membrane (SPM) is placed between the solvent and solution, the solvent molecule will flow through the membrane from pure solvent to the solution. This process of flow of solvent is called osmosis.

The pressure applied on the ~~pressure~~ solution, which stop the asmosis is called asmotic pressure of the solution is represented by (π).
Experimentally, asmotic pressure is proportional to the molarity (C) of the solution at a given temperature
i.e. $\pi = CRT$
where R = Solution constant.
Because $C = \frac{n_2}{V}$
Therefore $\pi V = n_2 RT$
where V = Volume of solution
n_2 = no. of moles of solute.

<u>Formula for numericals</u>

$\pi = CRT$
or $\pi V = n_2 RT$

<u>Hints</u>:- (a) Use proper unit:-
T = in Kelvin $R = 0.082\,L\,atm\,K^{-1}\,mol^{-1}$
V = dm^3 or litre $R = 0.083\,L\,bar\,K^{-1}\,mol^{-1}$
π = atm or bar

(b) In case of dissociation, ionisation, or association use van't Hoff factor (i)
$\pi = iCRT$
OR $\pi V = i n_2 RT$

(c) For isotonic solutions:-
$\boxed{C_1 = C_2}$
or $\boxed{i_1 C_1 = i_2 C_2}$

Relative lowering of vapour pressure

We know that the vapour pressure of the solution containing non-volatile solute is less than that of pure solvent. Suppose the vapour pressure of pure solvent is p_1° and vapour pressure of solvent containing non-volatile solute is p_1, then

Lowering in vapour pressure $(\Delta p) = p_1^\circ - p_1$

$$\therefore \Delta p = p_1^\circ - p_1^\circ x_1 \quad (\because p_1 = p_1^\circ x_1)$$

$$\therefore \Delta p = p_1^\circ (1 - x_1)$$

$$\Delta p = p_1^\circ x_2$$

where x_2 = mole fraction of non-volatile solute.

Relative lowering in vapour pressure $= \dfrac{\Delta p}{p_1^\circ} = \dfrac{p_1^\circ x_2}{p_1^\circ} = x_2$

* Raoult's law for non-volatile solute-solution

The relative lowering in vapour pressure is equal to the mole fraction of the solute.

Formula for Numericals

Relative lowering in V.P $= \dfrac{p_1^\circ - p_1}{p_1^\circ} = x_2$

OR $= \dfrac{p^\circ - p_s}{p^\circ} = x_2$

where p° or p_1° = V.P of pure solvent or liquid
p_s or p_1 = V.P of liquid (or solution)
x_2 (mole fraction of solute) $= \dfrac{n_2}{n_1 + n_2}$

Hints (a) Use any unit of pressure but same.

(b) for very dilute solution or finding the molar mass of solute, use the following formula.

$$\frac{p^\circ - p_s}{p^\circ} = \frac{n_2}{n_1} \quad \left(\because x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n_1}\right)$$

(c) In case of ionization, dissociation or association, use van't Hoff factor(i)

$$\frac{p^\circ - p_s}{p^\circ} = i x_2$$

(d) At normal boiling point, $p^\circ = 1$ atm
At standard boiling point, $p^\circ = 1$ bar

Isotonic Solution

Two solution having same osmotic pressure at a given temperature are called isotonic solutions. For ex→ RBCs placed with 0.9% (W/V) NaCl solution, no osmosis occur because both are isotonic solution.

Hypertonic Solution

If we place the RBC, in a solution containing more than 0.9% (W/V) NaCl solution, water will flow out of the cell and they shrink. Such a solution is called hypertonic solution, the shrinking of the cell is called plasmolysis or Crenation

Hypotonic Solution

If we place the RBC, in a solution containing less than 0.9% (W/V) NaCl solution, the water will flow into the cell and they swell up and finally burst. Such a solution is called Hypotonic solution.

Edema.

Persons taking a lot of salt or salty food develop swelling of their tissues, a disease is called Edema. This is due to the retention of water in the tissue cell and intercellular space due to asmasis.

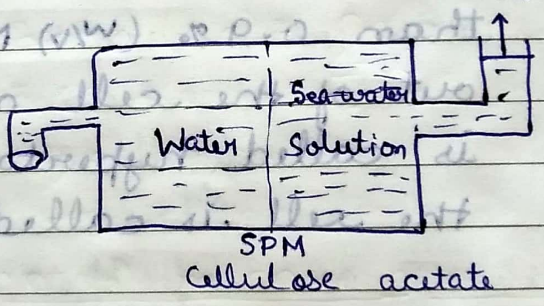
Preservation of meat by salty and fruits by adding Sugar

This is explain by the asmasis. This is because the bacteria lass water in the salted meat due to asmasis and die.

Reverse Asmasis

The direction of asmasis can be reversed if a pressure larger than asmotic pressure is applied to the solution side. This process is called reverse asmasis.

Reverse asmasis is used in disalination of sea water. The semi-permiable membrane used in this process is made up of cellulose acetate.



Cellulose acitate → Artificial SPM

Natural SPM → Animal membrane of brall bladder

* Asmotic pressure method is the best method for determining the molecular mass of solute. This is because as compared to other colligative property, its magnitude is large even for a very dilute solution. It is used to determining the molecular mass of bimolecules like protien which are unstable at high temperature. It is also used for polymers which has poor solubility.

Abnormal molecular mass

A molecular mass which is either lower and higher than the normal value is called Abnormal molar mass.

Abnormal molar mass is observed in case of dissociation or association of molecules in solvent.

Van't Hoff factor (i)

Van't Hoff factor may be defined as:-

$$i = \frac{\text{Normal molar mass}}{\text{Abnormal molarmass}}$$

OR $$i = \frac{\text{Experimentall colligative properties}}{\text{Calculated colligative properties}}$$

OR $$i = \frac{\text{Total no. of moles after dissociation or association}}{\text{Total no. of moles before dissociation or association}}$$

Degree of dissociation

Degree of dissociation may be defined as the ratio of total moles of the substances associate or dissociates

$$\alpha = \frac{\text{no. of moles dissociate or associated}}{\text{Total no. of moles taken}}$$

Hints:- α means no. of moles dissociate or associate.

Value of Van't hoff factor in case of dissociation

(a) $\boxed{i > 1}$

(b) In case of partial dissociation (α) →

(i) $AB \rightleftharpoons A^+ + B^-$

	AB	A^+	B^-
Before disso. moles	1	0	0
After disso. moles	$1-\alpha$	α	α

$$i = \frac{\text{Total no. of moles after dissociation}}{\text{Total no. of moles before dissociation}}$$

$$i = \frac{1 - \cancel{\alpha} + \cancel{\alpha} + \alpha}{1} = 1 + \alpha$$

(ii) $K_2SO_4 \rightleftharpoons 2K^+ + SO_4^{2-}$

Before disso. 1 0 0

After disso. $1-\alpha$ 2α α

$i = \frac{1-\cancel{\alpha}+2\alpha+\cancel{\alpha}}{1} = 1+2\alpha$

(iii) $K_3[Fe(CN)_6] \rightleftharpoons 3K^+ + [Fe(CN)_6]^{3-}$

Before diss. moles 1 0 0

After diss. moles $1-\alpha$ 3α α

$i = \frac{1-\alpha+3\alpha+\alpha}{1} = 1+3\alpha$

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

where n = no. of ions produced by one molecule

(c) In case of complete dissociation :-

$\alpha = 1$ then $i = \cancel{1}+n-\cancel{1} = n$

(d) Dissociation constant of acid $(K_a) = \frac{C\alpha^2}{1-\alpha}$

Where C = Molality or molarity.

Value of van't Hoff factor in case of association

(a) $i<1$

(b) In case of partial association (α):-

(i) For dimer, $2A \rightleftharpoons A_2$

Before ass. moles 1 0

After ass. moles $1-\alpha$ $\frac{\alpha}{2}$

$i = \frac{\text{Total no. of moles after ass.}}{\text{Total no. of moles before asso.}}$

$i = \frac{1-\alpha+\frac{\alpha}{2}}{1}$

$i = 1-\frac{\alpha}{2}$

(ii) For trimer, $3A \rightleftharpoons A_3$

Before ass moles 1 0

After ass. moles $1-\alpha$ $\frac{\alpha}{3}$

$i = 1 - \alpha + \frac{\alpha}{3}$

$i = 1 - \frac{2\alpha}{3}$

(iii) $i = 1 - \frac{(n-1)\alpha}{n}$

where $n=2$ (For dimer)
$n=3$ (For Trimer)
$n=4$ (For tetramer)

For complete

Comparison of colligative properties of different solutions

- $C.P \propto i \times M$
- $B.P \propto i \times M$
- $F.P \propto \frac{1}{i \times M}$
- Value of (i) for organic compound is 1 (except organic acid)

Problems

1. Calculate the boiling point of 0.1M solution of NaCl

$T_b^\circ = 100^\circ c$, $K_b = 0.52 K\ kg\ mol^{-1}$

For NaCl, $i=2$

$T_b - T_b^\circ = i\ K_b \times m$

$T_b - 100 = 2 \times 0.52 \times 0.1$

$T_b = 100 + 0.104$

$= 100.104^\circ c$

2. Calculate the osmotic pressure of a solution containing 3g of Urea (M.M = 60) in 2 l of water at 27° C:

$\pi = ?$

$W_2 = 3g$

$M_2 = 60$

$V = 2$ litre

$T = 27°C$

$\pi V = i n_2 RT$

$\pi = \frac{i n_2 RT}{V}$

$\pi = 1 \times \frac{3}{\cancel{60}} \times 0.082 \times \overset{5}{\cancel{300}}$

$\pi = 15 \times 0.082$

3. The freezing point depression of 0.1 molal solution of acetic acid in Benzene is 0.256 K. K_f for benzene is 5.12 K kg/mol. What conclusion can you draw about the molecular state of acetic acid in Benzene?

$\Delta T_f = 0.256 K$

$K_f = 5.12$ K kg / mol

$m = 0.1$

$\Delta T_f = i K_f m$

$\frac{0.256 \times 0.1}{5.120} = i$

$i = 1/2$ $(\because i < 1)$

So, acetic acid associates 50%. in benzene and form dimer.

4. 0.5g KCl (M.M. 74.5g/mol) was dissolve in 100 gram of water and the solution originally at 20°C and froze at −24°C. Calculate the % ionisation of salt. (K_f for water :- 1.86 K kg mol^{-1})

$$\Delta T_f = i K_f m$$

$$m = \frac{W_2}{M_2} \times \frac{1}{W_1}$$

$$m = \frac{0.50}{74.5} \times \frac{1}{0.1} = \frac{0.50}{7.450}$$

~~44 = i ×~~ $T_f^\circ - T_f = i K_f m$

$$0 - (-0.24) = i \times 1.86 \times \frac{50}{745}$$

$$i = \frac{0.24 \times 745}{50 \times 1.86} = 1.92$$

$$KCl \rightleftharpoons K^+ + Cl^-$$

	KCl	K^+	Cl^-
Before diss	1	0	0
After diss.	$1-\alpha$	α	α

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

$$\alpha = i - 1 = 1.92 - 1 = 0.92$$

$$\alpha = 92\%$$