

Chapter-1

SOLUTIONS

Introduction

When several non reacting substances are mixed, then there are three possible types of mixtures :

- (a) Coarse mixture (Sand + Salt and Sugar + Salt)
- (b) Colloidal dispersion (Gum + water and fine clay + water)
- (c) True Solution (Salt + water)

In the coarse mixture there exists heterogeneity where as in true solutions there is complete homogeneity, In colloidal dispersions the heterogeneity is not readily apparent and it is not homogeneous.

Distinction between Solute and Solvent

I. Phase Method

Let there be a substance 'A' in solid phase and 'B' in liquid phase then if the phase of the resulting mixture is

- (a) Solid, then Solute = B and Solvent = A.
- (b) Liquid, then Solute = A and Solvent = B

II. Amount Method

According to this method, the substance which is in larger proportion by mass is solvent while the one in lesser proportion is solute.

e.g. a solid mixture of A and B. if $W_A > W_B$ then solute is B and solvent is A.

In the solutions of solids in liquids, where the liquid is usually present in large excess over the solid, there is no ambiguity, here liquid is solvent and solid is solute.

However when we deal with solubility of liquid

e.g. Acetone + water, here the one which is in larger quantity is solvent.

Saturated, Unsaturated And Super Saturated Solutions

Saturated Solution :

A solution, which contains as much solute as it can hold at a given temperature is said to be a saturated solution.

Unsaturated Solution :

A solution which contains less solute than the amount of solute it can hold then it is called unsaturated solution.

Super Saturated :

A solution which contains more solute than the amount it can hold at a particular temperature is called a super saturated solution.

Factors Influencing Solubility

The extent to which a substance will dissolve in another varies greatly with the substance, and depends on nature of solute, solvent, temperature, and pressure.

1. The effect of pressure on solubility is small unless gases are involved.
2. The effect of temperature however is very pronounced. The direction in which the solubility of a substance in a solvent, changes with temperature depends on **heat of solution**.
 - (a) If the **dissolution is exothermic** then the **solubility decreases with increase in temperature**.
 - (b) If the **dissolution is endothermic** then the **solubility increases with increase in temperature**.
3. In general, the compounds with similar character are more readily soluble in each other. While those with entirely different chemical characteristics will be very much insoluble.

Hence with these two extreme ends, a considerable number of intermediate stages are possible, which we call as mutual solubilities e.g.

- (i) When ethyl alcohol and water are mixed, the two dissolve in each other in all proportions and hence there is no saturation limit. Such substances are **completely miscible**.
- (ii) When water and mercury are mixed they do not dissolve in each other at all and hence are called **completely immiscible**.
- (iii) Between these two extreme pairs we have liquid pairs as ether + water, phenol + water which dissolve in each other to a limited extent only. Liquid pairs of these kinds are called **partially miscible**.

Types of Binary Solutions (Table-1)

S.No.	Solute	Solvent	Example of solution
1.	Solid	Solid	Alloy (Brass)
2.	Liquid	Solid	Hydrated salts butter
3.	Gas	Solid	H ₂ /Ni adsorption
4.	Solid	Liquid	Sugar in water
5.	Liquid	Liquid	Alcohol in water
6.	Gas	Liquid	Cold Drinks
7.	Solid	Gas	Dust, Smoke
8.	Liquid	Gas	Fog
9.	Gas	Gas	Air

The Vapour Pressure of Binary Ideal solution Containing Volatile liquids

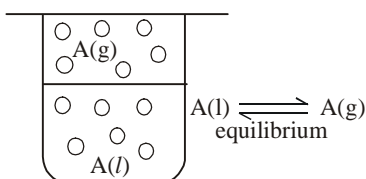
In a liquid, the molecules are always in the state of random motion, due to collision of molecules with each other and with walls of container. This leads to the molecules acquiring certain kinetic energy. The molecules of the liquid which possess high kinetic energy have a tendency to change to vapour state.

The minimum energy which the molecules of a liquid should acquire to transform from liquid state to vapour state is termed as escape energy. **Lesser the escape energy, greater is the volatility of a liquid** from liquid surface.

When a liquid is placed in a closed container then due to evaporation, vapours of liquid are produced which ultimately leads to an equilibrium state due to the tendency of the vapours to convert back to liquid.

Vapour Pressure

The pressure exerted by the vapours of the liquid which are in equilibrium with the liquid phase at the given temperature is called vapour pressure.



The vapour pressure of liquid depends upon

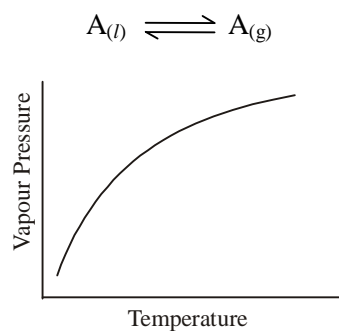
- (i) Nature of the liquid
- (ii) Temperature

Nature of Liquid

When the intermolecular forces of attractions are stronger then the vapour pressure will be low because less number of molecules can leave the liquid

Temperature

Higher the temperature, greater would be the vapour pressure. This is because when temperature is raised, kinetic energy of the molecules increase and therefore the number of molecules leaving surface of liquid, is large.

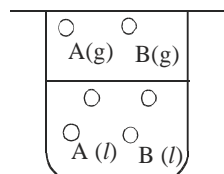


The Clausius Clapeyron equation gives the relationship for vapour pressure of liquid with temperature

i.e.
$$\log \frac{P_2}{P_1} = \frac{\Delta H}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right].$$

Vapour Pressure of Solution

Let two volatile liquids A and B dissolve in each other to form an ideal solution. Then the vapours above the solution will contain the vapours of A and B.



An ideal solution is one in which the activity of each constituent is equal to its mole fraction throughout complete range of concentration.

Hence applying Dalton's law of partial pressure the **vapour pressure** of the **solution** will be

$$\text{vapour pressure of solution} = P_{\text{solution}} = P_A + P_B$$

Where P_A and P_B are the partial vapour pressures of A and B.

Solution being dilute (Condition for ideality) *Raoult's law can be applied.*

Raoult's law for binary solutions state that "the vapour pressure of any volatile constituent of a binary solution at any given temperature is equal to the product of the vapour pressure of pure constituent and its mole fraction".

$$P_A = P_A^0 \chi_A$$

$$P_B = P_B^0 \chi_B$$

P_A^0 and P_B^0 are vapour pressure of pure A and B respectively

χ_A and χ_B are mole fraction of A and B respectively

Hence

$$P_s = P_A^0 \chi_A + P_B^0 \chi_B$$

Hence,

$$P_s = P_A^0(1 - \chi_B) + P_B^0 \chi_B \quad [\chi_A + \chi_B = 1]$$

$$P_s = P_A^0 + (P_B^0 - P_A^0)\chi_B$$

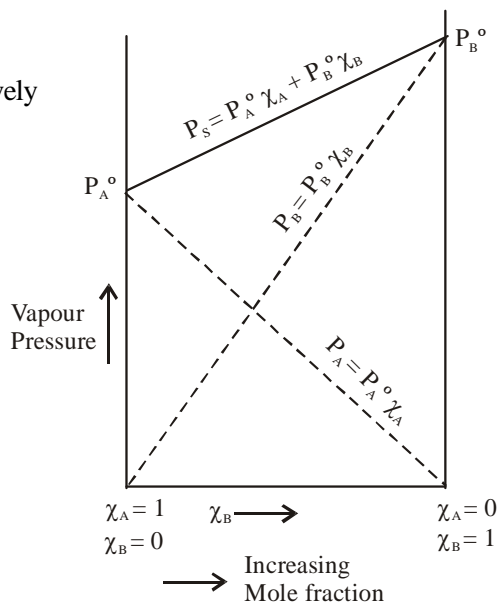
This equation is of the form $y = mx + c$

Where $y = P_s$, $c = P_A^0$, $x = \chi_B$, and $m = (P_B^0 - P_A^0)$

The value of m (slope) may be (+ve) or (-ve)

Depending upon whether $P_B^0 > P_A^0$ ($m = +ve$) or $P_B^0 < P_A^0$ ($m = -ve$)

Hence a plot of a graph of P_s vs χ_B will be a straight line with an intercept on y-axis.



Note: Formation of a true ideal solution is rare and largely exceptional. However a large number of solution are obtained which are found to be nearly ideal.

Ideal Solution

A few binary miscible liquid systems which obey *Raoult's law* throughout the complete range of concentration, are:

- (1) Ethylene dibromide and Propylene dibromide
- (2) Chlorobenzene and Bromobenzene
- (3) Benzene and Ethylene dichloride
- (4) $\text{CCl}_4 + \text{SnCl}_4$
- (5) $\text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH}$
- (6) n-Hexane + n-Heptane
- (7) Benzene + Toluene

Such systems are called nearly ideal or ideal solutions.

Such solutions obey Raoult's law and comply to the equation $P_s = P_A^0 \cdot \chi_A + P_B^0 \cdot \chi_B$.

To comply to this condition for ideality the two liquids A and B should fulfill the under mentioned conditions

1. The attractive forces between the particles A and B (*i.e.* A–B interactions) should be equal to the attractive forces between A and A (*i.e.* A–A interaction) and between B and B (*i.e.* B–B interaction)
2. Such an interaction can be equal if the structure and polarity are almost same. *e.g.* CH₃–OH and C₂H₅–O–H.

In such solutions

- (i) $\Delta V_{\text{mix}} = 0$ (ii) $\Delta S_{\text{mix}} > 0$ (iii) $\Delta H_{\text{mix}} = 0$.

Binary Non Ideal Solutions

There are certain liquid pair systems which deviate from the Raoult's law to a greater or lesser extent depending upon the nature of the liquids and the temperature.

Set-A

- (i) Ether + Acetone
- (ii) CCl₄ + CH₃OH
- (iii) C₆H₆ + acetone
- (iv) H₂O + C₂H₅OH
- (v) *n*-Hexane + Ethyl alcohols

Set-B

- (i) CH₃ OH + CH₃COOH
- (ii) H₂O + HNO₃
- (iii) H₂O + HCl
- (iv) H₂O + H₂SO₄
- (v) CHCl₃ + CH₃COOCH₃

Set A exhibits positive deviation while set B exemplify negative deviation.

Positive Deviation Solution

Here the **A Sets** of solution show a relationship where the vapour pressure of the solution observed is greater than the vapour pressure of solution under ideal conditions

i.e. $P_s(\text{obs}) > P_s(\text{ideal})$

or

$$P_s > P_i \quad \text{where } P_i = P_A^0 \chi_A + P_B^0 \chi_B$$

i.e. $P_s > P_A^0 \chi_A + P_B^0 \chi_B$

Such solutions are said to have a +ve deviation from ideality.

The graph obtained resembles as given below

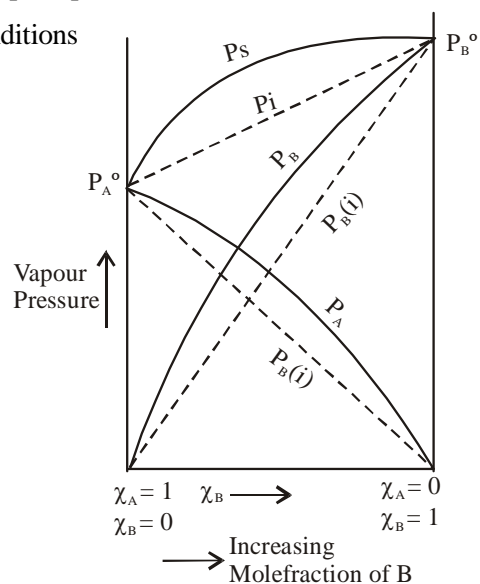
The reasons for such a +ve deviation could be linked to the fact that after mixing the interactions between the liquid A and B is less than the interaction between A–A particle and B–B particles

This leads to a less escape energy for the molecules of A and B liquids in the solution.

This also some times leads to an increase in volume of solution after mixing

$$\Delta V_{\text{mix}} > 0. \quad \Delta V_{\text{mix}} = V_{\text{obs}} - V_{\text{actual}}$$

$$\Delta S_{\text{mix}} > 0$$



Negative Deviation

The B set of solutions show a relationship where the vapour pressure of solution observed is lesser than the vapour pressure of the solution under ideal conditions i.e.

$$P_{s(\text{obs})} < P_{\text{solution (ideal)}}$$

$$P_s < P_i.$$

$$\Rightarrow P_s < P_A^0 \chi_A + P_B^0 \chi_B$$

Here this equation is due to the fact that when interactions increase the escape kinetic energy required, increases, leading to a lowering of vapour pressures such that $P_A < P_A^0 \chi_A$ and $P_B < P_B^0 \chi_B$

Hence the sum

$$P_A + P_B < P_A^0 \chi_A + P_B^0 \chi_B$$

$$\Rightarrow P_s < P_i$$

When the interactions between liquid A particles and liquid B particles increases

A–B interaction > A–A interaction and B–B interactions.

$$\Delta H_{\text{mix}} < 0 \Rightarrow \Delta H_{\text{mix}} = -\text{ve. and also}$$

$$\Delta V_{\text{mix}} < 0 \Rightarrow \Delta V_{\text{mix}} = -\text{ve}$$

$$\Delta S_{\text{mix}} > 0.$$

The graph corresponds to the one given.

Vapour Phase Composition

To obtain the relationship between the composition of solutions and the composition of the vapour above it.

Let γ_A and γ_B be the mole fraction of components A and B in the vapour phase above the liquid solution consisting of χ_A and χ_B mole fractions of A and B respectively.

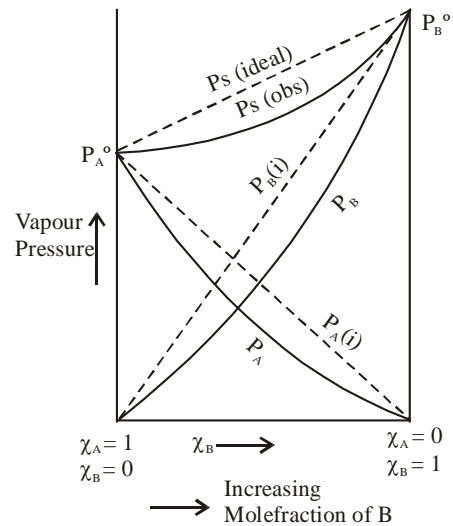
Then according to gas law

$$\frac{P_B}{P_{(s)}} = \gamma_B \quad \text{and} \quad \frac{P_A}{P_{(s)}} = \gamma_A \quad \left[\frac{P_A}{P_{(s)}} = \frac{n'_A}{n'_A + n'_B} = \gamma_A \right]$$

$$\Rightarrow \frac{P_B^0 \chi_B}{P_{(s)}} = \gamma_B = \frac{P_B^0 \chi_B}{P_A^0 \chi_A + P_B^0 \chi_B} = \text{Vapour phase composition of B}$$

$$\text{and} \quad \frac{P_A^0 \chi_A}{P_{(s)}} = \gamma_A = \frac{P_A^0 \chi_A}{P_A^0 \chi_A + P_B^0 \chi_B} = \text{Vapour phase composition of A.}$$

Generally the distillate composition is the vapour phase composition



Azeotropic Mixtures

The study of the vapour pressure curves of completely miscible liquid mixture is of great help in

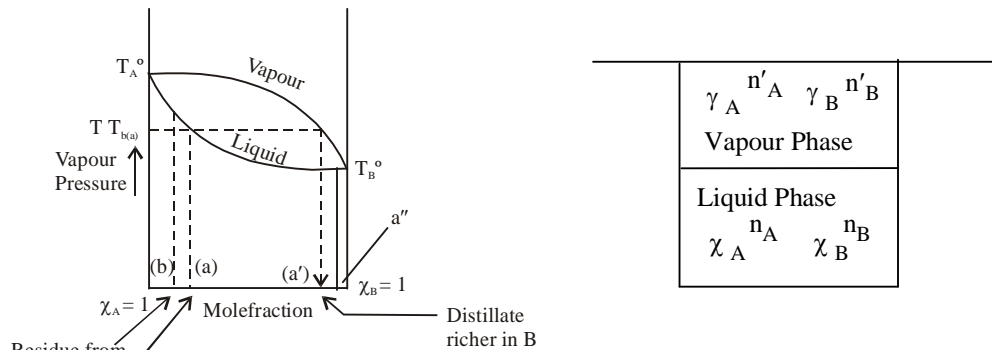
separating the constituents of the liquid mixtures by distillation.

Azeotropic mixture are those completely miscible liquid mixtures which distil over unchanged in composition and boil at constant temperature.

The separation by fractional distillation is possible only when the vapour phase has a composition different from that of the boiling mixture. Thus azeotropes can not be separated by fractional distillation.

When a plot of the boiling point temperature versus composition of solution is done then we get.

I For Ideal Solution



Graph for boiling point vs composition for ideal solution

Point 1: Mixture composition (a) taken richer in a component (A)

Point 2: Mixture composition (a) boils at $T_{b(a)}$ temperature

Point 3: Distillate (a') of (a) is the mixture composition richer in component B.

Point 4: 'b' is residue during distillation of mixture composition 'a'.

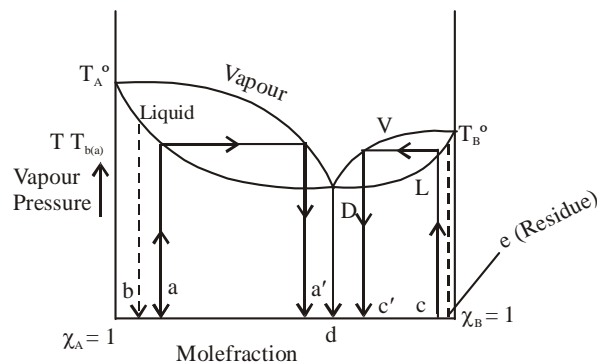
Hence such solution can be successfully separated into pure A and pure B

Successive distillation of 'a' give 'a'' and then finally pure B. as distillate.

II For non Ideal Solutions

A) +Deviation solution or (-ve boiling azeotropes)

When temperature versus composition graphs are drawn for +ve deviation solution we get



(Graph for boiling point vs composition for non-ideal solution showing +ve deviation)

Point 1: Here when mixture composition 'a' is boiled, then the distillate (a') becomes more rich in 'B' but, successive distillation of a' will finally lead to compositions ('d') where vapour phase and liquid phase compositions are same. Hence d(D) is a solution which cannot be separated into pure A and B. Hence it is a -ve boiling azeotropic mixture. But the residue 'b' becomes richer in 'A'.

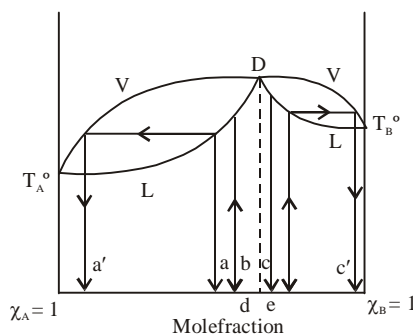
Point 2: When mixture composition 'c' is boiled then distillate is (c') richer in 'A' but successive distillation makes it to composition d(D) i.e. -ve boiling azeotropic mixture.

The distillate is 'e' richer in (B) component

Table for Minimum Boiling Azeotropic Mixtures					
Component A	B.pt	Component B	B.P.	B. pt of Azeotropic mixture	% of B
H ₂ O	100°C	CHCl ₃	61.2°C	56.12	97%
H ₂ O	100°C	C ₂ H ₅ OH	78.3°	78.13	96%
H ₂ O	100°C	C ₆ H ₆	80.2°C	69.25	91%
H ₂ O	100°C	C ₃ H ₇ OH	97.2°C	87.7	97%
Chloroform	61.2°C	CH ₃ OH	64.7°C	53.43	13.6%

B)-ve Deviation solutions (+ve Boiling azeotropic)

When temperature versus composition are drawn for the solutions showing -ve deviation the graph obtained is



(Graph of Boiling point V_s composition for non-ideal solutions -ve deviation)

Point 1: When mixture composition 'a' is taken, then on boiling.

- (i) Distillate a' is obtained which is richer in component A
- (ii) Residue is 'b'

Successive distillation of 'b' leads to azeotropic solution D. (+ve boiling azeotropic mixture)

- (iii) Successive distillation of a' will lead to pure (A)

Point 2: When mixture composition c is taken and boiled.

- (i) Distillate is c' which is richer in component B and successive distillation of distillates lead to solution becoming pure 'B'
- (ii) The residue of 'c' is 'e' successive distillation of 'e' makes the residue richer in 'D' which is +ve boiling azeotropic mixtures.

Table for Maximum Boiling Azeotropic Mixture

A	B.pt of A in °C	B	B.pt B in °C	B. pt of Azeotropic mix	% of B
HCl	-20°	H ₂ O	100	108.5	79.96
HNO ₃	86°	H ₂ O	100	120.5	32
CHCl ₃	61.2	Acetone	56.5	64.7°C	20
CHCl ₃	61.2	CH ₃ COOC ₂ H ₅	57	64.8	23

Ratio of Distillate to Residue Compositions

The relative proportions of the two liquids in the distillate can be calculated on the basis that the number of moles of each component present in the vapour phase is proportional to its vapour pressure.

If n'_A and n'_B are the number of moles of the components A and B in the vapour phase, then

$$n'_A/n'_B = p_A^\circ / p_B^\circ \quad (1)$$

If w_A and w_B represent the actual masses of the two components in the distillate and M_A and M_B their respective molecular masses, then Eq. (1) may be written as

$$\frac{w_A}{w_B} = \frac{n_A M_A}{n_B M_B} = \frac{p_A^\circ M_A}{p_B^\circ M_B} \Rightarrow \boxed{\frac{w_A}{w_B} = \frac{p_A^\circ M_A}{p_B^\circ M_B}}$$

Thus the masses of the liquids in the distillate will be in the ratio of their vapour pressures and molar masses.

Solubility of Gases In Liquids

Gases dissolve in liquids to form true solutions, the degree of solubility depends on the nature of the gas, the nature of the solvent, the pressure and the temperature. Gases like nitrogen, hydrogen and helium dissolve to a slight extent, while gases like hydrogen chloride and ammonia are very soluble. The large solubility of HCl and ammonia is accounted by the chemical reaction of these gases with the solvent to form hydrochloric acid, and ammonium hydroxide respectively.

Under the same pressure and temperature

- (a) N₂, CO₂ are more soluble in CH₃OH than in H₂O.
- (b) H₂S and NH₃, are more soluble in H₂O than in C₂H₅OH.

From this it is quite clear that chemical similarity between solute and solvent leads to higher solubility. **e.g.** Hydrocarbons vapours (non polar) are more soluble in other hydrocarbons (non polar) and other organic solvents than they do in water. HCl vapours (polar) more soluble in H₂O (polar) than in CS₂ (non polar)

Factors Influencing Solubility of Gases in Liquids

The solubility depends upon

- (i) Nature of solute or solvent
- (ii) Temperature
- (iii) Pressure (In case of gases)

1. Nature of Gas and Nature of Solvent

The solubility of gas in a given solvent varies considerably with nature of the gas. Generally speaking, the gases which are easily liquified, are more soluble in common solvents.

Thus CO₂ is more soluble than H₂ and O₂ in water or in any other solvent.

The gases which are capable of forming ions in aqueous solutions, are much more soluble in water than in other solvents, e.g. Hydrogen chloride is highly soluble in water but not in benzene, because HCl dissociates into H⁺ +Cl⁻ in water: Similarly NH₃ is highly soluble in H₂O than in benzene

The solubility of gases is generally expressed in terms of absorption coefficient (a). This is defined as the volume of the gas reduced to STP dissolved by a unit volume of a solvent at the temperature of the experiment and under a pressure of one atmosphere of the gas.

The absorption coefficient of few gases at 20°C in different solvents.

	H ₂	N ₂	O ₂	CO ₂
<i>Solvent</i>				
H ₂ O	0.017	0.015	0.028	0.88
C ₂ H ₅ OH	0.080	0.130	0.130	3.00
C ₆ H ₆	0.066	0.104	0.105	--

2. Effects of Temperature

It has been found that under constant pressure the solubility of a gas diminishes with rise in temperature. The absorption coefficient of a few gases at different temperatures are

Temperature	CO ₂	O ₂	N ₂
0	1.713	0.0484	0.0239
10	1.194	0.0380	0.0196
20	0.878	0.0380	0.0196
30	0.665	0.0260	0.0138
40	0.530	0.0231	0.0118

3. Effects of Pressure on solubility of gases in liquids

The effect of pressure on the solubility of a given gas in a particular liquid at constant temperature can be obtained by carefully observing the process in reverse direction viz. the gas as a solute which vapourizes to establish a vapour pressure above the solution.

Henry's Law :

It states that at constant temperature the solubility of a gas in a liquid is directly proportional to the pressure of the gas above it.

When several gases are dissolved simultaneously in a solvent, the solubility of each gas from a mixture of gases is directly proportional to the partial pressure of the gas mixture. The proportionality constant will however be different for each gas.

The strict applicability of Henry's law is limited to the lower pressure and at high pressures the law becomes less exact.

Generally, higher the temperature and lower the pressure, the more closely is the law obeyed.

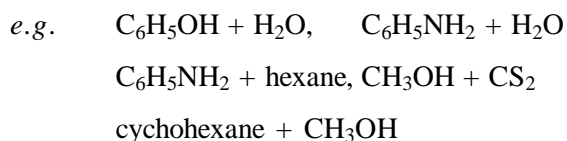
This law is not valid when the gas reacts with the solvent, or when the dissolved gas ionizes.

Solubility of Partially Miscible Liquids

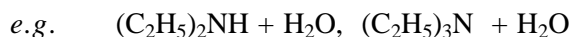
These are pairs of liquids which dissolve in each other to a limited extent only.

There are four types of such partially miscible liquid-liquid systems.

Case-1: Those in which partial miscibility increases with increase in temperature



Case-2: Those in which partial miscibility decreases with increase in temperature



Case-3 : Those in which partial miscibility increase both on increasing the temperature as well as decreasing the temperature, in certain ranges



Case-4: Those in which complete miscibility cannot be attained.



Nernst Distribution Law

H_3BO_3 is soluble in both water and amyl alcohol. But when a solution of H_3BO_3 in amylalcohol is shaken with water, it is found that H_3BO_3 distributes itself in such a way that the ratio of the concentration of H_3BO_3 in water and alcohol is a constant at a particular temperature.

Similarly iodine is soluble in H_2O and CCl_4 and the distribution of iodine in H_2O and CCl_4 remains constant at a particular temperature.

This is also one of the direct consequences of thermodynamic requirement for equilibrium.

Let a substance 'X' be miscible in two immiscible pairs of solvents A and B. Then

$$\frac{a_A}{a_B} = \text{Constant} = K$$

This equation $\frac{a_A}{a_B} = \text{Constant} = K$ is a mathematical representation of Nernst distribution law.

It states that a substance will distribute itself between two solvents until at equilibrium the ratio of the activities of the substances in two layers is a constant at any given temperature.

Assuming the solution to be dilute or when solute behaves ideally the activity becomes equal to concentration C and hence we have

$$K = \frac{C_B}{C_A}$$

where K = distribution or partition coefficient of solute between two solvents.

K depends upon

- (i) Nature of solute
- (ii) Nature of liquids involved.
- (iii) The temperature at which the liquids are maintained.
- (iv) The magnitude depends upon the manner in which the constant is represented C_A/C_B or C_B/C_A .

Colligative Properties of Solution

Solutions of Non Volatile Solute and Volatile Solvent

Colligative Properties

The properties which depend entirely upon the *number of particles of solute* in a given volume of solvent and not on the chemical nature of the solute molecule are defined as Colligative properties.

Here we shall consider four properties of solution containing non volatile solutes.

- (i) Lowering in vapour pressure.
- (ii) Elevation in boiling point
- (iii) Depression in freezing point
- (iv) Osmotic pressure

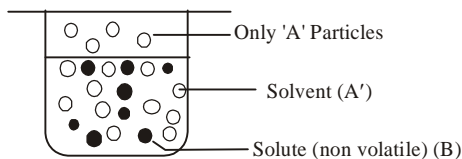
It is convenient to subdivide the solutions in the

- A. Solutions of non electrolytes
- B. Solutions of electrolytes
- A. Solutions of Non Electrolyte

Lowering in Vapour pressure

When a non volatile solute is present in the solution, the vapour pressure of the solution will be less than vapour pressure of pure solvent.

Let there be a solution of solute B. in solvent A



Since 'B' is non volatile it won't go to the vapour phase hence the vapours above solution will be only due to volatile solvent 'A'. Since

$$P_A \propto P_A^0 \chi_A$$

$\Rightarrow P_A < P_A^0$ so vapour pressure is lowered.

For a binary system $\chi_A + \chi_B = 1$.

Substituting the value of χ_A

$$\Rightarrow P_A = P_A^0 (1 - \chi_B)$$

$$P_A = P_A^0 - P_A^0 \chi_B$$

$\Rightarrow P_A^0 \chi_B = P_A^0 - P = \Delta P$ (Lowering in vapour pressure)

$$\Delta P = P_A^0 \chi_B$$

$\Rightarrow \Delta P \propto \chi_B$

⇒ Lowering in vapour pressure is directly proportional to the mole fraction of solute
 The relative lowering in vapour pressure is equal to the mole fraction of solute.

$$\frac{\Delta P}{P_A^0} = \chi_B$$

Hence

- (a) Lowering in vapour pressure is directly proportional to the mole fraction of solute in the solution.
 (b) Relative lowering in vapour pressure is equal to the mole fraction of solute.

1. Calculation of molecular mass of solute (B) in solvent (A)

$$\Delta P = P_A^0 \chi_B = P_A^0 \frac{n_B}{n_A + n_B}$$

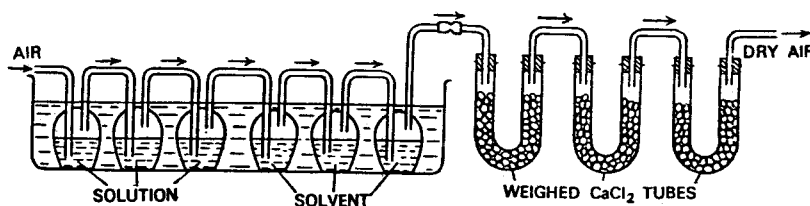
$$= P_A^0 \left[\frac{W_B / M_B}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} \right]$$

But when the solution is dilute then $\frac{W_B}{M_B} \ll \frac{W_A}{M_A}$ and hence $\frac{W_B}{M_B}$ can be neglected in the denominator

$$\Rightarrow \Delta P = P_A^0 \times \frac{W_B \times M_A}{W_A \times M_B}$$

or
$$M_B = \left[\frac{P^0}{\Delta P} \right] \times \left[\frac{W_B \times M_A}{W_A} \right]$$

2. The relative lowering in vapour pressure is determined by *Ostwald And Walker* Method. In this method a stream of dry air is passed successively through a set of weighed bulbs containing the solution and then through a set of merged bulbs containing pure solvent and finally through weighed U-shaped tubes containing anhydrous CaCl_2 .



- (a) Let the loss in weight of solution bulbs be = w_1 gm.
 (b) Loss in weight of solvent bulbs = w_2 gm
 (c) Loss in weight of solution bulbs (w_1) \propto vapour pressure of solution.
 (d) Loss in weight of solvent bulbs (w_2) \propto vapour pressure of solvent – vapour pressure of solution.

$$\Rightarrow P_s \propto w_1 \text{ and } (P^0 - P_s) \propto w_2$$

$$\Rightarrow \frac{P^0 - P_s}{P^0} = \frac{w_2}{w_1 + w_2} = \frac{\text{Loss in weight of solvent bulbs}}{\text{Total loss in weight of solution bulbs and solvent bulbs}} = X_B \text{ i.e. mole}$$

fraction of solute

Elevation in Boiling Point

When a liquid is heated then due to rise in temperature the liquid vapourises and the vapour pressure increases. When the vapour pressure of the liquid becomes equal to the atmospheric pressure, the liquid begins to boil. The temperature at which the equilibrium vapour pressure of the liquid becomes equal to the atmospheric pressure is called boiling point.

When a non volatile solute is added to the solvent the vapour pressure of the solvent in the solution decreases. Consequently the solution has to be heated to a higher temperature to have its vapour pressure equal to atmospheric pressure.

Relationship for elevation in Boiling points

Consider the graph of vapour pressure versus temperature in Kelvin scale.

Here Triangle ADB and ACE are similar

Hence

$$\frac{AD}{AE} = \frac{AB}{AC}$$

$$\frac{T_1 - T^0}{T_2 - T^0} = \frac{P^0 - P_1}{P^0 - P_2}$$

$$\Rightarrow T_1 - T^0 \propto P^0 - P_1$$

$$\Rightarrow \Delta T_B \propto \Delta P$$

Also

$$\Delta P \propto \chi_B$$

$$\Rightarrow \Delta T_B \propto \chi_B$$

$$\Delta T_B \propto \frac{n_B}{n_A + n_B}$$

$$\Delta T_B \propto \frac{n_B}{n_A} \text{ [Dilute solutions]}$$

$$\Delta T_B \propto \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

$$\Rightarrow \boxed{\Delta T_B = K_b \frac{W_B}{M_B \times W_A}}$$

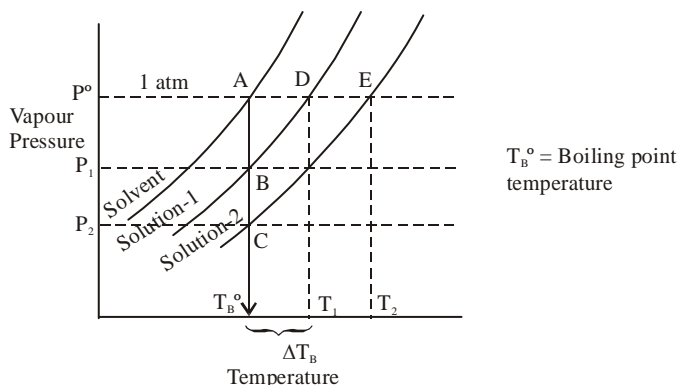
When $\frac{W_B}{M_B} = 1$ mole and $W_A =$ mass of solvent in kilogram (kg)

$$\Rightarrow \boxed{\Delta T_B = K_b \times m} \quad m = \text{molality of solution} \quad K_b = \text{Ebullioscopic constant}$$

$$\boxed{\Delta T_B \propto K_b} \text{ [when concentration is kept constant]. Hence elevation in boiling point depends upon}$$

K_b i.e., nature of solvent

$$\boxed{\Delta T_B \propto m} \text{ [When solvent taken is same]}$$



K_b is defined as the elevation in boiling point of a solvent when 1-gm mole of a non-volatile solute is dissolved in 1000 gm of solvent.

$$K_b = \frac{RT_b^2}{1000 l_v} \quad l_v = \text{latent heat of vapourization per gram of the solvent}$$

$$\text{Also } K_b = \frac{RT_b^2 \times M_0}{1000 \times \Delta H_v} \quad \text{where } M_0 = \text{molecular weight of solvent.}$$

$$\Delta T_B = \frac{K_b W_{\text{solute}}}{M_{\text{solute}} \times W_{\text{solvent}}} \times 1000$$

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

$W_B = W_{\text{solute}} = \text{Mass of solute taken}$

$M_B = M_{\text{solute}} = \text{Molecular weight of solute}$

$W_A = W_{\text{solvent}} = \text{Mass of solvent taken in grams}$

$$\Rightarrow M_{\text{solute}} = \frac{K_b W_B}{\Delta T_B \times W_A} \times 1000$$

$$\text{Also } \frac{T_{B(1)}}{\Delta T_{B(2)}} = \frac{K_{B(1)}}{K_{B(2)}} \quad \text{when concentration is same but solvent different}$$

$$\frac{\Delta T_{B(1)}}{\Delta T_{B(2)}} = \frac{m_1}{m_2} \quad \text{when solvent is same but concentration different}$$

$$\frac{\Delta T_{B(1)}}{\Delta T_{B(2)}} = \frac{M_{O(2)}}{M_{O(1)}} \Rightarrow \Delta T_B \propto \frac{1}{M_{O(1)}} \quad \text{when solvent same and amount of solute is same}$$

Depression in Freezing Point

When a solvent is cooled, a temperature is eventually reached at which solid begins to separate from the solution. The temperature at which this separation begins is called freezing point of solvent.

At freezing point liquid and solid are in equilibrium.



At the freezing point, the vapour pressure of liquid and solid will be same.

Addition of a non-volatile solute, decreases the vapour pressure of pure liquid. Therefore for a solid to have the same vapour pressure as the solution, the temperature would lower down. This phenomenon is called depression in freezing point.

Relationship for Depression in Freezing Point.

Here again.

$$\begin{aligned} \Delta T_f &\propto \Delta p & \Delta T_f &\propto \Delta P \\ \Delta p &\propto \text{molality} & \text{or } \Delta P &\propto X_B \\ \Delta T_f &\propto \text{molality} & \Delta T_f &\propto X_B \end{aligned}$$

$$\Rightarrow \Delta T_f \propto \frac{n_B}{n_A} \quad \text{for dilute solutions}$$

$$\Rightarrow \Delta T_f = K_f \frac{W_B}{M_B W_A} \quad \text{when } W_A \text{ is in kilogram}$$

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

$K_f = \text{molal depression constant}$

K_f is defined as the depression in freezing point of a solvent when 1-gm mole of a non-volatile solute is dissolved in 1000 gm of solvent. *i.e.*

$$\boxed{K_f = \frac{RT_f^2}{1000l_f}} \quad \text{also} \quad \boxed{K_f = \frac{RT_f^2 M_0}{1000\Delta H_f}}$$

where T_f = freezing point
 T_f = latent heat of fusion per gram

Also

$$\boxed{\Delta T_f = \frac{RT_f \times w \text{ solute}}{M \text{ solute} \times W \text{ solvent}} \times 1000}$$

Hence molecular weight of solute

$$\boxed{M_{\text{solvent}} = \frac{K_f \times W \text{ solute}}{\Delta T_f \times W \text{ solvent}} \times 1000}$$

Since $\Delta T_f = K_f m \Rightarrow \Delta T_f \propto K_f$ [When concentration is same but different solvents are taken]

$\Delta T_f \propto m$ [when solvent is same but different concentration are taken]

Osmotic Pressure

Osmosis

- The phenomenon of osmosis, first observed by Abbe Nollet, may be defined as a process in which pure solvent molecules pass through a semipermeable membrane from a solution of low concentration to a solution of higher concentration.
 - Exosmosis* is the outward flow of water from a cell containing an aqueous solution through a semipermeable membrane, e.g. grape in NaCl solution.
 - Endosmosis* is the inward flow of water into a cell containing an aqueous solution through a semipermeable membrane, e.g. grape in water.
- The most frequently used semipermeable membrane in laboratory is that of copper ferrocyanide, $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ because it is very strong and can withstand very high pressure. Remember that semipermeable membrane of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ does not work in non-aqueous solution because it gets dissolved in non-aqueous solvents. Other synthetic semipermeable membrane is that of calcium phosphate. Natural semipermeable membranes are parchment paper, cell walls, pig's bladder, skin surrounding white of an egg, membrane surrounding RBCs etc.

When a solution (say of sugar) is separated from the pure solvent (water in present case) by means of a semipermeable membrane (a membrane which allows only the solvent molecules but not the solute molecules to pass through it), the pure solvent passes through the membrane and goes to solution (osmosis) till the hydrostatic pressure of the liquid column exactly balances the tendency of water to pass inward through the semipermeable membrane. The hydrostatic pressure set up as a result of osmosis is a measure of the osmotic pressure of the solution. For instance, if the solution of density d rises to height h , then osmotic pressure is expressed as

$$\pi = h \times d \times g, \text{ where } g \text{ is the acceleration due to gravity.}$$

The osmotic pressure may be defined as the excess pressure which must be applied to a solution in order to prevent flow of solvent into the solution through the semipermeable membrane.

Osmotic pressure may also be defined in several other ways.

- (i) Osmotic pressure is the excess pressure which must be applied to a given solution in order to increase its vapour pressure until it becomes equal to that of the solution.
- (ii) Osmotic pressure is the negative pressure produced when a solution is separated from the solvent by a semipermeable membrane.
- (iii) Osmotic pressure is the hydrostatic pressure produced when a solution is separated from the solvent by a semipermeable membrane.

Laws of Osmotic Pressure

The different laws of osmotic pressure are

1. Boyle-Vant Hoff law
2. Charles-Vant Hoff law
3. Avogadro-Vant Hoff law
4. Vant Hoff theory of osmotic pressure

Vant Hoff Theory of Dilute solution :

Vant Hoff gave an idea that dilute solution behave like ideal gases and gas laws obeyed by ideal gas are also obeyed by dilute solution .

We know that

$$V \propto \frac{1}{\pi} \quad (\text{Boyle - van't Hoff Law})$$

$$V \propto T \quad (\text{Charles Van't Hoff law})$$

$$V \propto n \quad (\text{Avogadro - Van't Hoff law})$$

$$\Rightarrow V \propto \frac{n \times T}{\pi}$$

$$\Rightarrow V = \frac{nRT}{\pi} \quad R = \text{solution constant } (0.0821 \text{ l atm K}^{-1} \text{ mol}^{-1})$$

$$\Rightarrow \pi = \frac{n}{V} RT$$

$$\pi = CRT$$

Hence at a given temperature

$$\pi \propto C$$

Important relations concerning osmotic pressure, P or π

$$(i) \pi V = n RT \text{ or } \pi V = n ST \text{ or } \pi = \frac{n}{V} ST \text{ or } \pi = CST$$

where π = Osmotic pressure in atmospheres

n = Number of moles of the solute present in V litres of the solution

C = Concentration of the solution in moles per litre

T = Temperature in K

R or S = $0.0821 \text{ l atm deg}^{-1} \text{ mole}^{-1}$

$$(ii) \pi V = \frac{w}{M_0} ST \left(\because n = \frac{w}{M_0} \right)$$

$$M_0 = \frac{wST}{\pi V} \quad (M_0 = \text{Molecular weight of solute})$$

where w = Wt. of solute in g dissolved in V l of solution

m = Molecular wt. of the solute

$$(iii) \pi = h d g$$

where h = Height, d = density, g = Gravitational acceleration.

(iv) In isotonic solutions, since osmotic pressure, p is equal, their concentration (C) must also be equal, *i.e.*

$$\frac{n_1}{V_1} = \frac{n_2}{V_2}, \quad \frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

(v) If a number of solutes are present in the solutions and π_1, π_2, π_3 etc. are their individual osmotic pressures, then

$$\text{Total osmotic pressure} = \pi_1 + \pi_2 + \pi_3 + \dots$$

Reverse osmosis

If a pressure higher than osmotic pressure is applied on the solution, the solvent will flow from the solution into the pure solvent through the semipermeable membrane. Since here the flow of solvent is in the reverse direction to that observed in the usual osmosis, the process is called reverse osmosis. It is used in the desalination of sea water to obtain pure water.

Isotonic Solutions

A pair of solutions having the same osmotic pressure are known as isosmotic or isotonic solutions. Isotonic solutions have the same concentration. 0.85% NaCl solution is found to be isotonic with blood, while 0.9% NaCl solution is isotonic with human RBCs. A solution having lower or higher osmotic pressure than the other is to be hypotonic or hypertonic respectively in respect to other solution.

(i) When placed in water or hypotonic solutions, cell swell and burst (haemolysis).

(ii) When placed in hypertonic solutions, the fluid from the plant cells comes out and thus the cells contract in size (plasmolysis). When excess of fertilizers (like urea) are applied, plasmolysis takes place and plants dry up (wilt).

Osmolarity

Osmolarity is the term used by physiologists to discuss the osmotic behaviour of solutes which either dissociate or associate in solution. Mathematically,

$$\text{Osmolarity} = \text{Molarity} \times \text{No. of particles produced per formula unit of the solute}$$

B. Solution of Electrolytes

Abnormal Behaviour of Solutions

Since the colligative properties of solutions, viz. lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure, depend solely on the number of solute particles present in solution and not on their nature, colligative properties of the solutes which undergo dissociation (electrolytes) in solution would be higher than expected for the normal substances (non-electrolytes). For example, one mole of a solute like glucose, cane sugar, urea, etc. when dissolved in 1000 g of water depresses the freezing point of water by 1.86°C. However, solution of one mole of NaCl or BaCl₂ in 1000 g of water depress the freezing point of water by 3.72°C (2 × 1.86) and 5.58°C (3 × 1.86) respectively because each molecule of NaCl and BaCl₂ dissociates to give 2 (Na⁺ & Cl⁻) and three (Ba²⁺ and 2Cl⁻) ions respectively and each ion behaves as a particle in itself. Thus, among the 0.1 M solution of the various substances like cane sugar, NaCl, BaCl₂, Al₂(SO₄)₃, etc. the colligative effect will be maximum in Al₂(SO₄)₃ solution giving 5 ions per molecule.

Similarly, there are certain substances which associate when dissolved in a particular solvent. Hence the molecular weight of such substances as determined with the help of colligative properties will be more than the theoretically calculated value from the molecular formula. For example, the observed molecular weight of acetic acid when dissolved in benzene is found to be 118 which is nearly double the value (60) calculated from its molecular formula, CH₃COOH. This is due to the fact that acetic acid, in benzene, does not exist as CH₃COOH but as a dimer, i.e. (CH₃COOH)₂.

Vant'f Hoff Factor, *i*.

To account for the above anomalies, Van't Hoff introduced a factor '*i*' in the Van't Hoff equation ($\pi V = RT$) of osmotic pressure. The modified equation may thus be written as $\pi V = iRT$

The factor '*i*' was defined by the expression

$$i = \frac{\text{Observed osmotic pressure}}{\text{Normal osmotic pressure}}$$

The experimental value of *i* can be obtained by dividing the observed osmotic pressure of the solution under study with that of the solution of a normal substance (say sucrose) of the same concentration (molarity) as that of the substance under study.

Now since osmotic pressure behaves like other colligative properties, the factor *i* can also be applied to other colligative properties. Thus in general,

$$i = \frac{\text{Actual number of particles}}{\text{No. of particles when no ionisation/association}}$$
$$i = \frac{\text{Observed colligative property (experimental)}}{\text{Normal colligative property (calculated)}}$$

Now since molecular weight of a solute is inversely proportional to the colligative property, the factor i may also be defined in the following way

$$i = \frac{\text{Normal molecular wt. (calculated value)}}{\text{Observed molecular wt. (experimental value)}}$$

Evidently for a normal substance (which neither dissociates nor associates in solution), the factor i is always unity.

When the Van't Hoff factor is included then the colligative properties get modified as follows

(a) Relative Lowering in Vapour Pressure

$$\frac{P^0 - P_S}{P^0} = i \times X_B$$

Where i = van't Hoff factor

X_B = mole fraction of solute for dilute solution

$$\frac{P^0 - P_S}{P^0} = i \times \frac{n_B}{n_A}$$

n_B = number of moles of solute

n_A = number of mole of solvent

$$\Rightarrow \frac{P^0 - P_S}{P^0} = i \times \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

Where W_B = Amount of solute dissolved

W_A = Amount of solvent taken

M_B = Molecular mass of solute

M_A = Molecular mass of solvent

(b) Elevation in Boiling point

$$\Delta T_B = iK_b m$$

$$\Delta T_B = iK_b \times \frac{W_B}{M_B \times W_A (\text{gms})} \times 1000$$

(c) Depression in Freezing Point

$$\Delta T_f = iK_f m.$$

$$\Delta T_f = iK_f \times \frac{W_B}{M_B \times W_A (\text{gms})} \times 1000$$

(d) Osmotic Pressure

$$\pi v = inRT$$

$$\pi = iCRT$$

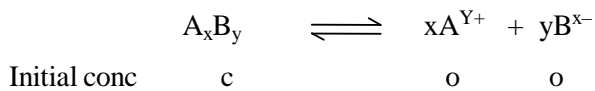
Relationship between Van't Hoff factor for Dissociation and association

1. Dissociation

Degree of dissociations : It is defined as the number of moles dissociated over the initial concentration taken.

$$\text{Van't Hoff Factor} : \frac{\text{Total number of particles at equilibrium}}{\text{Initial concentration}}$$

Let c moles per litre of an electrolyte A_xB_y be taken and let it dissociate as



∴ $yC\alpha$ moles of B_c^{x-} is formed

$$\begin{array}{ccccccc} & & c & & 0 & & 0 \\ \Rightarrow & A_x B_y & \rightleftharpoons & xA^{Y+} & + & yB^{x-} & \\ & (C - C\alpha) & & xC\alpha & & yC\alpha & \\ i = & \frac{[(C - C\alpha) + xC\alpha + yC\alpha]}{C} & & & & & \end{array}$$

$$\begin{aligned} \Rightarrow i &= \frac{1 - \alpha + x\alpha + y\alpha}{1} \\ &= 1 + [(x + y) - 1]\alpha \end{aligned}$$

Let $x + y = n =$ number of particles formed after dissociation

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

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

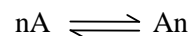
2. Association

Degree of Association : It may be defined as the number of molecules associated over initial concentration

$$\alpha = \frac{\text{number of moles associated}}{\text{Initial concentration}}$$

$$i = \frac{\text{Total number of moles of particles at equilibrium}}{\text{Initial concentration}}$$

Let n molecules of an electrolyte A undergo association



Let the initial concentration of $A = C$

The degree of association = α

when $C\alpha$ moles of A associate then $\frac{C\alpha}{n}$ moles of A_n are formed

number of moles of equilibrium $(C - C\alpha) \rightleftharpoons \frac{C\alpha}{n}$

$$\Rightarrow i = \frac{C - C\alpha + \frac{C\alpha}{n}}{C}$$

If $C = 1$

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

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

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

SOLVED EXAMPLES

Ex.1 : A solution contains 25% water, 25% ethanol and 50% acetic acid by weight. Find out the mole fraction of each component.

Sol.: Let us consider that total mass of the solution is 100 g

Mass of water = 25 g

Mass of ethanol = 25 g

Mass of acetic acid = 50 g

$$\text{Moles of water} = \frac{25}{18} = 1.388$$

$$\text{Moles of ethanol} = \frac{25}{46} = 0.543$$

$$\text{Moles of acetic acid} = \frac{50}{60} = 0.833$$

$$\text{Mole fraction of water} = \frac{1.388}{1.388 + 0.543 + 0.833} = \mathbf{0.502}$$

$$\text{Mole fraction of ethanol} = \frac{0.543}{1.388 + 0.543 + 0.833} = \mathbf{0.196}$$

$$\text{Mole fraction of acetic acid} = \frac{0.833}{1.388 + 0.543 + 0.833} = \mathbf{0.301}$$

Ex.2 : 4.45 g of pure sulphuric acid is added to 82.20 g water. The density of the solution was found to be 1.029 g/ml. Calculate (a) weight percent (b) mole fraction (c) mole percent (d) molality (e) molarity and (f) normality of sulphuric acid solution.

Sol.: Mass of H_2SO_4 = 4.450 g

Mass of water = 82.20 g

Mass of solution = 86.65 g

Density of solution = 1.029 g/ml

$$(a) \text{ Weight percent of } \text{H}_2\text{SO}_4 \text{ in solution} = \frac{4.45}{86.65} \times 100 = \mathbf{5.14}$$

$$(b) \text{ Moles of } \text{H}_2\text{SO}_4 = \frac{4.45}{98} = 0.0454$$

$$\text{Moles of } \text{H}_2\text{O} = \frac{82.20}{18} = 5.566$$

$$\text{Total no. of moles} = 0.0454 + 5.566 = 4.6114$$

$$\text{Mole fraction of } \text{H}_2\text{SO}_4 = \frac{0.0454}{4.6114} = \mathbf{0.0098}$$

$$\text{Mole fraction of water} = 1 - 0.0098 = \mathbf{0.9902}$$

(c) Mole percent

$$\begin{aligned}\text{Mole percent of solute} &= \frac{\text{Moles of solute}}{\text{Total moles in solution}} \times 100 \\ &= \text{Mole fraction of solute} \times 100 = 0.0098 \times 100 = \mathbf{0.98}\end{aligned}$$

$$\begin{aligned}\text{Mole percent of solvent} &= \text{Mole fraction of solvent} \times 100 \\ &= 0.9902 \times 100 = \mathbf{99.02}\end{aligned}$$

(d) Molality

$$\begin{aligned}\text{Molality} &= \frac{\text{Moles of solute}}{\text{Mass of solvent in g}} \times 1000 \\ &= \frac{0.0454}{82.2} \times 1000 = \mathbf{0.552}.\end{aligned}$$

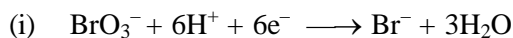
(e) Molarity

$$\begin{aligned}\text{Molarity} &= \frac{\text{Moles of solute}}{\text{Volume of solution in litres}} \\ \text{Volume of Solution} &= \frac{\text{Mass of solution in g}}{\text{Density of solution}} = \frac{86.65}{1.029 \times 1000} \text{ litre} \\ \text{Molarity} &= \frac{0.0454 \times 1000 \times 1.029}{86.65} = 0.539\end{aligned}$$

(f) Normality

$$\begin{aligned}\text{Normality} &= \frac{\text{No. of equivalents of solute dissolved}}{\text{No. of litres of solution made}} \\ \text{Equivalent of H}_2\text{SO}_4 &= \frac{4.45}{49} \\ \text{Volume of solution} &= \frac{86.65}{1.029 \times 1000} \\ \text{Normality} &= \frac{4.45 \times 1000 \times 1.029}{49 \times 86.65} = \mathbf{1.078}\end{aligned}$$

Ex.3 : Find out the mass of sodium bromate and molarity of solution necessary to prepare 85.5 ml of 0.672 N solution where the half cell reaction are



Sol.: For equation (i)

$$\text{Equivalent weight of NaBrO}_3 = \frac{\text{Molecular weight}}{6} = \frac{151}{6} = 25.167$$

$$\text{Mass of NaBrO}_3 \text{ is solution} = \text{N} \times \text{V in litre} \times \text{Equivalent weight.}$$

$$\begin{aligned}&= 0.672 \times \frac{85.5}{1000} \times 25.167 \\ &= \mathbf{1.446 \text{ g}}\end{aligned}$$

$$\text{Molarity} = \frac{\text{Normality}}{\text{No. of electrons accepted}} = \frac{0.672}{6} = 0.112$$

For equation (ii)

$$\text{Equivalent weight of NaBrO}_3 = \frac{\text{Mol. wt}}{10} = \frac{151}{10} = 15.1$$

$$\text{Mass of NaBrO}_3 \text{ in solution} = 0.672 \times \frac{85.5}{1000} \times 15.1 = \mathbf{0.867 \text{ g}}$$

$$\text{Molarity} = \frac{\text{Normality}}{\text{No. of electrons accepted}} = \frac{0.672}{10} = \mathbf{0.0672}$$

Ex.4 : Certain liquid X boils at 33.5° C at 1 atm. At what temperature will it boil at 750 mm. Latent heat of vaporization is 88.4 cal/g, R = 1.987 cal. and Mol. wt. of X is 74.

Sol.: We Known

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.302 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$P_1 = 760 \text{ mm}$$

$$P_2 = 750 \text{ mm}$$

$$\Delta H_v = 88.4 \times 74$$

$$T_1 = 33.5 + 273 = 306.5$$

$$T_2 = ?$$

$$\log \frac{750}{760} = \frac{88.4 \times 74}{2.303 \times 1.987} \left[\frac{T_2 - 306.5}{306.5 \times T_2} \right]$$

$$T_2 = 305.9 \text{ k}$$

$$= (305.9 - 273)^\circ \text{C} = \mathbf{32.9^\circ \text{C}}$$

Ex.5 : Solutions of two volatile liquids A and B obey Raoult's law. At certain temperature T, it is found that when the total pressure above a given solution is 400 mm Hg the mole fraction of A in the vapour phase is 0.45 and in the liquid it is 0.65. Find out the vapour pressure of two pure liquids at temp. T.

Sol.: Total Pressure = 400 mm

$$x_A = 0.65 \quad Y_A = 0.45 \quad P_A^\circ = ?$$

$$x_B = 0.35 \quad Y_B = 0.55 \quad P_B^\circ = ?$$

We know $P = P_A^\circ \cdot x_A + P_B^\circ \cdot x_B$

$$400 = P_A^\circ \cdot 0.65 + P_B^\circ \cdot 0.35$$

Also we know

$$Y_A = \frac{P_A}{P} = \frac{P_A^\circ \cdot x_A}{P}$$

$$0.45 = \frac{0.65 P_A^\circ}{400}$$

$$P_A^0 = \frac{400 \times 0.45}{0.65} = 277 \text{ mm}$$

Now,

$$400 = 277 \times 0.65 + P_B^0 \times 0.35$$

$$P_B^0 = \frac{400 - 180}{0.35} = 630 \text{ mm}$$

Ex.6 : At 30°C A and B have vapour pressures of 119.6 and 36.7 mm respectively. What are the partial pressures of each of these components and the total pressure over a solution consisting of equal weights of these two components at 30°C. What is the composition of the vapour in equilibrium with the solution at this temperature. Comment on the results. [mol. wt. of A = 78 and mol. wt. of B = 92].

Sol.: Say the amount taken is 92 g for each liquid.

$$\text{Moles of A} = \frac{92}{78} = 1.18$$

$$\text{Moles of B} = \frac{92}{92} = 1$$

$$x_A = \frac{1.18}{2.18} = 0.541$$

$$x_B = \frac{1}{2.18} = 0.459$$

$$P_A = 0.541 \times 119.5 = 64.7 \text{ mm}$$

$$P_B = 0.459 \times 36.7 = 16.8 \text{ mm}$$

$$\text{Total pressure} = 64.8 + 16.8 = 81.5$$

Composition of vapour

$$x_A \text{ in vapour phase} = \frac{64.7}{81.5} = 0.793$$

$$x_B \text{ in vapour phase} = 1 - 0.793 = 0.207.$$

This indicates that the vapour is always richer in the more volatile liquid.

Ex.7 : Aniline-water mixture boils at 98°C at a pressure of 1 atm. At this temperature the vapour pressure of water is 707 mm. If the system is distilled in steam what fraction of total weight of the distillate will be aniline

Sol.: $M_A = 93$ $P_A^0 = ?$ $W_A = ?$

$M_W = 18$ $P_W^0 = 707 \text{ mm}$ $W_W = ?$

We know

$$P = P_A^0 + P_W^0$$

$$760 = P_A^0 + 707$$

$$P_A^0 = 53 \text{ mm}$$

We know

$$\frac{W_A}{W_W} = \frac{P_A^0 \cdot M_A}{P_W^0 \cdot M_W} = \frac{53 \times 93}{707 \times 18} = \frac{4929}{12726}$$

$$x_A = \frac{W_A}{W_A + W_B} = \frac{4929}{4929 + 12726} = \mathbf{0.279}$$

$$\% \text{ of A} = 0.279 \times 100 = \mathbf{27.9 \%}.$$

Ex.8 : The vapour pressure of 2.1% aqueous solution of a non-electrolyte is 755 mm at 100°C. Find out the mol. wt. of solute.

Sol.: Vapour pressure of pure water at 100°C = 760 mm

Vapour pressure of solution at 100°C = 755 mm

Mass of solute = 2.1 g

Mass of water = 100 – 2.1 = 97.9 g

Moles of solute = $\frac{2.1}{m}$ (m = mol. wt. of solute)

Moles of water = $\frac{97.9}{18}$

We know

$$\frac{P - P_s}{P} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$$

$$\frac{760 - 755}{760} = \frac{\frac{2.1}{m}}{\frac{2.1}{m} + \frac{97.9}{18}}$$

$$\frac{5}{760} = \frac{\frac{2.1}{m}}{\frac{2.1}{m} + \frac{97.9}{18}}$$

$$\frac{2.1}{m} + \frac{97.9}{18} = \frac{2.1}{m} \times \frac{760}{5}$$

$$\frac{97.9}{18} = \frac{1596}{5m} - \frac{2.1}{m}$$

$$\frac{97.9}{18} = \frac{1585.5}{5m}$$

$$m = \frac{1585.5 \times 18}{97.9 \times 5} = \mathbf{58.30}.$$

Ex.9 : A very small amount of a non-volatile solute (non-electrolyte) is dissolved in 56.8 ml of benzene (density 0.889 g cm⁻³). At room temperature, vapour pressure of this solution is 98.88 mm Hg while that of benzene is 100 mm Hg. Find the molality of this solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene what is the value of cryoscopic constant of benzene.

Sol.: We know for a very dilute solution

$$\frac{P-P_s}{P} = \frac{w}{m} \cdot \frac{M}{W}$$

$$\frac{P-P_s}{P} \times \frac{1000}{M} = \text{molality of solution}$$

$$\frac{100 - 98.88}{100} \times \frac{1000}{78} = \text{molality} = \mathbf{0.1435\ m}$$

Further we know

$$\Delta T_f = K_f \times m$$

$$K_f = \frac{\Delta T_f}{m} = \frac{0.73}{0.1435}$$

$$= \mathbf{5.087\ K\ kg.\ mol^{-1}}$$

Ex.10: Dry air was passed through a solution (obtained by dissolving 50 g of solute in 100 g water) and then through pure water. The loss in weight of pure water is found to be 0.05 g. The wet air was then passed through concentrated H_2SO_4 . In the process H_2SO_4 gained 2 g. Find out the molecular weight of the solute.

Sol.: Loss in weight from pure water = 0.05g

Loss in weight from solution = $2 - 0.05 = 1.95\ \text{g}$

Total loss in weight = 2.0 g

We know

Loss in weight from solution $\propto P_s$

Total loss in weight $\propto P$

Also we know

$$\frac{P-P_s}{P} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}; \quad \frac{2.0-1.95}{2.0} = \frac{\frac{50}{m}}{\frac{50}{m} + \frac{100}{18}}$$

$$\frac{1}{40} = \frac{50 \times 18}{900 + 100m}$$

$$m = \mathbf{351}$$

Ex.11: Calculate the freezing point of an aqueous solution of non-electrolyte having an osmotic pressure of 2.0 atmosphere at 300 K. [Given $K_f = 1.86\ \text{K kg mole}^{-1}$ and $S = 0.0821\ \text{litre atm K}^{-1}\text{mol}^{-1}$]

Sol.: We know

$$\pi = CST$$

Given

$$\pi = 2.0\ \text{atm}$$

$$T = 300\ \text{K}$$

$$S = 0.0821\ \text{litre atm K}^{-1}\text{mol}^{-1}$$

$$C = ?$$

$$2.0 = C \times 0.0821 \times 300$$

$$C = \frac{2.0}{0.0821 \times 300} = 0.0812 \text{ mol litre}^{-1}$$

Since solution is very dilute molality may be taken as equal to molarity

$$\Delta T_f = K_f \times m$$

$$\Delta T_f = 1.86 \times 0.0812$$

$$= 0.151$$

$$\text{F.P.} = -0.151^\circ\text{C}$$

Ex.12: A tube of uniform bore ($a = 1 \text{ cm}^2$) is closed at one end with semipermeable membrane. A 5% (w/v) solution of glucose is filled in the tube and it is dipped in pure water at 27°C so that equilibrium is attained. Find out

(a) Osmotic pressure of the solution

(b) Height developed in vertical column

[Given density of the final sucrose solution is 2 g/cc]

Sol.: We know

$$\pi v = nRT$$

$$\pi v = \frac{w}{M} \cdot RT$$

$w = 5 \text{ g}$, $v = 100 \text{ ml}$ or 0.1 litre , $M = 180$, $R = 0.0821$, $T = 300 \text{ K}$

$$0.1 \pi = \frac{5}{180} \times 0.0821 \times 300$$

$$\pi = \frac{5 \times 0.0821 \times 300}{180 \times 0.1} = \mathbf{6.84 \text{ atm.}}$$

Further

$$\pi = 6.84 \text{ atm} = 6.84 \times 1.01 \times 10^5 \text{ Nm}^{-2}$$

$$d = 2 \text{ g/ml} = 2 \times 10^3 \text{ kg m}^{-3}$$

$$g = 9.81 \text{ m sec}^{-2}$$

we know

$$\pi = hdg$$

$$h = \frac{\pi}{dg} = \frac{6.84 \times 1.01 \times 10^5}{2 \times 10^3 \times 9.81}$$

$$= \mathbf{35.22 \text{ meters}}$$

Ex.13: Boiling point of an aqueous solution is found to be 100.5°C . Find out the osmotic pressure of this solution. [Given $K_b = 0.5 \text{ K kg mol}^{-1}$]

Sol.: B.P. of water = 100°C

$$\Delta T_b = 100.5 - 100 = 0.5$$

We know

$$\Delta T_b = 1000 K_b \cdot \frac{w}{m} \cdot \frac{1}{W}$$

or $\Delta T_b = K_b \times m$

$$0.5 = 0.5 \times m$$

$$\mathbf{m = 1}$$

Since solution is dilute molality = molarity

We know

$$\pi = CRT$$

$$\begin{aligned}\pi &= 1 \times 0.0821 \times 300 \\ &= \mathbf{24.63 \text{ atm}}\end{aligned}$$

Ex.14: The boiling point of pure benzene is 80°C. The boiling point of a solution containing 1g of a substance dissolved in 83.4 g of benzene is 80.175°C. If the latent heat of vaporization of benzene is 94 cal per g. Calculate the mol.wt., of solute.

Sol.: Latent heat of vaporization = 94 cal per g

Boiling point of benzene = 80°C = 353 K

We know

$$K_b = \frac{R \cdot T_b^2}{1000 l_v} = \frac{1.98 \times 353 \times 353}{1000 \times 94} = 2.624 \text{ K Kg mol}^{-1}$$

Further we know

$$m = \frac{1000 K_b \times w}{\Delta T_b \times W}$$

$$\Delta T_b = (80.175 - 80) = \mathbf{0.175^\circ C}$$

$$m = \frac{1000 \times 2.624 \times 1}{0.175 \times 83.4} = \mathbf{179.78}$$

Ex.15: 100 g of Sucrose solution in water is cooled to 272.5 K. Find out the weight of ice that will separate at this temperature. Assume that the solution started freezing at -38°C.

[$K_f = 1.86 \text{ K Kg mol}^{-1}$]

Sol.: Mass of solution = 100 g

Say mass of solute is w g and mass of solvent Wg

$$w = 100 - W$$

$$\Delta T_f = 38^\circ$$

Molecular weight of sucrose = 342

$$m = \frac{1000 \times 1.86}{38} \times \frac{100 - w}{W}$$

$$W = \mathbf{93.47 \text{ g}}$$

When the solution is cooled to -0.5°C let the mass of water left unfrozen = W_1 g

$$\Delta T_f = 0.5$$

$$m = \frac{1000 \times K_f \times w}{\Delta T_f \times w}$$

$$[w = 100 - 93.47 = 6.53 \text{ g}]$$

$$342 = \frac{1000 \times 1.86 \times 6.53}{0.5 \times W_1}$$

$$W_1 = 71.028 \text{ g}$$

Hence amount of water separated out = **22.43 g**.

OBJECTIVE QUESTIONS

- The correct relationship between the boiling points of very dilute solutions of AlCl_3 (t_1) and CaCl_2 (t_2) having the same molar concentrations
(a) $t_1 = t_2$ (b) $t_2 > t_1$ (c) $t_1 > t_2$ (d) $t_2 \geq t_1$
 - If a thin slice of sugar beet is placed in concentrated solution of NaCl then
(a) sugar beet loses water from its cell (b) sugar beet will absorb water from solutions
(c) sugar beet will neither absorb nor lose water (d) sugar beet will dissolve in water
 - 2N HCl solution will have same molar concentration as a
(a) 4.0 N H_2SO_4 (b) 0.5 N H_2SO_4
(c) 1N N_2SO_4 (d) 2N H_2SO_4
 - The solution having lower osmotic pressure when compared to another is called
(a) Isotonic solution (b) Hypertonic (c) Hypotonic (d) none of these
 - Which of the following gases are highly soluble in water
(a) HCl (b) SO_2 (c) NH_3 (d) H_2
 - Henry's law can be applied for which of the following gases for solubility in water
(a) H_2 (b) HCl (c) SO_2 (d) NH_3
 - Which of the following would be equal to zero when the liquid pairs form an ideal solution
(a) ΔH (b) ΔS (c) ΔG (d) ΔV
 - When HgI_2 is added to an aqueous solution of KI there will be
(a) increase in boiling point (b) decrease in freezing point
(c) increase in vapour pressure (d) both (a) and (b)
 - It takes larger time to cook food on hills than in plains. This is because
(a) high pressure of hills (b) low pressure on hills
(c) boiling increases on going up the hills (d) none of these
 - The lubricating action of an oil is more if it possesses
(a) high vapour pressure (b) low vapour pressure
(c) high surface tension (d) high density
 - The vapour pressure of a dilute solution of a solute is not influenced by
(a) temperature of solutions (b) melting point of solute
(c) mole fraction of solute (d) degree of dissociation of solute.
 - That solvent is better to be used during ebullioscopic measurements where the solvent has
(a) high K_b value (b) low K_b value
(c) where K_b and K_f values are equal for solvent (d) none of these
-

-
13. The melting points of most of the solid substances increase with an increase of pressure acting on them. However, ice melts at lower temperature than its usual melting point when the pressure increases. This is because
- (a) ice is less dense than H_2O (b) pressure generates heat
(c) the bonds break on pressure (d) ice is not a true solid
14. 'A' gms of non-volatile organic substance of molecular weight M_0 is dissolved in 250 gms of benzene. Molal elevation constant of benzene is K_b . The ΔT_b is equal to
- (a) $\frac{M_0}{K_b A}$ (b) $\frac{4K_b A}{M_0}$ (c) $\frac{16K_b A}{M_0}$ (d) none of these
15. An aqueous solution freezes at $-0.186^\circ C$ ($k_f = 1.86^\circ$, $K_b = 0.512$). The elevation in boiling point is
- (a) 0.186 (b) 0.512 (c) 0.275 (d) none of these
16. Dry air was successively passed through a solution of 5 gms of solute in 80 gm of water and then through pure water. The loss in weight of solution was 2.5 gms and that of pure water was 0.04 gms. The molecular wt. of solute is
- (a) 7.143 (b) 74.13 (c) 71.43 (d) none of these
17. In a solution of 7.8 g benzene (C_6H_6) and 46.0 g toluene ($C_6H_5CH_3$), the mole fraction of benzene is :
- (a) 1/6 (b) 1/5 (c) 1/2 (d) 1/3
18. At $40^\circ C$ the vapour pressures of pure liquids, benzene and toluene, are 160 mm Hg and 60 mm Hg respectively. At the same temperature, the vapour pressure of an equimolar solution of the two liquids, assuming the ideal solution should be :
- (a) 140 mm Hg (b) 110 mm Hg (c) 220 mm Hg (d) 100 mm Hg
19. The vapour pressure of ethanol and methanol are 42.0 mm and 88.5 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 46.0 g of ethanol with 16.0 g of methanol. The mole fraction of methanol in the vapour is :
- (a) 0.467 (b) 0.502 (c) 0.513 (d) none of these
20. 3% aqueous solution of dextrose (Mol. Wt. 180) is isotonic with 2% aqueous solution of another covalent solute in water at $25^\circ C$. The molar mass of the solute is
- (a) 60 (b) 120 (c) 180 (d) 90
21. Which of the following will form maximum boiling azeotropic mixture
- (a) $C_2H_5OH + C_3H_7OH$ (b) $C_2H_5OH + H_2O$
(c) $CH_3CHO + CHCl_3$ (d) $CH_3COOH + H_2O$
-

-
22. The boiling points of bromine (Br_2) and iodine monochloride (ICl) are 58.8°C and 97.4°C respectively. The boiling point of ICl is higher than that of Br_2 because
- (a) ICl is polar and Br_2 is non-polar
 - (b) the vapour pressure of ICl is higher than of Br_2 at room temperature
 - (c) ICl is ionic, while Br_2 is molecular compound.
 - (d) all of these
23. Two immiscible liquids A and B are distilled together and found to boil at 60°C temperature, at which the vapour pressure of A is found to be 360 mm. The distillate is found to contain 40% by weight of A. If the molecular weight of A is 82 then the molecular weight of B is
- (a) 40
 - (b) 50
 - (c) 60
 - (d) none of these
24. A salt MA_2 , ionises as : $\text{MA}_2 \rightleftharpoons \text{M}^{2+} + 2\text{A}^-$. It was found that a given solution of the salt had the same freezing point as a solution of glucose of twice the molarity. The apparent degree of ionisation of the salt is
- (a) 0.25
 - (b) 0.33
 - (c) 0.50
 - (d) 0.67
25. To 10 ml of 0.1 M BaCl_2 solution 0.2 ml of 3 M Na_2SO_4 is added. BaSO_4 is formed and is completely insoluble. All the salts are completely dissociated and change in volume is negligible. The
- (a) freezing point is raised
 - (b) freezing point is lowered
 - (c) freezing point does not change
 - (d) boiling point is lowered
26. The boiling point of an aqueous solution of a non volatile solute is 100.15°C . What is the freezing point of an aqueous solution obtained by diluting the above solution with an equal volume of water ? The values of K_b and K_f for water are 0.512°C and 1.86°C
- (a) -0.545°C
 - (b) -0.512°C
 - (c) -0.279°C
 - (d) -1.86°C
27. A mixture of water and bromobenzene was steam distilled at 95°C . The distillate contained 58.0 grams of water and 100 grams of bromobenzene. The vapour pressures of water and bromobenzene at the given temperature are 635 and 125 mm respectively. The molecular weight of bromobenzene is computed and found to be
- (a) 79
 - (b) 158
 - (c) 180
 - (d) 316
28. At 80°C benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will boil at 88°C at 1 atm pressure, benzene-toluene form an ideal solution.
- (a) 0.416
 - (b) 0.588
 - (c) 0.688
 - (d) 0.740
29. Two liquids A and B have vapour pressure in the ratio $p_A^0 : p_B^0 = 1 : 2$ at a certain temperature. Suppose that we have an ideal solution of A and B in the mole fraction ratio A : B = 1 : 2, the mole fraction of A in the vapour in equilibrium with the solution at the given temperature is
- (a) 0.25
 - (b) 0.2
 - (c) 0.5
 - (d) none of these
30. The mole fraction of H_2SO_4 in water is 0.15. Its molality is
- (a) 0.1 M
 - (b) 2.0 M
 - (c) 9.8 M
 - (d) none of these
-

MORE THAN ONE CORRECT ANSWER TYPE QUESTIONS

31. Which are the correct statements

- (a) Minimum boiling azeotropic mixture boils at temperature lower than either of the two pure components.
- (b) Maximum boiling azeotropic mixture boils at temperature higher than either of the two pure components.
- (c) Minimum boiling azeotropic mixture shows (+ve) deviation.
- (d) Maximum boiling azeotropic mixture shows (-ve) deviation.

32. Which of the following statements is/are correct?

- (a) 1 M NaCl solution has higher depression in freezing point than 1 M glucose solution
- (b) 1 M glucose solution has same elevation in boiling point as 1 m sucrose solution
- (c) 1 M urea is isotonic with 0.1 M NaCl
- (d) Van't Hoff factor (i) = 1 if solute undergoes association

33. With regard to the depression in freezing point experiment: Pick out correct statements

- (a) At the freezing point, liquid solvent and solid solvent are in equilibrium.
- (b) At the freezing point of solution only solvent solidifies.
- (c) At the freezing point of solution, solute also enters the solid phase.
- (d) Freezing point of solution will be lower than that of pure solvent.

34. Which of the following is correct for a non-ideal solution of liquids A and B, showing negative deviation?

- (a) ΔH_{mix} = negative
- (b) ΔV_{mix} = negative
- (c) ΔS_{mix} = positive
- (d) ΔG_{mix} = negative

35. Consider the following solutions;

I. 1 M aqueous glucose

II. 1 M aqueous NaCl

III. 1 M $\text{C}_6\text{H}_5\text{COOH}$ in C_6H_6

IV. 1 M $(\text{NH}_4)_3\text{PO}_4$

- (a) All are isotonic solution
- (b) III is hypotonic to I, II, IV
- (c) I, II, IV are hypertonic to III
- (d) IV is hypertonic to I, II, IV

36. Which of the following statements is/are correct about azeotropic mixture?

- (a) Azeotropic mixtures are non-ideal solution
- (b) The components of azeotropic mixture cannot be separated by fractional distillation
- (c) Azeotropes obey Raoult's law
- (d) Solution with positive deviation from Raoult's law, forms minimum boiling azeotrope

37. Which of the following are correct about the binary homogeneous liquid mixture?

- (a) H_2O and $\text{C}_2\text{H}_5\text{OH}$; $\Delta H_{\text{sol}} > 0$, $\Delta V_{\text{sol}} > 0$
 - (b) C_6H_6 and $\text{C}_6\text{H}_5\text{CH}_3$; $\Delta H_{\text{sol}} = 0$, $\Delta V_{\text{sol}} = 0$
 - (c) CH_3COCH_3 and CHCl_3 ; $\Delta H_{\text{sol}} < 0$, $\Delta V_{\text{sol}} < 0$
 - (d) H_2O and HCl ; $\Delta H_{\text{sol}} > 0$, $\Delta V_{\text{sol}} < 0$
-

38. Which of the following statements are correct for Van't Hoff factor ' i ' for a solution of weak electrolytes A_xB_y ?

- (a) $i = 1 - \alpha + x\alpha + y\alpha$ (b) $i > 1$ at normal dilution
(c) i increase more rapidly with dilution and attain a limiting value of $(x + y)$ at infinite dilution.
(d) The increases in (i) with dilution is due to increase in molality of solution with dilution.

39. Which of the following are correct about mixture of two miscible liquids forming azeotropes;

- (a) Has the lowest temperature at which the two liquids can exist in the liquid state.
(b) Has the lowest temperature attainable at which the two liquids forms eutectic mixture.
(c) Eutectic point has found application to attain low melting point solids which are eutectic mixtures.
(d) Composition of azeotrope and their boiling point vary with the external pressure.

40. Consider the following aqueous solution and assume 100% ionization in electrolytes:

- I. 0.1 m urea II. 0.04 m $Al_2(SO_4)_3$ III. 0.5 m $CaCl_2$ IV. 0.005 m $NaCl$

The wrong statement regarding the above solutions is

- (a) Freezing point will be lowest for solution I (b) Freezing point will be highest for solution IV
(c) Boiling point will be highest for solution IV (d) Vapour pressure will be highest for solution II
-

MISCELLANEOUS ASSIGNMENT

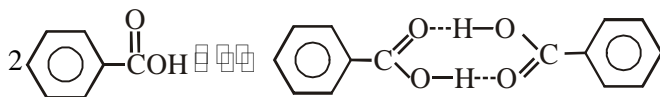
Comprehension-1

The various relations between colligative properties and molecular mass are applicable only to solutions of non-electrolytes and in dilute solutions. Out of various colligative properties, Osmotic pressure measurement is especially suitable for the determination of molecular masses of proteins whereas freezing point depression and other colligative properties are too small. Certain solutes which dissociate or associate in solutions affect the colligative property and hence molecular mass determination also. In case of association the observed molecular mass is more than normal and the correction factor $i < 1$. For dissociation of solute $i > 1$ and observed molecular mass is less than the normal molecular mass.

- Which of the following 0.1 m aqueous solution will have the lowest freezing point?
(a) $\text{Al}_2(\text{SO}_4)_3$ (b) $\text{C}_6\text{H}_{12}\text{O}_6$ (c) KI (d) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
- Correction factor i for 0.1 M ideal solution of $\text{C}_6\text{H}_{12}\text{O}_6$ is
(a) 0.1 (b) 1 (c) 0.01 (d) 2.0
- The Van't Hoff factor i for 0.1 M $\text{Ba}(\text{NO}_3)_2$ solution is 2.74. The degree of dissociation is
(a) 91.3% (b) 87% (c) 100% (d) 74%
- After adding a solute, freezing point of water decreases to -0.186°C . What is the value of ΔT_b ?
($k_b = 0.521$; $k_f = 1.86$)
(a) 0.521 (b) 0.0521 (c) 1.86 (d) 0.0186

Comprehension-2

Read the following sentence and answer the questions at the end of it. Benzoic acid dimerises in benzene but ionizes in aqueous solution



- Equimolar solution of (A) benzoic acid in benzene and (B) in aqueous solution are taken. Thus
(a) Van't Hoff factor of (A) $>$ (B) (b) Van't Hoff factor of (A) $<$ (B)
(c) Van't Hoff factor of (A) = (B) (d) Dimer formation or ionization is not possible

-
6. In the following equilibrium: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2$; NO_2 is 50% of the total volume. Hence, degree of dissociation (x) and Van't Hoff factor (i) respectively are
- (a) 0.5, 1.5 (b) 0.25, 1.25 (c) 0.33, 1.33 (d) 0.66, 1.66
7. Which has maximum freezing point?
- (a) 6 g Urea solution in 100 g H_2O (b) 6 g Acetic acid solution in 100 g H_2O
(c) 6 g Sodium chloride in 100 g H_2O (d) All have equal freezing point.
8. Aluminium phosphate is 100% ionized in 0.01 mol. aqueous solution. Hence $\Delta T_b/K_b$ is
- (a) 0.01 (b) 0.015 (c) 0.0175 (d) 0.02

MATRIX MATCH TYPE QUESTIONS

9. A. Lowest freezing point (p) 0.05 M NaCl
B. Lowest osmotic pressure (q) 0.025 M $\text{K}_3[\text{Fe}(\text{CN})_6]$
C. Highest boiling point (r) 0.0125 M AlCl_3
D. Highest Van't hof factor (s) 0.1 M $\text{C}_6\text{H}_{12}\text{O}_6$
10. A. +ve deviations from Raoult's law (p) $\text{CHCl}_3, \text{CH}_3\text{COCH}_3$
B. -ve deviations from Raoult's law (q) $\text{C}_2\text{H}_5\text{OH}, \text{H}_2\text{O}$
C. Azetropic mixtures (r) $\text{CH}_3\text{COOC}_2\text{H}_5, \text{H}_2\text{O}$
D. Mixture having low Boiling point (s) $\text{HNO}_3, \text{H}_2\text{O}$

INTEGER TYPE QUESTIONS

11. What weight of non volatile solute, Urea (NH_2CONH_2) needs to be dissolved in 90 g of water, in order to decrease the vapour pressure of water by 25%? The answer after dividing with 20 is:
12. 62 g of Ethylene glycol in 205 gm water is cooled to -9.3°C . K_f for water is $1.86 \text{ K Kg mol}^{-1}$. The amount of ice in grams that would be separated from solution is:
13. X gm of non volatile solute (Mol. Wt. = 36) is dissolved in 114 gm of Octane. Then vapour pressure is reduced to 80%. The value of X is:
14. A complex is represented as $\text{CoCl}_3 \cdot \text{XNH}_3$. Its 0.1 molal solution in water shows $\Delta T_f = 0.558^\circ\text{C}$ and K_f of H_2O is $1.86 \text{ K Kg Mol}^{-1}$. Assume 100% ionization of complex. So, the value of X is:
15. The osmotic pressure in atm of a decinormal solution of BaCl_2 at 27°C showing 71.2% of ionization is:
16. Depression in freezing point of 0.01 molal aqueous CH_3COOH solution is 0.02046. Also, a 1.0 molal aqueous solution of Urea freezes at -1.86°C . What is the pH of the above solution of acetic acid?
-

-
17. 17.4% (Mass/Vol) K_2SO_4 solution at $27^\circ C$ is isotonic to 5.85% (mass/vol) NaCl solution at $27^\circ C$. If NaCl is 100% ionized. The % ionization of K_2SO_4 in aqueous solution is $x \times 10$, then the value of x is:
18. The vapour pressure of two pure liquids A and B that forms an ideal solution at 300 and 800 torr, respectively at temperature T. A mixture of the vapour of A and B for which the mole fraction of A is 0.25 is slowly compressed at temperature T. The composition (mole fraction) of A in the solution whose normal boiling point is T is $x \times 10^{-2}$, then the value of x is:
19. A 0.001 molal solution of a complex represented as $Pt(NH_3)_4Cl_4$ in water had a freezing point depression of $0.00558^\circ C$. Given K_f for $H_2O = 1.86 \text{ K molality}^{-1}$. Assuming 100% ionization of this complex, and making necessary approximation, find how many ions will be given by this complex in solution?
20. Certain mass of a non electrolyte of molecular mass 90 is dissolved in 0.06 M solution of KCl and the osmotic pressure of the solution is found to be 5.49 atm at 300 K. Assuming KCl to undergo complete dissociation and the solution being dilute, find the mass of solute in grams dissolved in one litre.
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PREVIOUS YEAR QUESTIONS

IIT-JEE/JEE-ADVANCE QUESTIONS

- The van't Hoff factor for 0.1 M $\text{Ba}(\text{NO}_3)_2$ solution is 2.74. The degree of dissociation is
(a) 91.3% (b) 87% (c) 100% (d) 74%
- The elevation in boiling point, when 13.44 g of freshly prepared CuCl_2 are added to one kilogram of water, is. [Some useful data, $K_b = 0.52 \text{ kg K mol}^{-1}$, molecular weight of $\text{CuCl}_2 = 134.4 \text{ gm}$].
(a) 0.05 (b) 0.1 (c) 0.16 (d) 0.21
- 0.004 M Na_2SO_4 is isotonic with 0.01 M Glucose. Degree of dissociation of Na_2SO_4 is
(a) 75 % (b) 50 % (c) 25 % (d) 85 %
- During depression of freezing point in a solution, the following are in equilibrium
(a) liquid solvent, solid solvent (b) liquid solvent, solid solute
(c) liquid solute, solid solute (d) liquid solute, solid solvent
- A sugar syrup of weight 214.2 grams contains 34.2 grams of water. The molal concentration is
(a) 0.55 (b) 5.5 (c) 55 (d) 0.1
- An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 ml. The volume of 0.1 N NaOH required to completely neutralize 10 ml of this solution is
(a) 40 ml (b) 20ml (c) 10 ml (d) 4 ml
- The vapour pressure of solution of 5 g of non-electrolyte in 100 g of water at a particular temperature is 2985 Nm^{-2} . The vapour pressure of pure water at that temperature is 3000 Nm^{-2} . The molecular weight of the solute is
(a) 180 (b) 90 (c) 270 (d) 200
- The vapour pressure of benzene at a certain temperature is 640 mm Hg. A non-volatile-non-electrolyte and weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular weight of the solid substance?
(a) 6.96 (b) 65.3 (c) 63.8 (d) none of these
- When 20 g of naphthoic acid ($\text{C}_{11}\text{H}_8\text{O}_2$) is dissolved in 50 g of benzene ($K_f = 1.72 \text{ K kg mol}^{-1}$), a freezing point depression of 2 K is observed. The van't Hoff factor (i) is
(a) 0.5 (b) 1 (c) 2 (d) 3

Paragraph for Question Nos. 10 to 12

Properties such as boiling point, freezing point and vapour pressure of a pure solvent change when solute molecules are added to get homogeneous solution. These are called colligative properties. Applications of colligative properties are very useful in day-to-day life. One of its examples is the use of ethylene glycol and water mixture as anti-freezing liquid in the radiator of automobiles

A solution **M** is prepared by mixing ethanol and water. The mole fraction of ethanol in the mixture is 0.9

Given: Freezing point depression constant of water (K_f^{water}) = 1.86 K kg mol⁻¹
Freezing point depression constant of ethanol (K_f^{ethanol}) = 2.0 K kg mol⁻¹
Boiling point elevation constant of water (K_b^{water}) = 0.52 K kg mol⁻¹
Boiling point elevation constant of ethanol (K_b^{ethanol}) = 1.2 K kg mol⁻¹
Standard freezing point of water = 273 K
Standard freezing point of ethanol = 155.7 K
Standard boiling point of water = 373 K
Standard boiling point of ethanol = 351.5 K
Vapour pressure of pure water = 32.8 mm Hg
Vapour pressure of pure ethanol = 40 mm Hg
Molecular weight of water = 18 g mol⁻¹
Molecular weight of ethanol = 46 g mol⁻¹

In answering the following questions, consider the solutions to be ideal dilute solutions and solutes to be non-volatile and non-dissociative.

10. The freezing point of the solution **M** is
(a) 268.7 K (b) 268.5 K (c) 234.2 K (d) 150.9 K
11. The vapour pressure of the solution **M** is
(a) 39.3 mm Hg (b) 36.0 mm Hg (c) 29.5 mm Hg (d) 28.8 mm Hg
12. Water is added to the solution **M** such that the mole fraction of water in the solution becomes 0.9. The boiling point of this solution is
(a) 380.4 K (b) 376.2 K (c) 375.5 K (d) 354.7 K
13. The Henry's law constant for the solubility of N₂ gas in water at 298 K is 1.0 × 10⁵ atm. The mole fraction of N₂ in air is 0.8. The number of moles of N₂ from air dissolved in 10 moles of water at 298 K and 5 atm pressure is:
(a) 4.0 × 10⁻⁴ (b) 4.0 × 10⁻⁵ (c) 5.0 × 10⁻⁴ (d) 4.0 × 10⁻⁶
14. Dissolving 120 g of urea (mol. wt. 60) in 1000 g of water gave a solution of density 1.15 g/mL. The molarity of the solution is
(a) 1.78 M (b) 2.00 M (c) 2.05 M (d) 2.22 M
15. The freezing point (in °C) of a solution containing 0.1g of K₃[Fe(CN)₆] (Mol. Wt. 329) in 100 g of water ($K_f = 1.86 \text{ K kg mol}^{-1}$) is
(a) -2.3×10^{-2} (b) -5.7×10^{-2} (c) -5.7×10^{-3} (d) -1.2×10^{-2}
16. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solute in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take $K_b = 0.76 \text{ K kg mol}^{-1}$)
(a) 724 (b) 740 (c) 736 (d) 718
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17. A compound H_2X with molar weight of 80 g is dissolved in a solvent having density of 0.4 g ml^{-1} . Assuming no change in volume upon dissolution, the molality of a 3.2 molar solution is
18. MX_2 dissociates into M^{2+} and X^- ions in an aqueous solution, with a degree of dissociation of (α) of 0.5. The ratio of the observed depression of freezing point of the aqueous solution to the value of the depression of freezing point in the absence of ionic dissociation is

DCE QUESTIONS

1. An X molal solution of a compound in benzene has mole fraction of solute equal to 0.2. The value of X is
(a) 14 (b) 3.2 (c) 1.4 (d) 2
2. What does not change on changing temperature?
(a) mole fraction (b) normality (c) molarity (d) None of these
3. The freezing point of equimolal aqueous solutions will be highest for
(a) $C_6H_5NH_3Cl$ (b) $Ca(NO_3)_2$ (c) $La(NO_3)_2$ (d) Glucose
4. Blood is isotonic with 0]
(a) 0.16 M NaCl (b) Conc. NaCl (c) 50% NaCl (d) 30% NaCl
5. The O.P. of equimolar solution of Urea, $BaCl_2$ and $AlCl_3$ will be in the order
(a) $AlCl_3 > BaCl_2 > Urea$ (b) $BaCl_2 > AlCl_3 > Urea$
(c) $Urea > BaCl_2 > AlCl_3$ (d) $BaCl_2 > Urea > AlCl_3$
6. When common salt is dissolved in water
(a) M. P. of solution increases (b) B.P. of solution increases
(c) B. P. of solution decreases (d) Both M.P. and B.P. decreases
7. The molarity of a solution of Na_2CO_3 having 10.6 g/500 ml of solution is
(a) 0.2 M (b) 2 M (c) 20 M (d) 0.02 M
8. 60 gm of Urea (mol. wt 60) was dissolved in 9.9 moles of water. If the vapour pressure of pure water is P_o , the vapour pressure of solution is
(a) 0.10 P_o (b) 1.10 P_o (c) 0.90 P_o (d) 0.99 P_o
9. In coagulating the colloidal solution of As_2S_3 which has the minimum coagulating value
(a) NaCl (b) KCl (c) $BaCl_2$ (d) $AlCl_3$
10. Depression in freezing point is 6 K for NaCl solution if K_f for water is 1.86 K/kg mole amount of NaCl desolved in 1 kg water is
(a) 3.42 (b) 1.62 (c) 3.24 (d) 1.71
11. A 5% solution of sugarcane (mol.wt. = 342) is isotonic with 1% solution X under similar conditions. The mol. wt. g X is
(a) 136.2 (b) 64.4 (c) 34.2 (d) 171.2
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AIEEE/JEE-MAINS QUESTIONS

- If α is the degree of dissociation of Na_2SO_4 the vant Hoff's factor (i) used for calculating the molecular mass is
(a) $1 + \alpha$ (b) $1 - \alpha$ (c) $1 + 2\alpha$ (d) $1 - 2\alpha$
 - Which one of the following aqueous solutions will exhibit highest boiling point?
(a) 0.015 M urea (b) 0.01 M KNO_3 (c) 0.01 M Na_2SO_4 (d) 0.015 M glucose
 - 6.02×10^{20} molecules of urea are present in 100 ml of its solution. The concentration of urea solution is
(Avogadro constant, $N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$)
 - To neutralised completely 20 mL of 0.1 M aqueous solution of phosphorous acid (H_3PO_3), the volume of 0.1 M aqueous KOH solution required is
(a) 40 mL (b) 20 mL (c) 10 mL (d) 60 mL
 - Which of the following liquid pairs shows a positive deviation from Raoult's law?
(a) Water - nitric acid (b) Benzene - methanol
(c) Water - hydrochloric acid (d) Acetone - Chloroform
 - Which one of the following statements is **False**?
(a) The correct order of osmotic pressure for 0.01 M aqueous solution of each compound is $\text{BaCl}_2 > \text{KCl} > \text{CH}_3\text{COOH} > \text{Sucrose}$
(b) The osmotic pressure (π) of a solution is given by the equation $\pi = MRT$, where M is the molarity of the solution
(c) Raoult's law states that the vapour pressure of a component over a solution is proportional to its mole fraction.
(d) Two sucrose solutions of same molality prepared in different solvents will have the same freezing point depression
 - In a mixture A and B components show negative deviation as
(a) $\Delta V_{\text{mix}} > 0$ (b) $\Delta H_{\text{mix}} > 0$
(c) A — B interaction is weaker than A — A and B — B interaction
(d) None of the above reason is correct
 - If liquids A and B form an ideal solution
(a) the entropy of mixing is zero
(b) the free energy of mixing is zero
(c) the free energy as well as the entropy of mixing are each zero
(d) the enthalpy of mixing is zero
 - 25 ml of a solution of barium hydroxide on titration with a 0.1 molar solution of hydrochloric acid gave a titre value of 35 ml. The molarity of barium hydroxide solution was
(a) 0.14 (b) 0.28 (c) 0.35 (d) 0.07
 - An aqueous solution freezes at -0.186°C ($K_f = 1.86$, $K_b = 0.512$). What is the elevation in boiling
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- point?
- (a) 0.186 (b) 0.512 (c) 0.86 (d) 0.0512
11. In a 0.2 molal aqueous solution of a weak acid HX, the degree of ionization is 0.3. Taking K_f for water as 1.85, the freezing point of the solution will be nearest to
(a) -0.360°C (b) -0.260°C (c) $+0.480^\circ\text{C}$ (d) -0.480°C
12. Density of a 2.05 M solution of acetic acid in water is 1.02 g/mL. The molality of the solution is
(a) 0.44 mol kg^{-1} (b) 1.14 mol kg^{-1}
(c) 3.28 mol kg^{-1} (d) 2.28 mol kg^{-1}
13. 18 g of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is added to 178.2 g of water. The vapour pressure of water for this aqueous solution at 100°C is
(a) 752.40 Torr (b) 759.00 Torr (c) 7.60 Torr (d) 76.00 Torr
14. The density (in g mL^{-1}) of a 3.60 M sulphuric acid solution that is 29% H_2SO_4 (Molar mass = 98 g mol^{-1}) by mass will be
(a) 1.22 (b) 1.45 (c) 1.64 (d) 1.88
15. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be
(a) 700 (b) 360 (c) 350 (d) 300
16. A 5.25% solution of a substance is isotonic with a 1.5% solution of urea (molar mass = 60 g mol^{-1}) in the same solvent. If the densities of both the solutions are assumed to be equal to 1.0 g cm^{-3} , molar mass of the substance will be []
(a) 105.0 g mol^{-1} (b) 210.0 g mol^{-1}
(c) 90.0 g mol^{-1} (d) 115.0 g mol^{-1}
17. Two liquids X and Y form an ideal solution. At 300 K, vapour pressure of the solution containing 1 mol of X and 3 mol of Y is 550 mm Hg. At the same temperature, if 1 mol of Y is further added to this solution, vapour pressure of the solution increases by 10 mm Hg. Vapour pressure (in mm Hg) of X and Y in their pure states will be, respectively:
(a) 300 and 400 (b) 400 and 600 (c) 500 and 600 (d) 200 and 300
18. A binary liquid solution is prepared by mixing n-heptane and ethanol. Which one of the following statements is **correct** regarding the behaviour of the solution?
(a) The solution is non-ideal, showing +ve deviation from Raoult's Law.
(b) The solution is non-ideal, showing -ve deviation from Raoult's law
(c) n-heptane shows +ve deviation while ethanol shows -ve deviation from Raoult's law
(d) The solution formed is an ideal solution.
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19. If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f), when 0.01 mol of sodium sulphate is dissolved in 1 kg of water, is ($K_f = 1.86 \text{ K kg mol}^{-1}$).
- (a) 0.0744 K (b) 0.0186 K (c) 0.0372 K (d) 0.0558 K
20. On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25.0g of heptane and 35g of octane will be (molar mass of heptane = 100 g mol^{-1} and of octane = 114 g mol^{-1})
- (a) 96.2 kPa (b) 144.5 kPa (c) 72.0 kPa (d) 36.1 kPa
21. A 5.2 molal aqueous solution of methyl alcohol, CH_3OH , is supplied. What is the mole fraction of methyl alcohol in the solution?
- (a) 0.100 (b) 0.190 (c) 0.086 (d) 0.050
22. Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at -6°C will be:
(K_f for water = $1.86 \text{ K kg mol}^{-1}$, and molar mass of ethylene glycol = 62 g mol^{-1})
- (a) 804.32g (b) 204.30 g (c) 400.00g (d) 304.60g
23. The degree of dissociation (α) of a weak electrolyte, A_xB_y is related to van't Hoff factor (i) by the expression.
- (a) $\alpha = \frac{i-1}{(x+y-1)}$ (b) $\alpha = \frac{i-1}{x+y+1}$ (c) $\alpha = \frac{x+y-1}{i-1}$ (d) $\alpha = \frac{x+y+1}{i-1}$
24. The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is 1.15 g/mL. The molarity of this solution is
- (a) 0.50 M (b) 1.78 M (c) 1.02 M (d) 2.05 M
25. K_f for water is $1.86 \text{ K kg mol}^{-1}$. If your automobile radiator holds 1.0 kg of water how many grams of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) must you add to get the freezing point of the solution lowered to -2.8°C
- (a) 72 g (b) 93 g (c) 39 g (d) 27 g
26. Consider separate solutions of 0.500 M $\text{C}_2\text{H}_5\text{OH}(\text{aq})$, 0.100 M $\text{Mg}_3(\text{PO}_4)_2(\text{aq})$, 0.250 M $\text{KBr}(\text{aq})$ and 0.125 M $\text{Na}_3\text{PO}_4(\text{aq})$ at 25°C . Which statement is true about these solutions, assuming all salts to be [JEE-Mains 2014]
- (a) 0.125 M $\text{Na}_3\text{PO}_4(\text{aq})$ has the highest osmotic pressure
(b) 0.500 M $\text{C}_2\text{H}_5\text{OH}(\text{aq})$ has the highest osmotic pressure
(c) They all have the same osmotic pressure
(d) 0.100 M $\text{Mg}_3(\text{PO}_4)_2(\text{aq})$ has the highest osmotic pressure
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SUBJECTIVE PROBLEMS

1. Commercially available concentrated HCl is an aqueous solution containing 38% HCl by mass. It's density is 1.19 g ml^{-1} . Calculate
 - (a) Molarity of the solution
 - (b) How many ml of this HCl are required to make 1 litre of 0.1 M HCl.
 2. One litre of an aqueous solution contains 15 g of a solute of mol.wt 150. If the density of the solution is 1.005 g cm^{-3} , find out the mole fraction of solute.
 3. Find out the molarity of 20% solution of NaOH.
 4. Calculate normality of the solution obtained by mixing 40 ml of 0.05 N HCl and 60 ml of 0.1 N H_2SO_4 .
 5. The vapour pressure of $\text{C}_2\text{H}_5\text{OH}$ is 135.5 mm of Hg at 40°C and 542.5 mm of Hg at 70°C . Calculate the molar heat of vaporization and vapour pressure of ethanol at 50°C .
 6. A solution containing 30 g of a non-volatile solute in exactly 90 g water has vapour pressure of 21.85 mm Hg at 25°C . Further 18 g water is added to the solution. The resultant solution has a vapour pressure 22.15 mm of Hg at 25°C . Find out
 - (a) Molecular weight of the solute
 - (b) Vapour pressure of water at 25°C .
 7. The vapour pressure of pure benzene at 25°C is found to be 639.7 mm of Hg and vapour pressure of a solution in benzene at the same temperature is 631.9 mm of Hg. Find out molality of solution.
 8. A solution of sucrose is prepared by dissolving 68.4 g of sucrose per litre of the solution. Calculate the osmotic pressure of the solution at 300 K.
 9. The molal elevation constant for water is $0.56 \text{ K kg mol}^{-1}$. Find out the boiling point of solution obtained by dissolving 6 g of urea in 200 g water.
 10. A solution is prepared by dissolving 0.3 g of X in 30 g of CCl_4 . The elevation in boiling point was found to be 0.392. Find out the K_b for CCl_4 . [Given molecular weight of solute = 128]
 11. Two elements A and B form compounds having formula AB_2 and AB_4 . When dissolved in 20 g of benzene, 1.0 g of AB_2 lowers the freezing point by 2.3°C whereas 1.0 g of AB_4 lowers the freezing point by 1.3°C . The molal depression constants for benzene in 1000 g is 5.1°C . Calculate atomic masses of A and B.
 12. The molal freezing point constant of benzene is 4.90 and its melting point is 5.51°C . A solution of 0.816 g of a compound (A) when dissolved in 7.5 g of benzene freezes at 1.59°C . Find out the mol. wt. of A.
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13. A solution of X and Y with 30 mol percent of X is in equilibrium with its vapour which contain 60 mol percent of X. Assuming ideality of the solution and the vapour, calculate the ratio of the vapour pressure of pure X to that of pure Y.
14. A mixture of two immiscible liquids X and Y are distilled under equilibrium conditions at 1 atm pressure. Assuming ideal gas behaviour calculate the mole fraction of X in the distillate if the vapour pressure of Y is 425 torr.
15. The osmotic pressure of human blood due to presence of various solutes in the blood is 7.65 atm. at 27°C. Assuming that molarity equals molality find out the freezing point of blood.
16. A certain nonvolatile nonelectrolyte contains 40.0% carbon, 6.7% hydrogen, and 53.3% oxygen. An aqueous solution containing 5.00% by mass of the solute boils at 100.15°C. Determine the molecular formula of the compound. [$K_b = 0.52 \text{ K kg mol}^{-1}$]
17. The osmotic pressure of a solution of a synthetic polyisobutylene in benzene was determined at 25°C. A sample containing 0.20 g of solute/100 cm³ of solution developed a rise of 2.4 mm at osmotic equilibrium. The density of the solution was 0.88 g/cm³. What is the molecular weight of the polyisobutylene ?
18. A solution of crab hemocyanin, a pigmented protein extracted from crabs, was prepared by dissolving 0.750 g in 125 cm³ of an aqueous medium. At 4°C an osmotic pressure rise of 2.6 mm of the solution was observed. The solution had a density of 1.00 g /cm³. Determine the molecular weight of the protein.
19. A certain solution of benzoic acid in benzene has a freezing point of 3.1° C and a normal boiling point of 82.6°C. Explain these observations, and suggest structures for the solute particles at the two temperatures.
20. Calculate the ebullioscopic constant (K_b) of water. Given latent heat of vaporization is 2224 J and boiling point of water is 100°C.
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ANSWERS

Objective Questions

- | | | | | |
|---------------|-------------|-------------|---------------|-------------|
| 1. (c) | 2. (a) | 3. (a) | 4. (c) | 5. (a,b,c) |
| 6. (a) | 7. (a,d) | 8. (c) | 9. (b) | 10. (b) |
| 11. (b) | 12. (a) | 13. (a) | 14. (b) | 15. (d) |
| 16. (c) | 17. (a) | 18. (b) | 19. (c) | 20. (b) |
| 21. (c) | 22. (a) | 23. (d) | 24. (c) | 25. (b) |
| 26. (a) | 27. (b) | 28. (d) | 29. (b) | 30. (c) |
| 31. (a,b,c,d) | 32. (a,b) | 33. (a,b,d) | 34. (a,b,c,d) | 35. (b,c,d) |
| 36. (a,b,d) | 37. (a,b,c) | 38. (a,b,c) | 39. (a,b,c,d) | 40. (a,c,d) |

Miscellaneous Assignment

- | | | | | |
|--|---------|---------|---------|---------|
| 1. (a) | 2. (b) | 3. (b) | 4. (b) | 5. (b) |
| 6. (c) | 7. (a) | 8. (d) | | |
| 9. A-(p),(q),(s); B-(r); C-(p),(q),(s); D-(q),(r) | | | | |
| 10. A-(q),(r); B-(p),(s); C-(p),(q),(r),(s); D-(q),(r) | | | | |
| 11. (5) | 12. (5) | 13. (9) | 14. (5) | 15. (3) |
| 16. (3) | 17. (5) | 18. (8) | 19. (3) | 20. (9) |

Previous Year Questions

IIT-JEE/JEE-ADVANCE QUESTIONS

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (b) | 2. (c) | 3. (a) | 4. (a) | 5. (a) |
| 6. (a) | 7. (a) | 8. (b) | 9. (a) | 10. (d) |
| 11. (a) | 12. (b) | 13. (a) | 14. (c) | 15. (a) |
| 16. (a) | 17. (8) | 18. (2) | | |

DCE QUESTIONS

- | | | | | |
|---------|--------|--------|--------|---------|
| 1. (b) | 2. (a) | 3. (d) | 4. (a) | 5. (a) |
| 6. (b) | 7. (a) | 8. (a) | 9. (a) | 10. (b) |
| 11. (b) | | | | |

MAINS QUESTIONS

- | | | | | |
|---------|---------|---------|---------|---------|
| 1. (c) | 2. (c) | 3. (b) | 4. (a) | 5. (b) |
| 6. (d) | 7. (b) | 8. (d) | 9. (d) | 10. (d) |
| 11. (d) | 12. (d) | 13. (a) | 14. (a) | 15. (c) |
| 16. (b) | 17. (b) | 18. (a) | 19. (d) | 20. (c) |
| 21. (c) | 22. (a) | 23. (a) | 24. (d) | 25. (b) |
| 26. (c) | | | | |
-

Subjective Problems

- 12.38 M, 8.07 ml
 - 0.00181
 - 5 M
 - 0.0363 N
 - $\Delta H_u = 9880 \text{ cal/mol}$, V.P. at $50^\circ\text{C} = 221 \text{ mm}$
 - 78.83, 23.65 mm
 - 0.156
 - 4.926 atm.
 - 100.28°C
 - $5.02 \text{ k kg mol}^{-1}$
 - $A = 25.59$, $B = 42.64$
 - 136
 - 3.5
 - 0.441
 - 0.577°C
 - $\text{C}_6\text{H}_{12}\text{O}_6$
 - 2.4×10^5
 - 5.4×10^5
 - $m = 0.47$, $m = 0.99$, Associated freezing temperature and dissociated at boiling temperature.
 - 0.52.
-