



Knowledge... Everywhere

Chemistry

Solutions

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A solution is a homogenous mixture of two or more substances, the composition of which may vary within limits. "A solution is a special kind of 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**. A solution is termed as binary, ternary and quaternary if it consists of two, three and four components respectively.

1. Solubility.

Solubility of a substance in the solvent is the measure of the capacity of the latter to dissolve the former at a given temperature and pressure. "Solubility of a substance may be defined as the amount of solute dissolved in 100gms of a solvent to form a saturated solution at a given temperature". A **saturated solution** is a solution which contains at a given temperature as much solute as it can hold in presence of dissolved 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**. It is metastable.

2. Kinds of solutions.

All the three states of matter (gas, liquid or solid) may behave either as solvent or solute. Depending on the state of solute or solvent, mainly there may be following nine types of binary solutions.

| Solvent | Solute | Example |
|---------|--------|--|
| Gas | Gas | Mixture of gases, air. |
| Gas | Liquid | Water vapors in air, mist. |
| Gas | Solid | Sublimation of a solid into a gas, smoke. |
| Liquid | Gas | CO ₂ gas dissolved in water (aerated drinks). |
| 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, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. |
| Solid | Solid | Homogeneous mixture of two or more metals (alloys), e.g., copper in gold, zinc in copper. |

Among these solutions the most significant type of solutions are those which are in liquid phase and may be categorized as: (i) Solid in liquid solutions, (ii) Liquid in liquid solutions and (iii) Gas in liquid solutions.

(i) **Solid in liquid solutions:** For the solid in liquid solutions the solid is referred to as solute. The amount of solute that is dissolved in 100g of a solvent, to form a saturated solution at a particular temperature is called **solubility**. The solubility of a solid solute in liquid depends upon

(a) Nature of solute and solvent

(b) Temperature: Usually the solubility of the solute increases with increase in temperature

(e.g., KI , KNO_3 , NH_4Br) but in some cases increase in solubility is negligible (e.g. NaCl) and in cases of some salts (e.g., NaOH , Na_2SO_4 , CeSO_4) solubility decreases with increase in temperature.

Cause of miscibility of solids in liquids : The basic cause of solubility of solid solute in liquid solvent can be summed up in one line, i.e., "Similia similibus solvanter" meaning **like dissolves like** which implies that polar solvents dissolve polar solutes and non-polar solvents dissolve non-polar solutes.

For ionic solutes, the solubility, in general, is related to the magnitude of **hydration (or salvation) energy** and **lattice energy**. In general if the magnitude of hydration energy is greater than lattice energy, the solute is soluble otherwise it is insoluble.

(ii) **Liquid in liquid solutions:** When two liquids are mixed, the mixture may be of the following types:

(a) The two components may be almost immiscible: In this case, one of the liquids is polar while the other is of non-polar nature. For example, benzene and water.

(b) The miscibility of the component may be partial: If the intermolecular attraction of one liquid is different from intramolecular attraction of the other, there may be a partial miscibility of the two liquids. For example, ether and water.



(c) The two components may be completely miscible: In this case, the two liquids are of the same nature, i.e., they are either polar (like alcohol and water) or non-polar (like benzene and hexane).

Cause of Miscibility of Liquids

(a) Chemically alike liquids dissolve in one another more freely as compared to others, for example, alkanes are miscible in all proportions with one another. Alkanes are however, not miscible with water because they cannot form H-bonds with water molecules.

(b) Dipole-Dipole interactions also play an important role in forming liquid solutions.

(c) Molecular sizes of liquids which are mutually soluble, are also approximately same.

(iii) **Gas in Liquid solutions:** Most of the gases are soluble in water to some extent. The solubility of gas in water generally depends upon the following factors

(a) Nature of the gas: In general the gases which are easily liquefiable are more soluble in water.

(b) Temperature: The dissolution of gas in water is exothermic process. Hence, the solubility of gas decreases with rise in temperature.

(c) Pressure: Effect of pressure on the solubility of gas is explained by "**Henry's law**". According to Henry's law "mass of gas dissolved in a given volume of solvent, at a constant temperature, is proportional to the pressure of the gas with which it is in equilibrium."

Solubility \propto Pressure; $S = KP$ where K is Henry's constant.

Higher the value of K at given pressure, the lower is the solubility of the gas in the liquid. Value of K increases with increase in temperature while solubility of gas decreases. It is due to this reason that aquatic species are more comfortable in cold water rather than hot water.

Applications of Henry's law: Henry's law finds several applications in industry and explains some biological phenomena. Notable among these are:

(i) To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

(ii) To minimize the painful effects accompanying the decompression of deep sea divers, oxygen diluted with less soluble helium gas is used as breathing gas.

(iii) In lungs, where oxygen is present in air with high partial pressure of oxygen to form oxohaemoglobin. In tissues where partial pressure of oxygen is low. Oxohaemoglobin releases oxygen for utilization in cellular activities.



3. Methods of expressing concentration of solution.

Concentration of solution is the amount of solute dissolved in a known amount of the solvent or solution. The concentration of solution can be expressed in various ways as discussed below.

(1) **Percentage:** It refers to the amount of the solute per 100 parts of the solution. It can also be called as parts per hundred (pph). It can be expressed by any of following four methods:

$$(i) \text{ Weight to weight percent (\% w/w)} = \frac{\text{Wt. of solute}}{\text{Wt. of solution}} \times 100$$

e.g., 10% Na_2CO_3 solution w/w means 10g of Na_2CO_3 is dissolved in 100g of the solution. (It means 10g Na_2CO_3 is dissolved in 90g of H_2O)

$$(ii) \text{ Weight to volume percent (\% w/v)} = \frac{\text{Wt. of solute}}{\text{Volume of solution}} \times 100$$

e.g., 10% Na_2CO_3 (w/v) means 10g Na_2CO_3 is dissolved in 100cc of solution.

$$(iii) \text{ Volume to volume percent (\% v/v)} = \frac{\text{Vol. of solute}}{\text{Vol. of solution}} \times 100$$

e.g., 10% ethanol (v/v) means 10cc of ethanol dissolved in 100cc of solution.

$$(iv) \text{ Volume to weight percent (\% v/w)} = \frac{\text{Vol. of solute}}{\text{Wt. of solution}} \times 100$$

e.g., 10% ethanol (v/w) means 10cc of ethanol dissolved in 100g of solution.

(2) **Parts per million (ppm) and parts per billion (ppb):** When a solute is present in trace quantities, it is convenient to express the concentration in parts per million and parts per billion. It is the number of parts of solute per million (10^6) or per billion (10^9) parts of the solution. It is independent of the temperature.

$$ppm = \frac{\text{mass of solute component}}{\text{Total mass of solution}} \times 10^6; \quad ppb = \frac{\text{mass of solute component}}{\text{Total mass of solution}} \times 10^9$$

(3) **Strength:** The strength of solution is defined as the amount of solute in grams present in one litre (or dm^3) of the solution. It is expressed in g/litre or (g/dm^3).

$$\text{Strength} = \frac{\text{Mass of solute in grams}}{\text{Volume of solution in litres}}$$



(4) **Normality (N):** It is defined as the number of gram equivalents (equivalent weight in grams) of a solute present per litre of the solution. Unit of normality is gram equivalents litre⁻¹. Normality changes with temperature since it involves volume. When a solution is diluted x times, its normality also decreases by x times. Solutions in term of normality generally expressed as,

N = Normal solution; $5N$ = Penta normal, $10N$ = Deca normal; $N/2$ = semi normal

$N/10$ = Deci normal; $N/5$ = Penti normal

$N/100$ or $0.01N$ = centinormal, $N/1000$ or $0.001N$ = millinormal

Mathematically normality can be calculated by following formulas,

$$(i) \text{ Normality } (N) = \frac{\text{Number of g.eq. of solute}}{\text{Volume of solution } (l)} = \frac{\text{Weight of solute in g.}}{\text{g. eq. weight of solute} \times \text{Volume of solution } (l)}$$

$$(ii) N = \frac{\text{Wt. of solute per litre of solution}}{\text{g eq. wt. of solute}},$$

$$(iii) N = \frac{\text{Wt. of solute}}{\text{g. eq. wt. of solute}} \times \frac{1000}{\text{Vol. of solution in ml}}$$

$$(iv) N = \frac{\text{Percent of solute} \times 10}{\text{g eq. wt. of solute}},$$

$$(v) N = \frac{\text{Strength in g } l^{-1} \text{ of solution}}{\text{g eq. wt. of solute}}$$

$$(vi) N = \frac{\text{Wt}\% \times \text{density} \times 10}{\text{Eq. wt.}}$$

(vii) If volume V_1 and normality N_1 is so changed that new normality and volume N_2 and V_2 then,

$$\boxed{N_1 V_1 = N_2 V_2} \text{ (Normality equation)}$$

(viii) When two solutions of the same solute are mixed then normality of mixture (N) is

$$\boxed{N = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}}$$

(ix) Vol. of water to be added i.e., $(V_2 - V_1)$ to get a solution of normality N_2 from V_1 ml of normality N_1

$$V_2 - V_1 = \left(\frac{N_1 - N_2}{N_2} \right) V_1$$

(x) If Wg of an acid is completely neutralized by V ml of base of normality N

$$\frac{\text{Wt. of acid}}{\text{g eq. wt. of acid}} = \frac{VN}{1000}; \text{ Similarly, } \frac{\text{Wt. of base}}{\text{g eq. wt. of base}} = \frac{\text{Vol. of acid} \times N \text{ of acid}}{1000}$$

(xi) When V_a ml of acid of normality N_a is mixed with V_b ml of base of normality N_b



(a) If $V_a N_a = V_b N_b$ (Solution neutral)

(b) If $V_a N_a > V_b N_b$ (Solution is acidic)

(c) If $V_b N_b > V_a N_a$ (Solution is basic)

$$(xii) \text{ Normality of the acidic mixture} = \frac{V_a N_a + V_b N_b}{(V_a + V_b)}$$

$$(xiii) \text{ Normality of the basic mixture} = \frac{V_b N_b + V_a N_a}{(V_a + V_b)}$$

$$(xiv) N = \frac{\text{No. of meq * of solute}}{\text{Vol. of solution in ml}} \quad (* 1 \text{ equivalent} = 1000 \text{ milliequivalents or meq.})$$

(4) **Molarity (M):** Molarity of a solution is the number of moles of the solute per litre of solution (or number of millimoles per ml. of solution). Unit of molarity is **mol/litre** or **mol/dm³** For example, a molar (1M) solution of sugar means a solution containing 1 mole of sugar (i.e., 342 g or 6.02×10^{23} molecules of it) per litre of the solution. Solutions in term of molarity generally expressed as,

1M = Molar solution, 2M = Molarity is two, $\frac{M}{2}$ or 0.5 M = Semimolar solution,

$\frac{M}{10}$ or 0.1 M = Decimolar solution, $\frac{M}{100}$ or 0.01 M = Centimolar solution

$\frac{M}{1000}$ or 0.001 M = Millimolar solution

- Molarity is most common way of representing the concentration of solution.
- Molarity is depend on temperature as, $\text{Molarity} \propto \frac{1}{\text{Temperature}}$
- When a solution is diluted (x times), its molarity also decreases (by x times)

Mathematically molarity can be calculated by following formulas,

$$(i) \quad M = \frac{\text{No. of moles of solute } (n)}{\text{Vol. of solution in litres}}$$

$$(ii) \quad M = \frac{\text{Wt. of solute (in gm) per litre of solution}}{\text{Mol. wt. of solute}}$$

$$(iii) \quad M = \frac{\text{Wt. of solute (in gm)}}{\text{Mol. wt. of solute}} \times \frac{1000}{\text{Vol. of solution in ml.}}$$

$$(iv) \quad M = \frac{\text{No. of millimoles of solute}}{\text{Vol. of solution in ml}}$$



$$(v) \quad M = \frac{\text{Percent of solute} \times 10}{\text{Mol. wt. of solute}}$$

$$(vi) \quad M = \frac{\text{Strength in } g l^{-1} \text{ of solution}}{\text{Mol. wt. of solute}}$$

$$(vii) \quad M = \frac{10 \times \text{Sp. gr. of the solution} \times \text{Wt.\% of the solute}}{\text{Mol. wt. of the solute}}$$

(viii) If molarity and volume of solution are changed from M_1, V_1 to M_2, V_2 . Then,

$$M_1 V_1 = M_2 V_2 \text{ (Molarity equation)}$$

(ix) In balanced chemical equation, if n_1 moles of reactant one react with n_2 moles of reactant two. Then,

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

(x) If two solutions of the same solute are mixed then molarity (M) of resulting solution.

$$M = \frac{M_1 V_1 + M_2 V_2}{(V_1 + V_2)}$$

(xi) Volume of water added to get a solution of molarity M_2 from V_1 ml of molarity M_1 is

$$V_2 - V_1 = \left(\frac{M_1 - M_2}{M_2} \right) V_1$$

Relation between molarity and normality

$$\text{Normality of solution} = \text{molarity} \times \frac{\text{Molecular mass}}{\text{Equivalent mass}}$$

$$\text{Normality} \times \text{equivalent mass} = \text{molarity} \times \text{molecular mass}$$

$$\text{For an acid, } \frac{\text{Molecular mass}}{\text{Equivalent mass}} = \text{basicity}$$

So, Normality of acid = molarity \times basicity.

$$\text{For a base, } \frac{\text{Molecular mass}}{\text{Equivalent mass}} = \text{Acidity}$$

So, Normality of base = Molarity \times Acidity.



(6) **Formality (F):** Formality of a solution may be defined as the number of gram formula masses of the ionic solute dissolved per litre of the solution. It is represented by F . Commonly, the term formality is used to express the concentration of the ionic solids which do not exist as molecules but exist as network of ions. A solution containing one gram formula mass of solute per litre of the solution has formality equal to one and is called formal solution. It may be mentioned here that the formality of a solution changes with change in temperature.

$$\text{Formality (F)} = \frac{\text{Number of gram formula masses of solute}}{\text{Volume of solution in litres}} = \frac{\text{Mass of ionic solute (g)}}{(\text{gm. formula mass of solute}) \times (\text{Volume of solution (l)})}$$

$$\text{Thus, } F = \frac{W_B(g)}{GFM \times V(l)} \quad \text{or} \quad \frac{W_B(g) \times 1000}{GFM \times V(ml)}$$

(7) **Mole fraction (X):** Mole fraction may be defined as the ratio of number of moles of one component to the total number of moles of all the components (solvent and solute) present in the solution. It is denoted by the letter X . It may be noted that the mole fraction is independent of the temperature. Mole fraction is dimensionless. Let us suppose that a solution contains the components A and B and suppose that $W_A g$ of A and $W_B g$ of B are present in it.

$$\text{Number of moles of } A \text{ is given by, } n_A = \frac{W_A}{M_A} \text{ and the number of moles of } B \text{ is given by, } n_B = \frac{W_B}{M_B}$$

Where M_A and M_B are molecular masses of A and B respectively.

$$\text{Total number of moles of } A \text{ and } B = n_A + n_B$$

$$\text{Mole fraction of } A, X_A = \frac{n_A}{n_A + n_B}; \text{ Mole fraction of } B, X_B = \frac{n_B}{n_A + n_B}$$

The sum of mole fractions of all the components in the solution is always one.

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1.$$

Thus, if we know the mole fraction of one component of a binary solution, the mole fraction of the other can be calculated.



Relation between molality of solution (m) and mole fraction of the solute (X_A).

$$X_A = \frac{m}{55.5 + m}$$

(8) **Mass fraction:** Mass fraction of a component in a solution is the mass of that component divided by the total mass of the solution. For a solution containing $w_A gm$ of A and $w_B gm$ of B

$$\text{Mass fraction of A} = \frac{w_A}{w_A + w_B}; \text{ Mass fraction of B} = \frac{w_B}{w_A + w_B}$$

Note: It may be noted that molality, mole fraction, mass fraction etc. are preferred to molarity, normality, etc. because the former involve the weights of the solute and solvent whereas later involve volumes of solutions. Temperature has no effect on weights but it has significant effect on volumes.

(9) **Demal unit (D):** The concentrations are also expressed in "Demal unit". One Demal unit represents one mole of solute present in one litre of solution at $0^\circ C$.

4. 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. The four well known examples of the colligative properties are

- (1) Lowering of vapor pressure of the solvent.
- (2) Osmotic pressure of the solution.
- (3) Elevation in boiling point of the solvent.
- (4) 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 any other and thus if one property is measured, the other can be calculated. The study of colligative properties is very useful in the calculation of molecular weights of the solutes.

5. Lowering of vapor pressure.

The pressure exerted by the vapors above the liquid surface in equilibrium with the liquid at a given temperature is called vapor pressure of the liquid. The vapor pressure of a liquid depends on

(1) Nature of liquid: Liquids, which have weak intermolecular forces, are volatile and have greater vapor pressure. For example, dimethyl ether has greater vapor pressure than ethyl alcohol.

(2) Temperature: Vapor 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 vapor phase.

(3) Purity of liquid: Pure liquid always has a vapor pressure greater than its solution.

Raoult's law: When a non-volatile substance is dissolved in a liquid, the vapor pressure of the liquid (solvent) is lowered. According to Raoult's law (1887), at any given temperature the partial vapor pressure (p_A) of any component of a solution is equal to its mole fraction (X_A) multiplied by the vapor pressure of this component in the pure state (p_A^0). That is, $p_A = p_A^0 \times X_A$

The vapor 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 vapor pressures p_A and p_B .

$$P_{total} = p_A + p_B = (p_A^0 \times X_A) + (p_B^0 \times X_B)$$

Alternatively, Raoult's law may be stated as "the relative lowering of vapor pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution."

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

Mole fraction of the solute is defined as the ratio of the number of moles of solute to the total number of moles in solution.

Thus according to Raoult's law,



$$\frac{p^0 - p}{p^0} = \frac{n}{n + N} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$$

Where, p = Vapor pressure of the solution; p^0 = Vapor 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.

6. Ideal and Non-Ideal solution.

(1) **Ideal solution:** An ideal solution may be defined as the solution which obeys Raoult's law over the entire range of concentration and temperature and during the formation of which no change in enthalpy and no change in volume takes place. So for ideal solutions the conditions are,

(i) It should obey Raoult's law, i.e., $P_A = P_A^0 X_A$ and $P_B = P_B^0 X_B$.

(ii) $\Delta H_{\text{mixing}} = 0$

(iii) $\Delta V_{\text{mixing}} = 0$

The solutions in which solvent-solvent and solute-solute interactions are almost of the same type as solvent-solute interactions, behave nearly as ideal solutions.

This type of solutions are possible if molecules of solute and solvent are almost of same size and have identical polarity. For example, solutions of following pairs almost behave as ideal solutions, n-Heptane and n-hexane.; Chlorobenzene and bromobenzene.

Benzene and toluene; Ethyl bromide and ethyl iodide.

Ethylene bromide and ethylene chloride; Carbon tetrachloride and silicon tetrachloride.

For such solutions the vapor pressure of the solution is always intermediate between the vapor pressures of pure components A and B, i.e., P_A^0 and P_B^0 .



(2) **Non-Ideal solution:** The solutions which do not obey Raoult's law and are accompanied by change in enthalpy and change in volume during their formation are called non-ideal solutions. So, for non-ideal solutions the conditions are:

(i) It does not obey Raoult's law. $P_A \neq P_A^0 X_A; P_B \neq P_B^0 X_B$

(ii) $\Delta H_{\text{mixing}} \neq 0$

(iii) $\Delta V_{\text{mixing}} \neq 0$

Either component of non-ideal binary solution do not follow Raoult's law. The non-ideal solutions are further divided into two types:

(a) Solutions showing positive deviations. (b) Solutions showing negative deviations.

(a) **Solutions showing positive deviation:** In this type of deviations, the partial vapor pressure of each component (say A and B) of solution is greater than the vapor pressure as expected according to Raoult's law. This type of deviations are shown by the solutions in which solvent-solvent and solute-solute interactions are stronger than solvent-solute interactions.

For the non-ideal solutions exhibiting positive deviation.

$P_A > P_A^0 X_A, P_B > P_B^0 X_B; \Delta H_{\text{mixing}} = +ve; \Delta V_{\text{mixing}} = +ve$

E.g. of solutions showing positive deviations

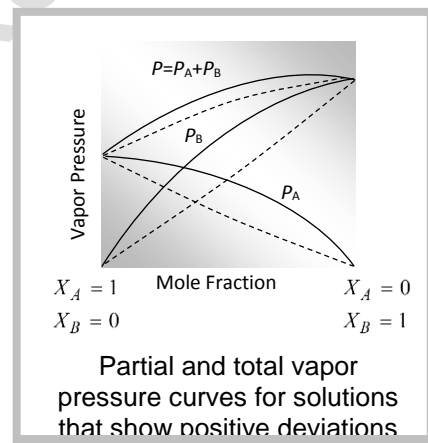
$(CH_3)_2CO + CS_2; (CH_3)_2CO + C_2H_5OH$

$C_6H_6 + (CH_3)_2CO; CCl_4 + C_6H_6$

$CCl_4 + CHCl_3; CCl_4 + C_6H_5CH_3$

$H_2O + CH_3OH; H_2O + C_2H_5OH$

$CH_3CHO + CS_2; CHCl_3 + C_2H_5OH$

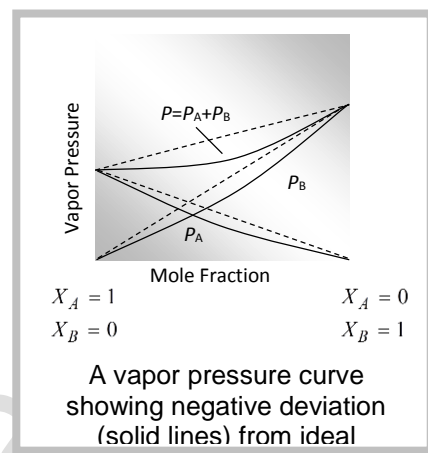
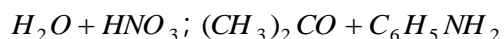
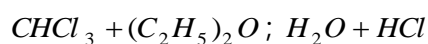
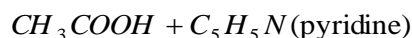


(b) **Solutions showing negative deviation:** In this type of deviations the partial vapor pressure of each component of solution is less than the vapor pressure as expected according to Raoult's law. This type of deviations are shown by the solutions in which solvent-solvent and solute-solute interactions are weaker than solvent-solute interactions.

For non-ideal solution showing negative deviation.

$$P_A < P_A^0 X_A, P_B < P_B^0 X_B; \Delta H_{\text{mixing}} = -ve; \Delta V_{\text{mixing}} = -ve$$

E.g. of solutions showing negative deviations



Differences between ideal and non-ideal solutions

| Ideal solutions | Solutions with positive deviations | Solutions with negative deviations |
|--|--|--|
| A.....B interactions are similar to A.....A and B.....B interactions | A.....B interactions are smaller than A.....A and B.....B interactions | A.....B interactions are greater than A.....A and B.....B interactions |
| $P_A = P_A^0 X_A; P_B = P_B^0 X_B$ | $P_A > P_A^0 X_A; P_B > P_B^0 X_B$ | $P_A < P_A^0 X_A; P_B < P_B^0 X_B$ |
| $\Delta H_{\text{sol.}} = 0$ | $\Delta H_{\text{sol.}} > 0$ | $\Delta H_{\text{sol.}} < 0$ |
| $\Delta V_{\text{mix}} = 0$ | $\Delta V_{\text{mix}} > 0$ | $\Delta V_{\text{mix}} < 0$ |
| Do not form azeotrope | Exhibit minimum boiling point azeotropy | Exhibit maximum boiling azeotropy |



7. Azeotropic mixture.

Azeotropes are defined as the mixtures of liquids which boil at constant temperature like a pure liquid and possess same composition of components in liquid as well as in vapor phase. Azeotropes are also called constant boiling mixtures because whole of the azeotropes changes into vapor state at constant temperature and their components cannot be separated by fractional distillation. Azeotropes are of two types as described below:

(1) **Minimum boiling azeotrope:** For the solutions with positive deviation there is an intermediate composition for which the vapor pressure of the solution is maximum and hence, boiling point is minimum. At this composition the solution distills at constant temperature without change in composition. This type of solutions are called minimum boiling azeotrope. e.g.

| Components | | Mass % of B | Boiling points (K) | | |
|--------------|----------------|-------------|--------------------|-------|-----------|
| A | B | | A | B | Azeotrope |
| H_2O | C_2H_5OH | 95.57 | 373 | 351.3 | 351.1 |
| H_2O | $C_2H_5CH_2OH$ | 71.69 | 373 | 370 | 350.72 |
| $CHCl_3$ | C_2H_5OH | 67 | 334 | 351.3 | 332.3 |
| $(CH_3)_2CO$ | CS_2 | 6.8 | 329.25 | 320 | 312.2 |

(2) **Maximum boiling azeotrope:** For the solutions with negative deviations there is an intermediate composition for which the vapor pressure of the solution is minimum and hence, boiling point is maximum. At this composition the solution distills at constant temperature without the change in composition. This type of solutions are called maximum boiling azeotrope. e.g.

| Components | | Mass % of B | Boiling points (K) | | |
|------------|----------|-------------|--------------------|-----|-----------|
| A | B | | A | B | Azeotrope |
| H_2O | HCl | 20.3 | 373 | 188 | 383 |
| H_2O | HNO_3 | 58.0 | 373 | 359 | 393.5 |
| H_2O | $HClO_4$ | 71.6 | 373 | 383 | 476 |



8. Osmosis and Osmotic pressure of the solution.

The flow of solvent from pure solvent or from solution of lower concentration into solution of higher concentration through a semi-permeable membrane is called **Osmosis**. Osmosis may be divided in following types,

(1) **Exo-Osmosis:** The outward osmotic flow of water from a cell containing an aqueous solution through a semi-permeable membrane is called as Exo-osmosis. For example, egg (after removing hard shell) placed in conc. NaCl solutions, will shrink due to Exo-osmosis.

(2) **Endo-osmosis:** The inward flow of water into the cell containing an aqueous solution through a semi-permeable membrane is called as endo-osmosis. e.g., an egg placed in water swells up due to endo-osmosis.

(3) **Reverse osmosis:** If a pressure higher than osmotic pressure is applied on the solution, the solvent will flow from the solution into the pure solvent through the semi-permeable membrane. Since here the flow of solvent is in the reverse direction to that observed in the usual osmosis, the process is called reverse osmosis.

Differences between osmosis and diffusion

| Osmosis | Diffusion |
|--|--|
| In osmosis movement of molecules takes place through a semi-permeable membrane. | In diffusion there is no role of semi-permeable membrane. |
| It involves movement of only solvent molecules from one side to the other. | It involves passage of solvent as well as solute molecules from one region to the other. |
| Osmosis is limited to solutions only. | Diffusion can take place in liquids, gases and solutions. |
| Osmosis can be stopped or reversed by applying additional pressure on the solution side. | Diffusion can neither be stopped nor reversed |



Osmotic pressure (π): Osmotic pressure may be defined in following ways,

The osmotic pressure of a solution at a particular temperature may be defined as the excess hydrostatic pressure that builds up when the solution is separated from the solvent by a semi-permeable membrane. It is denoted by π .

Or

Osmotic pressure may be defined as the excess pressure which must be applied to a solution in order to prevent flow of solvent into the solution through the semi-permeable membrane.

Or

Osmotic pressure is the excess pressure which must be applied to a given solution in order to increase its vapor pressure until it becomes equal to that of the solution.

Or

Osmotic pressure is the negative pressure which must be applied to (i.e. the pressure which must be withdrawn from) the pure solvent in order to decrease its vapor pressure until it becomes equal to that of the solution.

Measurements of osmotic pressure: Following methods are used for the measurement of osmotic pressure: (i) Pfeffer's method, (ii) Morse and Frazer's method, (iii) Berkeley and Hartley's method, (iv) Townsend's negative pressure method, (v) De Vries plasmolytic method.

Determination of molecular mass of non-volatile solute from osmotic pressure (π):

According to Van't Hoff equation,

$$\pi = \frac{n_B}{V} RT; \quad M_B = \frac{W_B RT}{\pi V} \quad \text{Where, } W_B = \text{known mass of solute in gm}$$

This method is especially suitable for the determination of molecular masses of macromolecules such as proteins and polymers. This is due to the reason that for these substances the values of other colligative properties such as elevation in boiling point or depression in freezing point are too small to be measured. On the other hand, osmotic pressure of such substances are measurable. Conditions for getting accurate value of molecular mass are,

- (i) The solute must be non-volatile.
- (ii) The solution must be dilute.
- (iii) The solute should not undergo dissociation or association in the solution.



Van't Hoff's solution equation:

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. Osmotic pressure is related to the number of moles of the solute by the following relation:

$$\pi V = nRT \text{ or } \pi = \frac{n}{V} RT \Rightarrow \boxed{\pi = CRT}; \text{ here, C = concentration of solution in moles per litre}$$

R = gas constant; T = temperature; n = number of moles of solute; V = volume of solution

Above eq. is called Van't Hoff's solution equation

Relation of osmotic pressure with different colligative properties: Osmotic pressure is related to relative lowering of vapor pressure, elevation of boiling point and depression of freezing point according to the following relations.

$$(1) \pi = \left(\frac{P_A^\circ - P_A}{P_A^\circ} \right) \times \frac{dRT}{M_B} \quad (2) \pi = \Delta T_b \times \frac{dRT}{1000 \times K_b} \quad (3) \pi = \Delta T_f \times \frac{dRT}{1000 \times K_f}$$

In the above relations, π = Osmotic pressure; d = Density of solution at temperature T; R = Universal gas constant; M_B = 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, | $C_1 = C_2$ | } Secondary |
| or | $\frac{n_1}{V_1} = \frac{n_2}{V_2}$ | |
| or | $\frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$ | |

.....(ii)

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

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

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

(c) 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.

9. Elevation in boiling point of the solvent (Ebullioscopy).

Boiling point of a liquid may be defined as the temperature at which its vapor pressure becomes equal to atmospheric pressure, i.e., 760 mm. Since the addition of a non-volatile solute lowers the vapor pressure of the solvent, solution always has lower vapor pressure than the solvent and hence it must be heated to a higher temperature to make its vapor 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 (ΔT or ΔT_b) is called the elevation of boiling point.

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

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.

Important relations concerning elevation in boiling point

(i) The elevation of boiling point is directly proportional to the lowering of vapor pressure, i.e.,

$$\Delta T_b \propto p^0 - p$$

(ii) $\Delta T_b = K_b \times m$

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 1000g of the solvent; ΔT_b = Elevation in boiling point

$$(iii) \Delta T_b = \frac{1000 \times K_b \times w}{m \times W} \text{ or } m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

Where, K_b is molal elevation constant and defined as the elevation in B.P. produced when 1 mole of the solute is dissolved in 1 kg of the solvent. Sometimes the value of K_b is given per 0.1kg (100g), in such case the expression becomes



$$m = \frac{100 \times K_b \times w}{\Delta T_b \times W}$$

Where w and W are the weights of solute and solvent and m is the molecular weight of the solute.

$$(iv) K_b = \frac{0.002(T_0)^2}{l_v}$$

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 $0.52 \text{ deg} - kg \text{ mol}^{-1}$

10. Depression in freezing point of the solvent (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 vapor 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 (ΔT or ΔT_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.

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.

Important relations concerning depression in freezing point.

(i) Depression in freezing point is directly proportional to the lowering of vapor pressure.

$$\Delta T_f \propto p^0 - p$$

(ii) $\Delta T_f = K_f \times m$



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); ΔT_f = Depression in freezing point

$$(iii) \Delta T_f = \frac{1000 \times K_f \times w}{m \times W} \text{ or } m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

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 1kg of the solvent. Sometimes the value of K_f is given per 0.1kg (100g), in such case the expression becomes

$$m = \frac{100 \times K_f \times w}{\Delta T_f \times W}$$

Where w and W are the weights of solute and solvent and m is the molecular weight of the solute.

$$(iv) K_f = \frac{R(T_0)^2}{l_f 1000} = \frac{0.002(T_0)^2}{l_f}$$

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

Relative lowering of vapor pressure, elevation in boiling point and depression in freezing point are directly proportional to osmotic pressure.

11. Colligative properties of electrolytes.

The colligative properties of solutions, viz. lowering of vapor pressure, osmotic pressure, elevation in b.p. and depression in freezing point, depend solely on the total number of solute particles present in solution. Since the electrolytes ionize 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.

Points to remember

- (i) Colligative properties \propto Number of particles
- \propto Number of molecules (in case of non-electrolytes)
- \propto Number of ions (In case of electrolytes)
- \propto Number of moles of solute



\propto Mole fraction of solute

(ii) For different solutes of same molar concentration, the magnitude of the colligative properties is more for that solution which gives more number of particles on ionization.

(iii) For different solutions of same molar concentration of different non-electrolyte solutes, the magnitude of the colligative properties will be same for all.

(iv) For different molar concentrations of the same solute, the magnitude of colligative properties is more for the more concentrated solution.

(v) For solutions of different solutes but of same percent strength, the magnitude of colligative property is more for the solute with least molecular weight.

(vi) For solutions of different solutes of the same percent strength, the magnitude of colligative property is more for that solute which gives more number of particles, which can be known by the knowledge of molecular weight and its ionization behavior.

12. Abnormal molecular masses.

Molecular masses can be calculated by measuring any of the colligative properties. The relation between colligative properties and molecular mass of the solute is based on following assumptions.

(1) The solution is dilute, so that Raoult's law is obeyed.

(2) The solute neither undergoes dissociation nor association in solution.

In case of solutions where above assumptions are not valid we find discrepancies between observed and calculated values of colligative properties. These anomalies are primarily due to

(i) Association of solute molecules.

(ii) Dissociation of solute molecules.

(i) **Association of solute molecules:** Certain solutes in solution are found to associate. This eventually leads to a decrease in the number of molecular particles in the solutions. Thus, it results in a decrease in the values of colligative properties. As already discussed, the colligative properties are inversely related to the molecular mass,

Colligative property $\propto \frac{1}{\text{molecular mass of solute}}$, therefore, higher values are obtained for molecular masses than normal values for unassociated molecules.



(ii) **Dissociation of solute molecules:** A number of electrolytes dissociate in solution to give two or more particles (ions). Therefore, the number of solute particles, in solutions of such substances, is more than the expected value. Accordingly, such solutions exhibit higher values of colligative properties. Since colligative properties are inversely proportional to molecular masses, therefore, molecular masses of such substances as calculated from colligative properties will be less than their normal values.

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:

$$\text{Relative lowering of vapor pressure} = \frac{P_A^o - P_A}{P_A^o} = i X_B$$

$$\text{Elevation of boiling point, } \Delta T_b = i k_b m$$

$$\text{Depression in freezing point, } \Delta T_f = i k_f m$$

$$\text{Osmotic pressure, } \pi = \frac{i n R T}{V}; \quad \pi = i C R T$$

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.

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

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 a bigger molecules.

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

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