Class XII

CHEMISTRY

SOLUTIONS (CHAPTER-2)

Solution – A homogeneous mixture of two or more substances mixed in varied proportions.

Solution = Solute + Solvent

Binary solution contains one solute dissolved in a solvent

Ternary solution contains two solutes dissolved in a solvent.

Types of solutions:

Type of solution	Solute	Solvent	Example
Gaseous solutions	Gas	Gas	Mixture of O_2 and N_2 gases
	Liquid	Gas	Chloroform + N_2 gas
	Solid	Gas	Camphor in N_2 gas
Liquid solutions	Gas	Liquid	O_2 dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid solutions	Gas	Solid	Solution of H_2 in Palladium
	Liquid	Solid	Amalgam of Hg with Na
	Solid	Solid	Copper dissolved in Gold

Important Formulas:

1) **Molarity** = No. of moles of solute dissolved in 1 L of solution

   M = No. of moles of solute / Volume of solution in L

   $$M = \frac{w_B \times 1000}{M_B \times V_{solution}(mL)}$$

   Unit = M or Molar or moles/L

2) **Molality** = No. of moles of solute dissolved in 1 Kg of solvent

   M = No. of moles of solute / Weight of solvent in Kg

   $$M = \frac{w_B \times 1000}{M_B \times w_A\,(g)}$$

   Unit = m or Molal or moles/Kg

   ➤ Molality is preferred over molarity as molarity is temperature dependent term because volume of solution changes with temperature.

   ➤ Concentration of 1 M > 1 m because 1 Kg > 1 L

3) **Normality** = No. of gram equivalents of solute in 1 L of solution

   Gram equivalents = M.Mass / n-factor

   Where n-factor = acidity or basicity or no. of electrons

   $$N = \frac{w_B \times 1000 \times n\text{-}factor}{M_B \times V_{solution}(mL)}$$

4) **Mole fraction (χ)**: $X_A = \dfrac{\text{no. of moles of component A}}{\text{Total no. of moles}} = \dfrac{n_A}{n_A + n_B}$

   $X_A + X_B = 1$

5) **Mass percentage** = $\dfrac{\text{Given mass of component}}{\text{Total mass}} \times 100$

6) **Parts per million (ppm)** = $\dfrac{\text{No. of atoms of component}}{\text{Total no. of atoms}} \times 10^6$

   $= \dfrac{\text{Given mass of component}}{\text{Total mass}} \times 10^6$

Solubility: The maximum amount of solute that can be dissolved in 100gm of solvent.

Saturated solution: When no more solute can be added in the solvent.

1) **Solubility of solid in liquid**: Like dissolves like
   Such as NaCl + H$_2$O
   When solid is added to the solvent, concentration of solute increases and a stage is reached when an equilibrium is achieved where the number of solute particles going into the solution becomes equal to solute particles separating out.
   Solute + Solvent ↔ Solution (Dissolution)

   At this stage, solution is known as saturated solution.

   <u>Effect of temperature on solubility of solids in liquids:</u>

   Solubility usually increases with increase in temperature.

   As according to Le Chatelier's principle,
   solubility should increase with increase in temperature if dissolution process is mostly endothermic ($\Delta H > 0$)

   Solute + Solvent + E ↔ Solution

   While solubility should decrease with increase in temperature if dissolution process is exothermic ($\Delta H < 0$)

   Solute + Solvent ↔ Solution + E

   <u>Effect of pressure</u>: Pressure has no significant effect on solubility of solids in liquids because solids are incompressible.

2) **Solubility of gas in liquid**:

Oxygen is found in dissolved form in sea water, dry HCl gas is highly soluble in water.

Effect of temperature: As temperature increases, solubility of gases decreases in liquids because on increasing temperature, K.E. of molecules increases.
Q. Aquatic species are more comfortable in cold water or in warm water?

Effect of pressure:
Solubility of gases increase with increase in pressure.

Q. Why does gas fizz out from the bottle of aerated drinks when it is opened?
As pressure increases, there is increase in number of gaseous particles per unit volume over the solution due to which solubility increases until a new equilibrium is attained between gaseous particles and solution.

It is explained by **Henry's Law**, a quantitative relationship between Pressure and solubility of gas in a solvent.
Pressure of a gas is directly proportional to solubility of a gas.
i.e. $P \propto \chi$
$P = K_H \chi$ where K_H is known as Henry's constant.

$K_H = P / \chi$

Different gases have different K_H values at the same temperature. This suggests that K_H is a function of the nature of the gas.

Higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid.
K_H values at 293K: $N_2 > H_2 > O_2$.

Q. What should be the order for their solubilities?

Applications of Henry's Law:
a) To increase the solubility of CO_2 in soft drinks, bottles are sealed under high pressure.

b) At high altitudes, partial pressure of oxygen is less than that at normal level. This leads to less solubility of oxygen in blood and tissues of human. Hence, mountaineers should carry oxygen cylinders with them to avoid anoxia.

c) Scuba divers generally take tanks filled Helium (11.7%), Nitrogen (56.2%) and Oxygen (32.1%) to avoid a condition known as bends and toxic effects of bubbles of N_2.
Bend is a condition in the blood which is formed due to changing pressure condition which can block blood capillaries and could be harmful to life while coming out of deep water.

Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood.

When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life.

Related numericals E.g. 2.4, intext Q 2.6, 2.7

Vapour Pressure: It is a pressure exerted by vapours on the surface of liquid when rate of evaporation is equal to rate of condensation.

Evaporation ↔ Condensation

Effect on Vapour Pressure: When volatile solute is used, vapour pressure increases due to increase in the amount of vapours in the system and vice versa.

Raoult's Law: It gives a relationship between partial pressure of any component and its mole fraction.

Raoult's law for non-volatile solute: According to it, vapour pressure of any component is directly proportional to the product of pressure of pure component and its mole fraction.

$P_A \propto P^0_A X_A$

i.e. $P_A = P^0_A X_A$ & $P_B = P^0_B X_B.$

E.g. of non-volatile solute – NaCl, $CaCl_2$

Raoult's law for volatile solute: According to it, partial vapour pressure of any component is directly proportional to its mole fraction.

$P_A \propto X_A$ i.e. $P_A = P^0_A X_A$ & $P_B = P^0_B X_B.$
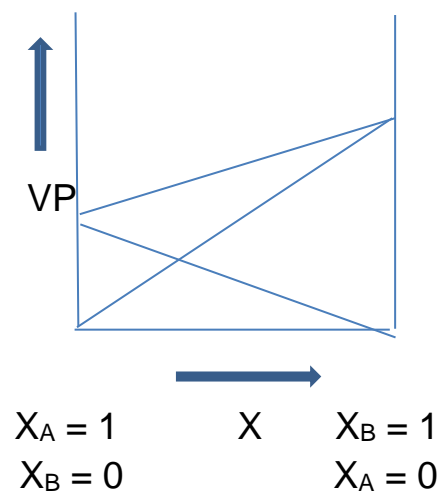
Derivation:

For ideal solutions

By Dalton's law of partial pressure, $P_{solution} = P_A + P_B = P^0_A X_A + P^0_B X_B$

$P_T = P^0_A (1 - X_B) + P^0_B X_B$

$P_T = P^0_A + X_B (P^0_B - P^0_A)$ ---(i)

& $P_T = P^0_A X_A + P^0_B (1 - X_A)$

$P_T = P^0_B + X_A (P^0_A - P^0_B)$ ---(ii)

$X_A = 1$ X $X_B = 1$
$X_B = 0$ $X_A = 0$

Raoult's law in vapour phase:

$P_A = P_{solution} . y_A$

Therefore,

mole fraction in vapour phase: $y_A = P_A / P_{solution}$ & $y_B = P_B / P_{solution}$

Raoult's law is a special case of Henry's law if $P^0_A = K_H$.

S. No.	Ideal Solution	Non-Ideal Solution
1	Solutions that obey Raoult's law	Solutions that do not obey Raoult's law
2	A-A & B-B interactions = A-B interactions	A-A & B-B interactions ≠ A-B interactions
3	Enthalpy Change, $\Delta H_{mixing} = 0$	$\Delta H_{mixing} \neq 0$
4	Volume Change, $\Delta V_{mixing} = 0$	$\Delta V_{mixing} \neq 0$
5	E.g. (a) Mixture of n-Hexane & n-Heptane; (b) Mixture of benzene & toluene; (c) Mixture of bromoethane & chloroethane.	E.g. (a) Mixture of Chloroform & acetone; (b) Mixture of alcohol & water.

Types of non-ideal solutions:

S.No.	Positive deviation	Negative deviation
1	$P_A > P^0_A X_A$	$P_A < P^0_A X_A$
2	A-A & B-B interactions > A-B interactions	A-A & B-B interactions < A-B interactions
3	Enthalpy Change, $\Delta H_{mixing} > 0$	Enthalpy Change, $\Delta H_{mixing} < 0$
4	Volume Change, $\Delta V_{mixing} > 0$	Volume Change, $\Delta V_{mixing} < 0$
5	They are minimum boiling azeotropes	They are maximum boiling azeotropes
6	E.g. (a) Mixture of Chloroform & CCl_4 ; (b) Mixture of alcohol & water.	E.g. (a) Mixture of Chloroform & acetone; (b) Mixture of nitric & water.

Azeotropes – Some liquids form azeotropes on mixing known as binary mixtures. They are the mixtures having same composition in liquid and vapour phase and boil at constant temperature.

| Ideal solution | Positive deviation | Negative deviation |
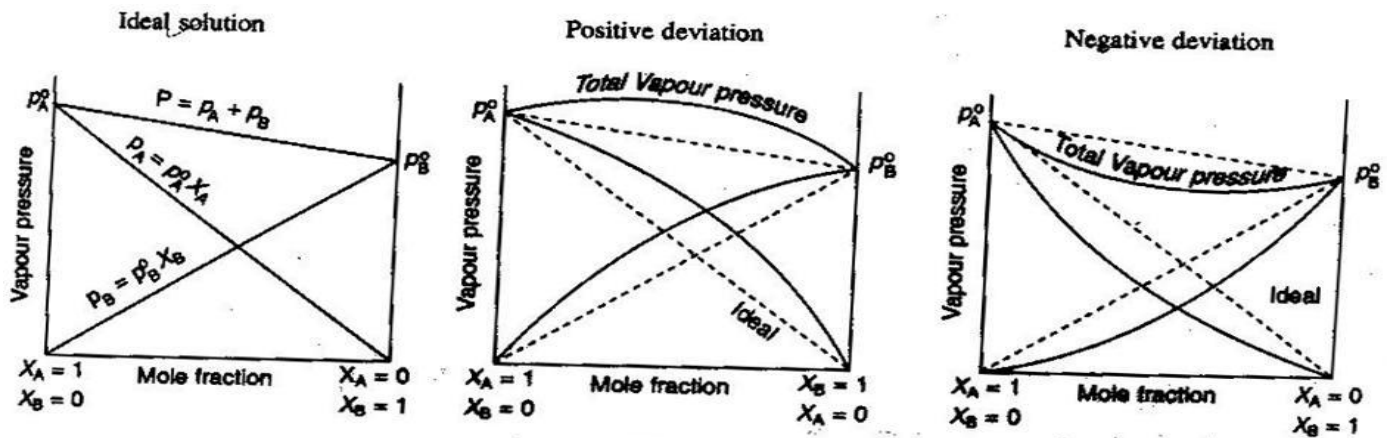
Colligative Properties: Those properties which depend on the number or amount of solute particles and do not depend upon the nature of particles.

1) **Relative lowering of vapour pressure**:

As amount of non-volatile solute increases, vapour pressure deceases. i.e.

$P^0_A > P_A$

$\Delta P = P^0_A - P_A = P^0_A - P^0_A X_A$

Lowering of Vapour Pressure $= P^0_A - P_A = P^0_A (1 - X_A)$

Relative lowering of vapour pressure $= \dfrac{P^0_A - P_A}{P^0_A} = 1 - X_A = X_B = \dfrac{n_B}{n_B + n_A}$

If $n_B << n_A$, then, $\dfrac{P^0_A - P_A}{P^0_A} = \dfrac{n_B}{n_A}$

$\dfrac{P^0_A - P_A}{P^0_A} = \dfrac{w_B \ X \ M_A}{M_B \ X \ w_A}$

2) **Elevation in boiling point**:

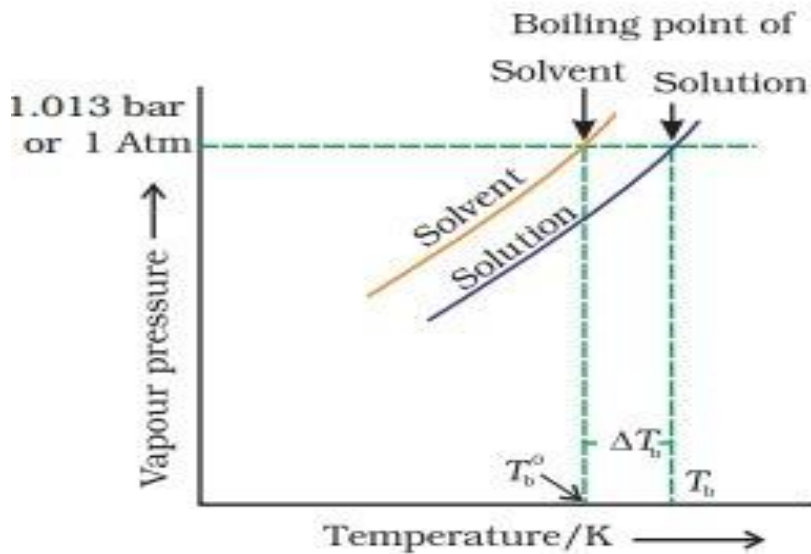On adding non-volatile solute, boiling point of solution increases.

$T_b > T^0_b$

$\Delta T_b = T_b - T^0_b$

& ΔT_b is directly proportional to molality of solution

Hence, $\Delta T_b = K_b \ m$

$\Delta T_b = \dfrac{K_b \ w_B \ X \ 1000}{M_B \ X \ w_A}$

Where K_b = Ebullioscopic constant or molal elevation constant. It is the elevation in boiling point of a solution having unit molality.
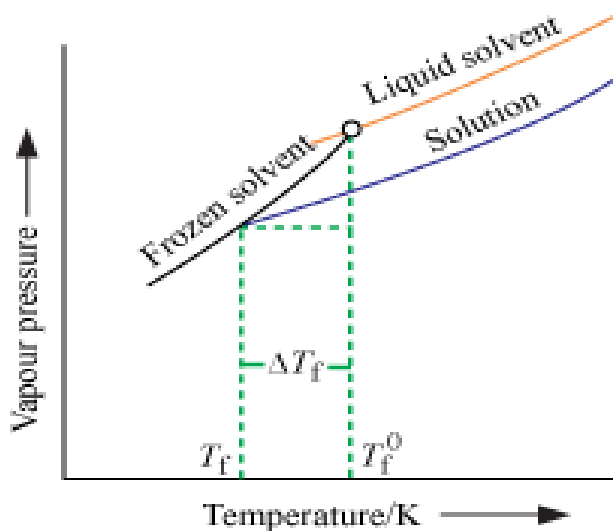
3) **Depression in freezing point**:

$T_f < T^0_f$

$\Delta T_b = T^0_f - T_f$

& ΔT_f is directly proportional to molality of solution

Hence, $\Delta T_f = K_f \cdot m$

$\Delta T_f = \dfrac{K_f \, w_B \times 1000}{M_B \times w_A}$

Where K_f = Cryoscopic constant or molal depression constant. It is the depression in freezing point of a solution having unit molality.

Note: Values of K_b and K_f for water are 0.52 KKg/mol and 1.86 KKg/mol respectively.

4) Osmotic Pressure:

Osmosis – The process of movement of solvent particles from high concentration to low concentration through semi permeable membrane such as pig bladder, cellophane paper, parchment paper, cellulose acetate.

Osmotic Pressure – It is the pressure exerted to stop the flow of solvent i.e. to stop osmosis.

Π α Concentration

$$\Pi = CRT = \frac{n_B \ RT}{V} = \frac{w_B RT}{M_B \ V}$$ where Concentration = moles/L

Value of R (universal Gas Constant) = 0.083 L bar mol^{-1} K^{-1}

Q. Which colligative property is preferred to determine the mass of macromolecules? Give reason.

Ans. Osmotic Pressure is preferred because it depends inversely on molar mass, so relatively small amount of pressure in suitable condition can be used to calculate molecular mass of a macromolecule. Also, pressure measurement is easy at room temperature and depends upon molarity.

Reverse Osmosis – The process of movement of solvent particles from low concentration to high concentration under the condition of exerted pressure is greater than π.

Application- Desalination of water.

Types of Solutions:

a) Isotonic solution – solution which has same π, as compared to surrounding. E.g. π of our blood = π of 0.9% NaCl solution.

b) Hypertonic solution – if the amount of solute is more in the solution than in the surroundings. So, when an animal cell or RBC is put into a hypertonic solution, then the cell will shrink, solvent will move out due to exosmosis.

c) Hypotonic solution – if the amount of solute is less in the solution than in the surroundings. So, when an animal cell or RBC is put into a hypotonic solution, then the cell will swell, solvent will move into the cell due to endosmosis.

Abnormal Molar Masses:

Calculate molar mass ≠ Experimental molar mass due to either Association or Dissociation of solute particles.
$KCl \leftrightarrow K^+ + Cl^-$ (i > 1)
Dimerization of acid $2 CH_3COOH \leftrightarrow (CH_3COOH)_2$ (i < 1)
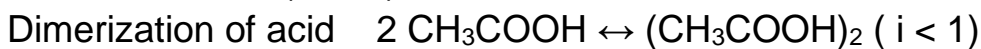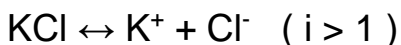
For the correction of the formulas of colligative properties:
Van't Hoff factor (i) = Normal molar mass / Abnormal molar mass
                = Observed colligative property / Calculated colligative property
= Total no. of moles after dissociation or association / total no. of moles initially

The extent to which a solute is dissociated or associated can be expressed by α.
Degree of dissociation (α) = (i – 1) / (n – 1)
where n = no. of moles formed after dissociation

Degree of association (α) = (1 – i) / (1 – 1/n)
Where n = no. of moles associated

Dissociation or Association constant (K_a) = $C\alpha^2$ / (1 – α)
Where C = concentration or molarity in moles/L

Corrected formulas:

a) $\dfrac{P^0_A - P_A}{P^0_A} = i\, X_B$

b) $\Delta T_b = i\, K_b\, m$

c) $\Delta T_f = i\, K_f\, m$

d) $\Pi = i\, CRT$

Note: Above mentioned formulas must be used in case of all compounds that can undergo dissociation or association even if it is not given in the question.

Value of 'i': (when no value of colligative property is given)

(a) Na_2SO_4 $i = 3$

(b) Tetramerization of an acid $i = \frac{1}{4}$

(c) $K_4[Fe(CN)_6]$ $i = 5$

(d) $Al_2(SO_4)_3$ $i = 5$

(e) Dimerization of an acid $i = \frac{1}{2}$

(f) $CaCl_2$ $i = 3$

(g) Polymerization $i = 1/n$.