

2. Solutions

Solution

Solution is a homogeneous mixture of two or more chemically non-reacting substances whose composition can be varies within certain limits. A solution is regarded as a single phase having more than one components.

A solution which contains only two components is called a binary solution.

The component which is present in smaller amount is called solute and the other present in larger amount is called the solvent.

The following table shows the list of solutions and their examples.

State	Solvent	Example
Solid	Solid	Alloys
Solid	Liquid	Sugar, salt in water
Solid	Gas	Iodine vapours in air
Liquid	Solid	NaHg, ZnHg Amalgam
Liquid	Liquid	Alcohol in water
Liquid	Gas	Chloroform in N ₂
Gas	Solid	Occluded hydrogen on Pd, Pt. Ni. etc. O ₂ on W
Gas	Liquid	Aerated water
Gas	Gas	Air, mixture of non reacting gases

Solutions of Solids in Liquids

- * Saturated solution is a solution which remains in contact with excess of solute.
- * The amount of solute dissolved per 100 g of solvent in a saturated solution at a specific temperature represents the solubility of the solute
- * For exothermic substances such as KOH, CaO, Ca(OH)₂, M₂CO₃, M₂SO₄ etc., solubility is inversely proportional to temperature.
(M = Alkali metals)
- * For endothermic substances such as NaCl, KNO₃, NaNO₂, glucoes etc. solubility is directly proportional to temperature.

Solubility of Gases

- * Solubility of gases is mostly expressed in terms of absorption coefficient, that is the volume of the gas (at NTP), dissolved by unit volume of

solvent, at 1 atm pressure and a specific temperature.

- * The solubility of a gas in a liquid depends upon
 1. **Temperature** – Solubility is inversely proportional to temperature as dissolution of a gas is exothermic in most cases.
 2. **Nature of gas** – Gases having a higher value of van der Waals force of attraction, that is, gases that are more easily liquefied are more soluble. For example, SO₂ and CO₂ are more soluble in water than O₂, N₂ and H₂.
 3. **Nature of solvent** – Gases which can ionize in aqueous solution are more soluble in water as compared to the other solvents.
 4. **Pressure of the gas (Henry's law)** According to this law, "At constant temperature, the solubility of a gas in a given volume of liquid is directly proportional to the pressure of the gas over the liquid".

$$m \propto P$$

$$M = KP$$
 or
$$\frac{m}{P} = K \text{ (At constant temperature)}$$
 Here K = Henry's constant
 Henry's law is obeyed only when
 1. Pressure is not too high
 2. Temperature is not too low.
 3. Gas does not dissociate.
 4. Gas is not highly soluble in the solvent.
 5. Gas does not chemically react with the solvent.

Vapour Pressure

Vapour Pressure of a Liquid

- * Vapour pressure is the pressure exerted by vapours when they are in equilibrium with the liquid phase at a given temperature. It depends on the nature of the liquid and temperature.
- * Vapour pressure of pure liquid is always greater than the vapour pressure of its solution.
- * Vapour pressure of a liquid helps us to have an idea of forces of attraction between the molecules of a liquid. More the force of attraction, lower is the vapour pressure and vice versa.

- * Vapour pressure of a liquid increase with increase in temperature due to increase in kinetic energy of molecules.
- * The variation of vapour pressure with temperature can be given by Clausius - Clapeyron equation as follows.

$$\log_{10} \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

Vapour Pressure of a Solution

- * When a miscible solute is added to a pure solvent, it results in the formation of solution. As some molecules of solute replace the molecules of the solvent from the surface, the escaping tendency of solvent molecules decreases. This causes a lowering of the vapour pressure.
- * The vapour pressure of a solution is less than that of pure solvent.
- * If the vapour pressure of a solvent is p^0 and that of solution is p_s then, lowering of vapour pressure = $p^0 - p_s$.
- * The vapour pressure of a solution decreases as the surface area occupied by the solvent molecules decreases and density increases.

Raoult's Law

Raoult's law for Volatile Solutes

Raoult's law states that in a solution, the vapour pressure of a component at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that component in the pure state.

The total vapour pressure of a solution containing two components A and B is

$$p_A = p_A^0 \times x_A$$

$$p_B = p_B^0 \times x_B$$

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

As we know that

$$x_A + x_B = 1$$

$$x_A = (1 - x_B)$$

$$P = (1 - x_B)p_A^0 + p_B^0 x_B$$

$$P = (p_A^0 - p_B^0) x_B + p_A^0$$

Raoult's Law For Non-Volatile Solutes

Raoult's law state that the relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution

$$\frac{P^0 - P_s}{P^0} = \frac{n_2}{n_1 + n_2} = x_2$$

Here, x_2 = Mole fraction of solute

n_1 = moles of solvent

n_2 = Moles of solute

p_s = Vapour pressure of the solution

p^0 = Vapour pressure of pure solvent

Ideal Solutions

Ideal solutions are the solutions in which solute-solute and solvent-solvent interactions are almost similar to solute-solvent interactions (A - B = A - A or B - B interactions) and such solutions satisfy the following requirements:

1. They obey Raoult's law for all ranges of concentrations and temperature.
2. $\Delta H(\text{mix}) = 0$
3. $\Delta V(\text{mix}) = 0$
4. $(V.P.)_{\text{obs}} = (V.P.)_{\text{exp}}$
 $(B.P.)_{\text{obs}} = (B.P.)_{\text{exp}}$
5. No dissociation or association takes place here.
6. No chemical reaction between solute and solvent.
7. It does not form azeotrope mixture.

Examples :

1. Benzene + toluene
2. Hexane + heptane
3. Ethyl bromide + ethyl iodide
4. chlorobenzene + bromobenzene
5. CCl_4 + SiCl_4
6. All dilute solutions

Non-ideal solutions

Non-ideal solutions are the solutions in which solute solvent interactions are different from solute-solute and solvent-solvent interactions. These solution do not obey Raoult's law for all concentration and

1. $\Delta H(\text{mix}) \neq 0$
2. $\Delta V(\text{mix}) \neq 0$

Types of non-ideal solutions

- a) Non-ideal solutions showing positive deviations
Positive deviation occurs when total vapour pressure for any mole fraction is more than what is expected according to Raoult's law. This happens when the new interactions are weaker than the interaction in the pure component (A-B < A - A or B - B interactions)

- * $\Delta H = +ve, \Delta V = +ve$
- * $(V.P.)_{obs} > (V.P.)_{exp}$
- * $P_T > P_A^0 X_A + P_B^0 X_B$
- * It forms minimum boiling azeotrope, for example, $C_2H_5OH +$ cyclohexane. The H-bonding present in pure C_2H_5OH are cut off on adding cyclohexane. For such solution, ΔV and ΔH are positive.

Examples :

- * Acetone + carbon disulphide
 - * Acetone + benzene
 - * Carbon tetrachloride + chloroform or Toluene
 - * Methylalcohol + water
 - * Acetone + C_2H_5OH
- b) Non-ideal solutions showing negative deviations
Negative deviation is seen when total vapour pressure for any mole fraction is less than that expected from Raoult's law. This happens when the new interactions are stronger than the interactions in the pure components ($A-B > A-A$ or $B-B$ interactions)
- * $\Delta H = -ve, \Delta V = -ve$
 - * $(V.P.)_{obs} < (V.P.)_{exp}$
 - * $P_T < P_A^0 X_A + P_B^0 X_B$
 - * It forms maximum boiling azeotrope, for example, $CHCl_3 + CH_3COCH_3$. For such solutions ΔV and ΔH are negative.

Examples :

1. Chloroform + benzene
2. Acetone + aniline
3. Nitric acid + water
4. Acetic acid + pyridine

Azeotropic Mixture

An azeotropic mixture is a mixture of two liquids having the same boiling point. These two liquids cannot be separated by simple distillation because of similar boiling point of the liquids. These mixtures are thus called constant-boiling mixtures. These are formed by non-ideal solutions

Azeotropic Mixture and Composition Curves.

- * These are the mixture of two liquids which boils at one particular temperature like pure liquid and distills over in the same composition i.e., these are constant boiling mixtures. These are formed by non-ideal solutions.

- * The study of the vapour pressure curves of such miscible liquids is of great help in separating the constituents of the liquid mixtures by distillation.
- * The separation by fractional distillation is possible only when the vapour phase has a composition different from that of the boiling liquid mixture.

Types of azeotropic mixture

These are of the following two types

- * Azeotropic Mixture with minimum boiling point
The mixture of two liquids whose boiling point is less than either of the two pure components.
- * This is formed by that composition of a non-ideal solution showing positive deviation for which the vapour pressure is maximum. These comprise non-ideal solutions which show positive deviation from Raoult's law and for which, the vapour pressure is maximum. For example, ethanol(95.5 %) + water (4.5%) mixture boils at 351.5 K.
(B.P. of ethanol = $78.1^\circ C$, B.P. of water = $100^\circ C$)
- * Such mixture on distillation will give first fraction upto point M in pure state. After this, the temperature will rise and the second component will pass over. Hence in such solutions also complete separation is not possible.
- 2. Azeotropic Mixtures with Maximum boiling point
The mixture of two liquids whose boiling point is more than either of the two pure components
- * This is formed by that composition of a non-ideal solution showing negative deviation for which the vapour pressure is minimum.
e.g., $-HNO_3(68\%) +$ water (32%) mixture boils at 393.5 K.
e.g., an aqueous solution of hydrochloric acid when subjected to distillation gives initially pure water and later forms a constant boiling mixture at $100^\circ C$ which contains 20.24% acid.
- * In a mixture of two volatile liquids A and B, If A is more volatile and present in excess, then during distillation the vapours will be rich of component A and the liquid part will be richer in component B. Finally we reach the point N where vapour pressure is minimum and the boiling point is maximum as shown in the figure
- * At this stage, the mixture distills unchanged in composition i.e., complete separation of components from this type of solution into pure state is impossible.

3. **Mixture Showing ideal Behaviour or Zeotropic Mixture** – Those liquid mixtures which distill with a change in composition are called zeotropic mixture.

- * For this type of containing liquids A and B, vapour pressure composition curve is a straight line. On distillation, A being more volatile, will collect as distillate.
- * The remaining fraction will be poorer in A and richer in B. By repeating the process of distillation again and again, we can get both the components in pure state e.g., methanol–water mixture.

Solubility of Partially Miscible Liquids

Conjugate solution

Many liquids are partially miscible and form two liquid layers at a particular temperature. Such liquid solutions in which different compositions of components coexist are called conjugate solutions, for example, phenol and water.

Critical temperature The miscibility of liquids varies with temperature. At a certain temperature the two layers become completely miscible. This temperature is called critical temperature or consolute temperature.

Colligative properties

Colligative properties are properties of a solution which depend only on the number of particles like ions or molecules of the solute in a definite amount of the solvent but not on the nature of the solute. These are properties of a dilute solution. These are as follows.

1. Relative lowering of vapour pressure
2. Osmotic pressure
3. Elevation in boiling point
4. Depression in freezing point.

Relative Lowering of Vapour Pressure

When a non-volatile solute is added in a volatile solvent the V.P of solution becomes less than the V.P. of pure solvent. It is due to increase in density which decreases rate of evaporation .

$$(r \propto \frac{1}{\sqrt{d}})$$

If p^0 = vapour pressure of pure solvent

p = vapour pressure of solvent in solution.

- * The lowering of vapour pressure

$$\Delta p = (p^0 - p)$$

* The relative lowering of vapour pressure is defined as the ratio between lowering of vapour pressure and the vapour pressure of pure solvent.

$$\frac{\Delta P}{P^0} = \frac{P^0 - P}{P^0} = \text{Relative lowering of}$$

Vapour pressure

* When a solution is prepared by mixing the non-volatile solute B and solvent A

$$x_A + x_B = 1$$

$$x_B = 1 - x_A$$

Here, x_B is the mole fraction of solute.

$$\text{As } \frac{P_A}{P_A^0} = x_A$$

$$1 - \frac{P_A}{P_A^0} = 1 - x_A = x_B \quad 1 - x_A = x_B$$

$$\frac{P_A^0 - P_A}{P_A^0} = x_B = \frac{\Delta P}{P_A^0} = \frac{n}{n + N}$$

Here, n = Number of moles of the solute

N = Number of moles of the solvent

* In a dilute solution, N is far greater than n , and hence ,

$$x_B = \frac{n}{N} = \frac{w/M}{W/m}$$

Here, w = Weight of solute

W = Weight of solvent

m = Molecular weight of solute

M = Molecular weight of solvent

$$\text{So, } \frac{P_A^0 - P_A}{P_A^0} = \frac{\Delta P}{P^0} = \frac{w/M}{W/m} = \frac{m \times M}{1000}$$

m = molality

* the molecular weight of a solute can be determined with the help of the relative lowering of vapour pressure method.

R.L.V.P. is measured by ostwald walker method.

$$\frac{P - P_s}{P} = \frac{\text{loss in mass of solvent bulbs}}{\text{Gain in CaCl}_2 \text{ tube}}$$

Osmotic pressure

- * Osmotic pressure is the equilibrium hydrostatic pressure of the column set up as a result of osmosis.

It is the minimum pressure that must be applied on the solution to prevent the entry of the solvent into the solution through the semi-permeable membrane.

It is the minimum pressure needed to apply on a solution to make its vapour pressure equal to vapour pressure of the solvent.

- * It is denoted by P or π .
- * It is measured by Pfeffer's method, Berkely-Hartley's method, Townsend's method.

Van't Hoff equation of osmotic pressure

π -CRT

Here, π = Osmotic pressure.

C = concentration of solution in mol/L

S or R = Solution constant

(= 0.0821 Latm/degmol)

T = Absolute temperature in K

So, $\pi \propto C$ (At constant temperature)

$$\pi = \frac{n}{V} RT \quad (C = n/V)$$

$$\pi V = nRT$$

Here, n = Numbers of moles the solute,

V = Volume of solution

$$\pi V = \frac{w}{M} RT$$

As $n = w/M$

M = Molar mass of solute

w = Gram weight of solute

Determination of molecular weight from osmotic pressure

$$\frac{M}{W} = \frac{RT}{\pi}$$

$$M = \frac{WRT}{\pi}$$

- * When solute is dissolved in V litre then $\pi V = nRT$ ($n = W/M$)

$$\pi V = \frac{W}{M} RT$$

$$M = \frac{W \times RT}{\pi \times V}$$

- * Accurate molecular weight is obtained under following conditions

1. Solution must be very dilute
2. Solute must be non-volatile
3. Solute should not undergo dissociation or association in the solution.

- * When height is involved then,

$$\pi = hdg$$

Isotonic solution

Solutions having equal molar concentration or equal osmotic pressure are called isotonic solutions. For example, 0.91% solution of pure aqueous NaCl is isotonic with human RBC.

$$P_1 = P_2 \text{ or } \pi_1 = \pi_2$$

$$\frac{w_1}{M_1 V_1} = \frac{w_2}{M_2 V_2}$$

- * In an isotonic solution net osmosis is zero.

Elevation in Boiling Point

Boiling point is the temperature of a liquid at which its vapour pressure becomes equal to the atmospheric pressure.

- * Elevation in the boiling point is also termed as ebullioscopy.
- * It is the increase in boiling point of solvent due to the addition of non-volatile solute in it. It is denoted by ΔT_b .

- * It is measured by Lands Berger's method and Koltrell's method.

- * The elevation in boiling point is given as $\Delta T_b \propto m$ or $\Delta T_b = K_b \cdot m$

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

Molecular weight of solute, $m_w = \frac{K_b \times w \times 1000}{\Delta T_b \times W}$

Here w = Weight of solute

W = Weight of solvent

K_b = Molal elevation constant or

ebullioscopic constant

If molality of the solution is one, then

$$\Delta T_b = K_b$$

$$K_b = \frac{RT^2}{1000L_v}$$

Here, L_v = Latent heat of vaporization

- * If molar elevation in boiling point constant (K_b) is to be calculated, then replace 1000 with 100 in the above mentioned formula, that is,

$$K = 10K_b$$

Depression in Freezing point

Freezing point is the temperature at which the liquid and the solid form of the same substance are in an equilibrium and have the same vapour pressure. Due to lower vapour pressure of the solution, solid form of a solution separates out at a lower temperature.

- * It is the decrease in freezing point of a solvent due to the addition of a non volatile solute.
- * This is also termed as cryoscopy.
- * Depression in freezing point (ΔT_f) = Freezing point of pure solvent – Freezing point of solution
- * It is measured by Beckmann's thermometer method and Rast's method.

$$\Delta T_f \propto m \text{ or } \Delta T_f = K_f \cdot m$$

$$M_2 = \frac{k_f \times w \times 1000}{\Delta T_f \times W}$$

m_w = mol. wt

Here w = Weight of solute

W = Weight of solvent

K_f = Molal depression constant or cryoscopic constant

- * If molality of the solution is one, then

$$\Delta T_f = k_f$$

$$K_f = \frac{RT^2}{1000L_f}$$

Here, L_f = Latent heat of fusion.

- * If molar depression in freezing point constant (K_f) is to be calculated, then replace 1000 with 100 in the above mentioned formula, that is,

$$K = 10K_f$$

Van't Hoff Factor

- * Certain solutes which undergo dissociation or association in solution, are found to show abnormal molecular mass. Due to this, the colligative property becomes abnormal which can be explained by van't Hoff factor.

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

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

$$i = \frac{\text{Actual number of particles or species}}{\text{Expected number of particles or species}}$$

- * For solutes showing dissociation, the van't Hoff factor $i > 1$

$$i = 2 \text{ for } MX, MNO_3, MSO_4$$

$$i = 3 \text{ for } MX_2, M_2O, M(NO_3)_2$$

$$i = 4 \text{ for } MX_3, K_3Fe(CN)_6$$

$$i = 5 \text{ for } M_2X_3, M_2(SO_4)_3, M_3(PO_4)_2, K_4Fe(CN)_6$$

For example, $FeCl_3 \longrightarrow Fe^{3+} 3Cl^-$ for $i = 4$

- * For solutes showing association, the van't Hoff factor $i < 1$, for example, dimerization of acids like benzoic acid in benzene.

- * For solutes showing neither dissociation nor association, the van't Hoff factor i is 1, for example, urea, glucose, sucrose

$$\text{Degree of dissociation, } \alpha = \frac{i-1}{n-1}$$

Here n = Number of species formed after dissociation

$$\text{Degree of association, } \alpha = \frac{n(1-i)}{n-1} = \frac{1-i}{n-1}$$

Here n = Number of species formed after association

$$1) \Delta T_b = i \cdot K_b \cdot M \quad 3) \pi = iCRT$$

$$2) \Delta T_f = i \cdot K_f \cdot M \quad 4) \frac{P - P_s}{P} = i \frac{n}{n+N}$$

Raoult's Law

- a) Raoult's law for volatile solutes

$$P = p_A + p_B = P_A^0 X_A + P_B^0 X_B$$

$$P = (1 - X_B) P_A^0 + P_B^0 X_B$$

$$P = (P_B^0 - P_A^0) X_B + P_A^0$$

- b) Raoult's law for non-volatile solute

$$\frac{P^0 - P_s}{P^0} = \frac{n_2}{n_1 + n_2} = x_2$$

$$\frac{\Delta P}{P^0} = \frac{P^0 - P}{P^0} \text{ Relative lowering of vapour pressure}$$

- * When a solution is prepared by mixing the non volatile solute B and solvent A.

$$X_A + X_B = 1$$

$$X_B = 1 - X_A$$

$$\frac{P_A^0 - P_A}{P_A^0} = X_B = \frac{\Delta P}{P_A^0} = \frac{n}{n+N}$$

Here n = number of moles of solute

N = solvent

* In dilute solution $N \gg n$ and hence

$$X_B = \frac{n}{N} = \frac{w/m}{W/M} = \frac{wM}{Wm}$$

$$\text{So, } \frac{P_A^0 - P_A}{P_A^0} = \frac{\Delta P}{P_A^0} = \frac{wM}{Wm} = \frac{m \times M}{1000}$$

Van't Hoff Equation of Osmotic Pressure

$$\pi = CST$$

$$\pi = \frac{n}{V} ST \quad (C = n/V)$$

$$\pi V = nST$$

$$\pi V = \frac{w}{M} RT$$

As $n = w/M$

Determination of Molecular Weight from Osmotic Pressure

$$\frac{M}{W} = \frac{ST}{\pi}$$

$$M = \frac{WST}{\pi}$$

* When solute is not dissolved in one litre or it is dissolved in V litre then

$$\pi V = nST \quad (n = W/M)$$

$$\pi V = \frac{W}{M} ST$$

$$M = \frac{W \times ST}{\pi \times V}$$

* When height is involved then

$$\pi = h \rho g$$

Isotonic Solution

$$\frac{w_1}{M_1 V_1} = \frac{w_2}{M_2 V_2}$$

Elevation of Boiling point

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

Molecular weight of solute.

$$m_w = \frac{k_b \times w \times 1000}{\Delta T_b \times W}$$

If molality of the solution is one, then

$$\Delta T_b = K_b$$

$$K_b = \frac{RT^2}{1000L_v}$$

Here L_v = Latent heat of vaporization.

Depression in Freezing Point

$$* \Delta T_f = K_f \times \frac{w}{m_w} \times \frac{1000}{W}$$

$$* m_w = \frac{k_f \times w \times 1000}{\Delta T_f \times W}$$

* If molality of the solution is one, then

$$\Delta T_f = K_f$$

$$K_f = \frac{RT^2}{1000L_f}$$

Here L_f = Latent heat of fusion

Van't Hoff Factor

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

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

Degree of Dissociation

$$\text{Degree of dissociation, } \alpha = \frac{i-1}{n-1}$$

Degree of Association

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

Here n = Number of species formed after association

$$\frac{P - P_S}{P} = i \frac{n}{n+N}$$

Henry's Law

$$M = KP$$

$$\text{or, } \frac{M}{P} = K \quad (\text{At constant temperature})$$

Introduction, Types of Solution

- The example of solution of liquid in gas is
 - dry air
 - alcohol in water
 - mercury in gold
 - moist air
- When the solution contains more solute than would be necessary to saturate it then it is known as
 - saturated solution
 - unsaturated solution
 - supersaturated solution
 - dilute solution
- Which of the following is not a solution?
 - smoke
 - air
 - salt solution
 - a gold ring
- When water is added to the solution its
 - concentration increases
 - concentration decreases