

II PUC CHEMISTRY

SOLUTIONS

Solution is a single phase mixture of two more components. The component of solution present in excess and in the same state as the solution is called solvent and the other solute.

- **Solute and Solvent.** In a binary solution, the component present in smaller amount is called solute while the other present in larger amount is called solvent. If water is the solvent, solution is called aqueous solution.

Saturated Solution:

A solution that does not dissolve anymore of solute at the same temperature is called as saturated solution.

Particle size in solutions: In the solution, all the particles are of molecular size, i.e., upto 10^{-9} m in diameter and hence cannot be separated by filtration or centrifugation etc.

Aqueous and non-aqueous solutions: Solutions in water are called aqueous solutions and the solutions in which water is not the solvent are called non-aqueous solutions.

Types of solutions: Depending upon the physical state of the component, the solutions are classified into following different types:

S.No.	Solute	Solvent	Examples
Solid solutions			
1.	Solid	Solid	Alloys, e.g., brass (Cu + Zn), German silver, (Cu + Zn + Ni), bronze (Cu + Zn) etc.
2.	Liquid	Solid	Hydrated salts, Amalgam of Hg with Na
3.	Gas	Solid	Dissolved gases in mineral
Liquid solutions			
4.	Solid	Liquid	Salt/Sugar solution in water
5.	Liquid	Liquid	Alcohol in water
6.	Gas	Liquid	Aerated drinks, O ₂ in water
Gaseous solutions			
7.	Solid	Gas	Iodine vapour in air
8.	Liquid	Gas	Water vapour in air
9.	Gas	Gas	Air (O ₂ + N ₂)

Importance of Solutions: The use of a solution depends upon its composition, e.g.,

- (i) 1 part per million parts (1 ppm) of fluoride ions in water prevents tooth decay, 1.5 ppm causes teeth to become mottled (coloured) and still higher concentration acts as a poison for rats.
- (ii) Solutions of intravenous injections should have the same ionic concentration as that of blood plasma.

Concentration units and ways of expressions

Mass percentage

It may be defined as number of parts by mass of solute per hundred parts by mass of solution.

$$\text{Mass percentage} = \frac{\text{wt. of solute}}{\text{wt. of solution}} \times 100$$

Volume percentage

It may be defined as number of parts by volume of solute per hundred parts by volume of solution.

$$\text{Volume percentage} = \frac{\text{Volume of solute}}{\text{Volume of Solution}} \times 100$$

Molality

Molality of a solution is defined as the number of moles of solute dissolved in 1 Kg of the solvent.

$$m = \frac{\text{moles of solute}}{\text{weight of solvent (in kg)}}$$

Molarity

The molarity of a solution gives the number of gram molecules of the solute present in one litre of the solution. Thus, if one gram molecule of a solute is present in 1 litre of the solution, the concentration of the solution is said to be one molar.

$$M = \frac{\text{no. of moles of solute}}{\text{volume of solution in lit}}$$

Normality

The normality of a solution gives the number of gram equivalents of the solute present in one litre of the solution. Thus, if one gram equivalent of a solute is present in one litre of the solution, the concentration of the solution is said to be one normal.

$$N = \frac{\text{no. of gm equivalents of solute}}{\text{volume of solution (in lit)}}$$

Mole fraction

The mole fraction of any component in a solution is the ratio of the number of moles of that component to the total number of moles of all components present in the solution.

$$X_{\text{solute}} = \frac{N}{n + N} \text{ and}$$

$$X_{\text{solvent}} = \frac{n}{n + N}$$

n = moles of solute and N = moles of solvent.

Note: Sum of the mole fractions of all the components in the solution is equal to unity.

Relation between Mole fraction (X_2), Molarity (M) and Molality (m) is

$$\begin{aligned} \text{Mole fraction of solute } (X_2) &= \frac{\text{Molality} \times \text{Mol. mass of solvent}}{1 + \text{molality} \times \text{Mol. mass of solvent}} \\ &= \frac{\text{Molality} \times \text{Mol. mass of solvent}}{\text{Molarity} (\text{Mol. mass of solvent} - \text{Mol. mass of solute}) + d} \\ &= \frac{MM_1}{M(M_1 - M_2) + d} \end{aligned}$$

(where d is the density of solution in kg/L, M_2 = mol. mass of solute in kg mol^{-1} , M_1 = mol. mass of solvent in kg mol^{-1} and molality 'm' is in moles/kg of the solvent)

Relationships between molality (m), molarity (M) and density (d) of the solution

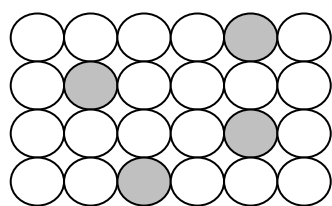
$$\begin{aligned} \text{Molality (m)} &= \frac{\text{Molarity}}{1000d - (\text{Molarity} \times \text{Mol.mass of solute})} \times 1000 \\ &= \frac{M}{1000d - MM_2} \times 1000 \text{ (where d is in } \text{g cm}^{-3} \text{ and } M_2 \text{ is the molar mass of solute in g} \\ &\text{mol}^{-1}\text{)} \end{aligned}$$

Solid solutions (Solutions of solids in solids):

These are those solutions in which both the components are solids. These are of two types.

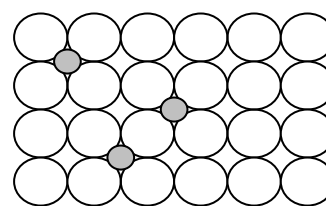
- (a) Substitutional solid solutions in which atoms, ions or molecules of one substance take the place of the other substance in the crystal lattice, e.g., brass (Cu + Zn), bronze (Cu + Zn + Sn), monel metal (Cu + Ni), steel (Fe + Cu or Ni or Mn) Etc.

- (b) Interstitial solid solutions in which atoms, ions or molecules of one substance enter into the voids or interstices of the host lattice, e.g., tungsten carbide, WC.



○ = Solvent ● = Solute

(a)



○ = Solvent ● = Solute

(b)

(a) Substitutional solid solution (b) Interstitial solid solution

Solutions of solids in liquids:

Solubility of ionic and non-ionic solids: Ionic solids like NaCl, KNO₃, CuSO₄ etc. dissolve in polar solvent like water whereas non-ionic (molecular) solids like iodine (I₂), naphthalene etc. dissolve in non-polar solvents like benzene, CCl₄ etc. Certain non-ionic compounds like glucose, sucrose (cane sugar), etc. dissolve in water due to hydrogen bonding.

Saturated, Unsaturated and Supersaturated solutions:

- (i) When in a solution, no more solute can be dissolved at a particular temperature, the solution is said to be saturated.
- (ii) When more solute can be dissolved in the given solution at a particular temperature, it is said to be unsaturated.
- (iii) When a solution contains more solute than the saturation point (due to superheating etc.) at a particular temperature, it is called supersaturated solution. It is metastable.

Solubility of solids in liquids: The solubility of a solid in a liquid at any temperature is defined as the maximum amount of the solid (solute) in grams which can dissolve in 100 g of the liquid (solvent) to form a saturated solution at that temperature.

Solubility in terms of lattice energy and hydration energy. The solubility of an ionic solid in a liquid depends upon 'Lattice energy' and 'Hydration energy'.

Lattice energy is the amount of energy required to dissociate one mole of an ionic crystal into its ions.

Hydration energy is the amount of energy released when one mole of ions undergo hydration.

If hydration energy > lattice energy, the solid dissolves otherwise not.

Effect of temperature on solubility: The dissolution can be exothermic or endothermic. The effect of temperature on solubility can be predicted by applying Le Chatelier's principle. For example,

- (i) NaNO_3 , KNO_3 , NaCl , KCl etc. dissolve with the absorption of heat, i.e., their dissolution is endothermic. Hence, their solubility increases with increase in temperature.
- (ii) Li_2CO_3 , $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3$ etc. dissolve with evolution of heat, i.e., their dissolution is exothermic. Their solubility decreases with increase in temperature.
- The plots of solubility versus temperature, called solubility curves, for the above cases are continuous. However, in some cases, e.g., $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ or NH_4NO_3 etc., the solubility curves are discontinuous. This is because at a particular temperature called **transition temperature**, one form of the crystalline solid changes into another form and at that point, the trend of solubility changes.

Solutions of Gases in liquids:

Solubility of a gas in a liquid: It is defined as the volume of the gas in cc's (converted to STP) that can dissolve in unit volume of the liquid to form a saturated solution at the temperature of the experiment and under one atmospheric pressure. The solubility of the gas in a liquid can also be expressed in the gas in a liquid can also be expressed in mol L^{-1} or in terms of mole fraction of the gas.

Factors affecting the solubility of a gas in a liquid:

- (i) **Nature of the gas and the solvent:** Gases like H_2 , O_2 , N_2 , etc. dissolve in water only to a small extent whereas gases like CO_2 , NH_3 , HCl , H_2S etc. are highly soluble in water. The greater solubility is again due to chemical similarity between the gas and the solvent.
- (ii) **Pressure (Henry's law):** **The solubility of a gas** (mass dissolved) in given volume of a liquid at a particular temperature is directly proportional to the pressure of the gas above the liquid. This is called **Henry's law**. Thus, $m \propto p$ or $m = k p$

where k is called Henry's constant

For a mixture of gases in equilibrium with a liquid, the solubility of any gas, expressed in terms of mole fraction (x_A) of that gas in the solution is directly proportional to its partial pressure, i.e.,

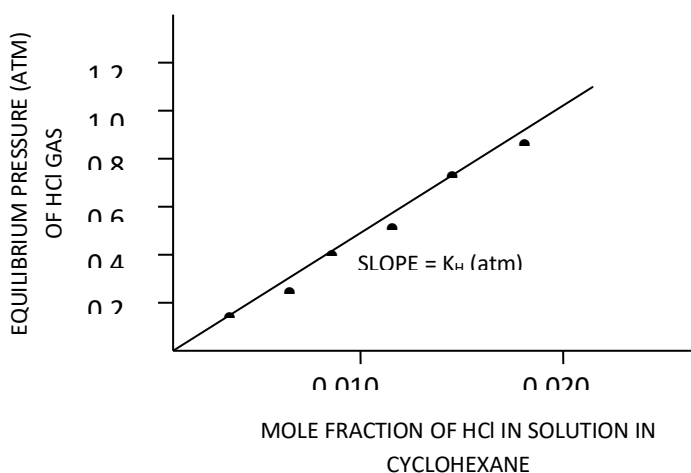
$$x_A = K_H p_A$$

(Units of $K_H = \text{atm}^{-1}$ or bar^{-1})

or it is written as $p_A = K_H x_A$

(Units of $K_H = \text{atm}$ or bar)

Thus, a plot of p_A versus x_A is a straight line passing through the origin with slope = K_H .



Henry's law constants for O₂ and N₂ in water:

Temp.	O ₂	N ₂
293 K	34.86 kbar	76.48 kbar
303 K	46.82 kbar	88.84 kbar

Thus,

- (a) K_H is a function of nature of the gas.
- (b) Greater the value of K_H, lower is the solubility at the same pressure
(as p_A = K_Hx_A).
- (c) K_H increases with increase of temperature implying that solubility decreases with increase of temperature at the same pressure.

(iii) Temperature: The solubility of a gas in a liquid decreases with increase of temperature.

Quantitatively, the effect of temperature on solubility is given by an equation similar

to van't Hoff equation as $\ln \frac{c_2}{c_1} = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

where c₁ and c₂ are concentrations of the solution at temperatures T₁ and T₂ respectively and ΔH is the heat of solution of 1 mole of the gas at the average temperature.

ΔG, ΔH and ΔS for solubility of a gas in a liquid:

ΔS = -ve (as gas in solution is less random)

ΔG = -ve (as process is spontaneous)

ΔH = -ve (as only then ΔG can be -ve according to the equation, ΔG = ΔH - TΔS)

Thus, dissolution of gas in water is always **exothermic**.

Applications of Henry's law:

- (i) In production of carbonated beverages: Under high pressure, solubility of CO₂ increases. On opening the bottle to atmospheric pressure, solubility decreases and the gas bubbles out.
- (ii) In deep sea diving: Compressed air cylinder is used to get more oxygen in the blood but N₂ dissolved causes a disease called decompression sickness. Hence, air diluted with helium is used.
- (iii) In the function of lungs: In the lungs, partial pressure of O₂ is high. It combines with haemoglobin to form oxyhaemoglobin. In the tissues, partial pressure of O₂ is low. Therefore, O₂ is released from oxyhaemoglobin for functions of the cells.
- (iv) For climbers or people living at high altitude: Concentration of O₂ in the blood and tissues is so low that they feel weak and are unable to think properly, a disease called anoxia.

Ideal and non-ideal solutions (of two liquids)

1. For an ideal solution ΔV_{mixing} = 0 and ΔH_{mixing} = 0

Ideal solution obeys 'Raoult's law of solution containing volatile solute'.

2. Raoult's law

Vapour pressure of any component in a solution is equal to the product of the mole fraction (x) of the component and its vapour pressure in the pure state, p^0 at the same temperature.

$$p = x p^0$$

Ideal solutions

1. In a solution let x_A and x_B be the mole fractions of the two components A and B. Let their vapour pressure in the pure state at the given temperature be p_A^0 and p_B^0 respectively. Then

$$p_A = p_A = x_A p_A^0 \text{ and } p_B = x_B p_B^0$$

2. From Raoult's law for an ideal solution, total vapour pressure

$$P = p_A + p_B = x_A p_A^0 + x_B p_B^0$$

Some examples for ideal solutions are

- (a) benzene and toluene
- (b) hexane and heptane
- (c) ethyl bromide and ethyl iodide
- (d) Bromobenzene and chlorobenzene

Non-ideal solution of two liquids

For non-ideal solutions $\Delta V_{\text{mixing}} \neq 0$ and $\Delta H_{\text{mixing}} \neq 0$

Further, non-ideal solutions do not obey Raoult's law.

$$\text{So, } P \neq x_A p_A^0 + x_B p_B^0$$

Types of non-ideal solutions

Solutions showing positive deviation from Raoult's law

1. $p_A > x_A p_A^0$ and $p_B > x_B p_B^0$. Hence $P > x_A p_A^0 + x_B p_B^0$

Examples

- (a) Ethanol + water
 - (b) Methanol + water
 - (c) Ethanol + acetone
 - (d) Benzene + acetone
2. (a) ΔV_{mixing} is positive and
(b) ΔH_{mixing} is positive

Solutions showing negative deviation from Raoult's law

1. $p_A < x_A p_A^0$ and $p_B < x_B p_B^0$. Hence $P < x_A p_A^0 + x_B p_B^0$.

Examples

- (a) HCl + water (b) HNO₃ + water
(c) chloroform + acetone (d) chloroform + benzene
(e) acetone + aniline
2. For solutions showing negative deviation
(a) ΔV_{mixing} is negative and
(b) ΔH_{mixing} is negative

Colligative properties

1. Colligative properties the values of which depend only on the number of solute particles present in the solution and not on its nature, size or chemical constitution.
2. Some of the colligative properties of dilute solutions are :
- Osmotic pressure
 - Lowering of vapour pressure
 - Elevation of boiling point
 - Depression in freezing point
3. Osmosis is a phenomenon where the solvent from the region of dilute solution moves to the region of concentrated solution through a semipermeable membrane.
4. The external pressure which must be applied to a solution in order to stop the flow of solvent into the solution through a semipermeable membrane is called osmotic pressure.

Laws of osmotic pressure

1. Van't Hoff - Boyle's law

At a constant temperature, the osmotic pressure is directly proportional to the concentration of the solution. $\pi \propto C$ (that is, $\pi \propto \frac{1}{V}$ where V is the volume of the solution containing one mole of the substance)

2. Van't Hoff - Charles law

Concentration being a constant, the osmotic pressure of a solution is directly proportional to the absolute temperature T.

$$\pi \propto T$$

3. Van't Hoff - Avogadro's law

The law states that equal volumes of solutions exerting same osmotic pressure at the same temperature should contain equal number of solute molecules.

$$\pi \propto n$$

4. Combined solution equation

$$\pi V = n R T$$

$$\text{No. of moles } n = \frac{w}{M} \quad \text{Hence } M = \frac{wRT}{\pi V}$$

Isotonic solutions

1. Solutions having same osmotic pressure are called isotonic solutions.
2. Molar concentrations of isotonic solutions are same.

Let w_1 and w_2 be the mass of the substances A and B dissolved in a litre of the solutions.

Let M_1 and M_2 are the molecular masses.

$$\text{Then } \frac{w_1}{w_2} = \frac{M_1}{M_2}$$

- **For isotonic solutions $\pi_1 = \pi_2$ and**

$$\frac{W_1}{M_1 \cdot V_1} = \frac{W_2}{M_2 \cdot V_2} \quad (\text{if both the solutes are non-electrolytes})$$

If M_1 of known, M_2 can be calculated

- When two solutions are mixed, first of all calculate their molar concentration (C_1 and C_2) in the final solution. Then

$$\pi_{\text{total}} = \pi_1 + \pi_2 = C_1RT + C_2RT = (C_1 + C_2) RT$$

$$\text{Or } \pi_{\text{total}} = \left(\frac{n_1 + n_2}{V} \right) RT$$

Where n_1 and n_2 are the number of moles of solutes 1 and 2 respectively

Relative lowering of vapour pressure

The ratio $\frac{p^0 - p}{p^0}$ is known as relative lowering of vapour pressure.

Raoult's law of dilute solutions

For a dilute solution the relative lowering of vapour pressure is equal to the mole fraction of the solute present in the solution.

$$\frac{p^0 - p}{p^0} = X_2 = \frac{n_2}{n_1 + n_2}$$

Limitations of Raoult's law

1. This law holds good only for dilute solutions.
2. It is applicable only for solutions containing dissolved solutes which are non-volatile.
3. In solution particles should not undergo association or dissociation.

Variation of vapour pressure with temperature

(Clausius-Clapeyron equation)

$$\log \frac{p_2}{p_1} = \frac{\Delta H_{\text{vap}}}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Here p_1 and p_2 are the vapour pressure of the liquid at temp. T_1 and T_2 respectively ($T_2 > T_1$) and ΔH_{vap} . Is the enthalpy of vapourisation of the liquid

Elevation of boiling point

1. Boiling point of a solution is always higher than that of the solvent. For example, boiling point of sodium chloride solution is more than that of water.

2. $\Delta T_b \propto m$ or $\Delta T_b = K_b m$

K_b is a constant. It is called **molal elevation constant** or **ebullioscopic constant**.

The value of K_b is a constant for a given solvent, but it is different for different solvents.

3. The value of K_b for water and benzene are 0.52 and 2.53 respectively.

4. Molecular mass of a solute and elevation in boiling point are related as

$$M_2 = \frac{1000 K_b w_2}{\Delta T w_1}$$

where w_1 and w_2 are the masses of the solvent and solute respectively.

Depression of freezing point

1. Freezing point of a solution is always lower than that of the solvent.

For example, freezing point of sodium chloride solution is less than that of water.

2. $\Delta T \propto m$ or $\Delta T = K_f m$

K_f is a constant. It is called **molal depression constant** or **cryoscopic constant**.

The value of K_f is a constant for a given solvent, but it is different for different solvents.

3. The value of K_f for water and benzene are 1.86 and 5.12 respectively.

4. Molecular mass of a solute and depression in freezing point are related as

$$M_2 = \frac{1000 K_f w_2}{\Delta T w_1}$$

where w_1 and w_2 are the masses of the solvent and solute respectively.

van't Hoff factor (i) :

When the solute undergoes dissociation or association in solution, the number of particles in solution increases or decreases and thus, the colligative property changes accordingly. In 1886, van't Hoff introduced a factor 'i' known as van't Hoff factor to express the extent of dissociation or association of the solute in solution.

van't Hoff factor, i

$$\begin{aligned}
 &= \frac{\text{Observed colligative property}}{\text{Theoretical or normal colligative property}} \\
 &= \frac{\text{No. of particles after dissociation or association}}{\text{No. of particles when there is no dissociation or association}} \\
 &= \frac{\text{Normal molecular mass of the solute}}{\text{Observed molecular mass of the solute}}
 \end{aligned}$$

From the value of 'i' it is possible to determine the degree of dissociation or association.

In case of dissociation 'i' is greater than 1.

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

where, n is the number of particles per molecule and α is the degree of dissociation.

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

Similarly, in case of association, 'i' is less than 1.

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

where, n is the number of molecules which are associated to form one giant molecule and α is the degree of association.

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

Molecular masses of electrolytes observed by the methods based on colligative properties are always less than normal molecular masses.

- For electrolytes undergoing complete dissociation, I = No. of particles formed from one formula unit. E.g, for NaCl, i = 2, for BaCl₂, i = 3 and so on
- **Expressions for colligative properties when association/dissociation occurs.**

Relative lowering of vapour pressure $= iX_{\text{solute}} = \frac{p^{\circ} - p}{p^{\circ}} = iX_2$

Elevation in boiling point $\Delta T_b = iK_b m$

Depression in freezing point $\Delta T_f = iK_f m$

Osmotic pressure $= icRT$

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

Azeotropes

Azeotropic mixtures or constant boiling mixtures are such mixtures whose liquid phase compositions are similar to that of vapour phase composition and due to this nature, they can not be separated by simple distillation.

To separate each component successfully a third component named entrainer is mixed which form heteroazeotrope with one of the component and having different boiling point (lower and higher) than previous azeotropes boiling point and thus make it easy to separate.

For example:

Water (weight – 4.5%, boiling point – 100°C) and Ethyl alcohol (weight – 95.5%, boiling point – 78.5°C) form low boiling point azeotrope (78.15°C) if desired further separation to obtain pure ethyl alcohol, benzene is added (known as entrainer) to former azeotropic mixture and makes it hetero-azeotrope with alcohol having boiling point 67.8°C. It then boils quickly than the remaining mixture and maximum of alcohol is separated further with benzene.

Azeotropic mixture with positive deviation (minimum boiling)

Components name		Composition by weight% of B	Boiling Point (K)		
A	B		A	B	Azeotropic mixture
H ₂ O	C ₂ H ₅ OH	95.37	373	351.3	351.15
H ₂ O	C ₃ H ₇ OH	71.69	373	370.19	350.72
Acetone	CS ₂	67	329.25	319.25	312.25
CHCl ₃	C ₂ H ₅ OH	6.8	334.2	351.3	332.3

Azeotropic mixture with negative deviation (maximum boiling)

Components name		Composition by weight% of B	Boiling Point (K)		
A	B		A	B	Azeotropic mixture
H ₂ O	HCl	20.3	373.0	188	383
H ₂ O	HI	57.0	373.0	239	400
H ₂ O	HNO ₃	68.0	373.0	359	393.5

H ₂ O	HClO ₄	71.6	373.0	383	476
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