8

Solutions

A solution is a mixture in which substances are intermixed so intimately that they cannot be observed as separate components. The dispersed phase or the substance which is to be dissolved is called solute, while the dispersion medium in which the solute is dispersed to get a homogenous mixture is called the solvent. And the Solubility of a substance may be defined as the amount of solute dissolved in 100 g of a solvent to form a saturated solution at a given temperature as with change in temperature solubility changes.

A saturated solution is a solution which contains at a given temperature as much solute as it can hold in presence of dissolve ding solvent. Any solution may contain less solute than would be necessary to saturate it. Such a solution is known as unsaturated solution. When the solution contains more solute than would be necessary to saturate it then it is termed as supersaturated solution.

An *aqueous solution* is a *solution* in which the solvent is water. Example of an *aqueous solution*: acetic acid as solute and water as solvent and nonaqueous solvents are ethyl acetate, used in nail polish removers, and turpentine, used to clean paint brushes. Aqueous-solution reactions can lead to the formation of a solid, as when a solution of potassium chromate (K_2CrO_4) is added to an aqueous solution of barium nitrate $Ba[NO_3]_2$ to form solid barium chromate ($BaCrO_4$) and a solution of potassium nitrate (KNO_3).

We have primarily discussed liquid solutions, and in particular aqueous solutions. It should be stressed, however, that solutions can also exist in the gaseous or solid phases. The air we breathe is a solution, not a compound; there is no such thing as an "air molecule" in its place, it is made up of diatomic elements; monatomic elements; one element in a triatomic molecule; and two compounds

The "solvent" in air is nitrogen, a diatomic element that accounts for 78% of Earth's atmosphere. Oxygen, also diatomic, constitutes an additional 21%. Argon, which like all noble gases is monatomic, ranks a distant third, with 0.93%. The remaining 0.07% is made up of traces of other noble gases; the two compounds mentioned, carbon dioxide and water (in vapour form); and, high in the atmosphere, the triatomic form of oxygen known as ozone (O_3).

An alloy is a mixture or metallic solid solution composed of two or more elements and the properties of alloys are usually different from those of its component elements. Alloy constituents are usually measured by mass. Some well-known alloys include bronze (three-quarters copper, one-quarter tin); brass (two-thirds copper, one-third zinc); pewter (a mixture of tin and copper with traces of antimony); and numerous alloys of iron-particularly steel-as well as alloys involving other metals.

Kinds of Solutions: Gas, liquid and solid, these three states of matter either behave as solvent or solute Depending on the state of solute or solvent, mainly there may be following nine types of binary solutions. Among these solutions the most significant type of solutions are those which are in liquid phase and may be categorised as:

- Solid in liquid solutions,
- Liquid in liquid solutions
- Gas in liquid solutions.

Table 8.1: Solvent**,** Solute and Example

Solvent	Solute	Example
Gas	Gas	Mixture of gases, air.
Gas	Liquid	Water vapours in air, mist.
Gas	Solid	Sublimation of a solid into a gas, smoke.
Liquid	Gas	CO_2 gas dissolved in water .
Liquid	Liquid	Mixture of miscible liquids, *e.g.,* alcohol in water.
Liquid	Solid	Salt in water, sugar in water.
Solid	Gas	Adsorption of gases over metals; hydrogen over palladium.
Solid	Liquid	Mercury in zinc, mercury in gold, $CuSO_4.5H_2O$
Solid	Solid	Homogeneous mixture of two or more metals (alloys), *e.g.,* copper in gold.

Water and oil and immiscible due to their respective molecule structures, and hence their inherent characteristics of intermolecular bonding. Water molecules are polar, meaning that the positive electric charge is at one end of the molecule, while the negative charge is at the other end. Oil, on the other hand, is non-polar-charges are more evenly distributed throughout the molecule. The immiscible quality of oil and water in relation to one another explains a number of phenomena from the everyday world.

The dispersion of two substances in an emulsion is achieved through the use of an emulsifier or surfactant. Made up of molecules that are both water-and oil-soluble, an emulsifier or surfactant acts as an agent for joining other substances in an emulsion. The two words are virtually synonymous, but "emulsifier" is used typically in reference to foods, whereas "surfactant" most often refers to an ingredient in detergents and related products.

In an emulsion, millions of surfactants surround the dispersed droplets of solute, known as the internal phase, shielding them from the solvent or external phase. Surfactants themselves are often used in laundry or dish detergent, because most stains on plates or clothes are oil-based, whereas the detergent itself is applied to the clothes in a water-based external phase. The emulsifiers in milk help to bond oily particles of milk fat (cream) and protein to the external phase of water that comprises the majority of milk's volume.

Colligative Properties: Certain properties of dilute solutions containing non-volatile solute do not depend upon the nature of the solute dissolved but depend only upon the concentration i.e., the number of particles of the solute present in the solution. Such properties are called colligative properties.

- Lowering of vapour pressure of the solvent.
- Osmotic pressure of the solution.
- Elevation in boiling point of the solvent.
- Depression in freezing point of the solvent.

Since colligative properties depend upon the number of solute particles present in the solution, the simple case will be that when the solute is a non-electrolyte. In case the solute is an electrolyte, it may split to a number of ions each of which acts as a particle and thus will affect the value of the colligative property. Each colligative property is exactly related to other, Relative lowering of vapour pressure, elevation in boiling point and depression in freezing point are directly proportional to osmotic pressure.

Vapour Pressure: The pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperature is called vapour pressure of the liquid. The vapour pressure of a liquid depends on:

- **Nature of Liquid:** Liquids, which have weak intermolecular forces, are volatile and have greater vapour pressure. For example, dimethyl ether has greater vapour pressure than ethyl alcohol.
- **Temperature:** Vapour pressure increases with increase in temperature. This is due to the reason that with increase in temperature more molecules of the liquid can go into vapour phase.
- **Purity of Liquid:** Pure liquid always has a vapour pressure greater than its solution.

Raoult's Law: When a non-volatile substance is dissolved in a liquid, the vapour pressure of the liquid (solvent) is lowered. According to Raoult's law (1887), at any given temperature the partial vapour pressure (p_A) of any component of a solution is equal to its mole fraction (X_A) multiplied by the vapour pressure of this component in the pure state (p°_A). That is, $p_A = p^\circ_A \times X_A$

The vapour pressure of the solution (P_{total}) is the sum of the partial pressures of the components, i.e., for the solution of two volatile liquids with vapour pressures p_A and p_B.

$$P_{total} = p_A + p_B = (p^\circ_A \times X_A) + (p^\circ_B \times X_B)$$

Relative lowering of vapour pressure is defined as the ratio of lowering of vapour pressure to the vapour pressure of the pure solvent. It is determined by Ostwald-Walker method.

Thus according to Raoult's law, $\dfrac{p^\circ - p}{p^\circ} = \dfrac{n}{n+N} = \dfrac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$

Where, $p =$ Vapour pressure of the solution

$p^\circ =$ Vapour pressure of the pure solvent

$n =$ Number of moles of the solute

$N =$ Number of moles of the solvent

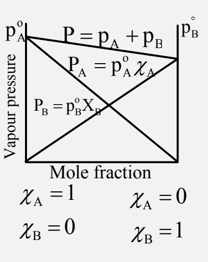
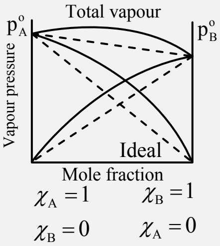
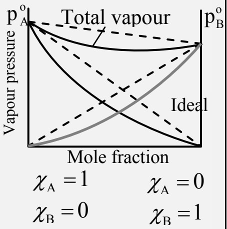
w and $m =$ weight and mol. wt. of solute

W and $M =$ weight and mol. wt. of the solvent.

Limitations of Raoult's Law

- Raoult's law is applicable only to very dilute solutions.
- Raoult's law is applicable to solutions containing non-volatile solute only.
- Raoult's law is not applicable to solutes which dissociate or associate in the particular solution.

Table 8.2: Ideal and Non-ideal Solutions

Ideal solutions	**Non-ideal solutions**	
	Positive deviation from Raoult's law 	Negative deviation from Raoult's law 

Obey Raoult's law at every range of concentration.	Do not obey Raoult's law.	Do not obey Raoult's law.
$\Delta H_{mix} = 0$; neither heat is evolved nor absorbed during dissolution.	$\Delta H_{mix} > 0$. Endothermic dissolution; heat is absorbed.	$\Delta H_{mix} < 0$. Exothermic dissolution; heat is evolved.
$\Delta V_{mix} = 0$; total volume of solution is equal to sum of volumes of the components.	$\Delta V_{mix} > 0$. Volume is increased after dissolution.	$\Delta V_{mix} < 0$. Volume is decreased during dissolution.
$P = p_A + p_B$ $= p_A^o X_A + p_B^o X_B$ i.e., $p_A = p_A^\circ X_A : p_B$ $= p_B^\circ X_B$	$p_A > p_A^o X_A$ $p_B > p_B^o X_B$ $\therefore\ p_A + p_B > p_A^\circ$ $X_A + p_B^\circ X_B$	$p_A < p_A^o X_A$; $p_B < p_B^o X_B$ $\therefore\ p_A + p_B <$ $p_A^\circ X_A + p_A^\circ X_B$
A–A, A–B, B–B interactions should be same, i.e., 'A' and 'B' are identical in shape, size and character.	A–B attractive force should be weaker than A–A and B–B attractive forces. 'A' and 'B' have different shape, size and character.	A–B attractive force should be greater than A–A and B–B attractive forces. 'A' and 'B' have different shape, size and character.
Escaping tendency of 'A' and 'B' should be same in pure liquids and in the solution.	'A' and 'B' escape easily showing higher vapour pressure than the expected value.	Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.
Examples: Dilute solutions; benzene + toluene: n-hexane + n-heptane; chlorobenzene + bromobenzene; ethyl bromide+ ethyl iodide; n-butyl chloride + n-butyl bromide	Examples: Acetone + ethanol acetone + CS_2: water + methanol; water + ethanol; CCl_4+ toluene; CCl_4+$CHCl_3$; acetone + benzene; CCl_4+CH_3OH; cyclohexane + ethanol	Examples: Acetone + aniline; acetone + chloroform; CH_3OH + CH_3COOH; H_2O + HNO_3 chloroform + diethyl ether; water + HCl; acetic acid + pyridine; chloroform + benzene

Osmotic Pressure (π): The osmotic pressure is a colligative property. For a given solvent the osmotic pressure depends only upon the molar concentration of solute but does not depend upon its nature. The following relation relates osmotic pressure to the number of moles of the solute,

According to Boyle Van't

Hoff law (at conc. temp.) $\pi \propto C$ . . .(*i*)

According to Gay lussac Van't Hoff law (at conc. temp.)

$$\pi \propto T \qquad ...(ii)$$

From equation (*i*) and (*ii*) we get $\pi \propto CT$

$\pi = CRT$ (Van't Hoff equation)

$$\pi = \frac{n}{V}RT \qquad \left(\therefore\ C = \frac{n}{V}\right)$$

$$\pi = \frac{w}{m}\frac{RT}{V} \qquad \left(\therefore\ n = \frac{w}{m}\right)$$

Here, C = concentration of solution in moles per litre

R = gas constant

T = temperature

n = number of moles of solute

V = volume of solution

m = molecular weight of solute

w = weight of solute

Relation of Osmotic Pressure with Different Colligative Properties: Osmotic pressure is related to relative lowering of vapour pressure, elevation of boiling point and depression of freezing point according to the following relations,

(a) $\pi = \left(\dfrac{P_A^o - P_A}{P_A^o}\right) \times \dfrac{dRT}{M}$

(b) $\pi = \Delta T_b \times \dfrac{dRT}{1000 \times K_b}$

(c) $\pi = \Delta T_f \times \dfrac{dRT}{1000 \times K_f}$

In the above relations,

π = Osmotic pressure

d = Density of solution at temperature T

R = Universal gas constant

M = Mol. Mass of solute

K_b = Molal elevation constant of solvent

K_f = Molal depression constant of solvent

Isotonic, Hypertonic and Hypotonic Solutions

- **Isotonic or iso-osmotic solutions:** Two solutions of different substances having same osmotic pressure at same temperature are known as isotonic solutions.

  For isotonic solutions, $\pi_1 = \pi_2$ Primary Condition . . .(*i*)

  Also, $C_1 = C_2$

  $$\left.\begin{array}{l} \text{or} \quad \dfrac{n_1}{V_1} = \dfrac{n_2}{V_2} \\ \text{or} \quad \dfrac{w_1}{m_1V_1} = \dfrac{w_2}{m_2V_2} \end{array}\right\} \text{Secondary Conditions} \qquad ...(ii)$$

  Equation (*ii*) holds good only for those solutes which neither possess the tendency to get associate nor dissociate in solution, *e.g.,*

  Urea and glucose are isotonic then, $\pi_1 = \pi_2$ and $C_1 = C_2$

  Urea and $\underset{\text{(dissociate)}}{\text{NaCl}}$ are isotonic then, $\pi_1 = \pi_2$ but $C_1 \neq C_2$

  Urea and $\underset{\text{(associate)}}{\text{Benzoic acid}}$ are isotonic then, $\pi_1 = \pi_2$ but $C_1 \neq C_2$

- **Hypertonic and Hypotonic Solution:** The solution which has more osmotic pressure than the other solution is called as hypertonic solution and the solution which has lesser osmotic pressure than the other is called as hypotonic solution. The flow of solvent is always from lower osmotic pressure to higher osmotic pressure *i.e.* from hypotonic to hypertonic solution.

Ebullioscopy: Elevation in boiling point is determined by Landsberger's method and Cottrell's method. Study of elevation in boiling point of a liquid in which a non-volatile solute is dissolved is called as ebullioscopy.

Boiling point of a liquid may be defined as the temperature at which its vapour pressure becomes equal to atmospheric pressure, i.e., 760 mm. Since the addition of a non-volatile solute lowers the vapour pressure of the solvent, solution always has lower vapour pressure than the solvent and hence it must be heated to a higher temperature to make its vapour pressure equal to atmospheric pressure with the result the solution boils at a higher temperature than the pure solvent. Thus sea water boils at a higher temperature than distilled water. If T_b is the boiling point of the solvent and T is the boiling point of the solution, the difference in the boiling point $(\Delta T$ or (ΔT_b) is called the elevation of boiling point.

$$T - T_b = \Delta T_b \text{ or } \Delta T$$

Important Relations Concerning Elevation in Boiling Point

- The elevation of boiling point is directly proportional to the lowering of vapour pressure, *i.e.,* $\Delta T_b \propto p^0 - p$
- $\Delta T_b = K_b \times m$

  Where, K_b= molal elevation constant or ebullioscopic constant of the solvent; m = Molality of the solution, i.e., number of moles of solute per 1000 g of the solvent; $\Delta T_b =$ Elevation in boiling point.
- $\Delta T_b = \dfrac{1000 \times K_b \times w}{m \times W}$ or $m = \dfrac{1000 \times K_b \times w}{\Delta T_b \times W}$

  Where, K_b is molal elevation constant and defined as the elevation in b.pt. produced when 1 mole of the solute is dissolved in 1 kg of the solvent. W and w are the weights of solute and solvent and m is the molecular weight of the solute.
- $K_b = \dfrac{0.002(T_0)^2}{l_V}$

  Where T_0= Normal boiling point of the pure solvent; l_v= Latent heat of evaporation in cal/g of pure solvent; K_b for water is $0.52 \text{ deg}-\text{kg mol}^{-1}$.

Cryoscopy: Depression in freezing point is determined by Beckmann's method and Rast's camphor method. Study of depression in freezing point of a liquid in which a non-volatile solute is dissolved in it is called as cryoscopy.

Freezing point is the temperature at which the liquid and the solid states of a substance are in equilibrium with each other or it may be defined as the temperature at which the liquid and the solid states of a substance have the same vapour pressure. It is observed that the freezing point of a solution is always less than the freezing point of the pure solvent. Thus, the freezing point of sea water is low than that of pure water. The depression in freezing point $(\Delta T$ or $\Delta T_f)$ of a solvent is the difference in the freezing point of the pure solvent (T_s) and the solution $(T_{sol.})$.

$$T_s - T_{sol} = \Delta T_f \text{ or } \Delta T$$

$NaCl$ or $CaCl_2$ (anhydrous) are used to clear snow on roads. They depress the freezing point of water and thus reduce the temperature of the formation of ice.

Important Relations Concerning Depression in Freezing Point

- Depression in freezing point is directly proportional to the lowering of vapour pressure. $\Delta T_f \propto p^0 - p$
- $\Delta T_f = K_f \times m$

  Where $K_f =$ molal depression constant or cryoscopic constant; $m =$ Molality of the solution (i.e., no. of moles of solute per $1000g$ of the solvent); $\Delta T_f =$ Depression in freezing point.
- $\Delta T_f = \dfrac{1000 \times K_f \times w}{m \times W}$ or $m = \dfrac{1000 \times K_f \times w}{\Delta T_f \times W}$

  Where K_f is molal depression constant and defined as the depression in freezing point produced when 1 mole of the solute is dissolved in 1 kg of the solvent. W and w are the weights of solute and solvent and m is the molecular weight of the solute.
- $K_f = \dfrac{R(T_0)^2}{l_f 1000} = \dfrac{0.002(T_0)^2}{l_f}$

  Where, $T_0 =$ Normal freezing point of the solvent; $l_f =$ Latent heat of fusion/g of solvent; K_f for water is $1.86 \text{ deg}-\text{kg mol}^{-1}$

Colligative Properties of Electrolytes: The colligative properties of solutions, viz. lowering of vapour pressure, osmotic pressure, elevation in b.p. and depression in freezing point, depend on the total number of solute particles present in solution. Since the electrolytes ionise and give more than one particle per formula unit in solution, the colligative effect of an electrolyte solution is always greater than that of a non-electrolyte of the same molar concentration. All colligative properties are used for calculating molecular masses of non-volatile solutes. However osmotic pressure is the best colligative property for determining molecular mass of a non-volatile substance.

Van't Hoff's Factor (*i*): In 1886, Van't Hoff introduced a factor '*i*' called Van't Hoff's factor, to express the extent of association or dissociation of solutes in solution. It is ratio of the normal and observed molecular masses of the solute*, i.e.,*

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

In case of association, observed molecular mass being more than the normal, the factor *i* has a value less than 1. But in case of dissociation, the Van't Hoff's factor is more than 1 because the observed molecular mass has a lesser value than the normal molecular mass. In case there is no dissociation the value of '*i*' becomes equal to one.

Since, colligative properties are inversely proportional to molecular masses, the Van't Hoff's factor may also be written as,

$$i = \frac{\text{Observed value of colligative property}}{\text{Calculated value of colligative property assuming no association or dissociation}}$$

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

Introduction of the Van't Hoff factor modifies the equations for the colligative properties as follows,

Relative lowering of vapour pressure $= \frac{P_A^o - P_A}{P_A^o} = iX_B$

Elevation of boiling point, $\Delta T_b = ik_b m$

Depression in freezing point, $\Delta T_b = ik_f m$

Osmotic pressure, $\pi = \frac{inRT}{V}; \pi = iCRT$

From the value of '*i*', it is possible to calculate degree of dissociation or degree of association of substance.

Degree of Dissociation (α)

It is defined as the fraction of total molecules which dissociate into simpler molecules or ions.

$\alpha = \frac{i-1}{m-1}1$ m = number of particles in solution

Degree of Association (α): It is defined as the fraction of the total number of molecules which associate or combine together resulting in the formation of bigger molecules.

$\alpha = \frac{i-1}{1/m-1}$; m = number of particles in solution.

Multiple Choice Questions

1. **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 K kg mol^{-1})**

   (a) 724 (b) 740
   (c) 736 (d) 718

2. **The vapour pressure of acetone at 20ºC is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20ºC, its vapour pressure was 183 torr. The molar mass (g mol^{-1}) of the substance is:**

   (a) 32 (b) 64
   (c) 128 (d) 488

3. **18 g glucose ($C_6H_{12}P_6$) is added to 178.2 g water. The vapor pressure of water (in torr) for this aqueous solution is :**

   (a) 7.6 (b) 76.0
   (c) 752.4 (d) 759.0

4. **Mixture(s) showing positive deviation from Raoult's law at 35ºC is(are):**

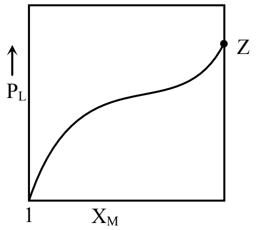
   (a) carbon, tetrahedral + methanol
   (b) carbon disulphide + acetone
   (c) benzene + toluene
   (d) phenol + aniline

5. **The freezing point of benzene decreases by 0.45°C when 0.2 g of acetic acid is added to 20 g of benzene. If acetic acid associates to form a dimer in benzene, percentage association of acetic acid in benzene will be: (for benzene = 5.12 K kg)**

   (a) 94.6% (b) 64.6%
   (c) 80.4% (d) 74.6%

6. **For a solution formed by mixing liquids L and M. the vapour pressure of L plotted against the mole fraction of M in solution is shown in the following figure. Here**

X_L and X_M represent mole fractions of L and M, respectively, in the solution. The correct statement(s) applicable to this system is(are):



(a) Attractive intermolecular interactions between L – L. in pure liquid L and M – M in pure liquid M are stronger than those between L – M when mixed in solution

(b) The point Z represents vapour pressure of pure liquid M and Raoult's law is obeyed when $x_L \longrightarrow 0$

(c) The point Z represents vapour pressure of pure liquid *M* and Raoult's law is obeyed from $x_L \longrightarrow 0$ to $x_L \longrightarrow 1$

(d) The point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L \longrightarrow 1$

7. **For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point?**

(a) $[Co(H_2O)_3Cl_3].3H_2O$ (b) $[Co(H_2O)_6]Cl_3$

(c) $[Co(H_2O)_5Cl]Cl_2.H_2O$ (d) $[Co(H_2O)_4Cl_2]Cl.2H_2O$

8. **An aqueous solution contains an unknown concentration of Ba^{2+}. When 50 mL of a 1 M solution of Na_2SO_4 is added, $BaSO_4$ just begins to precipitate. The final volume is 500 mL. The solubility product of $BaSO_4$ is 1×10^{-10}. What is original concentration of Ba^{2+}?**

(a) 1×10^{-10} M (b) 5×10^{-9} M

(c) 2×10^{-9} M (d) 1.1×10^{-9} M

9. **When metal 'M' is treated with NaOH, a white gelatinous precipitate 'X' is obtained, which is soluble in excess of NaOH. Compound 'X' when heated strongly gives an oxide which is used in chromatography as an adsorbent. The metal 'M' is:**

(a) Fe (b) Zn (c) Ca (d) Al

10. **An aqueous solution contains 0.10 M $H_2S$and 0.20 M HCl. If the equilibrium constant for the formation of HS^- is 1.0×10^{-7} and that of S^{2-} from HS^- ions is 1.2×10^{-13} then the concentration of S^{2-} ions in aqueous solution is:**

(a) 5×10^{-19} (b) 5×10^{-8}

(c) 3×10^{-20} (d) 6×10^{-21}

11. **The vapour pressures of pure liquids A and B are 400 and 600 mmHg, respectively at 298 K. On mixing the two liquids, the sum of their initial volumes is equal to the volume of the final mixture. The mole fraction of liquid B is 0.5 in the mixture. The vapour pressure of the final solution, the mole fraction of components A and B in vapour phase, respectively are:**

(a) 500 mmHg, 0.5, 0.5

(b) 450 mmHg, 0.4, 0.6

(c) 450 mmHg, 0.5, 0.5

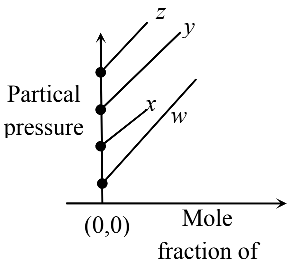
(d) 500 mmHg, 0.4, 0.6

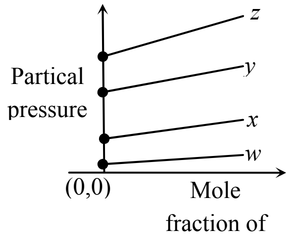
12. **If solubility product of $Zr_3(PO_4)_4$ is denoted by K_{sp} and its molar solubility is denoted by S, then which of the following relation between S and K_{sp} is correct.**

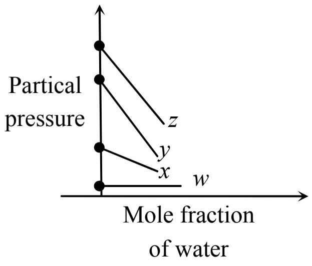
(a) $S=\left(\frac{K_{sp}}{929}\right)^{1/9}$ (b) $S=\left(\frac{K_{sp}}{216}\right)^{1/7}$

(c) $S=\left(\frac{K_{sp}}{144}\right)^{1/6}$ (d) $S=\left(\frac{K_{sp}}{6912}\right)^{1/7}$

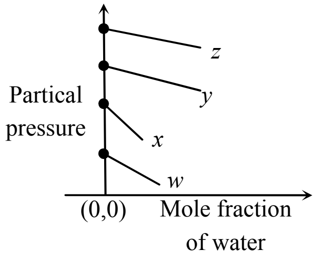
13. **For the solution of the gases w, x, y and z in water at 298K, the Henry's law constants (KH) are 0.5, 2, 35 and 40 kbar, respectively. The correct plot for the given data is:**

(a)


(b)


(c)


(d)



14. Which one of the following statements regarding Henry's law not correct?

(a) The value of K_H increases with function of the nature of the gas.

(b) Higher the value of K_H at a given pressure, higher is the solubility of the gas in the liquids.

(c) The partial of the gas in vapour phase is proportional to the mole fraction of the gas in the solution.

(d) Different gases have different K_H (Henry's law constant) values at the same temperature.

15. A solution of sodium sulfate contains 92 g of Na^+ ions per kilogram of water, the molality of Na^+ ions in that solution in mol kg^{-1} is:

(a) 16 (b) 8

(c) 4 (d) 12

16. Liquids A and B form an ideal solution in the entire composition range. At 350 K, the vapor pressures of pure A and pure B are 7×10^3 Pa and 12×10^3 Pa, respectively. The composition of the vapor in equilibrium with a solution containing 40 mole percent of A at this temperature is:

(a) $x_A = 0.37; x_B = 0.63$ (b) $x_A = 0.28; x_B = 0.72$

(c) $x_A = 0.76; x_B = 0.24$ (d) $x_A = 0.4; x_B = 0.6$

17. The amount of sugar ($C_{12}H_{22}O_{11}$) required to prepare 2 L of its 0.1 M aqueous solution is:

(a) 68.4 g (b) 17.1 g

(c) 34.2 g (d) 136.8 g

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

(a) $K_b = 0.5\ K_f$ (b) $K_b = 2\ K_f$

(c) $K_b = 1.5\ K_f$ (d) $K_b = K_f$

19. The concentration of dissolved oxygen (DO) in cold water can go upto:

(a) 10 ppm (b) 14 ppm

(c) 16 ppm (d) 8 ppm

20. 8g of NaOH is dissolved in 18g of H_2O. Mole fraction of NaOH in solution and molality (in mol kg^{-1}) of the solutions respectively are:

(a) 0.167, 11.11 (b) 0.2, 22.20

(c) 0.2, 11.11 (d) 0.167,22.20

21. If K_{sp} of Ag_2CO_3 is 8×10^{-12}, the molar solubility of Ag_2CO_3 in 0.1M $AgNO_3$ is :

(a) 8×10^{-12} M (b) 8×10^{-10} M

(c) 8×10^{-11} M (d) 8×10^{-13} M

Paragraph for Question Nos. 22 to 23

The electrochemical cell shown below is a concentration cell. $M|M^2$+ (saturated solution of sparingly soluble salt, MX_2)$|M^{2+}$(0.001 mol dm^{-3})|M The emf of the cell depends on the difference in concentration of M^{2+} ions at the two electrodes. The emf of the cell at 298 K is 0.059 V.

22. The value of ΔG (kJ mol^{-1}) for the given cell is (take 1 F = 96500 C mol^{-1})

(a) –5.7 (b) 5.7

(c) 11.4 (d) –11.4

23. The solubility product (K_{sp}; $mol^3\ dm^{-9}$) of at 298 K based on the information available for the given concentration cell is (take 2.303 × R × 298/F = 0.059 V)

(a) 1×10^{-15} (b) 4×10^{-15}

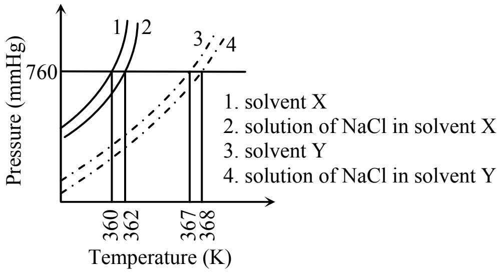
(c) 1×10^{-12} (d) 4×10^{-12}

24. A compound H_2X with molar weight of 80 g 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:

25. The mole fraction of a solute in a solution is 0.1. At 298 K, molarity of this solution is the same as its molality. Density of this solution at 298 K is 2.0 g cm^{-3}. The ratio of the molecular weights of the solute and solvent, $\frac{MW_{solute}}{MW_{solvent}}$, is:

26. Liquids A and B form ideal solution over the entire range of composition. At temperature T, equimolar binary solution of liquids A and B has vapour pressure 45 Torr. At the same temperature, a new solution of A and B having mole fractions x_A and x_B, respectively, has vapour pressure of 22.5 Torr. The value of x_A/x_B in the new solution is ___. (given that the vapour pressure of pure liquid A is 20 Torr at temperature T)

27. The plot given below shows P – T curves (where P is the pressure and T is the temperature) for two solvents X and Y and isomolal solutions of NaCl in these solvents. NaCl completely dissociates in both the solvents.



On addition of equal number of moles of a non-volatile solute S in equal amount (in kg) of these solvents, the elevation of boiling point of solvent X is three times that of solvent Y. Solute S is known to undergo dimerization in these solvents. If the degree of dimerization is 0.7 in solvent Y, the degree of dimerization in solvent X is _____.

28. Mole fraction of urea in 900 gram water is 0.05. Density of solution is 1.2 g/cm^3. Find molarity of solution.

ANSWERS and SOLUTIONS

1. (a) $\Delta T_L = k_b \times m = k_b \times \frac{W_s}{M_s \times W_{solution}}$

$$2 = 0.76 \times \frac{2.5 \times 1000}{M_s \times 100}$$

$$M_s = \frac{0.76 \times 2.5 \times 1000}{100 \times 2} = 9.5$$

$$\frac{760 - x}{760} = X_s = \frac{n_s}{n_{solution}}$$

$$= \frac{\frac{W_s}{W_s}}{\frac{W_{solv}}{M_{solv}}} = \frac{2.5 \times 18}{9.5 \times 100} = 36.0$$

$$x = 760 - 36 = 724$$

2. (b) $\frac{P^0 - P}{P^0} = X_{solute} = \frac{n_1}{n_1 + n_2}$

$$\frac{185 - 183}{185} = \frac{2}{185} = \frac{1.2/M}{\frac{1.2}{M} + \frac{100}{58}}$$

$\Rightarrow$ $M = 64$

3. (c or Bonus) Moles of glucose = $\frac{18}{180} = 0.1$

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

$\Rightarrow$ $n_{Total} = 10$

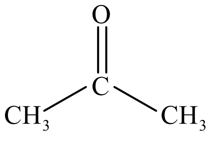
$\Rightarrow$ $\frac{\Delta P}{P^\circ} = \frac{0.1}{10}$

$\Rightarrow$ $\Delta P = 0.01 P^\circ$

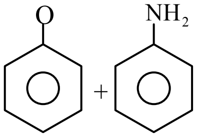
$= 0.01 \times 760 = 7.6$ torr

$P_S = 760 - 7.6 = 752.4$ torr

4. (a, b)(a) $CCl_4 + CH_3OH \Rightarrow$ Positive deviation from Raoult's law

(b) $CS_2 +$  $\Rightarrow$ Positive deviation from Raoult's law

(c) $C_6H_6 + C_7H_8 \Rightarrow$ Ideal solution

(d) 

$\Rightarrow$ Negative deviation from Raoult's law.

5. (a) In benzene $2CH_3COOH \quad (CH_3COOH)_2$

$i = 1 + \left(\frac{1}{2} - 1\right)\alpha \quad i = 1 - \frac{\alpha}{1}$ here, α is a degree of association

$\Delta T_f = iK_f m \qquad 0.45 = \left(1 - \frac{\alpha}{2}\right)(5.12)\frac{(0.2/60)}{20/100}$

$1 - \frac{\alpha}{2} = 0.527$

$\Rightarrow$ α=0.945% degree of association = 94.5%

6. (a, d) Attractive intermolecular interactions between L – L. in pure liquid L and M – M in pure liquid M are stronger than those between L – M when mixed in solution. The point Z represents vapour pressure of pure liquid L and Raoult's law is obeyed when $x_L \rightarrow 1$.

7. (a) The solution which shows maximum freezing point must have minimum number of solute particles.

(a) $[Co(H_2O)_3Cl_3].3H_2O \longrightarrow [Co(H_2O)_3Cl_3] i = 1$

(b) $[Co(H_2O)_6]Cl_3 \longrightarrow [Co(H_2O)_6]^{3+} + 3Cl^-, i = 4$

(c) $[Co(H_2O)_5Cl]Cl_2.H_2O \longrightarrow [Co(H_2O)_5Cl]^{2+} + 2Cl^-,\ i = 3$

(d) $[Co(H_2O)_4Cl_2]Cl.2H_2O \longrightarrow [Co(H_2O)_5Cl]^+ + Cl^-,\ i = 2$

So, Solution of 1 molal $[Co(H_2O)_3Cl_3].3H_2O$

will have minimum number of particles in aqueous state. Hence, option (a) is correct.

8. (d) Final concentration of $[SO_4^{--}]$

$$= \frac{[50 \times 1]}{[500]} = 0.1M$$

K_{sp} of $BaSO_4$, $[Ba^{2+}][so_4^{2-}] = 1 \times 10^{-10}$

$$[Ba^{2+}][0.1] = \frac{10^{-10}}{0.1} = 10^{-9} M$$

Concentration of Ba^{2+} in final solution

$= 10^{-9}$M Concentration of Ba^{2+} in the original solution.

$M_1V_1 = M_2V_2$

$M_1 (500 - 50) = 10^{-9}(500)$

$M_1 = 1.11 \times 10^{-9}$ M

So, option (d) correct

9. (d) $Al^{3+} \xrightarrow{NaOH} \underset{\text{White gelatinous ppt.}}{Al(OH)_3 \downarrow} \xrightarrow{\text{Excess NaOH}} \underset{\text{Sodium meta aluminate (soluble)}}{NaAlO_2}$

$$2Al(OH)_3 \xrightarrow{\text{Strong heating}} Al_2O_3 + 3H_2O$$

Al_2O_3 is used in column chromatography.

10. (c) In presence of external H^+

$H_2S \quad 2H \quad S^2 \ , K_{a_1}, K_{a_2} \quad K_{eq}$

$$\therefore \quad \frac{[H^+]^2[S^{2-}]}{H_2S} = 1 \times 10^{-7} \times 1.2 \times 10^{-13}$$

$$\frac{[0.2]^2[S^{2-}]}{[0.1]} = 1.2 \times 10^{-20}$$

$[S^{2-}] = 3 \times 10^{-20}$

11. (d) $P_{total} = X_A.P_A^0 = X_B.P_B^0 = 0.5 \times 400 + 0.5 \times 600$

$= 500$ mmHg

Now, mole fraction of A in vapour,

$$Y_A = \frac{P_A}{P_{total}} = \frac{0.5 \times 400}{500} = 0.4$$

and mole fraction of B in vapour,

$Y_B = 1 - 0.4 = 0.6$

12. (d) $Zr_3(PO_4)_4(s) \qquad \underset{3S\ M}{3Zr^{4+}(aq.)} + \underset{4S\ M}{4\ PO_4^{3-}(aq.)}$

$$K_{sp} = [Zr^{4+}]^3\ [PO_4^{3-}]^4 = (3S)^3.(4S)^4 = 6912\ S^7$$

$$\therefore \quad S = \left(\frac{K_{sp}}{6912}\right)^{1/7}$$

13. (c) $P = k_H \times \left(\frac{n_{gas}}{n_{H_2O} + n_{gas}}\right)$

$$= k_H \times \left(1 - \frac{n_{H_2O}}{n_{H_2O} + n_{gas}}\right)$$

$\Rightarrow \quad p = k_H - k_H \times \chi_{H_2O}$

$p = (-k_H) \times \chi_{H_2O} + k_H$

14. (b) Liquid solution

$P_{gas} = KH \times X_{gas}$

More is K_H less is solubility, lesser solubility is at higher temperature. So more is temperature more is K_H.

15. (d) $n_{Na} = \frac{92}{23} = 4$

So, molality = 4

16. (b) $x_A = \frac{P_A}{P_{Tolal}} = \frac{P_A^O X_A}{P_A^O X_A \times P_B^O X_B}$

$$= \frac{7 \times 10^3 \times 0.4}{7 \times 10^3 \times 0.4 + 12 \times 10^3 \times 0.6}$$

$$= \frac{2.8}{10} = 0.28 \Rightarrow x_B = 0.72$$

17. (a) $\text{Molarity} = \frac{(n)_{solute}}{V_{solution}(\text{in lit})}$

$$0.1 = \frac{wt/342}{2}$$

wt ($C_{12}H_{22}O_{11}$) = 68.4 gram

18. (b) $\frac{\Delta T_b}{\Delta T_f} = \frac{i.m \times k_b}{i \times m \times k_f}$

$\frac{2}{2} = \frac{1 \times 1 \times k_b}{1 \times 2 \times k_f}$ $K_b = 2\ K_f$

19. (a) In cold water, dissolved oxygen (DO) can reach a concentration up to 10 ppm.

20. (a) 8g NaOH, mol of NaOH

$$= \frac{8}{40} = 0.2\text{mol}$$

18g H_2O, mol of $H_2O = \frac{18}{18} = 1$mol

$$\therefore \quad X_{NaOH} = \frac{0.2}{1.2} = 0.167$$

$$\text{Molality} = \frac{0.2 \times 1000}{18} = 11.11\ m$$

21. (b) $Ag_2CO_3\ (s) \qquad \underset{(0.1+2S)M}{2Ag^+}\ (aq.) + \underset{M\,S}{CO_3^{-2}}\ (aq)$

$K_{sp} = [Ag^+]^2[CO_3^{-2}]$

$8 \times 10^{-12} = (0.1 + 2S)^2\ (S)$

$S = 8 \times 10^{-10}$ M

22. (d) $\Delta G = -nFE_{cell}$

$= -2\times 96500 \times 0.059$

$= -11.387\ \text{kJ mol}^{-1}$

$= -11.4\ \text{kJ}$

23. (b) $E = \dfrac{-0.0591}{2}\log_{10}\dfrac{C}{10^{-3}}$

$$0.059 = \frac{-0.0591}{2}\log_{10}\left(\frac{C}{10^{-3}}\right)$$

$$10^{-2} = \frac{C}{10^{-3}} \Rightarrow C = [M^{2+}] = 10^{-5}\,M.$$

$$K_{sp} = [M^{+2}][X^-]^2 = 4s^3 = 4(40^{-5})^3 = 4\times 10^{-15}$$

24. Here, $V_{solution} \approx V_{solvent}$

Since, in 1 solution, 3.2 moles of solute are present,

So, 1 solution $\approx$ 1 solvent

$(d = 0.4\,g/ml) \approx 0.4\ kg$

$$\text{So, molality(m)} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{3.2}{0.4} = 8$$

25. $$\text{Molality (m)} = \frac{x_{solute}\times 1000}{X_{solvent}\times M_{solvent}} = \frac{0.1\times 1000}{0.9\times M_{solvent}}$$

$$\text{Molarity (M)} = \frac{0.1\times 2\times 1000}{0.1\,M_{solute} + 0.9\,M_{solvent}}$$

As Molality = Molarity,

So $$\frac{0.1\times 1000}{0.9\times M_{solvent}} = \frac{0.1\times 2\times 1000}{0.1\,M_{solute} + 0.9\,M_{solvent}}$$

So $0.1\,M_{solute} + 0.9\,M_{solvent}$

$= 1.8\,M_{solvent}$.

So $\dfrac{M_{solute}}{M_{solvent}} = 9$

So, Answer is = 9

26. $P_A^\circ = 20\,\text{Torr}$

For equimolar binary solution:

$$x_A = x_B = \frac{1}{2}$$

$\therefore$ $\dfrac{P_A^\circ + P_B^\circ}{2} = 45$

$\Rightarrow$ $P_B^\circ = 70\,\text{Torr}$

If mole fractions are x_A & x_B

$P_B^\circ + (P_A^\circ - P_B^\circ)x_A = 22.5$

$\Rightarrow$ $70 + (20-70)x_A = 22.5$

$\Rightarrow$ $x_A = \dfrac{47.5}{50}$ and $x_B = \dfrac{2.5}{50}$

$$\frac{x_A}{x_B} = \frac{47.5}{2.5} = 19.00$$

27. When, NaCl as solute is used

For solvent X	For solvent Y
$2 = 2K_b m$	$1 = 2\times K'_b\, m$

$\therefore$ $\dfrac{K_b}{K'_b} = 2$

When solute S is used then molality in both solvent is equal.

For solvent X	For solvent Y
$i = 1 - \dfrac{\alpha}{2}$	$i = 1 - \dfrac{0.7}{2} = 0.65$
$\Delta T_b = \left(1-\dfrac{\alpha}{2}\right)K_b m$	$\Delta T'_b = (0.65)K'_b\, m$

$$3 = \frac{\Delta T_b}{\Delta T'_b} = \frac{\left(1-\frac{\alpha}{2}\right)\times 2}{0.65}$$

$$1 - \frac{\alpha}{2} = \frac{3}{2}\times 0.65$$

$$\frac{\alpha}{2} = 1 - \frac{3}{2}\times 0.65$$

$\alpha = 0.05$

28. **(3)** $wt_{H_2O} = 900g$

$\Rightarrow$ $n_{H_2O} = \dfrac{900}{18} = 50$

Let moles of urea = y

$\Rightarrow$ $x_{urea} = \dfrac{y}{y+50} = 0.05 \Rightarrow y = \dfrac{50}{19}$

$\therefore$ $Wt_{urea} = \left(\dfrac{50}{19}\right)\times 60 = \dfrac{3000}{19}$

$\therefore$ $Wt_{solution} = \dfrac{3000}{19} = 900 = \dfrac{(201)}{19}\times 100$

$\rho_{solution} = 1.2\,g/cm^3$

$\Rightarrow$ $V_{solution} = \dfrac{wt}{\rho} = \left(\dfrac{201}{19}\right)\times\dfrac{100}{1.2}$

$$\Rightarrow\ M_{urea} = \frac{n_{urea}}{V_{ml}}\times 1000 = \frac{\left(\frac{50}{19}\right)\times 1000}{\left(\frac{201}{19}\right)\times\frac{100}{1.2}}$$

$$\frac{(500)(1.2)}{201}\quad \frac{600}{201}\quad 2.985$$

Answer after truncation = 2.98