

CHAPTER - 12

SOLUTION

SYNOPSIS

Solution: A homogeneous mixture of two or more non-reacting substances. Binary solution contains only two components

Solvent is the component that is present in relatively higher amount and the other component is solute. If the two components are in different phases (physical states), the component which is in the same physical state as that of the solution is considered as the solvent (even though the amount is small).

Considering the three states of matter, $3^2 = 9$ types of binary solutions are possible.

	Solvent	Solute	Examples
I. Gaseous solutions	Gas	Gas	Mixtures of O_2 and N_2
	Gas	Liquid	$CHCl_3$ in N_2 gas
	Gas	Solid	Camphor in N_2 gas; I_2 vapour in air
II. Liquid solutions	Liquid	Gas	O_2 dissolved in water
	Liquid	liquid	Ethanol in water
	Liquid	Solid	Sugar in water
III. Solid solutions	Solid	Gas	N_2 in Ti , H_2 in Pd
	Solid	Liquid	Hg in gold, Amalgam of Hg with Na
	Solid	Solid	Alloys like brass, bronze etc (Substitutional solid solution)

Expressing concentrations of solutions

(i) Mass percentage (w/w) : Mass % of a component =

$$\frac{\text{Mass of the component in the solution} \times 100}{\text{Total mass of the solution}}$$

(ii) Volume percentage (v/v): vol% of a component = $\frac{\text{Volume of the component} \times 100}{\text{Total volume of the solution}}$

Solutions containing liquids are commonly expressed in this unit

(iii) Mass by volume percentage (w/v) : This is commonly used in pharmacy

$$\text{Mass by volume \% of a component} = \frac{\text{Mass of the component} \times 100\text{mL}}{\text{Vol : of the solution in mL}}$$

(i.e mass of the solute dissolved in 100ml of the solution)

$$(iv) \text{ Parts per million (ppm)} = \frac{\text{Number of parts of the component} \times 10^6}{\text{Total no : of parts of all the components of the solution}}$$

ppm can be expressed as mass to mass, volume to volume or mass to volume. ppm unit is used when the amount of the solute is in traces. The concentration of pollutant in water or atmosphere is often expressed in terms of the $\mu\text{g mL}^{-1}$ or ppm

(v) Mole fraction (Symbol x)

$$\text{Mole fraction of a component} = \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}}$$

In binary solutions x_1 denotes the mole fraction of solvent and x_2 denotes the mole fraction of solute.

If there are several components in the solution, mole fraction of the i^{th} component

$$= \frac{n_i}{n_1 + n_2 + n_3 + \dots n_i} = \frac{n_i}{\sum n_i}$$

$x_1 + x_2 = 1$ in a binary solution

$x_1 + x_2 + x_3 = 1$, in a ternary solution

(vi) **Molarity (M)**

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of the solution in litre}}$$

i.e molarity (M) is the number of moles of solute per litre of the solution

(One litre = one cubic decimetre i.e $1\text{L} = 1\text{dm}^3$)

(vii) **Molality (m)** It is the no: of moles of the solute per kg of the solvent

$$\text{i.e molality} = \frac{\text{number of moles of solute}}{\text{mass of solvent in kg}}$$

(viii) **Formality (F)** For ionic substances like NaCl, KCl etc, where the crystal does not contain discrete molecules, but only ions, formality can be used.

$$\text{Formality (F)} = \frac{\text{No. of formula weights of the ionic solute}}{\text{Vol. of the solution in litre}}$$

(ix) **Normality (N)** It is the number of gram equivalents of the solute per litre of the solution.

$$N = \frac{\text{No : of gram equivalent of solute}}{\text{Vol. of the solution in litre}}$$

$$(x) \text{ Mass fraction} = \frac{\text{Mass of the component}}{\text{Total mass of all the components}}$$

Molality, mole fraction and mass fraction are independent of temperature as they do not involve volumes. But molarity, normality and formality involves volume and they may vary slightly with temperature. For

very accurate work, therefore, molality, mole fraction or mass fraction are preferred.

Important relations

1. $V_1 N_1 = V_2 N_2$ (used in volumetric titrations and during dilution of solutions)
2. $V_1 N_1 + V_2 N_2 = V_3 N_3$ (Two solutions at different normalities of the same solute are mixed together)
3. $V_1 M_1 = V_2 M_2 \rightarrow$ used during dilutions
4. $\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$ (when the two substances are reacting not in equimolar amounts).

For eg: $n_1 A + n_2 B \rightarrow$ Products.

But when $n_1 = n_2$, $M_1 V_1 = M_2 V_2$ can be used for volumetric calculations.

Solubility: Solubility of a substance is the maximum amount that can be dissolved in a specified amount of solvent at a specified temperature. It depends on the nature of the solute and solvent as well as temperature and pressure.

Generally polar solutes dissolve in polar solvents while non polar solutes dissolve in nonpolar solvents – “like dissolves like”.

If the dissolution of a solid in a solvent is endothermic i.e. $\Delta H_{sol} > 0$, solubility should increase with temperature. Solutes like KCl, NH_4Cl , KNO_3 etc. dissolves in water by the absorption of heat. But if the dissolution of a solute in a solvent is exothermic i.e. $\Delta H_{soln} < 0$ (heat liberated), solubility should decrease with rise in temperature.

Eg: $\text{Co}_2(\text{SO}_4)_3$, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, Li_2CO_3 dissolves in water with liberation of heat. Pressure has no significant effect on the solubilities of solids and liquids. (Reason: - solids and liquids are incompressible)

Solubility of gases in liquids

Solubility of gases depends on the nature of the gas and the solvent. NH_3 , HCl etc are highly soluble in water, while N_2 , O_2 , H_2 etc are less soluble at the same temperature and pressure.

Henry's law: The mass of a gas dissolved in a given volume of the solvent at a particular temperature is directly proportional to the pressure of the gas at equilibrium with the liquid.

$$m = K_H \cdot P$$

(K_H = Henry's law constant, unit of K_H in this expression will be (mass) (pressure)⁻¹)

m = mass of the gas; P = Pressure

Instead of mass, we can use mols litre⁻¹ also, then the unit of K_H should be mol litre⁻¹ atm⁻¹.

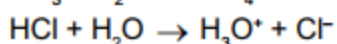
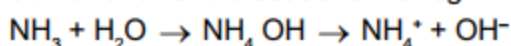
Henry's law is also expressed as $x = K_H \cdot P$ where x is the mole fraction of the gas in the solution and P is the partial pressure of gas in equilibrium with the liquid (Here unit of K_H is atm⁻¹ or bar⁻¹)

The most commonly used form of Henry's law: States that the partial pressure of the gas in the vapour phase (P) is proportional to the mole fraction (x) of the gas in the solution.

$$P = K_H \cdot x \text{ (Here the unit of } K_H \text{ will be same as that of pressure)}$$

This form of equation is used when different gases are dissolving in the same solvent. Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid. For many gases K_H value increases with increasing temperature, indicating that the solubility of gases decrease with temperature.

NB:- Henry's law is not valid, when the gas is highly soluble in a solvent and it enters into chemical combination and dissociation for eg: NH_3 , HCl etc in H_2O .



Henry's law and Scuba divers : During deep sea diving, some nitrogen from the oxygen air mixture will dissolve in the blood (due to high pressure). But when the diver comes to the surface, due to the decrease

of pressure, dissolved N_2 forms bubbles in blood and this causes severe pain to the diver and this condition is called 'bends' or caisson disease. To decrease the solubility of N_2 in blood vessels, the oxygen - nitrogen mixture for breathing is diluted with Helium (11.7% He, 56.2% N_2 and 32.1% O_2)

Vapour pressure of liquid solutions: For a binary solution of two volatile liquids, let P_1 and P_2 be the partial vapour pressures and x_1 and x_2 their mole fractions in the liquid mixture, then Raoult's law states that $P_1 = x_1 P_1^0$ and $P_2 = x_2 P_2^0$. P_1^0 and P_2^0 are the vapour pressures of the pure components 1 and 2 at the same temperature at which P_1 and P_2 are measured. According to Dalton's law of partial pressures, total vapour pressure above the solution is $P_1 + P_2$ i.e. $P_{\text{total}} = P_1 + P_2$. Substituting the values of P_1 and P_2

$$P_{\text{total}} = x_1 P_1^0 + x_2 P_2^0 = (1 - x_2) P_1^0 + x_2 P_2^0$$

$$\text{or } P_{\text{total}} = P_1^0 + (P_2^0 - P_1^0) x_2 \rightarrow (A)$$

$$\begin{aligned} \text{(OR) } P_{\text{total}} &= x_1 P_1^0 + (1 - x_1) P_2^0 \\ &= P_2^0 + (P_1^0 - P_2^0) x_1 \rightarrow (B) \end{aligned}$$

From equations A and B it is clear that total vap: pressure over the solution is linearly dependent on the mole fraction of any one component. When a solution obeys Raoult's law over the entire range of concentration, it is called an ideal solution, otherwise it is non ideal. Examples of ideal solution:

1. n hexane + n heptane
2. Ethyl chloride + ethyl bromide
3. Chlorobenzene + bromobenzene
4. Benzene + Toluene

For ideal solutions $\Delta V_{\text{mix}} = 0$ and $\Delta H_{\text{mix}} = 0$ i.e total vol: does not change on mixing. Similarly no heat change on mixing.

In pure liquids A and B there are only A – A interactions and B – B interactions. But on mixing them there will be additional A – B interactions. If the A – B interactions are nearly the same as A – A and B – B interactions, the solution will be ideal.

Non ideal solution : Non ideal solutions may exhibit +ve or –ve deviations from Raoult's law. If the total vapour pressure is higher than that predicted by Raoult's law, it is +ve deviation. This is due to weaker A – B interactions compared to more strong A – A and B – B interactions. For such non-ideal systems exhibiting +ve deviations from Raoult's law, $\Delta V_{\text{mix}} > 0$ and ΔH_{mix} is +ve or greater than zero

Example of systems exhibiting +ve deviations

1. Acetone + Ethanol
2. Acetone + CS_2
3. Water + ethanol
4. Water + methanol
5. CCl_4 + Toluene
6. CCl_4 + $CHCl_3$
7. Acetone + Benzene
8. Cyclohexane + Ethanol
9. CCl_4 + methanol
10. Water + Propanol

If the total vapour pressure is less than that predicted by Raoult's law, we have –ve deviations. Here A – B

interactions are stronger than A – A or B – B attractions. Here $\Delta V_{\text{mix}} < 0$ and $\Delta H_{\text{mix}} < 0$ (ΔH is –ve).

Examples for –ve deviations

1. Acetone + CHCl_3
2. Acetone + Aniline
3. Phenol + Aniline
4. Methanol + Acetic acid
5. H_2O + HCl
6. H_2O + HNO_3
7. H_2O + H_2SO_4
8. CHCl_3 + diethyl ether
9. CHCl_3 + Benzene
10. Acetic acid + Pyridine

Azeotropes : Several non ideal solutions form azeotropes or constant boiling mixture. These are solutions which cannot be separated completely into pure components by fractional distillation. Example. Ethyl alcohol water mixture shows +ve deviation and it forms an Azeotropic mixture with minimum boiling point. 95.5% ethanol and 4.5% water by weight is a constant boiling mixture. i.e it will distill without any change in composition. i.e the vapour will also have the same composition.

Boiling point of H_2O is 373K

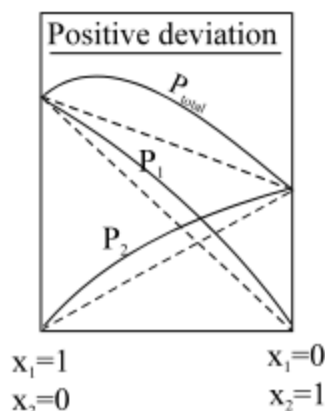
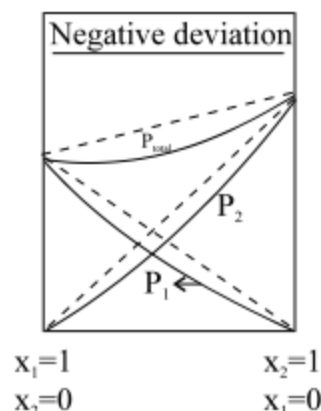
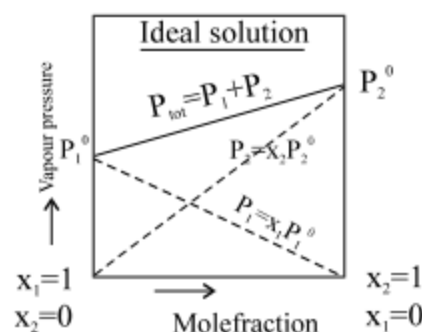
B.P of Ethanol is 351.3K

B.P of Azeotrope is 351.1°K

Non ideal systems with –ve deviations will form Azeotropes of maximum boiling point. A mixture containing 68% HNO_3 and 32% H_2O by mass has the boiling point 393.5K

Vapour pressure curves for ideal and non ideal solutions

dotted line for ideal solutions



Raoult's law is a special case of Henry's law

According to Raoult's law, the vapour pressure of a volatile component in a given solution is given by $P_i = x_i P_i^0$. In the solution of a gas in a liquid, one of the components is too volatile that it exists as a gas and for gases, dissolved in a liquid solvent we have Henry's law $P = K_H \cdot x$ [This is the most commonly used form of Henry's law].

If we compare those two equations, only the proportionality constant is differing. Thus, Raoult's law becomes a special case of Henry's law in which K_H becomes equal to P_i^0 .

Composition of the vapour phase in ideal solutions

If y_1 and y_2 are the mole fractions of the components 1 and 2 respectively in the vapour phase, then

$$P_1 = y_1 P_{\text{total}}; \quad \therefore y_1 = \frac{P_1}{P_{\text{total}}} \text{ and } y_2 = \frac{P_2}{P_{\text{total}}}$$

$$\text{we know } P_1 = x_1 P_1^0 \text{ and } P_2 = x_2 P_2^0; \quad \therefore y_1 = \frac{x_1 P_1^0}{x_1 P_1^0 + x_2 P_2^0} \text{ and } y_2 = \frac{x_2 P_2^0}{x_1 P_1^0 + x_2 P_2^0}$$

Vapour pressure of solutions of solids in liquids

When a solute like, urea, glucose, cane sugar or sodium chloride is dissolved in water, vapour pressure of the resulting solution is less than that of the pure solvent (water) at the same temperature. Similarly I_2 or sulphur dissolved in CS_2 (liquid solvent) lowers the vapour pressure of the solvent. The decrease in the vapour pressure of water by adding 1 mole of sucrose to 1 kg of water is nearly similar to that produced by adding 1 mole of urea to the same quantity of water at the same temperature.

Raoult's law in its general form

For any solution, the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction. In a binary solution containing a non volatile solute, only the solvent molecules are present in the vapour phase. Let P_1 be the vapour pressure of the solvent and x_1 its mole fraction in the solution. Let P_1^0 be its vapour pressure in the pure state. According to Raoult's law.

$$P_1 \propto x_1 \text{ or } P_1 = x_1 P_1^0 (P_1^0 \text{ is the proportionality constant})$$

$$\text{But } x_1 = 1 - x_2$$

$$\therefore P_1 = (1 - x_2) P_1^0 \text{ ie } P_1 = P_1^0 - x_2 P_1^0$$

$$\Rightarrow P_1^0 - P_1 = x_2 P_1^0 \text{ or } \frac{P_1^0 - P_1}{P_1^0} = x_2$$

P_1^0 is the vapour pressure of the pure solvent

P_1 is the vapour pressure of the solution at the same temperature. Since the solute is non volatile, P_1 can be replaced by P_s

$$\therefore \frac{P_1^0 - P_s}{P_1^0} = x_2 \quad (P_s = \text{Vap. pressure of solution})$$

i.e Relative lowering of vapour pressure in a solution containing a non volatile solute is equal to the mole fraction of the solute. This is the form of the Raoult's law generally used for dealing with solutions of solids in liquids.

$$\text{Lowering of vapour pressure} = P_1^0 - P_s$$

$$\therefore \text{Relative lowering} = \frac{P_1^0 - P_s}{P_1^0}$$

$$x_2 = \text{mole fraction of solute} = \frac{n_2}{n_1 + n_2} \quad n_2 = \text{no. of moles of solute, } n_1 = \text{no. of moles of solvent}$$

$$\therefore \frac{P_1^0 - P_s}{P_1^0} = \frac{n_2}{n_1 + n_2}$$

But in a dilute solution $n_1 \gg n_2$ \therefore n_2 in the denominator can be neglected so that

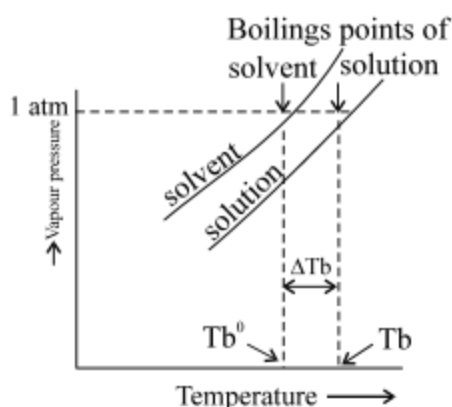
$$\frac{P_1^0 - P_s}{P_1^0} = \frac{n_2}{n_1} \quad \text{but } n_2 = \frac{w_2}{M_2} \quad w_2 = \text{mass of solute ; } M_2 = \text{Molecular mass of solute and } n_1 = \frac{W_1}{M_1}, W_1 = \text{mass of solvent; } M_1 = \text{Molecular mass of solvent}$$

This expression can be used to find out the molecular mass of unknown solute using Raoult's law (i.e from lowering of vapour pressure)

Colligative properties and determination of molar mass or molecular mass of solute

When a non volatile solute is added to a volatile solvent, the escaping tendency of solvent molecules to the vapour phase is decreased and it leads to a lowering of vapour pressure. There are many properties of solutions which are connected with this decrease of vapour pressure. These are (1) Relative lowering of vapour pressure of solvent (2) Depression of freezing point of the solvent (3) Elevation of boiling point of the solvent and (4) Osmotic pressure of the solution. Since these properties are all bound together through their common origin, they are called colligative properties. Common origin is the lower value of chemical potential of the solvent in the solution, compared to its chemical potential in the pure solvent. All the four colligative properties depend on the number of solute particles irrespective of their nature relative to the total no. of particles present in the solution.

Elevation in boiling point (ΔT_b) : Boiling point is the temperature at which vapour pressure becomes equal to the atmospheric pressure (1 atm or 1.013 bar or 760 torr or 760mm Hg). Since vapour pressure of a solution is less than that of pure solvent, the boiling point of solution is greater than that of pure solvent.



ΔT_b is proportional to the molality (m) of the solution

i.e $\Delta T_b \propto m$ or $\Delta T_b = K_b \times m$

K_b is called molal elevation constant (Ebullioscopic constant)

when $m = 1$, $\Delta T_b = K_b$

Therefore K_b is defined as the elevation in boiling point of a 1 molal solution.

The unit of $K_b = K \text{ kg mol}^{-1}$ or K/m (Kelvin per molality)

K_b is characteristic of the solvent. It has nothing to do with solute

<u>Solvent</u>	<u>K_b value</u>
Water	0.52
Benzene	2.67
Methanol	0.80
CHCl_3	3.88
Ethanol	1.20
CCl_4	5.03

$\Delta T_b = K_b \times \text{molality of solution}$

$$\Delta T_b = K_b \times \frac{W_2}{M_2} \times \frac{1000}{W_1} \quad \text{But molality} = \frac{\left(\frac{W_2}{M_2}\right)}{\left(\frac{W_1}{1000}\right)} = \frac{\text{no. of moles of solute}}{\text{mass of solvent in Kg}}$$

$$\therefore M_2 = \frac{K_b \times W_2 \times 100}{\Delta T_b \times W_1} \quad \text{Here } W_2 = \text{mass in gms of solute}$$

$$W_1 = \text{mass in gms of solvent}$$

K_b is related to heat of vaporization of the solvent

$$K_b = \frac{RT_b^2}{1000\ell_v} \quad \text{where } T_b = \text{boiling point of pure solvent in Kelvin}$$

$R = \text{gas constant}$

$$= \frac{RT_b^2 M_1}{1000\Delta H_{\text{vap}}} \quad \ell_v = \text{latent heat of vapourisation per gm of solvent}$$

$$\text{But } \ell_v = \frac{\Delta H_{\text{vap}}}{M_1}$$

$\Delta H_{\text{vap}} = \text{molar heat of vapourisation of solvent}$

$M_1 = \text{Molecular mass of solvent (or molar mass)}$

Depression in freezing point (ΔT_f)

The freezing point of a solution is less than that of pure solvent $\Delta T_f = T_f^0 - T_f$

$\Delta T_f \propto \text{molality}$ or $\Delta T_f = k_f \times m$ (K_f = cryoscopic constant)

Molecular mass of solute can be calculated using the expression,

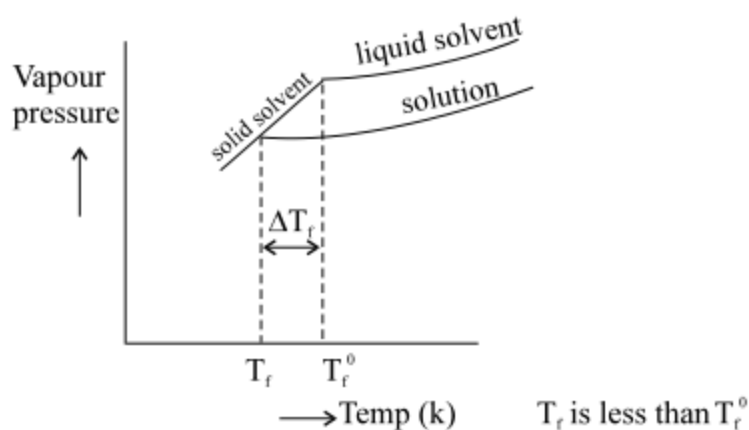
$$M_2 = \frac{K_f \times W_2 \times 1000}{\Delta T_f \times W_1}$$

Molal depression constant or cryoscopic constant for some solvents.

Solvent	K_f (K kg mol⁻¹)
Water	1.86
C ₆ H ₆ (Benzene)	5.12
Phenol	7.27
Acetic acid	3.90
Naphthalene	6.90
Cyclohexane	20.0
Camphor	39.70

Cause of depression in F.P

The lowering of vapour pressure of a solution causes a lowering of the freezing point compared to that of the pure solvent. The freezing point of a substance is the temperature at which the vapour pressure of the substance in its liquid phase is equal to that of the vapour pressure in the solid phase. A solution will freeze when its vapour pressure equals the vapour pressure of the pure solid solvent (see diagram)



K_f is also characteristic of the solvent. It is related to the latent heat of fusion of the solid solvent.

$$K_f = \frac{RT_f^2}{1000\ell_f} \text{ where}$$

T_f = F.P of the solvent (In Kelvin)

R = gas constant

ℓ_f = heat of fusion per gram of solvent

(If R is in Joules ℓ_f also should be in Joules)

but $\ell_f = \frac{\Delta H_f}{M_1}$ where M_1 = Molecular mass of solvent and ΔH_f is the molar heat of fusion

$$\therefore K_f = \frac{RT_f^2 \cdot M_1}{\Delta H_{fus} \times 1000}$$

Experimental methods for ΔT_f measurement are Beckmann method and Rast method.

For measuring ΔT_b , Landsberger method and Cottrell's method are used.

Osmosis and Osmotic pressure

The migration of solvent particles from pure solvent or dilute solution towards the concentrated solution when they are separated by a semipermeable membrane is called osmosis.

Osmotic pressure (π) is the excess hydrostatic pressure which builds up as a result of osmosis (OR) The excess pressure that must be applied to a solution to prevent osmosis.

Example of Semipermeable membranes

- | | | |
|------------------|---|----------------------------------|
| (1) Natural :- | (1) Skin of an egg | (2) Pig's bladder |
| | (3) Membrane of plant cells | (4) RBC membrane. |
| (2) Artificial:- | (1) $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ | (2) $\text{Ca}_3(\text{PO}_4)_2$ |

Reverse osmosis:- If a pressure greater than osmotic pressure is applied to the solution side, the solvent particles migrate from solution to solvent side, through the membrane. Desalination of sea water is by this technique.

Isotonic solutions:- Solutions having the same osmotic pressure. They are also called Isopiestic solutions.

A 0.9% aq: solution: of NaCl is isotonic with blood: Average osmotic pressure of blood is about 7.6 atm.

Hypertonic and hypotonic solutions:- When comparing the osmotic pressure of two solutions, the one with lower value of O.P is hypotonic and the other with higher O.P is called hypertonic solutions.

Vant Hoff's eqn: for O.P : $\pi = CRT$, where C = molarity of the solution.

$$C = \frac{n}{V} \quad n = \text{no: of moles of solute; } V = \text{Vol: of the solution in litres}$$

$$\therefore \pi = CRT \text{ or } \pi = \frac{n}{V} RT$$

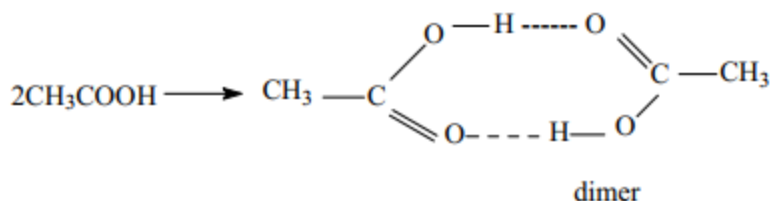
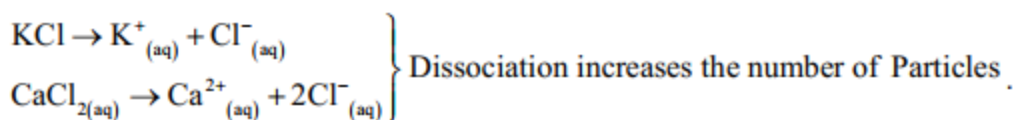
Here π is in atmospheres, when R is in litre atmosphere and V is in litres

$$\pi = \frac{nRT}{V} \text{ can be written as } \pi = \frac{W_B}{M_B} \times \frac{RT}{V}$$

$$\text{or } M_B = \frac{W_B RT}{\pi V} . \text{ Hence mol: wt. of solute (or molecular mass) can be determined.}$$

Osmotic pressure method is suitable to find out the molecular mass of macromolecules (or polymers)

Abnormal colligative properties :- For electrolytes like NaCl, KBr etc which dissociates in aqueous solution, the values of the colligative properties will be higher than the theoretical values. Acetic acid, benzoic acid etc, which associates in benzene, give a lower value of the colligative properties. Hence molecular masses of such solutes determined by colligative property measurements will be abnormal values.



Association decreases the no: of particles

$$\text{molecular mass} \propto \frac{1}{\text{colligative property}}$$

Molecular mass of KCl obtained by colligative property method is 40.5 (actual mol. mass = 74.5). The value of mol. mass obtained shows that KCl is not completely dissociated. Had there been 100% dissociation, the molecular mass obtained would have been $\frac{1}{2}(74.5) = 37.25$. The mol: mass of acetic acid using benzene solvent is 120. (Actual mol. mass = 60). This shows that acetic acid exists as a dimer in benzene.

Van't Hoff factor (i) :- To compensate for the variation in colligative properties, a parameter 'i' called Van't Hoff factor is used in the equation for colligative properties.

$$\frac{P^0 - P_s}{P^0} = ix_2 \quad \Delta T_b = i K_b \times m \quad \Delta T_f = i K_f \times m \quad \pi = i CRT$$

In the case of association $i < 1$ and for dissociation $i > 1$ when there is dissociation, $i = 1 + \alpha(n-1)$

Where α is the degree of dissociation and 'n' is the no. of particles (ions) obtainable theoretically from one molecule. For KCl, $n = 2$, for CaCl_2 $n = 3$ etc

$$\text{When there is association, } i = 1 + \alpha \left(\frac{1}{n} - 1 \right)$$

Here α is the degree of association and n is the no: of molecules associated together. For acetic acid, benzoic acid etc in benzene $n = 2$ since dimer is formed.

$$\text{Degree of association } \alpha = \frac{i-1}{\left(\frac{1}{n}-1\right)} = \frac{(i-1)n}{(1-n)}; \quad \text{Degree of dissociation } \alpha = \left(\frac{i-1}{n-1}\right)$$

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}} = \frac{M}{M_0}, i = \frac{\text{Observed value of colligative property}}{\text{Theoretical value of colligative property}}$$

$$i = \frac{\text{No. of particles after association or dissociation}}{\text{No. of particles before association or dissociation}}$$

$$\text{Degree of dissociation } \alpha = \frac{(M_{\text{theoretic}} - M_{\text{obs}})}{M_{\text{obs}}(n-1)}; \text{ Degree of association } \alpha = \left(\frac{M_{\text{obs}} - M_{\text{theor}}}{M_{\text{obs}}} \right) \frac{n}{n-1}$$

PART-I (JEE MAIN)

SECTION-I- Straight objective type questions

- From the following, select the temperature independent concentration term
 1) Molarity 2) Normality 3) Molality 4) Volume percent
- If 100 cm³ of 0.3 M NaCl and 150 cm³ of 0.1 M CaCl₂ solutions are mixed, the molarity of Cl⁻ in the final mixture will be:
 1) 0.24 2) 0.18 3) 0.5 4) 0.6
- Which of the following statements are CORRECT with respect to Henry's law constant (K_H)?
 I) K_H is a function of nature of the gas
 II) K_H of N₂ is 76.48 kbar at 303 K and 88.84 kbar at 293 K
 III) Highly soluble gases have low K_H (in kbar units) at a given temperature and pressure
 IV) K_H has a unit of pressure or (pressure)⁻¹
 1) I, IV only 2) I, II, III only 3) II, III, IV only 4) I, III, IV only
- Liquids A and B form an ideal solution in the entire composition range. At 350 K, the vapour pressure of pure A and pure B are 7 × 10³ Pa and 12 × 10³ Pa, respectively. The vapour pressure of a solution of A and B containing 40 mol percent of A at this temperature is:
 1) 1.9 × 10⁴ Pa 2) 10⁴ Pa 3) 9.5 × 10³ Pa 4) 10³ Pa
- Which of the following correctly represents the changes in thermodynamic properties during the formation of an ideal binary solution?
 1) $\Delta H_{\text{mix}} = 0$, $\Delta G_{\text{mix}} = 0$, $T\Delta S_{\text{mix}} = 0$
 2) $\Delta H_{\text{mix}} = 0$, $\Delta G_{\text{mix}} = +ve$, $T\Delta S_{\text{mix}} = -ve$
 3) $\Delta H_{\text{mix}} = 0$, $\Delta G_{\text{mix}} = -ve$, $T\Delta S_{\text{mix}} = +ve$
 4) $\Delta H_{\text{mix}} = -ve$, $\Delta G_{\text{mix}} = 0$, $T\Delta S_{\text{mix}} = +ve$
- Assertion : Both enthalpy of mixing and volume of mixing are negative for a binary mixture of aniline and phenol.

Reason : The intermolecular forces of attraction between aniline and phenol is stronger than aniline-aniline or phenol-phenol interactions.

In the light of the above statements choose the correct option:

- Both assertion and reason are true and the reason is the correct explanation of the assertion
- Both assertion and reason are true but reason is not the correct explanation of the assertion
- Assertion is true but reason is false
- Assertion is false but reason is true

7. Match the following

Column-I

- A) n-hexane + n-heptane
- B) Nitric acid + water
- C) Chlorobenzene + bromobenzene
- D) Ethanol + water

- 1) A-P, B-QR, C-P, D-RS
- 2) A-PR, B-QR, C-PR, D-RS
- 3) A-P, B-RS, C-P, D-QR
- 4) A-PR, B-RS, C-PR, D-QR

Column-II

- P) Ideal solution
- Q) Maximum boiling azeotrope
- R) Will not follow Raoult's law
- S) Minimum boiling azeotrope

8. Elevation in the boiling point for 1 molal solution of glucose is 2 K. The depression in the freezing point for 2 molal solution of glucose in the same solvent is 2 K. The relation between K_b and K_f is

- 1) $K_b = 0.5 K_f$
- 2) $K_b = 2 K_f$
- 3) $K_b = 1.5 K_f$
- 4) $K_b = K_f$

9. Which of the following solutions will show the maximum vapour pressure at 300 K?

- 1) 1M NaCl
- 2) 1M $CaCl_2$
- 3) 1M $AlCl_3$
- 4) 1M $C_{12}H_{22}O_{11}$

10. Which of the following aqueous solutions are isotonic at a given temperature? [Assume 100% dissociation/association in the case of dissociating/associating solutes]

- i) 0.15 M urea
- ii) 0.05 M $CaCl_2$
- iii) 0.1M $MgSO_4$
- iv) 0.15 M glucose
- 1) i & iv
- 2) ii & iii
- 3) i, ii & iv
- 4) ii, iii & iv

SECTION-II - Numerical Type Questions

11. How many of the following is/are examples of solid solutions?

- 1) glucose dissolved in water
- 2) Camphor dissolved in nitrogen
- 3) Copper dissolved in gold
- 4) Amalgam of mercury with sodium
- 5) Solution of hydrogen in palladium

12. Vapour pressure of water at 293 K is 17.535 mmHg. The vapour pressure of the solution at 293 K when 25 g of glucose is dissolved in 450 g of water is mmHg (molar mass of glucose = 180 $g\ mol^{-1}$)

13. If K_2SO_4 is completely dissociated in water then its van't Hoff factor will be

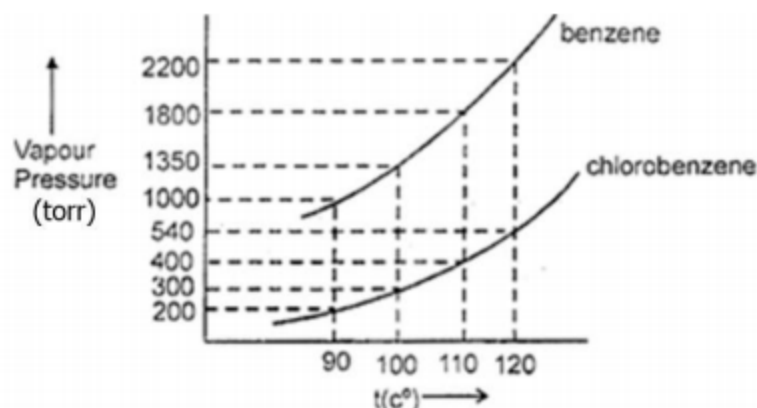
14. The osmotic pressure of 0.01 m aqueous solution of sodium chloride is $x \times 10^{-1}$ times that of 0.01 m urea solution. The value of x is (assume NaCl is 90% dissociated).

15. A solution of 12.2 g of benzoic acid (molar mass = 122 $g\ mol^{-1}$) in 100 g of benzene has a elevation in boiling point of 1.25°C. The degree of dimerisation of benzoic acid in this solution is (given K_b of benzene = 2.5 K kg mol^{-1}).

PART-II (JEE ADVANCED)

Section-III - Only one option correct type

16. Two liquids A and B are known to form an ideal solution. At 300 K, the vapour pressure of solution containing 1 mole of A and 3 mole of B is 550 mm Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm Hg. The vapour pressure of A and B in their pure states (in mm Hg) are respectively
 A) 400, 600 B) 300, 500 C) 600, 400 D) 500, 300
17. The boiling point elevation constant for toluene is $3.32 \text{ K kg mol}^{-1}$. The normal boiling point of toluene is 383 K. The enthalpy of vapourisation of toluene would be nearly (given $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$; atomic mass of C = 12 and H = 1)
 A) 17.0 kJ mol^{-1} B) 34.0 kJ mol^{-1} C) 51.0 kJ mol^{-1} D) 68.0 kJ mol^{-1}
18. It is more convenient to obtain the molecular weight of an unknown solute by measuring the freezing point depression than by measuring the boiling point elevation because
 A) freezing point depression is a colligative property whereas boiling point elevation is not
 B) freezing point depressions are larger than boiling point elevations for the same solution
 C) freezing point depressions are smaller than boiling point elevations for the same solution
 D) freezing point depression depends more on the amount of the solute than boiling point elevation
19. A 1.00 molal aqueous solution of $\text{PtCl}_4 \cdot 6\text{H}_2\text{O}$ has a depression in freezing point of 3.72°C . The correct formula of the complex is (assume 100% dissociation; $K_f(\text{H}_2\text{O}) = 1.86 \text{ K kg mol}^{-1}$)
 A) $[\text{Pt}(\text{H}_2\text{O})_6]\text{Cl}_4$ B) $[\text{Pt}(\text{H}_2\text{O})_4]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$
 C) $[\text{Pt}(\text{H}_2\text{O})_3\text{Cl}_3]\text{Cl} \cdot 3\text{H}_2\text{O}$ D) $[\text{Pt}(\text{H}_2\text{O})_2\text{Cl}_4]4\text{H}_2\text{O}$
20. Assuming the formation of an ideal solution, determine the boiling point of a mixture containing 1560 g of benzene (molar mass = 78) and 1125 g of chlorobenzene (molar mass = 112.5) using the given vapour pressure vs temperature diagram against an external pressure of 1000 torr



- A) 90°C B) 100°C C) 110°C D) 120°C

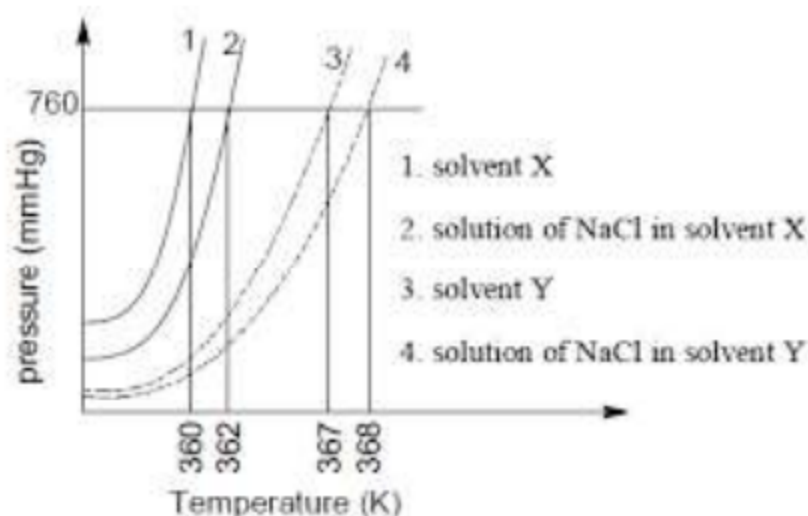
21. If a 1 molal solution of benzoic acid in benzene has a freezing point depression of 2.56°C ($K_f = 5.12^{\circ}\text{C mol}^{-1}\text{kg}$) and boiling point elevation of 2.53°C ($K_b = 2.53^{\circ}\text{C mol}^{-1}\text{kg}$) then select the correct statement(s) from the following
- 1) There is dimer formation when undergoing freezing
 - 2) There is no dimer formation when undergoing boiling
 - 3) There is no dimer formation when undergoing freezing
 - 4) There is dimer formation when undergoing both freezing and boiling
- A) 1, 2 B) 2, 3 C) 3, 1 D) Only 1

Section IV - One or more option correct type

22. On adding a non-volatile solute (A) into a liquid solvent (B).
- A) Vapour pressure of the solution (P_s) is given by $P_s = P_B^0 X_B$
 - B) Fraction of the liquid surface covered by the solvent molecules gets reduced
 - C) Number of solvent molecules escaping from the liquid remains the same
 - D) Number of solvent molecules in equilibrium with the liquid solution remains the same
23. Acetone and carbon disulphide form a binary liquid solution that shows positive deviations from Raoult's law. The normal boiling point of pure acetone is less than that of pure carbon disulphide. Pick out the incorrect statement(s) from the following
- A) Boiling temperature of mixture is always less than boiling temperature of pure carbon disulphide
 - B) Boiling temperature of azeotropic mixture is less than boiling temperature of pure acetone
 - C) When a small amount of carbon disulphide is added to excess of acetone boiling point of resulting mixture increases
 - D) A mixture of carbon disulphide and acetone can be completely separated by fractional distillation
24. Consider following solutions
- P: 1 M aqueous glucose
 Q: 1 M aqueous sodium chloride
 R: 1 M aqueous ammonium phosphate
 S: 1 M benzoic acid in benzene
- Choose the correct option(s)
- A) All are isotonic solutions
 - B) R is hypertonic to P, Q and S
 - C) S is hypotonic to P, Q and R
 - D) Q is hypotonic to R but hypertonic to P and S

Section V - Numerical type questions

25. The temperature of a city was found to be -9.3°C . A car was used, whose radiator was filled with 5L of water. What is the minimum quantity (in grams) of antifreezing agent (ethylene glycol) to be added to water of radiator in order to use the car for travelling? (K_f of water = $1.86 \text{ K kg mol}^{-1}$; molar mass of ethylene glycol = 62 g mol^{-1} ; density of water = 1 g mL^{-1})
26. A solution containing 81 g of ethylene glycol in 250 g of water is cooled to -10°C . If K_f for water is $1.86 \text{ K kg mol}^{-1}$, the amount of water separated as ice is g (molar mass of ethylene glycol = 62 g mol^{-1})
27. The plot given below shows P-T curves (where P is the pressure and T is the temperature) for two solvents X and Y and isomolal solution of NaCl in these solvents. NaCl completely dissociates in both the solvents



On addition of equal number of moles of a non-volatile solute S in equal amounts (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y. Solute S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent Y, the degree of dimerization in solvent X is $x \times 10^{-2}$, then value of x is

28. A soft drink was bottled with a partial pressure of CO_2 of 5 atm at 25°C . Before the bottle is opened, the concentration of CO_2 in the liquid is $x \times 10^{-1} \text{ mol L}^{-1}$ and after opening it is $y \times 10^{-5} \text{ mol L}^{-1}$. Find $x + y$. (Partial pressure of CO_2 in air is 0.0004 atm; $K_H = 3 \times 10^{-2} \text{ mol L}^{-1} \text{ atm}^{-1}$)
29. 0.1 M aqueous $\text{Pb}(\text{NO}_3)_2$ is titrated with 0.1 M aqueous KI at 300 K. The osmotic pressure of the final mixture at equivalence point will be atm. [Use $R = 0.08 \text{ L atm mol}^{-1} \text{ K}^{-1}$]

Section-VI - Matrix match type

30. Match the following

Column-I contains sets of two solutions A and B. Column-II contains properties of the system when solutions A and B of column-I are separated by a semipermeable membrane.

Column-I

I) 0.1 M glucose (A); 0.1 M urea (B)

II) 0.1 M NaCl (A); 0.1 M Na_2SO_4 (B)

III) 0.1 M NaCl (A); 0.1 M KCl (B)

IV) 0.1 M CuSO_4 (A); 0.1 M Sucrose (B)

A) I \rightarrow PQ; II \rightarrow S; III \rightarrow PQ; IV \rightarrow R

C) I \rightarrow PQ; II \rightarrow R; III \rightarrow PQ; IV \rightarrow S

Column-II

P) Isotonic solutions

Q) No net migration of solvent across the membrane

R) Solvent migrates from B to A

S) Solvent migrates from A to B

B) I \rightarrow R; II \rightarrow S; III \rightarrow PQ; IV \rightarrow S

D) I \rightarrow R; II \rightarrow S; III \rightarrow PQ; IV \rightarrow S