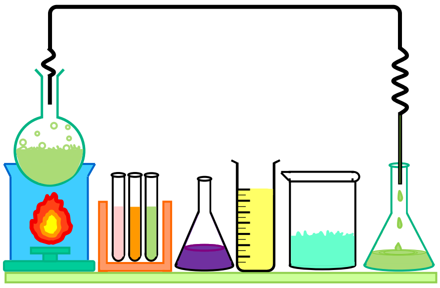
Chapter – 2

India's First Colour Smart Book



SOLUTION & COLLIGATIVE PROPERTIES

1 INTRODUCTION

- A solution is a homogeneous mixture of two or more pure substances, in same or different physical phases, the relative ratio of which can be changed within certain limits.
- The substances forming the solution are called components of the solution.
- On the basis of number of components a solution of two components is called binary solution, if three then tertiary, if four then quaternary and so on.
- The two constituents of the solution are: Solvent and Solute.
- Solvent (A): It is that component of the solution which is present in a relatively large proportion in the solution, and whose physical state is same as that of the resulting solution.
- Solute (B): It is the component of a solution which is present in relatively small proportion.

2 CLASSIFICATION OF SOLUTIONS

On the basis of physical state of solvent and solute:

Types of Solution	*Solute*	*Solvent*	*Examples*
Solid solution	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold
Liquid solution	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Gaseous solution	Gas	Gas	Mixture of oxygen & nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas

DO YOU KNOW ?

1. Aqueous solution: Binary solution in which water is solvent are called aqueous solution.
2. Non-aqueous solution: Solutions in which solvent is a liquid other than water such as ether, benzene, alcohol, carbon tetrachloride are called non-aqueous solution.

Amongst the nine types of solutions, the widely studied ones are:
(i) Solid – liquid solution, *(ii)* Liquid – liquid solution and *(iii)* Gas – liquid solution.

(i) Solid – liquid solution**:**

a) ***Dilute solution:*** A small amount of solute (usually ionic solids) is dissolved in a large quantity of solvent. If the amount of solvent is large as compared to solute, the solution is said to be as a dilute solution.
b) ***Saturated solution:*** A solution is said to be saturated if it holds the maximum amount of solute at a given temperature in a given quantity of the solution.
c) ***Unsaturated solution:*** A solution in which more solute can be dissolved without raising temperature is called an unsaturated solution.
d) ***Super-saturated solution:*** A solution which contains more solute than that would be necessary to saturate it at a given temperature is called a super-saturated solution.

Solubility

Definition: The maximum amount of solute that can be dissolved in 100 g solvent at a specified temperature.

- *The solubility of solid into liquid depends upon the following factors:*
  - *a) Nature of solvent & solute:* Dissolution of solid solutes in liquids can be summed up in a phrase 'like dissolves like'. This means, polar solutes dissolve in polar solvents & non-polar solutes dissolves in non-polar solvents. E.g., ionic substances like NaCl, KCl, etc, have large solubilities in polar solvents like water but they have poor solubilities in non-polar solvents like CCl_4, CS_2, etc.
  - *b) Temperature:* The solubility may increase or decrease with the rise in temperature depending upon the value of $\Delta_{sol}H$. The different variations in solubilities of different substances serves as the basis for fractional crystallization.
- *Causes of solubility:*

  The following types of forces of attraction are operated when a solute is mixed with a solvent:
  - a) *Inter-ionic attraction in the solute molecules:* Ions are held together in the lattice due to electrostatic forces. Due to these forces molecules are stabilized and the energy released is called lattice energy. This is defined as the energy released when 1 g mole of the compound is formed due to electrostatic attraction between the ions.
  - b) *Inter-molecular attraction between solvent molecules:* Water is a polar solvent because of the different in electro-negativity between hydrogen & oxygen atoms constituting water molecule. This difference gives rise to the development of a slight negative charge on oxygen and equal positive charge on hydrogen. A dipole is thus created giving rise to dipole-dipole attraction between water molecules.
  - c) *Solvation:* It represents force of attraction between solute and solvent molecules. If the solvent is water then the energy released is called hydration energy.

    If the hydration energy is greater than lattice energy, then solution is easily formed. Both the ions of the solute get hydrated to overcome the lattice energy of the solute.
  - d) *Temperature:* Saturated solution represents equilibrium between undissolved solute & dissolved solute.

    Undissolved Solute + solvent $\rightleftharpoons$ *Solution;* $\Delta_{sol}H = \pm x.$

    If $\Delta_{sol}H < 0$, i.e., negative, the dissolution process is exothermic. In this case, as the temperature increases, solubility decreases (Le Chatelier's principle).

    If $\Delta_{sol}H > 0$, i.e., positive, the dissolution process is endothermic. In this case, as the temperature increases then solubility increases (Le Chatelier's principle).

(ii) Liquid – liquid solution**:**

a) *Miscible liquids:* Two components are completely soluble. They are miscible only when they have similar nature or belongs to the same homologous series.

E.g., water & alcohol (both polar), benzene & toluene (both belongs to the same homologous series).

There is a rule discussed: like dissolves like' means, polar solutes dissolve in polar solvents & non-polar solutes dissolves in non-polar solvents.

b) *Partially miscible liquids:* This happens only when the intermolecular forces of one liquid is greater than that of other. Solubility, however, increases with increasing temperature. E.g., aniline – water, phenol – water, etc.

c) *Immiscible liquid pairs:* Two components are completely immiscible. This happens when one liquid is polar and the other non-polar. E.g., carbon tetrachloride – water, chloroform – water, etc.

(iii) Gas – liquid solution**:**

a) Nature of gas: Different gases dissolve to a different extent even in the same solvent & same gas has different solubilities in different solvents. Highly soluble gases in water do not dissolves in non-polar solvents like benzene, carbon tetrachloride, etc. because of their inability to react with these solvents. So, easily liquefiable gases are more generally soluble in common solvents.

b) Nature of liquid: Those gases which easily form ions in solution are more soluble in water than in other solvents. Ion formation in other solvents is not an easy process.

$HCl\,(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-\,(aq).$

c) Temperature: As a general rule, the solubility of a gas in water decreases as the temperature is raised. However, here helium show exception whose solubility first decreases & then increases as the temperature is increased. In some other liquid solvents also, the solubility of gases may increases with increase in temperature.

d) Pressure: For all practical purposes, the external pressure has no influence on the solubilities of liquids & solids, but for gases the solubilities are greatly affected by pressure of gas. (Henry law)

Memories

➢ *Energetics of Dissolution Process*

Three types of interparticle forces play significant role in dissolution of solute B in solvent A. These are solute-solute (B-B); solvent-solvent (A-A) and solvent-solute (A-B) interactions. A-A and B-B interactions have to be overcome which requires energy. A-B interactions get established which releases energy. If A-B interactions are stronger than those between A-A and B-B particles then solute particles break apart and dissolution process becomes energetically favourable, i.e., $\Delta_{sol} H < 0$. If A-B interaction, then dissolution is energetically not favourable, i.e., $\Delta_{sol} H > 0$. However dissolution in such a case is favoured by a large – ve value of ΔS.

Multiple Choice Questions (MCQ)

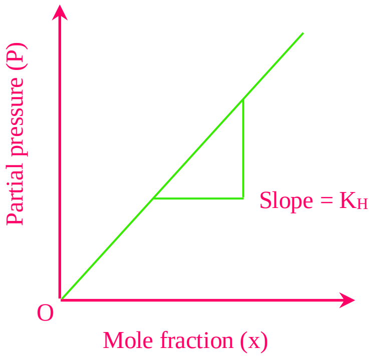
1. *Which of the following is not correct?*
   - (a) Mixture may contain two or more pure substances.
   - (b) Mixtures can be solid solution, liquid solutions or gaseous solution.
   - (c) Concentration of solutions is always mentioned as parts per million.
   - (d) All of these.
2. *Which of the following is not a homogeneous solution?*
   - (a) milk in water (b) salt in water (c) iodine in CCl_4 (d) CCl_4 in water
3. *A solution in which small amount of solute gets dissolved at a given temperature so that further dissolution of solute may also take place is called:*
   - (a) saturated solution (b) unsaturated solution (c) dilute solution (d) normal solution
4. *A beaker contains a solution of substance 'A'. Precipitation of substance 'A' takes place when small amount of 'A' is added to the solution. The solution is:*
   - (a) saturated (b) super-saturated (c) unsaturated (d) concentrated
5. *Which of the following is true about the effect of temperature on the solubility of Na_2SO_4 in water?*
   - (a) As the temperature increases, the solubility increases.
   - (b) As the temperature increases, the solubility decreases.
   - (c) Solubility of Na_2SO_4 is not affected by temperature.
   - (d) As the temperature increases, the solubility shows irregular behaviour.
6. *Maximum amount of a solid solute that can be dissolved in a specified amount of a given liquid solvent does not depend upon:*
   - (a) temperature (b) nature of solute (c) pressure (d) nature of solvent
7. *The solute can be separated from solution by:*
   - (a) filtration (b) evaporation (c) decantation (d) sedimentation
8. *The solubility of a gas in water depends on:*
   - (a) nature of gas (b) temperature (c) pressure of the gas (d) all of these
9. *Which among the following alloys is used in making instruments for electrical measurement?*
   - (a) Stainless steel (b) Manganin (c) Spiegeleisen (d) Duralumin
10. *An example of solid in solid solution is:*
    - (a) bronze (b) mercury amalgam
    - (c) sodium chloride in water (d) camphor in air

Answers of Multiple Choice Questions:

1. (c) Concentration of solutions can be expressed in several ways such as in parts per million(ppm), molarity(M), molality(m), etc.
2. (d) CCl_4 in water is a heterogeneous solution.
3. (b)
4. (b) A solute when added to its solution will precipitate out only if its solution is already supersaturated.
5. (d) As the temperature increases upto 32.8^0C, the solubility of sodium sulphate increases. When temperature is increased beyond 32.8^0C, the solubility of sodium sulphate decreases.
6. (c) Solids & liquids are incompressible. Hence, the solubility of solid in a given liquid solvent does not depend on change in pressure.
7. (b)
8. (d)
9. (b)
10. (a)

3 HENRY'S LAW

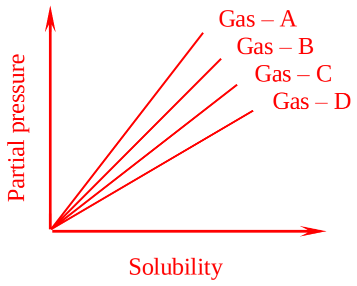
- *Definition:* It states that at constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas.
- The most commonly used form of Henry's law states that the partial pressure (p) of a gas in vapour phase is proportional to the mole fraction of the gas (x) in the solution and is expressed as: $p = K_H x$. Where, K_H is the Henry's law constant & 'x' is the mole fraction of the gas.



- *Limitations of Henry's law:*
  a) The pressure of the gas is not too high.
  b) The temperature is not too low.
  c) The gas should not undergo any chemical reaction with the solvent.
  d) The gas should not undergo dissociation in solution.
- *Applications of Henry's law:*
  a) Production of carbonated beverages: Soft drinks, soda water & other carbonated beverages contains dissolved carbon dioxide. In the preparation of these beverages, CO_2 is passed at high pressure to increase its solubility.
  b) Anoxia in climbers: At high altitudes, the partial pressure of oxygen is less than that the ground level. Thus, low blood oxygen causes climbers to become weak & make them unable to think clearly, which are symptoms of a condition known as anoxia.
  c) Deep sea diving: To avoid the toxic effects of high concentration of nitrogen in the blood, the tanks use by scuba divers are filled with air dilute with helium (11.7% helium, 56.2% nitrogen& 32.1% oxygen).
  d) Functioning of lungs: In lungs, oxygen present in the inhaled air dissolved in blood because of its high partial pressure and combine with haemoglobin t form oxyhaemoglobin. In tissues, where partial pressure of oxygen is low, oxyhaemoglobin release oxygen for its utilisation in cellular activities.

Questions Based On Henry's Law

1. *The relation between solubility of a gas in liquid at constant temperature & external pressure is stated by which law?*
   (a) Raoult's law (b) van't Hoff Boyle's law (c) Henry's law (d)van't Hoff Boyle's law
2. *Henry's law is applicable at:*
   (a) constant volume (b) constant concentration (c) constant pressure (d) constant temperature
3. *The statement, " If 0.003 moles of a gas are dissolved in 900 g of water under a pressure of 1 atm, 0.006 moles will be dissolved under a pressure of 2 atm", illustrates:*
   (a) Graham's law (b) Daltons law of partial pressure
   (c) Henry's law (d) Henry's law
4. For the given graph at constant temperature, which gas has the least solubility?



   (a) gas – D (b) gas – B (c) gas – C (d) gas - D
5. *Among the following gases which gas has the highest Henry's law constant, K$_H$ value in water at the same temperature?*
   (a) O_2 (b) N_2 (c) H_2 (d) He
6. *Which of the following is false?*
   (a) Henry's law is valid if the temperature is not too low.
   (b) The gas should not be highly soluble.
   (c) The breathing gas used by deep sea divers is the oxygen gas diluted with argon.
   (d) People living at high altitudes & climbers suffer anoxia & thus becomes weak.

7. *K_H values for Ar(g), CO_2(g), HCHO(g) & CH_4(g) are 40.39, 1.67, 1.83× 10^{-5} & 0.413 respectively. Arrange these gases in the order of their increasing solubility.*
   (a) HCHO < CH_4 < CO_2 < Ar
   (b) HCHO < CO_2 < CH_4 < Ar
   (c) Ar < CO_2 < CH_4 < HCHO
   (d) Ar < CH_4 < CO_2 < HCHO
8. *H_2S a toxic gas with rotten egg like smell, is used for the qualitative analysis. If the solubility of H_2S in water at STP is 0.195 mol kg^{-1}, calculate Henry's law constant.*
9. *Henry's law constant of CO_2 in water is 1.67× 10^8 Pa at 298 K. Calculate the quantity of CO_2 in 500mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.*
10. *O_2 is bubbled through water at 293 K. Assuming that O_2 exerts a partial pressure of 0.98 bar. Calculate the solubility of O_2 in gL^{-1}. The value of Henry's law constant for O_2 is 34.84 k bar.*

Answers of the Questions:

1. (d)
2. (d)
3. (d) As the pressure is double from 1 atm to 2 atm, the number of moles of gas dissolved is also doubled from 0.003 to 0.006. Thus the amount of gas dissolved in a given volume of solvent is proportional to pressure. This illustrates Henry's law.
4. (c) According to Henry's law, " the solubility of a gas in a liquid at constant temperature is proportional to the pressure of the gas above the solution", i.e., $S \propto P$.
   (where, S is solubility of the gas & P is pressure of the gas).
   If several gases are present, then the solubility of any gas may be evaluated by using P as partial pressure of that gas in the mixture.
   So, for the given graph it is observed that at any given partial pressure, gas – A has the least solubility.
5. (d) At 293K, Gas: He has 144.97 K_H/k bar
   Gas: N_2 has 76.48 K_H/k bar
   Gas: H_2 has 69.16 K_H/k bar
   Gas: O_2 has 34.86 K_H/k bar
6. (c)
7. (c) Solubility of a gas in a liquid decreases with increase in temperature. Lower the solubility, higher the K_H value of a gas. Hence, value of K_H increases with increase in temperature.
8. According to Henry's law, K_H. x = p or, K_H = p/x

   Here, p = 1 bar, solubility = 0.195 mol/kg

   Moles of H_2S (n_B) = 0.195

   Moles of water (n_A) = $\frac{1000\text{ (g)}}{18\text{ (g/mol)}} = 55.5$

   ∴ Mole fraction of H_2S (x) = $\frac{0.195}{0.195 + 55.5} = \frac{0.195}{55.695} = 3.5 \times 10^{-3}$

   $K_H = \frac{1\text{ (bar)}}{3.5 \times 10^{-3}} = 285.6$ bar.
9. Pressure of CO_2 (p) = 2.5 atm

   $= 2.5\text{ (atm)} \times 101325\text{ (Pa/atm)} = 253312.5\text{ Pa}$

   According to Henry's law, $^xCO_2 = \frac{p}{K_H} = \frac{253312.5\text{ (Pa)}}{1.67 \times 10^8\text{ (Pa)}} = 1.52 \times 10^{-3}$

   $^xCO_2 = \frac{n_{CO_2}}{n_{CO_2} + n_{H_2O}} = \frac{n_{CO_2}}{55.5}$

   $n_{CO_2} = 1.52 \times 10^{-3} \times 55.5 = 0.0844\text{ mol/L}$

   Moles of CO_2 present in 500 mL, $\frac{0.0844}{2}$ mol $= 0.0422$ mol

   Amount of CO_2 present in 500 mL, $0.0422\text{ mol} \times 44.0\text{ g/mol} = 1.86\text{ g}$.
10. According to Henry's law, $p_{O_2} = K_H \times x_{O_2}$

    Or, $x_{O_2} = \frac{p_{O_2}}{K_H} = \frac{0.098\text{ (bar)}}{34.84 \times 10^3\text{ (bar)}} = 2.81 \times 10^{-5}$

    Mole of H_2O in 1 L = 55.5

    $^xO_2 = \frac{n_{O_2}}{n_{O_2} + 55.5}$ or, $\frac{n_{O_2}}{55.5}$

    $n_{O_2} = 2.81 \times 10^{-5} \times 55.5 = 1.56 \times 10^{-3}$ mol

    Thus, solubility of O_2 = $1.56 \times 10^{-3}\text{mol/L} = 1.56 \times 10^{-3} \times 32\text{ g/L} = 0.05\text{ g/L}$

4 METHODS OF EXPRESSING CONCENTRATION OF SOLUTIONS

The concentration of solution is the amount of the solute present in the given quantity of solution or solvent. It can be expressed in any of the following ways:

1. *Mass percentage (w/w): It may be defined as mass of solute per 100g of solution.*

   $$\text{Mass \% of solute} = \frac{Mass\ of\ solute}{Total\ mass\ of\ the\ solution} \times 100$$

2. *Volume percentage (v/v): It may be defined as volume of solute per 100 mL of solution.*

   $$\text{Volume \% of solute} = \frac{Volume\ of\ solute}{Total\ volume\ of\ the\ solution} \times 100$$

3. *Mass by volume percentage (w/v): It may be defined as the mass of solute per 100 mL of the solution.*

   $$\text{Mass by volume \%} = \frac{Mass\ of\ solute}{Volume\ of\ the\ solution} \times 100$$

4. *Parts per million (ppm): It is the parts of a component per million (10^6) parts of the solution.*

   $$ppm = \frac{Number\ of\ parts\ of\ components}{Total\ number\ of\ parts\ of\ all\ components\ of\ the\ solution} \times 10^6$$

5. *Mole fraction (x): It may be defined as the ratio of the number of moles of one component (solute or solvent) to the total number of all the components present in the solution.*

   If in a solution, n_A & n_B are the number of moles of solvent & solute, respectively, then

   Mole fraction of solvent in the solution, $x_A = \frac{n_A}{n_A + n_B}$

   Mole fraction of solute in the solution, $x_B = \frac{n_B}{n_A + n_B}$

   In a solution, sum of the mole fractions of all the components is unity.

   For example, in a binary solution (having two components). $x_A + x_B = 1$

6. *Molarity (M): It is defined as number of moles of solute dissolved in one litre of solution.*

   $$Molarity = \frac{Moles\ of\ solute}{Volume\ of\ the\ solution\ (in\ litre)}$$

   Unit of molarity is mol/litre or M (molar).

   Molarity changes with change in temperature as volume changes with change in temperature.

7. *Molality (m): It is defined as the number of moles of the solute dissolved in one kilogram (kg) of the solvent & is expressed as:*

   $$Molarity = \frac{Moles\ of\ solute}{Mass\ of\ the\ solvent\ (in\ kg)}$$

   $$= \frac{Number\ of\ moles\ of\ solute}{Mass\ of\ solvent\ (in\ grams)} \times 1000$$

   Unit of molality is mol/kg.

   Molality is independent of temperature.

8. *Normality (N): It is defined as the number of gram-equivalents of the solute present per litre or per cubic decimetre of the solution.*

   It may be also expressed in terms of milliequivalents of solute present in one millilitre of solution.

   $$\text{Normality} = \frac{Gram-equivalents\ of\ solute\ (B)}{Volume\ of\ solution\ (in\ Litre)}$$

9. *Formality: It is defined as number of moles of ionic solute present in one litre (or dm^3) of solution.*

   $$Formality = \frac{Moles\ of\ ionic\ solute}{Volume\ of\ solution\ (in\ Litre)}$$

DO YOU KNOW ?

1. Concentration modes based on mass-volume relationship between solute & solution such as molarity, normality, formality and mass-volume percentage are temperature dependent.
2. Concentration modes based on mass-mass relationship such as percentage mass, molality, mole fraction, etc., are independent of temperature.

Important terms and formulas for solving numerical

A represents solvent

M_A = Molar mass of solvent

W_A = Mass of solvent

V = Volume of solution

GEM = Gram Equivalent Mass

B represents solute

M_B = Molar mass of solute

W_B = Mass of solute

d = Density of solution

GM = Gram Molecular mass

1. Mass percentage (w/w):

$$\text{Mass \% of solute} = \frac{\text{Mass of solute}}{\text{Total mass of the solution}} \times 100 \quad = \frac{W_B}{W_A + W_B} \times 100$$

2. Volume percentage (v/v):

$$\text{Volume \% of solute} = \frac{\text{Volume of solute}}{\text{Total volume of the solution}} \times 100 \quad = \frac{V_B}{V_A + V_B} \times 100$$

3. Mass by volume percentage (w/v):

$$\text{Mass by volume \%} = \frac{\text{Mass of solute}}{\text{Volume of the solution}} \times 100 \quad = \frac{W_B \times 100}{V\ (mL)}$$

4. Parts per million (ppm):

$$ppm = \frac{\text{Number of parts of components}}{\text{Total number of parts of all components of the solution}} \times 10^6 \quad = \frac{W_B}{W_A + W_B} \times 10^6$$

5. Mole fraction (x):

Mole fraction of solvent (A) in the solution, $x_A = \frac{n_A}{n_A + n_B}$

Mole fraction of solute (A) in the solution, $x_B = \frac{n_B}{n_A + n_B}$

$$x_A + x_B = 1$$

6. Molarity (M):

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of the solution (in litre)}} = \frac{n_B}{V\ (in\ L)} = \frac{W_B}{M_B \times V\ (in\ L)}$$

7. Molality (m):

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Mass of the solvent (in kg)}} = \frac{\text{Number of moles of solute}}{\text{Mass of solvent (in grams)}} \times 1000 = \frac{n_B}{W_A\ (in\ kg)} = \frac{W_B \times 1000}{M_B \times W_A\ (in\ g)}$$

8. Normality (N):

$$\text{Normality} = \frac{\text{Gram−equivalents of solute (B)}}{\text{Volume of solution (in Litre)}} = \frac{W_B}{GEM\ of\ solute \times V\ (in\ L)} = \frac{W_B \times 1000}{GEM_B \times V\ (in\ mL)}$$

9. Formality:

$$\text{Formality} = \frac{\text{Moles of ionic solute}}{\text{Volume of solution (in Litre)}} = \frac{\text{Mass of ionic solute (g)}}{\text{Formula mass (solute)} \times V_{sol}(L)} = \frac{W_B(g) \times 1000}{M_B \times V_L}$$

Important relationships for entrance examinations

1. Relationship between Molarity & Normality:

Normality × Equivalent mass (solute) = Molarity × Molar mass (solute)

2. Relationship between Molarity(M) & Mass percentage(p):

If p is the mass percentage & d is the density of the solution then,

$$\text{Molarity} = \frac{p \times d \times 10}{\text{Mol. mass (solute)}};$$

$$\text{Normality} = \frac{p \times d \times 10}{\text{Eq. mass (solute)}}$$

3. Relationship between Molarity (M) & Molality (m):

$$m = \frac{1000 \times M}{(1000 \times d) - (M \times GMM_B)}$$

4. Relationship between Molality (m) & mole fraction of solute (x_B):

$$x_B = \frac{m \times GMM_A}{1000 + m \times GMM_A}; \quad m = \frac{1000\ x_B}{x_A \times GMM_A}$$

5. Relationship between Molarity (M) & Mole fraction of solute (x_B):

$$x_B = \frac{m \times GMM_A}{M\ (GMM_A - GMM_B) + 1000\ d}; \quad M = \frac{1000 \times d \times x_B}{x_A \times GMM_A + x_B \times GMM_B}$$

Dilution formula

If the solution of some substance is diluted by adding solvent from volume V_1 to volume V_2, then :

$M_1 V_1 = M_2 V_2$

Or, $N_1 V_1 = N_2 V_2$

Molarity of a mixture

If V_1 mL of a solution of molarity M_1 is mixed with another solution of same substance with volume V_2 & molarity M_2, then ,molarity of the resulting mixture of solution (M) can be obtained as: $M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$

Numericals Based On Different Modes Of Concentration

1. *Calculate the volume of 80% H_2SO_4 by mass (density = 1.80 g/cm^3) that is required to obtain one litre of 20% H_2SO_4 by mass (density = 1.25 g/cm^3).*

Calculation of molarity of 80% H_2SO_4

% use of H_2SO_4 by mass = 80%

Molar mass of H_2SO_4 $(M)_B$ = 98g/mol

Density of sulphuric acid = 1.80 g/cm^3

Molarity of 80% H_2SO_4 is given by the formula,

$$M_1 = \frac{W_B}{M_B} \times \frac{1\times1000}{(100/d)} = \frac{80\ (g)}{98\ (g/mol)} \times \frac{1\times1000\ (cm^3/L)}{(100/1.80)cm^3} = 14.7\ mol/L$$

Similarly, Molarity of 20% H_2SO_4 can be calculated as

$$M_2 = \frac{20\ (g)}{98\ (g/mol)} \times \frac{1\times1000\ (cm^3/L)}{(100/1.25)cm^3} = 2.55\ mol/L$$

Let, V_1 be the volume of concentrated acid required.

Then by dilution formula, $M_1V_1 = M_2V_2$

Or, $V_1 = \frac{M_2V_2}{M_1} = \frac{2.55\ (mol/L)\times1(L)}{14.7\ (mol/L)} = 0.1734\ L$ Or, $173.4\ cm^3$.

∴ Volume of 80% acid required = 173.4 cm^3.

2. *Calculate molality & mole faction of a solution containing 2.5 g of ethanoic acid (CH_3COOH) in 75 g of benzene. Also calculate mass % of benzene in solution.*

Calculation of molality,

Mass of solute (W_B) = 2.5 g

Molar mass of solute M_B = 60 g/mol

Moles of solute $(n_B) = \frac{W_B}{M_B} = \frac{2.5\ g}{60\ g/mol} = 0.0417\ mol$

Mass of solvent (W_A) = 75 g = 75×10^{-3} kg

Molality (m) = $\frac{n_B}{W_A(kg)} = \frac{0.0417\ (mole)}{75\times10^{-3}\ (kg)} = 0.556\ mol/kg$

Calculation of mole fraction,

Moles of solute (n_B) = 0.0417 mole

Mass of solvent (W_A) = 75 g

Molar mass of benzene (M_A) = 78 g/mol

Moles of solvent $(n_A) = \frac{W_A}{M_A} = \frac{75\ g}{78\ g/mol} = 0.961\ mol$

Total moles $(n_A + n_B)$ = 0.417 + 0.96 = 1.0027 mol

Mole fraction of solute $(x_B) = \frac{n_A}{n_A+n_B} = \frac{0.0417}{1.0027} = 0.0416$

Mole fraction of solute $(x_A) = 1-(x_B) = 1-0.416 = 0.9584$

Calculation of mass % of benzene,

%of benzene = $\frac{Mass\ of\ benzene\ (W_A)\times100}{W_A+W_B} = \frac{75\ (g)\times100}{(75+2.5)g} = 96.78\%$

3. *Calculate the molarity of each of the following solutions (a) 30 g of $Co(NO_3)_2.\ 6H_2O$ in 4.3 L of solution. (b) 30 mL of 0.5 M H_2SO_4 diluted to 500 mL.*

(a) Mass of $Co(NO_3)_2.6H_2O$ (W_B) = 30 g

Molar mass of $Co(NO_3)_2.6H_2O$ (M_B) = 297 g/mol

Volume of solution, (V) = 4.3 L

Molarity (M) = $\frac{W_B}{M_B\times V\ (in\ L)} = \frac{30\ g}{297\ g/mol\times4.3\ (L)} = 0.023\ mol/L$

(b) Initial volume (V_1) = 30 mL

Molarity (M_1) = 0.5 mol/L

Final volume (V_2) = 500 mL

Final molarity (M_2) = ?

$M_2\ V_2 = M_1\ V_1$ or, $M_2 = \frac{M_1\ V_1}{V_2} = \frac{0.5\times30}{500} = 0.03\ mol/L.$

4. *Calculate the mass of urea (NH_2CONH_2) required in making (a) 2.5 kg of 0.25 molal aqueous solution, (b) 0.25 molal aqueous solution using 2.5 kg of water.*

(a) Let the mass of urea required be = (W_B) g

Molar mass of urea (NH_2CONH_2) = (M_B) = 60 g/mol

Mass of solution ($W_A + W_B$) = 2.5 kg = 2500 g

Mass of solvent (W_A) = (2500 – W_B) g

Molality (m) = 0.25 mol/kg

Molality (m) = $\frac{W_B \times 1000}{M_B \times W_A(kg)}$

$$W_B = \frac{m \times M_B \times W_A}{1000} = \frac{2.05 \times 60 \times (2500 - W_B)}{1000} = 36.94\ g$$

(b) Here, (W_A) = 2.5 kg = 2500 g

$$\therefore\ W_B = \frac{0.25 \times 60 \times 2500}{1000} = 37.5\ g$$

5. *Calculate (a) molality, (b) molarity of KI if the density of 20% (mass/mass) aqueous KI is 1.202 g/mL.*

Mass of KI (W_B) = 20 g;

Molar mass of KI (M_B) = 166 g/mol;

Mass of solution ($W_A + W_B$) = 100 g;

Density of solution (d) = 1.202 g/mL

Volume of solution, (V) $= \frac{mass}{density} = \frac{100(g)}{1.202(g/mL)} = 83.2\ mL$

Mass of solvent (W_A) = 100 – 20 = 80 g

(a) Molality (m) = $\frac{W_B \times 1000}{M_B \times W_A(kg)} = \frac{20\ (g) \times 1000\ (g/kg)}{166\ (g/mol) \times 80\ (g)} = 1.51\ mol/kg$

(b) Molarity (M) = $\frac{W_B \times 1000}{M_B \times V} = \frac{20\ (g) \times 1000\ (mL/L)}{166\ (g/mol) \times 83.2\ (mL)} = 1.45\ mol/L$

Multiple Choice Questions (MCQ)

1. *What is the mass of the precipitate formed when 50 mL of 16.9% (w/v) solution of $AgNO_3$ is mixed with 50 mL of 5.8% (w/v) NaCl solution? (Ag = 107.3, N = 14, O = 16, Na = 23, Cl = 35.5).*
   (a) 7 g (b) 14 g (c) 28 g (d) 3.5 g
2. *When a solute is present in trace amount, which of the following expression is used?*
   (a) Milligram% (b) Microgram% (c) Nanogram% (d) parts per million
3. *Unit of mole fraction is:*
   (a) mole/litre (b) mole/litre^2 (c) moles – litre (d) nil
4. *A mixture has 18 g of water & 414 g ethanol. The mole fraction of water in mixture is: (assume ideal behaviour of the mixture).*
   (a) 0.1 (b) 0.4 (c) 0.7 (d) 0.9
5. *What is the mole fraction of the solute in a 1.00m aqueous solution?*
   (a) 0.0354 (b) 0.0177 (c) 0.177 (d) 1.770
6. *2.0 molar solution is obtained when 0.5 mole solute is dissolved in:*
   (a) 250 mL solvent (b) 250 g solvent (c) 250 mL solution (d) 1000 mL solvent
7. *A solution of $CaCl_2$ is 0.5 mol/litre. The the moles of chloride ions in 500 mL will be:*
   (a) 0.25 (b) 0.50 (c) 0.75 (d) 1.00
8. *What is the weight (in g) of Na_2CO_3 (molar mass = 106) present in 250 mL of its 0.2 M solution:*
   (a) 0.53 (b) 5.3 (c) 1.06 (d) 10.6
9. *What will be the molality of a solution having 18 g of glucose (molecular weight = 180) dissolved in 500g of water?*
   (a) 1 mol/kg (b) 0.5 mol/kg (c) 0.2 mol/kg (d) 2 mol/kg
10. *The normality of 0.3 M phosphorous acid (H_3PO_4) is:*
    (a) 0.1 N (b) 0.9 N (c) 0.3 N (d) 0.6 N

Answers of the Questions:

1. (a) 16.9% (w/v) $AgNO_3$ solution means 100 mL of solution contains 16.9 g of $AgNO_3$.

5.8% (w/v) NaCl solution means 100 mL of solution contains 5.8 g of NaCl.

	$AgNO_3$ +	NaCl ⇒	AgCl ↓ +	$NaNO_3$
In 100 mL	16.9 g	5.8 g	--	--
In 1 L	169 g	58 g	--	--
	≡ 1 mol	≡ 1 mol		
In 50 mL	0.05 mL	0.05 mol	0.05 mol	--

When 0.05 mol of $AgNO_3$ reacts with 0.05 mol of NaCl, 0.05 mol of AgCl is formed.

∴ The mass of the precipitate formed = 0.05 mol × 142.8 g/mol = 7.14 g ≈ 7g.

2. (d)

3. (d) Mole fraction is unitless quantity.

4. (a) Number of moles of ethanol (n_A) $= \frac{W_A}{M_A} = \frac{414}{46} = 9$

Number of moles of ethanol (n_B) $= \frac{W_B}{M_B} = \frac{18}{18} = 1$

Mole fraction of water $= x_B = \frac{n_B}{n_A + n_B} = \frac{1}{9+1} = \frac{1}{10} = 0.1$

5. (b) Mass of water (W_A) = 1000 g ;

Number of moles of solute (n_B) = 1 mole

Number of moles of ethanol (n_A) $= \frac{W_A}{M_A} = \frac{1000}{18} = 55.55$

Mole fraction of water $= x_B = \frac{n_B}{n_A + n_B} = \frac{1}{55.55 + 1} = 0.0177.$

6. (c) Molarity $= \frac{Number\ of\ moles\ of\ solute}{Volume\ of\ solution\ in\ litre}$

$\therefore 2.0 = \frac{0.5}{Volume\ of\ solution\ in\ litre}$

∴ Volume of solution in litre $= \frac{0.5}{2.0} = 0.250\ litre = 250\ mL$

7. (b) $CaCl_2 \rightleftharpoons Ca^{+} + 2Cl^{-}$

(1 mole) (1 mole) (2 moles)

1 L of 0.5 M $CaCl_2$ solution will contain,

2 × 0.5 = 1 mole of Cl^{-} ions.

500 mL of 0.5 M $CaCl_2$ solution will contain,

1 × 0.5 = 0.5 mole of Cl^{-} ions.

8. (b) Molarity $= \frac{Mass}{Molar\ mass\ \times\ Volume\ in\ mL} \times 1000$

$\therefore Mass = \frac{0.2\ M \times\ 106 \times 250mL}{1000} = 5.3\ g$

9. (c) Molality $= \frac{Number\ of\ moles\ of\ solute}{Mass\ of\ solvent\ in\ g} \times 1000$

$$= \frac{Mass\ of\ solute}{Molar\ mass\ of\ solute} \times \frac{1000}{Mass\ of\ solvent\ in\ g}$$

Molality $= \frac{18 \times 1000}{180 \times 500} = 0.2 mol/kg$

10. (d) Normality of acid = molarity × basicity

H_3PO_3 is a dibasic acid;

Therefore, N = 0.3 × 2 = 0.6 N.

5 VAPOUR PRESSURE OF LIQUID SOLUTIONS

- When a liquid is taken in a closed vessel, a part of the liquid evaporates & its vapours occupy the available empty space. These vapours cannot escape as the vessel is closed. They would rather have a tendency to condense into liquid form.
- In fact an equilibrium is established between vapour phase & liquid phase & the pressure that its vapour exert is termed as vapour pressure.
- Thus, vapour pressure of a liquid may be defined as the pressure exerted by vapour above the liquid surface in equilibrium with the liquid phase at a given temperature.
- *The vapour pressure of a liquid depends on the following factors:*
  a) *Nature of liquid:* Liquid having weak intermolecular forces are volatile & therefore have great vapour pressure. E.g., dimethyl ether has larger vapour pressure than ethyl alcohol.
  b) *Temperature:* Vapour pressure of a liquid increases with increase in temperature. This is because with increase in temperature, the kinetic energy of the molecules increases & therefore large numbers of molecules are available for escaping from the surface of the liquid.

1. Vapour Pressure Of Solution Of Solids In Liquids

- Let us consider the addition of a small amount of a non-volatile solute such as, glucose, sucrose, sodium chloride, etc., to the liquid (solvent such as water) to form a solution.
- In such a case the vapour pressure of the solution is solely due to the solvent molecules, as the solute is non-volatile. It is found that the vapour pressure of the solution is lower than that of the pure solvent.
- *Raoult's law for a solution containing a non-volatile solute & volatile solvent:* It states that the relative lowering of vapour pressure is equal to mole fractions of solute which is non-volatile.
- Mathematically, $p = p_A + p_B$

  Or, $p = p_A$ (since solute B is non-volatile)

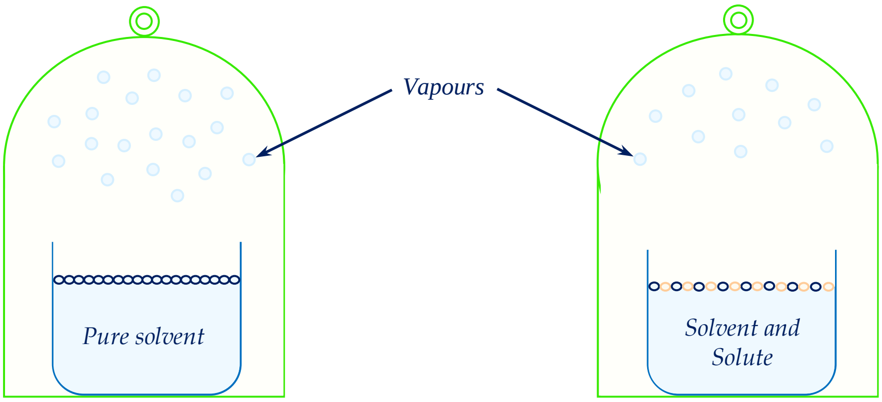
  $$p = p_A^0\, x_A$$
  $$p = p_A^0\,(1 - x_B) = p_A^0 - p_A^0\, x_B$$
  $$p_A^0\, x_B = p_A^0 - p$$

  Or, $\frac{p_A^0 - p}{p_A^0} = x_B$

  Or, Relative lowering of vapour pressure = Mole fraction of solute
- *Reason for lower vapour pressure of solution:*

i. The lowering of vapour pressure can be explained on the basis of the surface area of the liquid from which evaporation occurs.

ii. In case of the solution, a part of the liquid surface is occupied by solute particles, which are non-volatile. Therefore, evaporation of the liquid will take place from a lesser surface area. In other words, the particles (or molecules) of the liquid will now have a less tendency to escape into vapour state & this shall, therefore, results in lowering of vapour pressure.



Vapour pressure of pure liquid

Vapour pressure of solution

2. Vapour Pressure Of Solution Of Solids In Liquids

- *Raoult's law for volatile solute:* It states that for a solution of volatile liquids the partial pressure of each component is directly proportional to its mole fraction.
- Mathematically, $p_A \propto x_B \qquad p_B \propto x_B$

$$p_A = p_A^0\, x_A \qquad p_B = p_B^0\, x_B$$

Where, p_A & p_B are partial vapour pressure,

x_A & x_B are mole fraction,

p_A^0 & p_B^0 are the vapour pressure of pure components A & B respectively.

According to Raoult's law, $p_A = p_A^0\, x_A$ & $p_B = p_B^0\, x_B$

If p is total vapour pressure then according to Dalton's law of partial pressure,

$$p = p_A + p_B\,,$$
$$p = p_A^0\, x_A + p_B^0\, x_B$$
$$p = p_A^0\,(1 - x_B) = p_B^0\, x_B$$
$$p = p_A^0 + (p_B^0 - p_A^0)\, x_B$$

As p_A^0 & p_B^0 are constants at a given temperature it is evident from the above equations that the total vapour pressure varies linearly with the mole fraction x_B (or, x_A since $x_A = 1 - x_B$)

Let us assume that a solution has n_A moles of liquid A & n_B moles of liquid B.

Mole fraction of A, $x_A = \frac{n_A}{n_A + n_B}$

Mole fraction of B, $x_B = \frac{n_B}{n_A + n_B}$

- *Limitations of Raoult's law:*
  - i. When the solution is not dilute, there are significant interactions between solute & solvent particles & Raoult's law is not obeyed fully. There are positive & negative deviations from ideal behaviour.
  - ii. If solute molecules dissociates in solution, there are more particles in solution & therefore, lowering of vapour pressure shows an increased effect.

$$NaCl(s) \rightleftharpoons Na^+\,(aq.) + Cl^-\,(aq.)$$

  - iii. If the solute molecules associates in solution, there are less particles in solution, & therefore lowering of vapour pressure shows a decreased effect.

$$nAB \rightleftharpoons (AB)_n$$

E.g., $2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$

- *Dalton's law of partial pressure in combination with Raoult's law:*

From Raoult's law,

$p_A = p_A^0\, x_A$ .... (i)

From Dalton's law,

$p_A = y_A\, p$ .... (ii)

p_A = Partial pressure of A

y_A = Mole fraction of vapour of A in vapour phase

p = Total vapour pressure due to all components

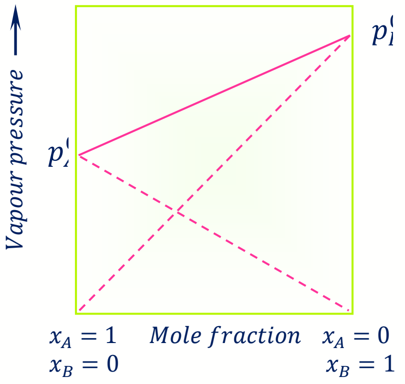
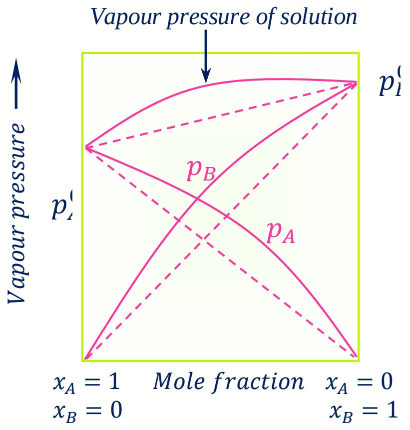
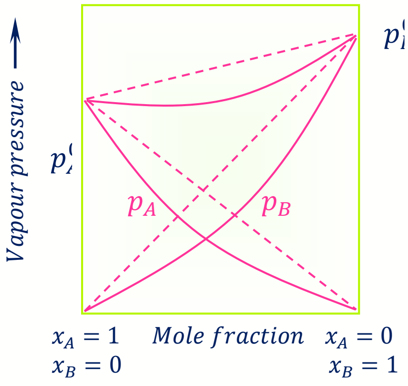
So, from (i) and (ii),

$$p_A^0\, x_A = y_A\, p$$
$$\frac{x_A}{y_A} = \frac{p}{p_A^0}$$

6 KONOWALOFF RULE

- ✓ At any fixed temperature, the vapour phase is always richer in the mole volatile component as compared to the solution phase.
- ✓ In other words, mole fraction of the more volatile component is always greater in the vapour phase than in the solution phase.
- ✓ The composition of the vapour phase in equilibrium with the solution can be determined from the partial pressure of the two components.
- ✓ If y_A & y_B are the mole fractions of components A & B respectively in the vapour phase,
  then, $p_A = y_A\, p_{total}$; $p_B = y_B\, p_{total}$.
  In general, $p_i = y_i\, p_{total}$.

7 COMPARISION BETWEEN IDEAL AND NON-IDEAL SOLUTIONS

Ideal Solution	Non-ideal Solution	
	Positive deviation (Raoult's law)	*Negative deviation (Raoult's law)*
1. *Obey Raoult's law at every range of concentration.*	1. *Do not obey Raoult's law.*	1. *Do not obey Raoult's law.*
2. $\Delta H_{mix} = 0$; *neither heat is evolved nor absorbed during dissolution.*	2. $\Delta H_{mix} > 0$; *Endothermic dissolution; heat is absorbed.*	2. $\Delta H_{mix} < 0$; *Exothermic dissolution; heat is evolved.*
3. $\Delta V_{mix} = 0$; *total volume of solution is equal to sum of volumes of the components.*	3. $\Delta V_{mix} > 0$; *Volume is increased after dissolution.*	3. $\Delta V_{mix} < 0$; *Volume is decreased during dissolution.*
4. $p = p_A + p_B$ $= p_A^0\, x_A + p_B^0\, x_B$ i.e., $p_A = p_A^0\, x_A$; $p_B = p_B^0\, x_B$	4. $p_A > p_A^0\, x_A$; $p_B = p_B^0\, x_B$ $\therefore p_A + p_B > p_A^0\, x_A + p_B^0\, x_B$	4. $p_A < p_A^0\, x_A$; $p_B = p_B^0\, x_B$ $\therefore p_A + p_B < p_A^0\, x_A + p_B^0\, x_B$
5. *A – A, A – B, B – B interactions should be same, i.e., 'A' & 'B' are identical in shape, size & character.*	5. *A – B attractive force should be weaker than A – A & B – B attractive forces. 'A' & 'B' have different shape, size & character.*	5. *A – B attractive force should be greater than A – A & B – B attractive forces. 'A' & 'B' have different shape, size & character.*
6. *Escaping tendency of 'A' & 'B' should be same in pure liquids & in the solution.*	6. *Escaping tendency of 'A' & 'B' easily showing higher vapour pressure than the expected value.*	6. *Escaping tendency of both 'A' & 'B' is lowered showing lower vapour pressure than the expected value.*
7. *Examples: dilute solution; mixture of benzene + toluene, n-hexane + n-heptane, methanol + ethanol, etc.*	7. *Examples: acetone + ethanol, water + methanol, water + ethanol,* CCl_4 *+ toluene,* CCl_4 *+* $CHCl_3$*, cyclohexane + ethanol.*	7. *Examples: acetone + aniline, acetone + chloroform,* HNO_3 *+ water, acetic acid + pyridine, hydrochloric acid + water.*
8. *Diagram representing vapour pressure for an ideal solution:*	8. *Diagram representing vapour pressure showing positive deviation:*	8. *Diagram representing vapour pressure showing negative deviation:*
		

Memories

➢ Vapour Pressure versus Temperature:

Vapour pressure of a liquid increases with temperature, as the formation of vapour pressure is an endothermic process.

If p_1 *and* p_2 *are the vapour pressure of a liquid at temperatures* T_1 *and* T_2*, then according to Clausius – Clapeyron equation.*

$$log_{10}\left(\frac{p_2}{p_1}\right) = \frac{\Delta H_{vap.}}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

If we plot a graph between p and T the above graph are obtained.

8 AZEOTROPES/AZEOTROPIC MIXTURE

- *Definition:* Azeotropes are binary mixtures having the same composition in liquid & vapour phase and boil at a constant temperature.
- *Types of Azeotropes:*

a) Minimum boiling Azeotropes:

- These are binary mixtures whose boiling point is less than either of the two components.
- The non-ideal solutions which shows a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.
- E.g., ethanol (b.p. = 351.3 K) & water (373 K) constitute minimum boiling azeotrope (b.p. 352.1 K) at the azeotrope composition of 95.57% by mass of ethanol.

b) Maximum boiling Azeotropes:

- These are the binary mixtures whose boiling point is more than either of the two components.
- The solution that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition,
- E.g., a mixture of 68% HNO_3 & 32% H_2O by mass.

Multiple Choice Questions (MCQ)

1. *Vapour pressure of pure A (p_A^0) = 100 mm Hg. Vapour pressure of B (p_B^0) = 150 mm Hg. 2 moles of liquid 'A' & 3 mole of liquid 'B' are mixed to form an ideal solution, the vapour pressure of solution will be:*
(a) 135 mm (b) 130 mm (c) 140 mm (d) 145 mm
2. *A solution has a 1:4 mole ratio of pentane to hexane. The vapour pressure of the pure hydrocarbons at 20^0C are 440 mm Hg for pentane & 120 mm Hg for hexane. The mole fraction of pentane in the vapour phase would be:*
(a) 0.549 (b) 0.200 (c) 0.786 (d) 0.478
3. *The vapour pressure of acetone at 20^0C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20^0C, its vapour pressure was 183 torr. The molar mass (g/mol) of the substance is:*
(a) 32 (b) 64 (c) 128 (d) 488
4. *In an experiment, 1 g of a non-volatile solute was dissolved in 100 g of acetone (molar mass = 58) at 298 K. The vapour pressure of the solution was found to be 192.5 mm Hg. The molecular weight of the solute is: (vapour pressure of acetone = 195 mm Hg)*
(a) 25.24 (b) 35.24 (c) 45.24 (d) 55.24
5. *On adding solute to a solvent having vapour pressure 0.80 atm, vapour pressure reduces to 0.60 atm. Mole fraction of solute is:*
(a) 0.25 (b) 0.75 (c) 0.50 (d) 0.33
6. *Vapour pressure of pure solvent & its solution at certain temperature are 660 mm & 600 mm of Hg, respectively. If 3.6×10^{-3} kg of solute is added into 40×10^{-3} kg of solvent, what is the molar mass of solute? (solvent = benzene, C = 12, H = 1)*
(a) 78.0 g/mol (b) 58.5 g/mol (c) 72.0 g/mol (d) 156 g/mol
7. *Heptane & octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kPa & 46.8 kPa, respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane & 35.0 g of octane?*
8. *The vapour pressure of water is 12.3 kPa at 300 K. Calculate the vapour pressure of 1 molal solution of a non-volatile solute in it.*
9. *The vapour pressure of pure liquids A & B are 450 mm Hg & 700 mm Hg at 350 K respectively. Find the composition of liquid mixture & also vapours if total vapour pressure is 600 mm Hg.*
10. *Benzene (C_6H_6) with b.pt 353.1 K & toluene (C_7H_8) with b.pt. 383.6 K are the two hydrocarbons which form nearly ideal solution. At 313 K, the vapour pressures of pure benzene & pure toluene are 21.2 kPa & 8.0 kPa respectively. Assuming an ideal solution behaviour, calculate the partial pressure of C_6H_6 & C_7H_8 & the total pressure in bar under the following conditions:*
(a) A solution made by mixing equal number of moles of C_6H_6 & C_7H_8.
(b) A solution made by mixing 4 moles of toluene & 1 mole of benzene.
(c) A solution made by mixing equal masses of toluene & benzene.

Answers of the Questions:

1. (b) $x_A = \frac{2}{5}$; $x_B = \frac{3}{5}$

$$p = p_A^0\, x_A + p_B^0\, x_B$$
$$= 100 \times \frac{2}{5} + 150 \times \frac{3}{5}$$
$$= 40 + 90 = 130\ mm$$

2. (d) The mole fraction of pentane in vapour phase = y_p

Mole ratio $n_p : n_h = 1:4$

$$x_p = \frac{n_p}{n_p + n_h} = \frac{1}{1+4} = \frac{1}{5}$$
$$x_h = \frac{n_h}{n_p + n_h} = \frac{4}{1+4} = \frac{4}{5}$$
$$p_T = p_p^0\, x_p + p_h^0\, x_h$$
$$= 440 \times \frac{1}{5} + 120 \times \frac{4}{5} = 88 + 96 = 184;$$
$$p_p^0\, x_p = y_p p_T = \frac{88}{184} = y_p;$$

Therefore, $y_p = 0.478$

3. (b) $\frac{p_A^0 - p_T}{p_A^0} = \frac{W_B}{M_B}\frac{M_A}{W_A}$

$$\therefore \frac{185-183}{185} = \frac{1.2 \times 58}{M_B \times 100}$$
$$M_B = \frac{1.2}{2} \times \frac{58}{100} \times 185$$
$$= 63.38\ g/mol\ \approx 64 g/mol$$

4. (c) $\frac{p_A^0 - p_T}{p_A^0} = \frac{W_B}{M_B}\frac{M_A}{W_A}$

$$\therefore \frac{195-192.5}{195} = \frac{1 \times 58}{M_B \times 100}$$
$$M_B = \frac{195}{2.5} \times \frac{58}{100} = 45.24$$

5. (a) According to Raoult's law,

$$x_B = \frac{p_A^0 - p_T}{p_A^0} = \frac{0.80 \times 0.60}{0.80} = 0.25$$

6. (a) $\frac{p_A^0 - p_T}{p_A^0} = \frac{W_B}{M_B}\frac{M_A}{W_A}$

$$\therefore \frac{660-600}{660} = \frac{3.6 \times 10^{-3} \times 78}{40 \times 10^{-3} \times M_B}$$
$$M_B = \frac{3.6 \times 10^{-3} \times 78}{40 \times 10^{-3} \times 0.09} = 78.0\ g/mol$$

7. Molar mass of heptane, C_7H_{16} = 100 g/mol

Molar mass of octane, C_8H_{18} = 114 g/mol

$$n_{C_7H_{16}} = \frac{26.0\ g}{100\ g/mol} = 0.26\ mol$$
$$n_{C_8H_{18}} = \frac{35.0\ g}{114\ g/mol} = 0.31\ mol$$
$$x_{C_7H_{16}} = \frac{n_{C_7H_{16}}}{n_{C_7H_{16}} + n_{C_8H_{18}}} = \frac{0.26}{0.26 + 0.31} = 0.456$$
$$x_{C_8H_{18}} = 1 - x_{C_7H_{16}} = 1 - 0.456 = 0.544$$
$$p_{C_7H_{16}} = 105.21\ kPa \times 0.456 = 47.97\ kPa$$
$$p_{C_8H_{18}} = p_{C_8H_{18}} \times x_{C_8H_{18}} = 46.8\ kPa \times 0.544 = 25.46\ kPa$$
$$p_{total} = p_{C_7H_{16}} + p_{C_8H_{18}} = 47.97 + 25.46 = 73.43\ kPa$$

Answers of the Questions:

8. 1 molal solution means 1 mol of the solute is present in 1000 g of the solvent, H_2O (assuming the solution to be dilute).

$$n_{H_2O} = \frac{1000}{18} = 55.5\ mol$$

$$\therefore x_{solute} = \frac{1}{1+55.5} = 0.0177$$

Also, $x_{solute} = \frac{p_A^0 - p_s}{p_A^0}$

$$0.0177 = \frac{12.3 - p_s}{12.3}$$

Or, $p_s = 12.08\ kPa$

9. Total vapour pressure $(p_T) = 600\ mmHg$

Let mole fraction of A is x_A & that of B is x_B

Vapour pressure of pure A (p_A^0) = 450 mm Hg

Vapour pressure of pure B (p_B^0) = 700 mm Hg

Now, $p_T = p_A^0\, x_A + p_B^0\, x_B$

$$600 = 450\, x_A + 700\, x_B = 450\, x_A + 700\,(1 - x_A) = 700 - 250\, x_A$$

Or, $x_A = 0;\ 4x_B = 1 - x_A = 1 - 0.4 = 0.6$

Mole fraction of A in vapour phase, $(y_A) = \frac{p_A^0 x_A}{p_T} = \frac{0.4 \times 450}{600} = 0.3$

Mole fraction of B in vapour phase, $(y_B) = \frac{p_B^0 x_B}{p_T} = \frac{0.6 \times 700}{600} = 0.7$

10. According to Raoult’s law, partial vapour pressure of benzene, $p_A = p_A^0\, x_A$

Where, p_A^0 is the vapour pressure of pure benzene & x_A is the mole fraction of benzene.

Partial vapour pressure of toluene, $p_A = p_A^0\, x_A$

Where, p_B^0 is the vapour pressure of pure toluene & x_B is the mole fraction of toluene.

Now, let us calculate the partial pressures of the solution.

(i) To calculate the vapour pressure of solution containing equal number of moles of benzene & toluene.

Let the number of moles of each liquid be $'a'$.

$$\therefore\ x_A = x_B = \frac{a}{a+a} = 0.5$$

Partial vapour pressure of benzene = $p_A^0\, x_A = 21.2 \times 0.5 = 10.6\ kPa$

Partial vapour pressure of toluene = $p_B^0\, x_B = 8.0 \times 0.5 = 4.0\ kPa$

$\therefore$ Total vapour pressure $= 10.6 + 4.0 = 14.6\ kPa = 14.6 \times 10^{-2}\ bar$

(ii) To calculate the vapour pressure of solution containing 4 moles of toluene & 1 mole of benzene.

$$x_A = \frac{No.of\ moles\ of\ benzene}{Total\ no.of\ moles\ of\ benzene\ \&\ toluene} = \frac{1}{1+4} = 0.2$$

$x_B = 1 - 0.2 = 0.8$

Partial vapour pressure of benzene, $p_A = p_A^0\, x_A = 21.2 \times 0.2 = 4.24\ kPa.$

Partial vapour pressure of toluene, $p_B = p_B^0\, x_B = 8.0 \times 0.8 = 6.4\ kPa.$

$\therefore$ Total vapour pressure $= 4.24 + 6.4 = 10.64\ kPa = 10.64 \times 10^{-2}\ bar.$

(iii) To calculate the vapour pressure of the solution containing equal masses of benzene & toluene.

Let the mass of benzene = mass of toluene = m g

$\therefore$ Moles of benzene = $\frac{m\ (g)}{78\ (g/mol)} = \frac{m}{78} mol$

Moles of toluene = $\frac{m\ (g)}{92\ (g/mol)} = \frac{m}{92} mol$

Mole fraction of benzene, $x_A = \frac{\frac{m}{78}}{\frac{m}{78} + \frac{m}{92}} = 0.541$

Mole fraction of benzene, $x_B = 1 - x_A = 1 - 0.541 = 0.459$

Partial vapour pressure of benzene = $p_A^0\, x_A = 21.2 \times 0.541 = 11.47\ kPa$

Partial vapour pressure of toluene = $8.0 \times 0.459 = 3.672\ kPa$

Total vapour pressure $= 11.47 + 3.672 = 15.142\ kPa$

$$= 15.142\ (kPa) \times 10^{-2} (bar/kPa) = 15.142 \times 10^{-2} bar$$

9 COLLIGATIVE PROPERTIES

- Those properties which depends on the number of solute particles (molecules, atoms or ions) but not upon their nature are called colligative properties.
- The following are the colligative properties:

  a) *Relative lowering of vapour pressure of the solvent.*
  b) *Elevation of boiling point of the solvent.*
  c) *Depression of freezing point of the solvent.*
  d) *Osmotic pressure of the solution.*

a) *Relative lowering of vapour pressure of the solvent.*

The addition of a non-volatile solute to a volatile solvent decreases the escaping tendency of the solvent molecules from the surface of solutions as some of the surface area is occupied by non-volatile solute particles. According to Raoult's law, the relative lowering of vapour pressure is equal to mole fraction of solute.

Thus, = $\frac{p_A^0 - p}{p_A^0} = x_B = \frac{n_B}{n_A + n_B}$

For a dilute solution, $n_B \ll n_A$, hence neglecting n_B in the denominator, we have

$$\frac{p_A^0 - p}{p_A^0} = \frac{n_B}{n_A} = \frac{W_B}{M_B} \times \frac{M_A}{W_A}$$

$$M_B = \frac{p_A^0}{p_A^0 - p} \times \frac{W_B \times M_A}{W_A}$$

$$M_B = \frac{W_B \times M_A \times p_A}{W_A . \Delta p}$$

Factors Affecting Vapour Pressure:

i. *Nature of liquid:*

- Liquids having weak cohesive forces are more volatile & have higher vapour pressure at a given temperature.
- Higher is the boiling point of a liquid, less is its vapour pressure at given temperature.
  E.g., vapour pressure of gasoline is higher than diesel oil.

ii. *Temperature:* Vapour and temperature of a liquid are related to each other by clapeyron equation:

$$2.303 \, log \frac{p_2}{p_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Here, p_1 & p_2 are vapour pressure at temperature T_1& T_2 respectively & ΔH = Enthalpy of evaporation & is always positive thus is $T_1 < T_2$ then $p_1 < p_2$.

iii. *Addition of non-volatile solute:*

When a non-volatile solute is added in a pure solvent its vapour pressure decreases, i.e., vapour pressure of a solution is always less than its solvent. It is known as lowering in vapour pressure. It is due to reduction in the relative surface area of liquid available for evaporation as a part of surface is occupied by non-volatile solute particles.

Let the vapour pressure of pure solvent is p^0 while that of its solution is p_s, then

Lowering in vapour pressure = $p^0 - p_s$.

& Relative lowering in vapour pressure = $\frac{p^0 - p_s}{p^0}$

Formula Chart (Relative Lowering Of Vapour Pressure)

1. $\frac{\Delta p}{p_A^0} = \frac{n_p}{n_A + n_B} = x_B$
2. $M_B = \frac{W_B \times M_A \times p_A^0}{W_A . \Delta p}$ [for very dilute solution]
3. $M_B = \frac{W_B \times M_A \times p_A}{W_A . \Delta p}$ [for very all solution]

$\Delta p = p_A^0 - p_A$;
W_B = Mass of solute ;
W_A = Mass of solvent ;
M_A & M_B molar masses of solvent & solute respectively.

Numericals Based On Relative Lowering Of Vapour Pressure

1. *The vapour pressure of 2% aqueous solution of a non-volatile substance X at 373 K is 755 torr. Calculate the molar mass of the solute. Vapour pressure of pure water at 373 K is 760 torr.*

Here, Mass of the solvent = W_A = 100 – 2 = 98 g
Mass of the solute W_B = 2 g
Molar mass of solvent = (M_A) = 18 g/mol
Molar mass of solute = (M_B) = ?
Vapour pressure of pure water (p_A^0) = 760 torr.
Vapour pressure of solution (p_A) = 755 torr.

Now, for dilute solution, $M_B = \frac{W_B \times M_A}{W_A}\left[\frac{p_A^0}{p_A^0 - p_A}\right]$

$$= \frac{2 \times 18}{98} \times \frac{760}{760 - 755}$$

$$= \frac{2 \times 18 \times 760}{98 \times 5} = 55.8\ g/mol.$$

2. *Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea (NH_2CONH_2) is dissolved in 850 g of water. Calculate the vapour pressure of water for this solution & its relative lowering of vapour pressure.*

Mass of water = W_A = 850 g

Moles of water = $n_A = \frac{850\ g}{15\ g/mol} = 47.22\ mol$

Mass of the urea = W_B = 50 g

Molar mass of urea = (M_B) = 60 g/mol

Moles of urea = $n_B = \frac{50\ g}{60\ g/mol} = 0.83\ mol$

Since the solution is not dilute we can use the formula, $\frac{\Delta p}{p_A^0} = \frac{n_p}{n_A + n_B}$; or, $\frac{\Delta p}{p_A^0} = \frac{n_B}{n_A}$

Thus, $\frac{p_A^0 - p_A}{p_A} = \frac{0.83}{47.22}$

$$\frac{p_A^0}{p_A} - 1 = \frac{0.83}{47.22}$$

$$\frac{p_A^0}{p_A} = 1 + \frac{0.83}{47.22} = 1.0175$$

$$p_A = \frac{p_A^0}{1.0175} = \frac{23.8}{1.0175} = 23.39\ mm\ Hg$$

Relative lowering vapour pressure = $\frac{p_A^0 - p_A}{p_A} = \frac{23.8 - 23.39}{23.8} = 0.0172$

3. *At 310 K, the vapour pressure of an ideal solution containing 2 moles of A & 3 moles of B is 550 mm of Hg. At the same temperature, if 1 mole of B is added to this solution, the vapour pressure of solution increases by 10 mm of Hg. Calculate the vapour pressure of A and B in their pure state.*

According to Raoult's law, $p = p_A^0\, x_A + p_B^0\, x_B$

Given that p = 550 mm, % n_A & n_B are 2 & 3 moles respectively.

$$550 = p_A^0 \times \left(\frac{2}{2+3}\right) + p_B^0 \times \left(\frac{3}{2+3}\right)$$

Or, $2p_A^0 + 3p_B^0 = 2750$ (initially) .... (i)

Now, adding 1 mole of B, & using Raoult's law again,

$$560 = p_A^0 \times \left(\frac{2}{2+4}\right) + p_B^0 \times \left(\frac{4}{2+4}\right)$$

$(\therefore p = 560mm, n_A = 2\ mole, n_B = 4\ mole)$

Or, $2p_A^0 + 4p_B^0 = 3360$ .... (ii)

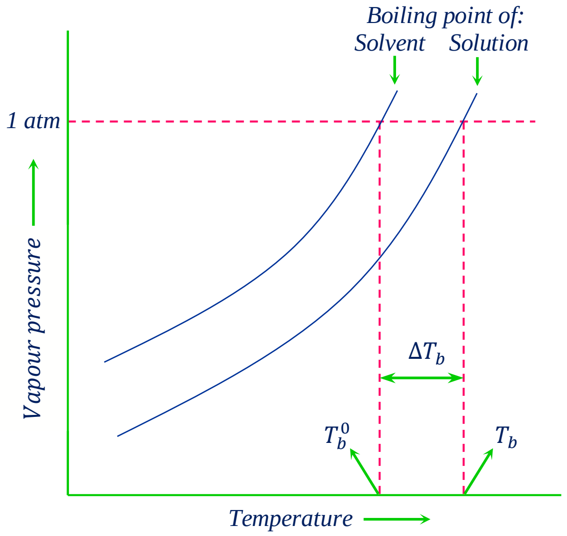
Solving equation (i) & (ii);

$p_A^0 = 460\ mm$; $p_B^0 = 610\ mm$

b) *Elevation of boiling point*

- Boiling point is the temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure.
- When a non-volatile solute is added to a volatile solvent, the vapour pressure of the solvent decreases.
- In order to make this solution boil its vapour pressure must be increased by raising the temperature above the boiling point of the pure solvent.
- The difference in the boiling point of solution (T_b^0) & that of pure solvent (T_b) is called *elevation of boiling point* (ΔT_b).
- Thus, elevation of boiling point $= \Delta T_b = T_b - T_b^0$.
- For *dilute solution*, it has been found that the elevation of boiling point is directly proportional to the molal concentration of the solute in the solution.
- Thus, $\Delta T_b \propto m$ or, $\Delta T_b = K_b m$
  Where, K_b is a constant called *boiling point elevation constant* or *molal elevation constant* or *ebullioscopic constant of the solvent*.
  When $m = 1\, mol/kg,\ \Delta T_b = K_b$
- Hence, *molal elevation constant* may be defined as the elevation in boiling point when 1 mole of a non-volatile solute is dissolved in 1 kilogram (1000 g) of solvent.
- The unit of K_b is $K\ kg\ mol^{-1}$.
- As, $m = \frac{W_B \times 1000}{M_B \times W_A}$
- Therefore, $\Delta T_b = \frac{K_b \times W_B \times 1000}{M_B \times W_A}$

$$M_B = \frac{K_b \times W_B \times 1000}{\Delta T_b \times W_A}$$



Vapour pressure temperature curves showing elevation in boiling point of solution

Formula Chart (Elevation Of Boiling Point)

1. $\Delta T_b = K_b m$
2. $M_B = \frac{K_b \times W_B \times p_A^0}{W_A . \Delta T_b}$ [for very dilute solution]
3. $K_b = \frac{M_A \times R T_b^2}{\Delta_{vap} H \times 1000}$ [for very all solution]
4. $\Delta T_b = K_b m = K_b = \frac{W_B \times 1000}{W_A \times M_B}$
5. $\Delta T_b = \frac{K_b \times W_B \times 1000}{W_A . M_B}$
6. $\Delta T_b = \frac{W_B \times 1000 K_b'}{W_A \times m}$
7. $K_b' = \frac{RT^2}{1000 \times l}$

$K_b =$ Molal elevation constant
$M_B =$ Molar mass of solute
$W_A =$ Mass of solvent
$\Delta T_b =$ Elevation in boiling point
$\Delta_{vap} H =$ Enthalpy of vaporization of
$m =$ Molality of solution
$M_A =$ Molar masses of solvent respectively.
$l =$ Heat of vaporization
R = Universal gas constant

Numericals Based On Elevation Of Boiling Point

1. *Dissolution of 10 g of a non-volatile solute in 100 g of benzene raise its boiling point by 1^0. Calculate the molar mass of solute. (K_b for benzene 2.53 K/m)*

   Mass of solute (W_B) = 10 g

   Mass of solvent (W_A) = 100 g

   Elevation in boiling point (ΔT_b) = 1^0

   $$\Delta T_b = K_b m = K_b = \frac{W_B \times 1000}{W_A \times M_B}$$

   Or, $M_B = \frac{K_b \times W_B \times 1000}{W_A \times \Delta T_b} = \frac{2.53 \times 10 \times 1000}{100 \times 1} = 253\ g/mol$

2. *A solution of glycerol ($C_3H_8O_3$; molar mass = 92 g/mol) in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42^0C. What mass of glycerol was dissolved to make this solution?*

   Given: M_B = 92 g/mol; W_A = 500 g; ΔT_b = 100.42 – 100 = 0.42^0C or 0.42 K;

   W_B = ? K_b = 0.512 K kg/mol^{-1}

   $$\Delta T_b = \frac{K_b \times W_B \times 1000}{W_A . M_B}$$

   $$0.42 = \frac{0.512\ K\ kg\ mol^{-1} \times W_B \times 1000}{92\ g/mol \times 500 g}$$

   $$W_B = \frac{0.42\ g \times 92\ g/mol \times 500\ g}{0.512\ K\ kg\ mol^{-1} \times W_B \times 1000} = 37.37\ g$$

3. *A solution of 2.5 g non-volatile solute in 100 g benzene boils at a higher temperature of 0.42^0C than boiling point of pure benzene. Calculate molecular mass of the solute. Molal elevation constant of benzene is 2.67.*

   Given, ΔT_b= 0.42^0C; W_B = 2.5 g; W_A = 100g; K_b' = 2.67 molality

   $$\Delta T_b = \frac{W_B \times 1000 K_b'}{W_A \times m}$$

   $$0.42 = \frac{1000 \times 2.67 \times 2.5}{100 \times m}$$

   $$m = 158.93$$

4. *On dissolving 6.0 g glucose in 50 g of water, 0.34^0C elevation is boiling point was recorded. Calculate molal elevation constant of water.*

   Given, ΔT_b= 0.34^0C; W_B = 6 g; W_A = 50 g; m = 180

   $$\Delta T_b = \frac{W_B \times 1000 K_b'}{W_A \times m}$$

   $$0.34 = \frac{1000 \times K_b' \times 6}{50 \times 180}$$

   $$K_b' = 0.51\ K\ molality^{-1}$$

5. *When 2.56 g of an element is dissolved in 100 g of carbon disulphide, boiling point is elevated by 0.24^0C. Find out atomicity of the element. Boiling point of CS_2 is 46^0C & its heat of vaporization is 84 calorie/g. (atomic mass of the element = 31.98).*

   Given, boiling point of CS_2 = 273 + 46 = 319 K, l = 84 cal/g

   $$\Delta T_b = \frac{W_B \times 1000 K_b'}{W_A \times m} \text{ .... (i)}$$

   $$K_b' = \frac{RT^2}{1000 \times l} \text{ .... (ii)}$$

   From equation (ii), $K_b' = \frac{2 \times 319 \times 319}{1000 \times 84} = 2.42\ K\ molality^{-1}$

   W_B = 256 g; W_A = 100 g; ΔT_b = 0.24 K; K_b = 2.42 $K\ molality^{-1}$

   From equation (i), $0.24 = \frac{1000 \times 2.42 \times 2.56}{100 \times m} \Rightarrow m = 258.13$

   Since, atomic mass = 31.98

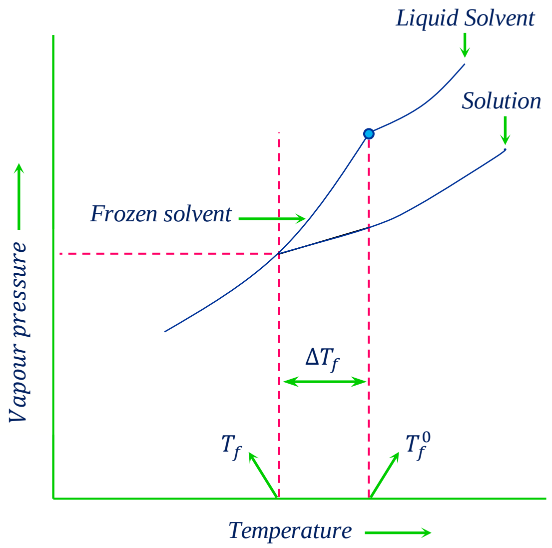
   Molecular mass = 258.13

   ∴ Atomicity (n) = $\frac{258.13}{31.98} \approx 8$

c) Depression in freezing point

- Freezing point is defined as the temperature at which the vapour pressure of a substance in its liquid phase is equal to its vapour pressure in the solid phase.
- A solution freezes when its vapour pressure equals the vapour pressure of the pure solid solvent.
- Whenever a non-volatile solute is added to the volatile solvent its vapour pressure decreases & it would become equal to that of solid solvent at a lower temperature.
- The difference in the boiling point of solution (pure solvent) (T_f^0) & that of pure solvent (T_f) is called *depression of freezing point* (ΔT_f).
- Thus, depression in freezing point $= \Delta T_f = T_f^0 - T_f$.
- For *dilute solution*, it has been found that the depression in freezing point is directly proportional to the molality of the solution.
- Thus, $\Delta T_f \propto m$ or, $\Delta f = K_f m$
  Where, K_f is a constant called *freezing point depression constant* or *molal depression constant* or *cryoscopic constant of the solvent*.
  When $m = 1\ mol/kg,\ \Delta T_f = K_f$
- Hence, *molal depression constant* may be defined as the depression in freezing point when 1 mole of a non-volatile solute is dissolved in 1 kilogram (1000 g) of solvent.
- The unit of K_b is $K\ kg\ mol^{-1}$.
- As, $m = \frac{W_B \times 1000}{M_B \times W_A}$
- Therefore, $\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A}$

$$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A}$$



Vapour pressure temperature curves showing depression in freezing point of solution

- The value of K_b & K_f, which depends upon the nature of the solvent & concentration of the solution, can be ascertained from the following relation:

$$K_b = \frac{R \times M_A \times (T_b^0)^2}{\Delta_{vap} H \times 1000}$$

$$K_f = \frac{R \times M_A \times (T_f^0)^2}{\Delta_{fus} H \times 1000}$$

Where, $K_b =$ Molal elevation constant
$T_b^0 =$ Boiling point of pure solvent
$T_f^0 =$ Freezing point of pure solvent
$\Delta_{vap} H =$ Enthalpy of vaporization of solvent
$\Delta_{fus} H =$ Enthalpy of fusion of solid solvent
$M_A =$ Molar masses of solvent
R = Universal gas constant

Formula Chart (Elevation Of Boiling Point)

1. $\Delta T_f = K_f m$
2. $M_B = \frac{K_f \times W_B \times 1000}{W_A . \Delta T_f}$
3. $K_f = \frac{R \times M_A \times (T_f^0)^2}{\Delta_{fus} H \times 1000}$
4. $\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A}$
5. $W_B = \frac{\Delta T_b \times M_B \times W_A}{K_f \times 1000}$

$K_f =$ Molal depression constant
$M_A =$ Molar masses of solvent
$M_B =$ Molar mass of solute
$W_A =$ Mass of solvent
$W_B =$ Mass of solute
$\Delta T_f =$ Depression in freezing point
$\Delta_{fus} H =$ Enthalpy of fusion of solvent
$m =$ Molality of solution

Numericals Based On Depression In Freezing Point

1. *Calculate the mass of ascorbic acid (Vitamin, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5^0C. K_f for acetic acid = 3.9 K kg mol^{-1}.*

Let mass of ascorbic acid required = W_B g

Molar mass of ascorbic acid ($C_6H_8O_6$) M_B = 176 g/mol

Mass of solvent, W_A = 75 g

Depression in melting point, ΔT_b = 1.5^0C

$$\Delta T_b = \frac{K_f \times W_B \times 1000}{M_B \times W_A}$$

$$\text{Or, } W_B = \frac{\Delta T_b \times M_B \times W_A}{K_f \times 1000} = \frac{1.5 \times 176 \times 75}{3.9 \times 1000} = 5.08\ g$$

2. *15.0 g of an unknown molecular material was dissolved in 450 g of water. The resulting solution was found to freeze at -0.34^0C. What is the molar mass of this material? (K_f of water = 1.86 K kg mol^{-1}).*

ΔT_f = 0^0C – (– 0.34^0C) = 0.34^0C or 0.34 K

W_B = 15.0 g; W_A = 450 g; K_f = 1.86 K kg mol^{-1}

Substituting these values in the expression,

$$M_B = \frac{K_f \times W_B \times 1000}{W_A . \Delta T_f}$$

$$= \frac{1.86\ K\ kg\ mol^{-} \times 15.0\ g \times 1000 g\ kg^{-1}}{0.34\ K \times 450\ g} = 182.35\ g\ mol^{-1}$$

3. *What mass of ethylene glycol (molecular mass = 62.0 g/mol) must be added to 5.50 kg of water to lower the freezing point of water from 0^0C to -10.0^0C? (K_f of water = 1.86 K kg mol^{-1})*

ΔT_f = 10 K; M_B = 62.0 g/mol; W_A = 5.50 kg or 5500 g; K_f = 1.86 K kg mol^{-1}

$$\text{We know that, } \Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A}$$

$$10 = \frac{1.86 \times W_B \times 1000}{62 \times 5500}$$

$$W_B = \frac{62 \times 5500 \times 10}{1000 \times 1.86} = \frac{3410000}{1860} = 1833.3\ g$$

4. *1.00 g of a non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. The freezing point depression constant of benzene is 5.12 K kg mol^{-1}. Find the molar mass of the solute.*

Substituting the values of various terms involved in equation,

$$M_B = \frac{K_f \times W_B \times 1000}{W_A . \Delta T_f}, \text{ we get}$$

$$M_B = \frac{5.12\ K\ kg\ mol^{-1} \times 1.00\ g \times 1000\ g/kg}{0.40\ K \times 50\ g} = 256\ g/mol$$

Thus, molar mass of the solute is 256 g/mol.

5. *Ethylene glycol (molecular mass = 62.0 g/mol) is a common automobile antifreeze. Calculate the freezing point of a solution containing 12.4 g of this substance in 100 g of water. Would it be advisable to keep this substance in the car radiator during summer?*

Given, K_f for water = 1.86 K kg mol^{-1}; K_b for water = 0.512 K kg mol^{-1}.

$$\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A}$$

$$= \frac{1.86\ K\ kg\ mol^{-1} \times 12.4\ g \times 1000\ gkg^{-1}}{62\ g\ mol^{-1} \times 100\ g} = 3.76\ K$$

Since, water freezes at 0^0C, so freezing point of the solution containing ethylene glycol will be – 3.76^0C.

$$\Delta T_b = \frac{K_b \times W_B \times 1000}{M_B \times W_A}$$

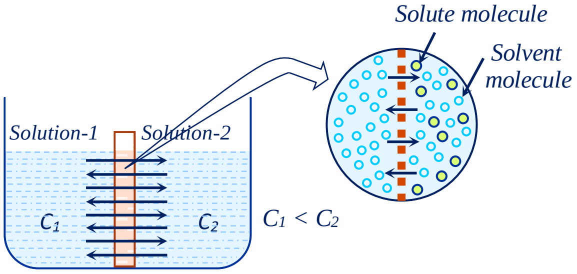
$$= \frac{0.512\ K\ kg\ mol^{-1} \times 12.4\ g \times 1000\ gkg^{-1}}{62\ g\ mol^{-1} \times 100\ g} = 1.024\ K$$

$$T_b = T_b^0 + \Delta T_b$$

= 100^0C + 1.024^0C = 101.024^0C

d) Osmosis and Osmotic pressure

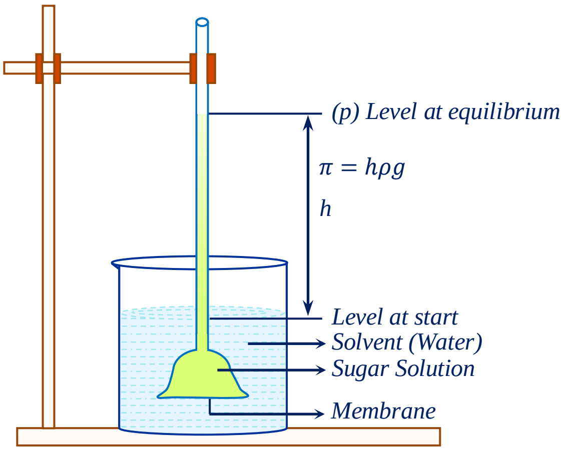
- *Osmosis:* When a solution is separated from its solvent by a semi-permeable membrane (SPM) there is a spontaneous flow of solvent molecules from solvent compartment to solution compartment. The phenomenon is called osmosis. The movement of solvent is only in one direction. In diffusion, however, movement takes place in both the direction.



Phenomenon of Osmosis

- *Semi-permeable membrane (SPM):* A membrane through which only solvent molecules can pass but not the solute ones. E.g., cellophane, parchment, copper ferrocyanide [$Cu_2[Fe(CN)_6]$].
- *Osmotic pressure (O.P or π):* The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis. i.e., to stop the passage of solvent molecules into it through semipermeable membrane.
  - ✓ Osmotic pressure (π) is proportional to molarity (C) of the solution at a given temperature T. Thus, $\pi = CRT$
  - ✓ $\pi = \frac{n_B}{V} RT = \frac{W_B \times R \times T}{M_B \times V}$

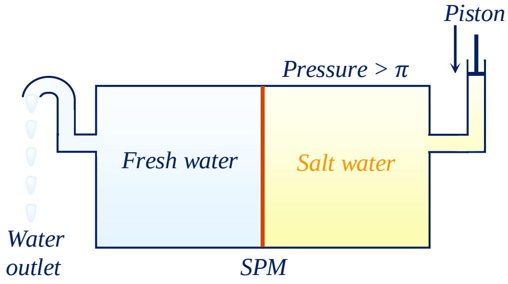
    Or, $M_B = \frac{W_B \times R \times T}{\pi \times V}$



Osmotic pressure

The pressure in excess of atmospheric pressure that must be applied to the solution to prevent it from raising in the tube is the osmotic pressure.

- *Reverse osmosis:* If a pressure larger than the osmotic pressure is applied to the solution side, the pure solvent (or water) flows out of the solution through the semi-permeable membrane. In this way the direction of osmosis is reversed and so the process is called reverse osmosis.
  - ✓ Thus, we can say that reverse osmosis is just opposite to the osmosis when an extra pressure is applied.
  - ✓ Reverse osmosis is used in desalination to get pure water from sea water.

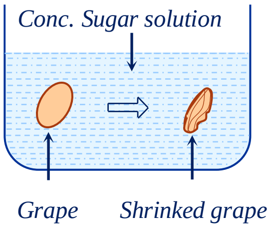


Reverse osmosis

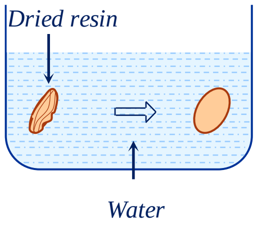
Reverse osmosis occurs when a pressure larger than osmotic pressure is applied in the solution.

- *Isotonic solution:* Two solutions are said to be isotonic when they exert the same osmotic pressure because they have the same molar concentration.

  E.g., All intravenous injections must be isotonic with the body.
- *Isosmotic solution:* When two isotonic solutions are separated by a semi-permeable membrane, no osmosis occurs, solution are called Isosmotic.
- *Hypotonic solution:* A solution having lower osmotic pressure than the other solution is called hypertonic with respect to the other solution.
- *Hypertonic solution:* A solution having higher osmotic pressure than the other solution is called hypertonic with respect to the other solution.
- *Isopiestic solution:* Different solutions having same vapour pressure are called isopiestic solution.



Exo-osmosis
In hypertonic solution



Endo-osmosis
In hypotonic solution

- *Application of Osmotic Pressure Phenomenon:*
  1. Chemical gardens: The silicate garden or chemical gardens are produced by dropping small crystals of various inorganic salts such as copper sulphate, nickel sulphate, alum, etc.
  2. Plasmolysis (or Crenation): When a cell is placed in hypertonic solution (or concentrated solution), it shrinks & this phenomenon is known as Plasmolysis.
  3. Haemolysis: When RBCs are placed in pure water or dilute solution than their sap. They swells up due to endo-osmosis & finally bursts. This phenomenon is known as haemolysis.
  4. Uptake of water by root hairs is also due to endo-osmosis of water present in soil to cells present at the tip of root.
  5. Wilting of plants in presence of excessive fertilizer present in soil is due to exo-osmosis.
  6. Preservation of jams, jellies or pickles by adding excessive sugar or salt is also based on osmotic phenomenon. In presence of concentrated solution, cells of microbes shrinks due to exo-osmosis.

Questions Based On Osmotic Pressure

1. *What will happen when red blood cells are placed in water?*

   They would swell due to osmosis & may even burst.

2. *At 27^{0}C, calculate the osmotic pressure of 5% by volume, urea solution.*

   Given, $w = 5g; V = \frac{100}{1000}L; T = 27 + 273 = 300K;$

   $m = 60 \ \& \ S = 0.0821\ L\ atm\ K^{-1}mol^{-1}$

   $\therefore \pi = \frac{w}{mV}ST = \frac{5 \times 0.0821 \times 300\ 1000}{60 \times 100} = 20.53\ atm$

3. *At 25^{0}C, a solution containing 0.2 g of polyisobutylene in 100 mL of benzene developed a rise of 2.4 mm at osmotic equilibrium. Calculate the molecular mass of polyisobutylene if the density of solution is 0.88 g/mL.*

   $O.P.(\pi) = h.d.g$

   Given, $h = 2.4\ mm; d = 0.88 g/mL \ \& \ g = 9.8\ ms^{-2}$

   $\pi = \frac{2.4}{10} \times 0.88 \times 981 = 207.187\ dyne\ cm^{-2}$

   $\pi V = nST$

   $207.187 \times 100 = \frac{0.2}{m} \times 8.314 \times 10^7 \times 298$

   $m = 2.39 \times 10^5$

4. *A solution of urea (molecular mass = 60) of strength 8.6 gL^{-1} is isotonic with a 5% (by volume) solution of a non-volatile organic compound (X). Calculate molecular mass of compound (X).*

   If association or dissociation of solute does not occur, then for isotonic solution,

   $C_1 = C_2$ or, $\frac{w_1}{m_1V_1} = \frac{w_2}{m_2V_2}$

   Given, For urea $w_1 = 8.6g; m_1 = 60$; V = 1 L

   For compound, X: $w_2 = 5g; m_2 = ?$; V = $\frac{10}{1000}L$

   $\frac{8.6}{60 \times 1} = \frac{5 \times 1000}{m_2 \times 100}$

   $\Rightarrow m_2 = 348.8$

5. *Calculate osmotic pressure of a solution obtained by mixing 100 mL of 3.4% solution (mass/volume) of urea (molecular mass = 60) & 100 mL of 1.6% solution (mass/volume) of cane-sugar (molecular mass = 342) at 20^{0}C.*

   Total moles in solution, $\frac{3.4}{60}(urea) + \frac{1.6}{342}(cane - sugar)$

   Total volume of solution = 200 mL (100 mL each)

   $\pi V = \left(\frac{3.4}{60} + \frac{1.6}{342}\right)ST$

   $\pi \times \frac{200}{100} = \left(\frac{3.4}{60} + \frac{1.6}{342}\right) \times 0.0821 \times 293$

   $= 7.38\ atm$

Abnormal Molar Masses

- The properties whose value does not depends upon the nature of solute but depends only upon the number of solute particles are known as colligative properties. *E.g.,* osmotic pressure, relative lowering of vapour pressure, elevation in boiling point and depression in freezing point.
- If $colligative\ properties_{Theot.} = colligative\ properties_{Exp.}$ (Normal)
- If $colligative\ properties_{Theot.} \neq colligative\ properties_{Exp.}$ (Abnormal)
- *The abnormality in colligative properties arises :*
  (i) As a result of change in molecular state of solute in solution due to dissociation or association.
  (ii) As a result of high solute concentrations where solute-solute interactions become effective.
- Thus, there may be two cases:
  (a) $colligative\ properties_{Theot.} < colligative\ properties_{Exp.}$ *(solute dissociates)*
  (b) $colligative\ properties_{Theot.} = colligative\ properties_{Exp.}$ *(solute associates)*

➢ Van't Hoff factor (*i*):

It may be defined as the ratio of normal molecular mass to the observed molecular mass of the solute.

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

Or, $$i = \frac{Observed\ colligative\ property}{Calculated\ value\ of\ colligative\ property}$$

Or, $$i = \frac{Total\ number\ of\ moles\ of\ particles\ after\ association\ /\ dissociation}{Number\ of\ particles\ before\ association/\ dissociation}$$

Van't Hoff factor (i) : expresses the extent of association or dissociation of the solute particles in the solutions.

In case of association, *i* < 1 (solute associates)
In case of dissociation, *i* > 1 (solute dissociates)
When there is neither association nor dissociation, *i* = 1.

a) Dissociation nature of solute:

- Dissociation leads to increase in the number of solute particles in the solution resulting in an increase in the value of colligative property.
- Since colligative property is inversely related to the molecular mass, therefore, molecular mass of such a substance as calculated from colligative property will be less than its normal value.
- For example, KCl is an electrolyte. When it is dissolved in water it dissociates into K^+ & Cl^{-1} ions & there would be double the number of particles if complete dissociation takes place. Hence, it is expected to have molecular mass, $37.25g\ \left(\frac{74.5}{2}\right)$.
- For those which dissociates in solvent, experimental colligative property higher than normal colligative property.
  i.e., Experimental colligative property > normal colligative property
  Or, Experimental osmotic pressure > normal osmotic pressure
  Experimental Δp > normal Δp
  Experimental ΔT_b > normal ΔT_b
  Experimental ΔT_f > normal ΔT_f
  And, because Colligative property $\propto \frac{1}{molacular\ mass}$
  So, experimental molecular mass < normal molecular mass.
- The degree of dissociation (α) can be calculated as follows consider an electrolyte, A_xB_y dissolved in water & it dissociates as:

$$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$$

	A_xB_y	xA^{+y}	yB^{-x}
Before dissociation,	1	0	0
After dissociation,	$1-\alpha$	$x\alpha$	$y\alpha$

Total number of particles after dissociation = $1-\alpha+x\alpha+y\alpha$ (α = degree of dissociation)

And, $$\alpha = \frac{Moles\ dissociated}{Moles\ present\ initially}$$

Experimental colligative property ∝ Actual no. of particles $\propto 1-\alpha+x\alpha+y\alpha$ after dissociation

Normal colligative property ∝ No. Of particles before dissociation ∝ 1 (i = van't Hoff factor)

$$i = \frac{Experimental\ colligative\ property}{Normal\ colligative\ property} = 1 - \alpha + x\alpha + y\alpha$$

$$i = 1 - \alpha + x\alpha + y\alpha$$

$$i - 1 = \alpha(x + y) - \alpha$$

$$= \alpha[(x + y) - 1$$

Or, $\alpha = \frac{i-1}{(x+y)-1}$; but, $x + y = n$

Total number particles formed by dissociation of one particle, $\boldsymbol{\alpha} = \frac{\boldsymbol{i-1}}{\boldsymbol{n-1}}$

And also Van't Hoff coefficient, $\boldsymbol{g} = \frac{\boldsymbol{i}}{\boldsymbol{n}} = \frac{\boldsymbol{i}}{\boldsymbol{(x+y)}}$

b) Association nature of solute:

- Association of molecules leads to decrease in number of particles in the solution resulting in a decrease in the value of colligative property.
- As colligative property is inversely related to the molecular mass. Therefore, higher value is obtained for molecular mass than normal values.
- For example, when ethanoic acid is dissolved in benzene it undergoes dimerisation & shows a molecular mass of 120 (normal molecular mass is 60).
- When solute undergoes association then,
  Experimental; colligative property < Normal colligative property &
  Experimental molar mass > Normal molar mass

	nA	$\rightleftharpoons$	$(A)_n$
Before dissociation,	1		0
After dissociation,	$1-\alpha$		α/n

Total number of particles after association = $1 - \alpha + \frac{\alpha}{n}$ (α = degree of association)

Total number of particles before association = 1

$$i = \frac{Experimental\ colligative\ property}{Normal\ colligative\ property} = \frac{1 - \alpha + (\alpha/n)}{1}$$

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

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

Or, $\alpha - n\alpha = n(i - 1)$;

$$\alpha(1 - n) = n(i - 1)$$

Total number particles formed by association of one particle, $\boldsymbol{\alpha} = \frac{\boldsymbol{n(i-1)}}{\boldsymbol{(1-n)}}$

Table showing van't Hoff factor (i) for different electrolytes

Solute type	*Example*	*Ionisation/association*	*No. of particles in soltn. from 1 mole solute*	*van't Hoff factor 'i'*
Non-electrolyte	*Urea, sucrose*		*1*	1
Binary electrolyte (AB type)	*NaCl, KCl, etc*	$AB \rightleftharpoons A^+ + B^-$ $1-\alpha \quad \alpha \quad \alpha$	*2*	$1+\alpha$
Tertiary electrolyte AB$_2$ type or A$_2$B type	*$CaCl_2$, H_2SO_4, $BaCl_2$, $K_2[PtCl_6]$, etc*	$AB_2 \rightleftharpoons A^{2+} + 2B^-$ $1-\alpha \quad \alpha \quad 2\alpha$ $A_2B \rightleftharpoons 2A^+ + B^{2-}$ $1-\alpha \quad 2\alpha \quad \alpha$	*3* *3*	$1+2\alpha$ $1+2\alpha$
Quaternary electrolyte AB$_3$ or A$_3$B type	*$AlCl_3$, $FeCl_3$, K_3PO_4,etc*	$AB_3 \rightleftharpoons A^{3+} + 3B^-$ $1-\alpha \quad \alpha \quad 3\alpha$ $A_3B \rightleftharpoons 3A^+ + B^{3-}$ $1-\alpha \quad 3\alpha \quad \alpha$	*4* *4*	$1+3\alpha$ $1+3\alpha$
Association of solute	*$C_7H_6O_2$ forms dimer in C_6H_6*	$nA \rightleftharpoons nB$ $1-\alpha \quad \alpha/2$	$\frac{1}{n}$	$\left[1-\left(1-\frac{1}{n}\right)\alpha\right]$
General electrolyte AB_{n-1}	*1 mole of solute giving n ion in solution.*	$AB_{n-1} \rightleftharpoons A^{+(n-1)} + (n-1)B^-$ $1-\alpha \quad \alpha \quad (n-1)\alpha$	n	$[1+(n-1)\alpha]$

Formula Chart (Osmotic pressure, Van't Hoff Factor, Association or Dissociation)

1. $\pi = CRT = \frac{n_B RT}{V}$
2. $M_B = \frac{W_B RT}{\pi V}$
3. For isotonic solution, $\pi_1 = \pi_2$; Or, $C_1 = C_2$ or, $n_1 = n_2$ for same V
4. $i = \frac{M_n}{M_0} = \frac{Observed\ colligative\ property}{Normal\ colligative\ property}$
5. $\Delta T_b = iK_b m$
6. $\Delta T_f = iK_f m$
7. $\frac{\Delta p}{p_A^0} = ix_B$
8. $\pi = iCRT$
9. $\alpha_{diss.} = \frac{i-1}{m-1} = \frac{M_n - M_0}{M_0\,(m-1)}$
10. $\alpha_{ass.} = \frac{i-1}{\left(\frac{1}{m}\right)-1} = \frac{M_n - M_0}{M_0} \times \frac{m}{1-m}$

π = Osmotic pressure
W_B = Mass of solution
n_B = Moles of solute
V = Volume of solution (dm^3 or L)
R = Universal gas constant (= 0.082 $atm\ K^{-1}\ mol^{-1}$ or, 0.082 $atm\ L\ K^{-1}\ mol^{-1}$)
i = Van't Hoff factor
M_n = Normal molar mass
M_0 = Observed molar mass
m = Number of particles into which each solute particle dissociates or,
Number of solute particles which associate to form single entity.

Questions Based On (Abnormal Molar Masses)

1. *0.5 g of KCl was dissolved in 100 g of water & the solution originally at 20^{0}C froze at –0.24^{0}C. Calculate the percentage ionisation of the salt. K_f for water is 1.86 K kg mol^{-1}.*

Mass of KCl (W_B) = 0.5 g
Mass of water (W_A) = 100 g
$\Delta T_f = 0 - (-0.24) = 0.24^0$
Molar mass of KCl (M_0) is given as,

$$M_0 = \frac{K_f \times W_B \times 1000}{W_A \times \Delta T_f}$$

$$= \frac{1.86\ (K\ kg\ mol^{-1}) \times 0.5\ (g) \times 1000\ (g)}{100\ (g) \times 1\ (kg) \times 0.24\ (K)} = 38.75\ g/mol$$

Normal molar mass of KCl (M_n) = 39 + 35.5 = 74.5 g/mol

Van't Hoff factor, i is given by, $i = \frac{M_n}{M_0} = \frac{74.5}{38.75} = 1.92$

Now, KCl ionises as K$^+$ + Cl$^-$ ions.

If α is degree of dissociation, $\alpha_{diss.} = \frac{i-1}{m-1} = \frac{1.92-1}{2-1} = 0.92$

Percentage dissociation = 0.92 × 100 = 92% .

2. *At 27^{0}C, 1.25 L of a solution containing 7.6 g KBr shows an osmotic pressure of 1.804 atm. What is the value of osmotic coefficient (g)?*

$$\pi_{theor.} = \frac{n}{v}ST = \frac{7.6}{119} \times \frac{1000}{1250} \times 0.0821 \times 300 = 1.258\ atm$$

But, $\pi_{exp.} = 1.804\ atm$

$$\therefore i = \frac{\pi_{exp.}}{\pi_{theor.}} = \frac{1.804}{1.258} = 1.434$$

$$i = 1.432\ \ \&\ \ n = 2$$

Now, osmotic coefficient (g) = $\frac{i}{n} = \frac{1.432}{2} = 0.717$

TRICK CARD OF SOLUTION & COLLIGATIVE PROPERTIES

1 INTRODUCTION

- A *solution* is a homogeneous mixture of two or more pure substances, in same or different physical phases, the relative ratio of which can be changed within certain limits.

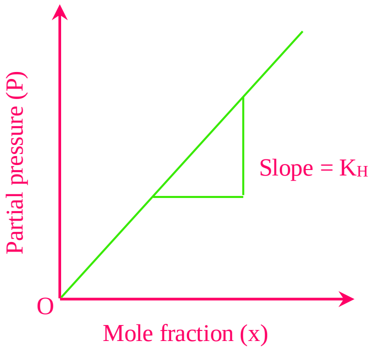
2 CLASSIFICATION OF SOLUTIONS

On the basis of physical state of solvent and solute:

Types of Solution	*Solute*	*Solvent*	*Examples*
Solid solution	Gas Liquid Solid	Solid Solid Solid	Solution of hydrogen in palladium Amalgam of mercury with sodium Copper dissolved in gold
Liquid solution	Gas Liquid Solid	Liquid Liquid Liquid	Oxygen dissolved in water Ethanol dissolved in water Glucose dissolved in water
Gaseous solution	Gas Liquid Solid	Gas Gas Gas	Mixture of oxygen & nitrogen gases Chloroform mixed with nitrogen gas Camphor in nitrogen gas

3 HENRY'S LAW

- *Definition:* It states that at constant temperature, the solubility of a gas in a liquid is directly proportional to the pressure of the gas.
- The most commonly used form of Henry's law states that the partial pressure (p) of a gas in vapour phase is proportional to the mole fraction of the gas (x) in the solution and is expressed as: $p = K_H x$. Where, K_H is the Henry's law constant & 'x' is the mole fraction of the gas.



- *Limitations of Henry's law:*
  a) The pressure of the gas is not too high.
  b) The temperature is not too low.
  c) The gas should not undergo any chemical reaction with the solvent.
  d) The gas should not undergo dissociation in solution.
- *Applications of Henry's law:*
  a) Production of carbonated beverages: Soft drinks, soda water & other carbonated beverages contains dissolved carbon dioxide. In the preparation of these beverages, CO_2 is passed at high pressure to increase its solubility.
  b) Anoxia in climbers: At high altitudes, the partial pressure of oxygen is less than that the ground level. Thus, low blood oxygen causes climbers to become weak & make them unable to think clearly, which are symptoms of a condition known as anoxia.
  c) Deep sea diving: To avoid the toxic effects of high concentration of nitrogen in the blood, the tanks use by scuba divers are filled with air dilute with helium (11.7% helium, 56.2% nitrogen& 32.1% oxygen).
  d) Functioning of lungs: In lungs, oxygen present in the inhaled air dissolved in blood because of its high partial pressure and combine with haemoglobin t form oxyhaemoglobin. In tissues, where partial pressure of oxygen is low, oxyhaemoglobin release oxygen for its utilisation in cellular activities.

DO YOU KNOW ?

Haemoglobin (A Henry's Law Deviator)

Under normal conditions oxygen gas is sparingly soluble in water. However, when oxygen comes in contact with blood in lungs, its solubility increases many fold due to the presence of high concentration of haemoglobin that associates with oxygen molecules. Due to association, Henry's law is not strictly followed in case of solubility of oxygen in blood.

4 RAOULT'S LAW

- *Raoult's law for volatile solute:* It states that for a solution of volatile liquids the partial pressure of each component is directly proportional to its mole fraction.
- Mathematically, $p_A \propto x_B$ $\quad p_B \propto x_B$

$$p_A = p_A^0\, x_A \qquad p_B = p_B^0\, x_B$$

Where, p_A & p_B are partial vapour pressure,

x_A & x_B are mole fraction,

p_A^0 & p_B^0 are the vapour pressure of pure components A & B respectively.

According to Raoult's law, $p_A = p_A^0\, x_A$ & $p_B = p_B^0\, x_B$

If p is total vapour pressure then according to Dalton's law of partial pressure,

$$p = p_A + p_B\,,$$
$$p = p_A^0\, x_A + p_B^0\, x_B$$
$$p = p_A^0\,(1 - x_B) = p_B^0\, x_B$$
$$p = p_A^0 + (p_B^0 - p_A^0)\, x_B$$

As p_A^0 & p_B^0 are constants at a given temperature it is evident from the above equations that the total vapour pressure varies linearly with the mole fraction x_B (or, x_A since $x_A = 1 - x_B$)

Let us assume that a solution has n_A moles of liquid A & n_B moles of liquid B.

Mole fraction of A, $x_A = \frac{n_A}{n_A + n_B}$

Mole fraction of B, $x_B = \frac{n_B}{n_A + n_B}$

- *Limitations of Raoult's law:*
  - i. When the solution is not dilute, there are significant interactions between solute & solvent particles & Raoult's law is not obeyed fully. There are positive & negative deviations from ideal behaviour.
  - ii. If solute molecules dissociates in solution, there are more particles in solution & therefore, lowering of vapour pressure shows an increased effect.

$$\text{NaCl(s)} \rightleftharpoons \text{Na}^+\text{(aq.)} + Cl^-\text{(aq.)}$$

  - iii. If the solute molecules associates in solution, there are less particles in solution, & therefore lowering of vapour pressure shows a decreased effect.

$$n\text{AB} \rightleftharpoons (\text{AB})_n$$

E.g., $2C_6H_5COOH \rightleftharpoons (C_6H_5COOH)_2$

Konowaloff Rule

- ✓ At any fixed temperature, the vapour phase is always richer in the mole volatile component as compared to the solution phase.
- ✓ In other words, mole fraction of the more volatile component is always greater in the vapour phase than in the solution phase.
- ✓ The composition of the vapour phase in equilibrium with the solution can be determined from the partial pressure of the two components.
- ✓ If y_A & y_B are the mole fractions of components A & B respectively in the vapour phase, then, $p_A = y_A\, p_{total}$; $p_B = y_B\, p_{total}$.

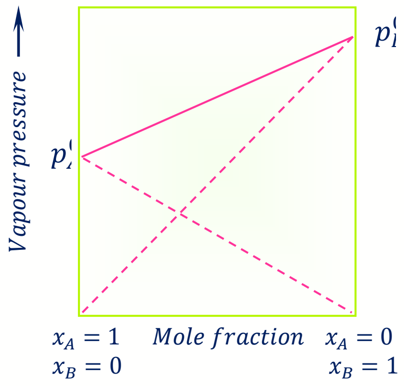
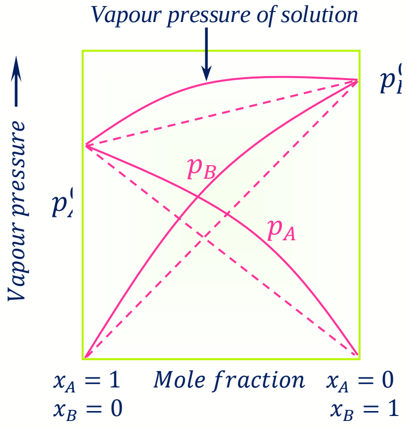
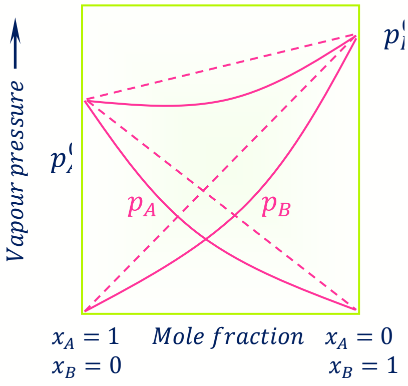
In general, $p_i = y_i\, p_{total}$.

DO YOU KNOW ?

Important Points To Be Remembered (Raoult's law & Henry law)

- ➢ Both Raoult's law and Henry law apply to the volatile component of the solution.
- ➢ The vapour pressure of solution in both the laws is directly proportional to the mole fraction of volatile component.
- ➢ However, the laws differ in their proportionality constants.

5 COMPARISION BETWEEN IDEAL AND NON-IDEAL SOLUTIONS

Ideal Solution	Non-ideal Solution	
	Positive deviation (Raoult's law)	*Negative deviation (Raoult's law)*
1. *Obey Raoult's law at every range of concentration.*	1. *Do not obey Raoult's law.*	1. *Do not obey Raoult's law.*
2. $\Delta H_{mix} = 0$; *neither heat is evolved nor absorbed during dissolution.*	2. $\Delta H_{mix} > 0$; *Endothermic dissolution; heat is absorbed.*	2. $\Delta H_{mix} < 0$; *Exothermic dissolution; heat is evolved.*
3. $\Delta V_{mix} = 0$; *total volume of solution is equal to sum of volumes of the components.*	3. $\Delta V_{mix} > 0$; *Volume is increased after dissolution.*	3. $\Delta V_{mix} < 0$; *Volume is decreased during dissolution.*
4. $p = p_A + p_B$ $= p_A^0\, x_A + p_B^0\, x_B$ *i.e.*, $p_A = p_A^0\, x_A$; $p_B = p_B^0\, x_B$	4. $p_A > p_A^0\, x_A$; $p_B = p_B^0\, x_B$ $\therefore p_A + p_B > p_A^0\, x_A + p_B^0\, x_B$	4. $p_A < p_A^0\, x_A$; $p_B = p_B^0\, x_B$ $\therefore p_A + p_B < p_A^0\, x_A + p_B^0\, x_B$
5. *A – A, A – B, B – B interactions should be same, i.e., 'A' & 'B' are identical in shape, size & character.*	5. *A – B attractive force should be weaker than A – A & B – B attractive forces. 'A' & 'B' have different shape, size & character.*	5. *A – B attractive force should be greater than A – A & B – B attractive forces. 'A' & 'B' have different shape, size & character.*
6. *Escaping tendency of 'A' & 'B' should be same in pure liquids & in the solution.*	6. *Escaping tendency of 'A' & 'B' easily showing higher vapour pressure than the expected value.*	6. *Escaping tendency of both 'A' & 'B' is lowered showing lower vapour pressure than the expected value.*
7. *Examples: dilute solution; mixture of benzene + toluene, n-hexane + n-heptane, methanol + ethanol, etc.*	7. *Examples: acetone + ethanol, water + methanol, water + ethanol,* CCl_4 *+ toluene,* CCl_4 *+* $CHCl_3$*, cyclohexane + ethanol.*	7. *Examples: acetone + aniline, acetone + chloroform,* HNO_3 *+ water, acetic acid + pyridine, hydrochloric acid + water.*
8. *Diagram representing vapour pressure for an ideal solution:* 	8. *Diagram representing vapour pressure showing positive deviation:* 	8. *Diagram representing vapour pressure showing negative deviation:* 

Memories

Vapour Pressure versus Temperature:

Vapour pressure of a liquid increases with temperature, as the formation of vapour pressure is an endothermic process.

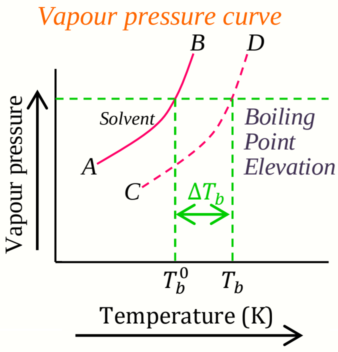
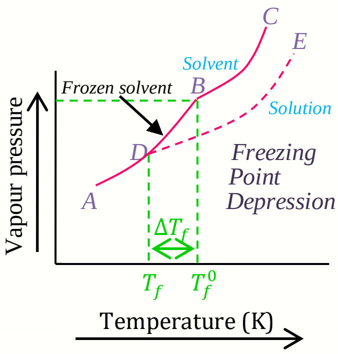
If p_1 *and* p_2 *are the vapour pressure of a liquid at temperatures* T_1 *and* T_2*, then according to Clausius – Clapeyron equation.*

$$\log_{10}\left(\frac{p_2}{p_1}\right) = \frac{\Delta H_{vap.}}{2.303\,R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

If we plot a graph between p and T the above graph are obtained.

6 COLLIGATIVE PROPERTIES:

Definition: Properties which depend only on the number of solute particles dissolved in a definite amount of the solvent & not on the nature of the solute are called *colligative properties*.

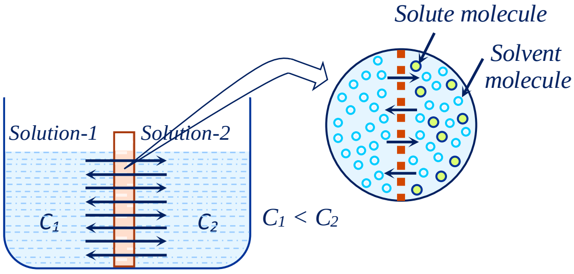
Colligative properties	Expression
Relative Lowering of Vapour Pressure When a non-volatile solute is dissolved in a solvent, vapour pressure of the solution is lower than that of the pure solvent which is known as lowering of vapour pressure. Relative lowering of vapour pressure is equal to the mole fraction of the solute in the solution.	$\frac{P_1^0 - P_1}{P_1^0} = x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n_1} = \frac{w_2 \times M_1}{M_2 \times w_1}$ (∴ for dilute solution, $n_2 \ll n_1$)
Elevation in Boiling Point The boiling point of a solution containing a non-volatile solute is always higher than the boiling point of the pure solvent. This increase in boiling point is termed as elevation in boiling point.  	$\Delta T_b = T_b - T_b^0$ $\Delta T_b \propto m$ $or, \Delta T_b = K_b m = K_b \left(\frac{w_2 \times 1000}{M_2 \times w_{1\,(in\,g)}}\right)$ $or, M_2 = \left(\frac{K_b \times w_2 \times 1000}{\Delta T_b \times w_{1\,(in\,g)}}\right)$ K_b is called boiling point elevation constant or molal elevation constant or Ebullioscopic constant, having unit $K\ kg\ mol^{-1}$.
Depression in Freezing Point The freezing point of a solution containing a non-volatile solute is always less than the freezing point of the pure solvent. This decrease in freezing point is termed as depression in freezing point.  	$\Delta T_f = T_f^0 - T_f$ $\Delta T_f \propto m$ $or, \Delta T_f = K_f m = K_f \left(\frac{w_2 \times 1000}{M_2 \times w_{1\,(in\,g)}}\right)$ $or, M_2 = \left(\frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_{1\,(in\,g)}}\right)$ K_f is called freezing point depression constant or molal depression constant or Cryoscopic constant, having unit $K\ kg\ mol^{-1}$.
Osmosis & Osmotic Pressure • When a solution is separated from the pure solvent with the help of a semipermeable membrane, the solvent molecules from the pure solvent move towards the solution. • The movement of solvent molecules from less concentrated solution to more concentrated solution through semipermeable membrane is termed as osmosis.	$\pi = CRT = \frac{n_2}{V} RT,$ $\pi V = \frac{w_2 RT}{M_2}$ $or, M_2 = \frac{w_2\, RT}{\pi V}$

Osmosis	*Diffusion*
1. In osmosis the movement of molecules takes place through semi-permeable membrane.	*1. In diffusion there is no role of semi-permeable membrane.*
2. It involves movement of only solvent molecules from one side to the other side.	*2. It involves passage of solvent as well as solute molecules from one region to the other region.*
3. Osmosis can be stopped or reversed by applying additional pressure on the solution side.	*3. Diffusion can neither be stopped nor be reversed.*

7 OSMOTIC PRESSURE

Osmosis and Osmotic pressure

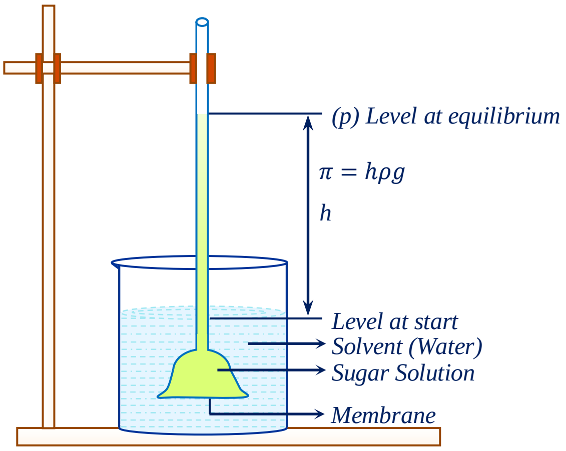
- *Osmosis:* When a solution is separated from its solvent by a semi-permeable membrane (SPM) there is a spontaneous flow of solvent molecules from solvent compartment to solution compartment. The phenomenon is called osmosis. The movement of solvent is only in one direction. In diffusion, however, movement takes place in both the direction.



Phenomenon of Osmosis

- *Semi-permeable membrane (SPM):* A membrane through which only solvent molecules can pass but not the solute ones. E.g., cellophane, parchment, copper ferrocyanide $[Cu_2[Fe(CN)_6]]$.
- *Osmotic pressure (O.P or π):* The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis. i.e., to stop the passage of solvent molecules into it through semipermeable membrane.
  - ✓ Osmotic pressure (π) is proportional to molarity (C) of the solution at a given temperature T. Thus, $\pi = CRT$
  - ✓ $\pi = \frac{n_B}{V} RT = \frac{W_B \times R \times T}{M_B \times V}$

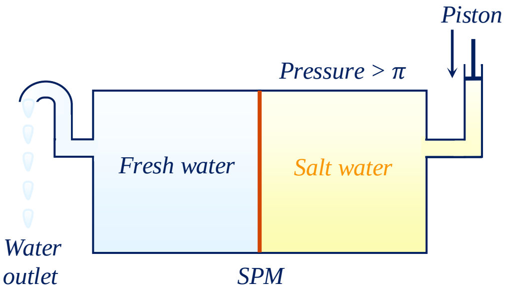
    Or, $M_B = \frac{W_B \times R \times T}{\pi \times V}$



Osmotic pressure

The pressure in excess of atmospheric pressure that must be applied to the solution to prevent it from raising in the tube is the osmotic pressure.

- *Reverse osmosis:* If a pressure larger than the osmotic pressure is applied to the solution side, the pure solvent (or water) flows out of the solution through the semi-permeable membrane. In this way the direction of osmosis is reversed and so the process is called reverse osmosis.
  - ✓ Thus, we can say that reverse osmosis is just opposite to the osmosis when an extra pressure is applied.
  - ✓ Reverse osmosis is used in desalination to get pure water from sea water.

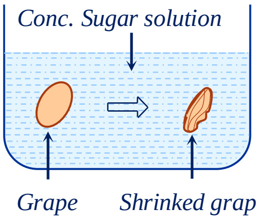


Reverse osmosis

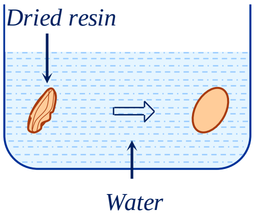
Reverse osmosis occurs when a pressure larger than osmotic pressure is applied in the solution.

- *Isotonic solution:* Two solutions are said to be isotonic when they exert the same osmotic pressure because they have the same molar concentration.

  E.g., All intravenous injections must be isotonic with the body.
- *Isosmotic solution:* When two isotonic solutions are separated by a semi-permeable membrane, no osmosis occurs, solution are called Isosmotic.
- *Hypotonic solution:* A solution having lower osmotic pressure than the other solution is called hypertonic with respect to the other solution.
- *Hypertonic solution:* A solution having higher osmotic pressure than the other solution is called hypertonic with respect to the other solution.



Exo-osmosis
In hypertonic solution



Endo-osmosis
In hypotonic solution

8 AZEOTROPES:

Definition: The mixture of liquids which boil at constant temperature like a pure liquid & possess same composition of components in liquid as well as vapour phase are called constant boiling mixtures or *azeotropic mixtures*.

Or,

A mixture of two liquids which boils at a constant temperature & distils over without any change in composition is called *azeotropic mixture*.

Types: Azeotropic mixtures are of two types:

(a) *Minimum boiling azeotropes:* These are formed by those liquid pairs which show positive deviations from ideal behaviour. *E.g.*, Ethanol-water mixture.

(b) *Maximum boiling azeotropes:* These are formed by those liquid pairs which show negative deviations from ideal behaviour. *E.g.*, nitric acid – water mixture.

Memories

➢ *Liquid Crystals: A Technology Boon*

- *Liquid crystals have both the properties of solid (directional order of molecules) and liquid (fluidity).*
- *Liquid crystals that change their properties with temperature are called thermotropic liquid crystals. These show the property of a unclear liquid just above the melting point due to the orderly alignment of some molecules. But at higher temperature, the liquid becomes clear. This property is called mesophase behaviour of a liquid crystal.*
- *This property was first observed by Austrian Biochemist Friedrich Reinitzer in 1988 while studying cholesterol.*

9 ABNORMAL MOLECULAR MASS

- When the molecular mass of a substance determined by any of the colligative properties comes out to be different than the expected value, the substance is said to show abnormal molecular mass.
- Abnormal molecular mass are observed when the solution is non-ideal (not dilute) or the solute undergoes association or dissociation.

10 VAN'T HOFF FACTOR

Definition: It is defined as the ratio of the experimental value of the colligative property to the calculated value of the colligative property.

- $i = \dfrac{Observed\ value\ of\ the\ colligative\ property}{Calculated\ value\ of\ the\ colligative\ property}$
- $i = \dfrac{Calculated\ molar\ mass}{Observed\ molar\ mass}$
- $Total\ number\ of\ moles\ of\ particles$

  $i = \dfrac{Total\ number\ of\ moles\ of\ particles\ after\ association/dissociation}{Total\ number\ of\ moles\ of\ particles\ before\ association/dissociation}$
- If $i > 1$, solute undergoes dissociation in the solution & if $i < 1$, solute undergoes association in the solution.
- $\propto_{dissociation} = \dfrac{i-1}{n-1}$ and $\propto_{association} = \dfrac{1-i}{1-\frac{1}{n}}$
- For substances undergoing association or dissociation in the solution, the various expressions for the colligative properties are modified as follows:

$$\frac{P_1^0 - P_1}{P_1^0} = i\,x_2\ ;\ \ \Delta T_b = iK_b m\ ;\ \ \Delta T_f = iK_f m\ ;\ \ \pi = iCRT.$$

DO YOU KNOW ?

Osmotic Coefficient (g): For a solution, osmotic coefficient is calculated by dividing van't Hoff factor (i) by 'n' (n = number of particles obtained from 1 mole solute after association of dissociation).

Practice Questions with Answers (Important for IIT JEE & NEET Aspirants)

1. Sea water contains $5.8 \times 10^{-3}\, g$ of dissolved oxygen per kilogram.

The concentration of oxygen in parts per million is

(a) $5.8\ ppm$ (b) $58.5\, ppm$ (c) $0.58\, ppm$ (d) $0.05\, ppm$

Solution: (a) Part per million $= \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6 = \frac{5.8 \times 10^{-3} g}{10^3 g} \times 10^6 = 5.8\, ppm$

2. Normality of a solution containing 9.8 g of H_2SO_4 in $250\ cm^3$ of the solution is

(a) $0.8\ N$ (b) $1N$ (c) $0.08\,N$ (d) $1.8\,N$

Solution: (a) Eq. wt. of $H_2SO_4 = \frac{\text{Mol. mass of } H_2SO_4}{\text{Basicity of } H_2SO_4} = \frac{98}{2} = 49$

$\therefore$ Number of g equivalent of $H_2SO_4 = \frac{\text{Weight in } g}{\text{Eq. mass}} = \frac{9.8}{49} = 0.2$

$250\ cm^3$ of solution contain $H_2SO_4 = 0.2 g$ equivalent

$\therefore$ $1000\ cm^3$ of the solution contain $H_2SO_4 = \frac{0.2}{250} \times 1000\ g$ equivalent $= 0.8 g$ equivalent

Hence normality of the solution $= 0.8\,N$

3. Amount of $NaOH$ present in $200\ ml$ of $0.5\,N$ solution is

(a) 40 g (b) 4 g (c) 0.4 g (d) 4.4 g

Solution: (b) Wt. of solute $= \frac{N \times V \times g\ eq.\ wt.}{1000} = \frac{0.5 \times 200 \times 40}{1000} = 4 g$

4. $50\ ml$ of $10\,N\ H_2SO_4$, $25\, ml$ of $12\,N\ HCl$ and $40\ ml$ of $5\,N\ HNO_3$ were mixed together and the volume of the mixture was made $1000\ ml$ by adding water. The normality of the resulting solution will be

(a) $1N$ (b) $2N$ (c) $3N$ (d) $4N$

Solution: (a) $N_1V_1 + N_2V_2 + N_3V_3 = N_4V_4$

$50 \times 10 + 25 \times 12 + 40 \times 5 = N_4 \times 1000$ or $N_4 = 1N$

5. Equal volumes of $0.1M\ AgNO_3$ and $0.2M\ NaCl$ are mixed.

The concentration of NO_3^- ions in the mixture will be

(a) $0.1M$ (b) $0.05\,M$ (c) $0.2\ M$ (d) $0.15\,M$

Solution: (b) $\underset{0.1M}{AgNO_3} + \underset{0.2M}{NaCl} \longrightarrow AgCl + NaNO_3$

$0.1M\ AgNO_3$ reacts with $0.1M\ NaCl$ to produce

$0.1M\ AgCl$ and $0.1M\ NaNO_3$

$\therefore NO_3^- = \frac{0.1M}{2} = 0.05\,M$

[$\because$ when equal volumes are mixed dilution occurs]

6. The molarity of H_2SO_4 solution that has a density of $1.84 g/cc$ at $35^o C$ and contains 98% by Weight is:

(a) $4.18\,M$ (b) $8.14\,M$ (c) $18.4M$ (d) $18\,M$

Solution: (c) Molarity $= \frac{\text{Wt. of solute}}{\text{Mol. wt.}} \times \frac{1000}{\text{Vol. of solution (in } ml.)} = \frac{98}{98} \times \frac{1000}{54.34} = 18.4M$

$\left(\text{Vol. of solution} = \frac{\text{mass}}{\text{density}} = \frac{100}{1.84} = 54.34\ ml \right)$

7. H_2SO_4 solution whose specific gravity is $1.98 g\ ml^{-1}$ and H_2SO_4 by volume is 95%.

The molality of the solution will be

(a) 7.412 (b) 8.412 (c) 9.412 (d) 10.412

Solution: (c) H_2SO_4 is 95% by volume

Wt. of $H_2SO_4 = 95\,g$

Vol. of solution $= 100\,ml$

$\therefore$ moles of $H_2SO_4 = \frac{95}{98}$ and weight of solution $= 100 \times 1.98 = 198\,g$

Weight of water $= 198 - 95 = 103\ g$

Molality $= \frac{95 \times 1000}{98 \times 103} = 9.412$

Hence molality of H_2SO_4 solution is 9.412

8. A solution has 25% of water, 25% ethanol and 50% acetic acid by mass. The mole fraction of each component will be

(a) 0.50, 0.3, 0.19 (b) 0.19, 0.3, 0.50 (c) 0.3, 0.19, 0.5 (d) 0.50, 0.19, 0.3

Solution: (d) Since $18\,g$ of water = 1mole

$25\,g$ of water = $\frac{25}{18} = 1.38$ mole

Similarly, $46\,g$ of ethanol = 1 mole

$25\,g$ of ethanol $= \frac{25}{46} = 0.55$ moles

Again, $60\,g$ of acetic acid = 1 mole

$50\,g$ of acetic acid $= \frac{50}{60} = 0.83$ mole

$\therefore$ Mole fraction of water $= \frac{1.38}{1.38 + 0.55 + 0.83} = 0.50$

Similarly, Mole fraction of ethanol $= \frac{0.55}{1.38 + 0.55 + 0.83} = 0.19$

Mole fraction of acetic acid $= \frac{0.83}{1.38 + 0.55 + 0.83} = 0.3$

9. 34.2 *g* of canesugar is dissolved in 180 *g* of water. The relative lowering of vapour pressure will be

(a) 0.0099 (b) 1.1597 (c) 0.840 (d) 0.9901

Solution: (a) $\frac{P_A^0 - P_A}{P_A^0} = \frac{W_B / M_A}{W_B / M_B + W_A / M_A} = \frac{34.2/342}{34.2/342 + 180/18} = \frac{0.1}{10.1} = 0.0099$

10. Vapour pressure of CCl_4 at 25^oC is 143 *mm Hg* 0.5 *g* of a non-volatile solute (mol. wt. 65) is dissolved in 100 *ml* of CCl_4. Find the vapour pressure of the solution.

(Density of $CCl_4 = 1.58\,g/cm^3$)

(a) 141.93 *mm* (b) 94.39 *mm* (c) 199.34 *mm* (d) 143.99 *mm*

Solution: (a) $\frac{P_A^0 - P_A}{P_A^0} = \frac{n_B}{n_A}$; $\frac{143 - P_s}{143} = \frac{0.5/65}{158/154}$ or $P_s = 141.93\,mm$

11. The vapour pressure of pure benzene and toluene are 160 and 60 torr respectively. The mole fraction of toluene in vapour pressure in contact with equimolar solution of benzene and toluene is

(a) 0.50 (b) 0.6 (c) 0.27 (d) 0.73

Solution: (c) For equimolar solutions, $X_B = X_T = 0.5$

$P_B = X_B \times P_B^0 = 0.5 \times 160 = 80\,mm$

$P_T = X_T \times P_T^0 = 0.5 \times 60 = 30\,mm$

$P_{\text{Total}} = 80 + 30 = 110\ mm$

Mole fraction of toluene in vapour phase $= \dfrac{30}{110} = 0.27$

12. Osmotic pressure is 0.0821 *atm* at a temperature of 300 *K*. find concentration in *mole*/*litre*

(a) 0.033 (b) 0.066 (c) 0.33×10^{-2} (d) 3

Solution: (c) $C = \dfrac{P}{RT} = \dfrac{0.0821}{0.0821 \times 300} = \dfrac{1}{300} = 0.33 \times 10^{-2}\ mole\ /\ litre$

13. A solution containing 3.3 *g* of a substance in 125 *g* of benzene (b.p. $80^{o}C$) boils at $80.66^{o}C$. If K_b for one litre of benzene is $3.28^{o}C$, the molecular weight of the substance shall be

(a) 127.20 (b) 131.20 (c) 137.12 (d) 142.72

Solution: (b) $M_2 = \dfrac{1000 \times K_b \times w}{W \times \Delta T_b} = \dfrac{1000 \times 3.28 \times 3.3}{125 \times 0.66} = 131.2$

14. The molal b.p. constant for water is $0.513^{o}C\,kg\,mol^{-1}$. When 0.1 mole of sugar is dissolved in 200 *g* of water, the solution boils under a pressure of 1 *atm* at

(a) $100.513^{o}C$ (b) $100.0513^{o}C$ (c) $100.256^{o}C$ (d) $101.025^{o}C$

Solution: (c) $\Delta T_b = K_b \times m = 0.513\left(\dfrac{0.1}{200} \times 1000\right) = 0.2565$; $\Delta T_b = 100.2565^{o}C$

15. An aqueous solution of a weak monobasic acid containing 0.1 *g* in 21.7 *g* of water freezes at 272.817*K*. If the value of K_f for water is 1.86 *K kg mol*$^{-1}$, the molecular mass of the acid is

(a) 46.0 (b) 48.6 (c) 48.8 (d) 46.8

Solution: (d) Mass of solvent $(W_A) = 21.7\,g$

Mass of solute $(W_B) = 0.1\,g$

Depression in freezing point, $(\Delta T_f) = 273 - 272.817 = 0.183\ K$

$$\Delta T_f = K_f \times m = K_f . \frac{W_B}{W_A} \times \frac{1000}{M_B}$$

$$M_B = \frac{K_f \times W_B \times 1000}{W_A \times \Delta T_f} = \frac{1.86 \times 0.1 \times 1000}{21.7 \times 0.183} = 46.8$$

16. A solution containing 6.8 *g* of a nonionic solute in 100 *g* of water was found to freeze at $-0.93^{o}C$. The freezing point depression constant of water is 1.86. Calculate the molecular weight of the solute

(a) 13.6 (b) 34 (c) 68 (d) 136

Solution: (d) $M_B = \dfrac{1000 \times K_f \times W_B}{\Delta T_f \times W_A} = \dfrac{1000 \times 1.86 \times 6.8}{100 \times 0.93} = 136$

17. The molar freezing point constant for water is $1.86^{o}C\,/\,mole$. If 342 *g* of cane sugar $(C_{12}H_{22}O_{11})$ is dissolved in 1000 *g* of water, the solution will freeze at

(a) $-1.86^{o}C$ (b) $1.86^{o}C$ (c) $-3.92^{o}C$ (d) $2.42^{o}C$

Solution: (a) $\Delta T_f = 1.86\left(\dfrac{342}{342}\right) = 1.86$

$$\Delta T_f = -1.86^{o}C$$

18. The Van't Hoff factor for 0.1 *M* $Ba(NO_3)_2$ solution is 2.74. The degree of dissociation is

(a) 91.3% (b) 87% (c) 100% (d) 74%

Solution: (b)

$$\begin{array}{lccc} & Ba(NO_3)_2 & \rightleftharpoons & Ba^{++} + 2NO_3^{-} \\ \text{Initial} & 0.1 & & 0 \qquad 0 \\ \text{At eq.} & (0.1-x) & & xM \qquad 2xm \end{array}$$

$$i = \frac{(0.1-x)+x+2x}{0.1} = \frac{0.1+2x}{0.1} = 2.74 = 0.1 + 2x = 0.274 \ \text{ or } \ x = \frac{0.174}{2} = 0.087$$

$$\%\alpha = \frac{x}{0.1} \times 100 = \frac{0.087}{0.1} \times 100 = 87\%$$

Multiple Choice Questions:

1. Which of the following options does not represents concentration of semi-molal aqueous solution of NaOH having $d_{solution} = 1.02\ g/mL$?
   (a) $Molarity = \frac{1}{2} M$
   (b) $X_{NaOH} = \frac{9}{1009}$
   (c) $\%\ w/w = 10\%$
   (d) $\%\ w/v = 2\%$

2. A solution of A & B with 30% moles of A in solution is in equilibrium with its vapour which contains 60% moles of A. What will be the ratio of the vapour pressure of pure A to that of pure B? (Assume ideal nature).
   (a) 1.5
   (b) 2.5
   (c) 3.5
   (d) 4.5

3. When 1.9g of a substance is dissolved in 128g water, freezing point of solution is depressed by -0.35^0C. Calculate molecular mass of the substance. (K_f of water is 1.86 K Kg mol^{-1}).
   (a) 58.12
   (b) 69.32
   (c) 78.88
   (d) 101.25

4. 200 mL of a very dilute aqueous solution of a protein contains 1.9g of the protein. If osmotic rise of such a solution at 300 K is found to be 38mm of solution then calculate molar mass of the protein.
   (a) 24630 g/mol
   (b) 123150 mg/mol
   (c) 517230 g/mol
   (d) 63644 g/mol

5. The vapour pressure of pure benzene at 25^0C is 639.7 mm of Hg & the vapour pressure of a solution of a solute in C_6H_6 at the same temperature is 631.9 mm of Hg. The molality of solution is
   (a) 0.269
   (b) 0.158
   (c) 0.486
   (d) 0.108

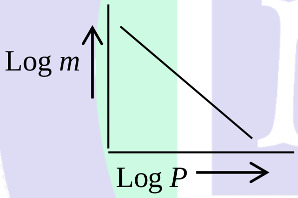
6. At 27^0C, 1.25L of a solution containing 7.6g of KBr shows an osmotic pressure of 1.804 atm. What is the value of van't Hoff factor?
   (a) 1.4
   (b) 1.8
   (c) 2.1
   (d) 0.8

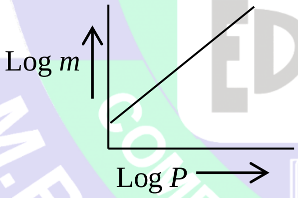
7. The Henry's law constant for the solubility of N_2 gas in water at 298K is 1.0×10^5 atm.
   The mole fraction of N_2 in air is 0.8.
   The number of moles of N_2 from air dissolved in 10 moles of water at 298K & 5 atm pressure is
   (a) 4.0×10^{-4}
   (b) 4.0×10^{-5}
   (c) 5.0×10^{-4}
   (d) 4.0×10^{-6}

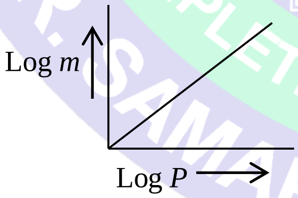
8. At 27^0C, 36g of glucose per litre has an osmotic pressure of 4.92 atm. If the osmotic pressure of another glucose solution is 1.5 atm at the same temperature. What should be its concentration?
(a) 1.23 M
(b) 5.86 M
(c) 0.061 M
(d) 0.21 M

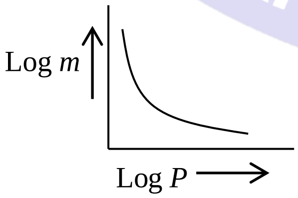
9. Normal boiling point (T_N) is defined as the temperature when vapour pressure of liquid becomes equal to 1 atm & standard boiling point (T_S) is defined as the pemerature when vapour pressure of liquid becomes equal to 1 bas. Which one is not correct if water is considered?
(a) $T_N = 100^0$C
(b) $T_S > 1000^0$C
(c) $T_S < 100^0$C
(d) $T_S < T_S$

10. In case of osmosis, solvent molecules move from
(a) higher vapour pressure to lower vapour pressure
(b) higher concentration to lower concentration
(c) lower vapour pressure to higher vapour pressure
(d) higher osmotic pressure to lower osmotic pressure

11. According to William Henry, the solubility of a gas in liquid depends on the pressure of the gas. if '*m*' is the molality of the gas & '*P*' is its pressure, then which of the following plot is in accordance with the law?
(a)


(b)


(c)


(d)


12. A very small amount of a non-volatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}). At room temperature, vapour pressure of this solution is 98.88 mm of Hg while that of benzene is 100 mm of Hg. Find the molality of this solution.
(a) 0.1452 m
(b) 0.73 m
(c) 2.591 m
(d) 5.028 m

13. For a 5% solution of H_2SO_4 by mass ($\rho = 1.01\ g\ mL^{-1}$), match the quantities in column I with their values in column – II.

Column – I	Column – II
P. Molarity of the solution	(i) 0.537
Q. Molalility of the solution	(ii) 0.0096
R. Mole fraction of H_2SO_4	(iii) 0.05
S. Mass fraction of H_2SO_4	(iv) 0.515

(a) P – (iii), Q – (iv), R – (ii), S – (i)
(b) P – (i), Q – (ii), R – (iv), S – (iii)
(c) P – (ii), Q – (iii), R – (i), S – (iv)
(d) P – (iv), Q – (i), R – (ii), S – (iii)

14. The vapour pressure of acetone at 20^0C is 185 torr. When 1.2g of a non-volatile substance was dissolved in 100g of acetone at 20^0C, its vapour pressure was 183 torr. The molar mass (g mol^{-1}) of the substance is
(a) 128
(b) 488
(c) 32
(d) 64

15. Consider separate solutions of 0.500M $C_2H_5OH_{(aq)}$, 0.100M $Mg_3\ (PO_4)_{2(aq)}$, 0.250m $KBr_{(aq)}$, & 0.125M $Na_3PO_{4(aq)}$ at 25^0C. Which statement is true about these solutions, assuming all salts to be strong electrolytes?
(a) 0.500M $C_2H_5OH_{(aq)}$ has the highest osmotic pressure.
(b) They all have the same osmotic pressure.
(c) 0.100M $Mg_3(PO_4)_{2(aq)}$ has the highest osmotic pressure.
(d) 0.125M $Na_3PO_{4(aq)}$ has the highest osmotic pressure.

16. For a dilute solution containing 2.5g of a non-volatile non-electrolyte solution in 100g of water, the elevation in boiling point at 1 atm pressure is 2^0C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is
(take $K_b = 0.76$ K Kg mol^{-1}).
(a) 724
(b) 740
(c) 736
(d) 718

17. The freezing point (in ^0C) of a solution containg 0.1g of $K_3[Fe(CN_6)]$ (mol. wt. = 329) in 100g of water ($K_f = 1.86$ K Kg mol^{-1}) is
(a) -2.3×10^{-2}
(b) -5.7×10^{-2}
(c) -5.7×10^{-3}
(d) -1.2×10^{-2}

18. Two solutions of same solute-solvent system exert osmotic pressures of 6 atm & 2 atm at 300K relatively. If these are separated by a semipermeable membrane, what would be the observations?
(a) Solvent will move from solution having 6 atm pressure to solution having 2 atm pressure.
(b) Solute will move from solution having 6 atm pressure to solution having 2 atm pressure.
(c) Solvent will move from solution having 2 atm pressure to solution having 6 atm pressure.
(d) No movement of solute or solvent takes place.

19. Density of 3M NaCl solution is 1.25 g/cc. The molality of the solution is
    (a) 2.79 molal
    (b) 0.279 molal
    (c) 1.279 molal
    (d) 3.85 molal

20. The density of 4M NaOH solution is 1.6g mL^{-1}. The molality of the solution is
    (a) 2.77
    (b) 14.28
    (c) 7.14
    (d) 57.14

21. The vapour pressure of the solution of two liquids A (P^0 = 80 mm) & B (P^0 = 120 mm) is found to be 100 mm of Hg when X_A = 0.4. The result shows that
    (a) solution exhibits ideal behaviour
    (b) $\Delta H_{solution} < 0$
    (c) solution shows positive deviation
    (d) solution will show positive deviation foe lower concentration & negative deviation for higher concentration.

22. A maxima or minima obtained in the temperature, composition curve of a mixture of two liquids indicates
    (a) an azeotropic mixture
    (b) an eutectic mixture
    (c) that the liquids are immiscible with one another
    (d) that the liquids are partially miscible at the maximum or minimum.

23. A solution has density 1.2 mL^{-1} & molality 2.0 m. If molar mass of the solute is 100g mol^{-1}, the molarity of the solute is
    (a) 0.5
    (b) 1.0
    (c) 1.5
    (d) 2.0

24. Which one of the following varies with temperature?
    (a) Molality
    (b) Mole fraction
    (c) Molarity
    (d) Mass per cent

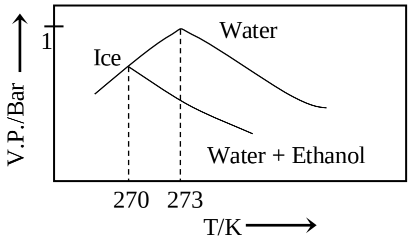
25. What is the molarity of 200g of pure water?
    (a) 18
    (b) 55.56
    (c) 20.0
    (d) 6.55

26. For 1 molal aqueous solution of the following compounds, which one will show the highest freezing point?
    (a) $[Co(H_2O)_4Cl_2]Cl.\ 2H_2O$
    (b) $[Co(H_2O)_3Cl_3].\ 3H_2O$
    (c) $[Co(H_2O)_6]Cl_3$
    (d) $[Co(H_2O)_5Cl]Cl_2.\ H_2O$

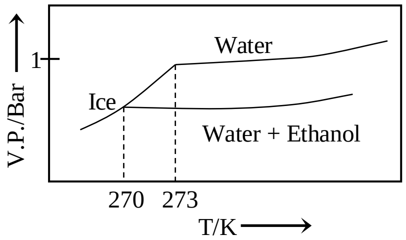
27. Pure water freezes at 273 K & 1 bar. The addition of 34.5 g of ethanol to 500 g of water changes the freezing point of the solution. Use the freezing point depression constant of water as 2 K kg mol^{-1}. The figures shown below represent plots of vapour pressure (V.P.) versus temperature (T). [Molecular weight of ehanol is 46 g/mol].

Among the following, the option representing change in the freezing point is:

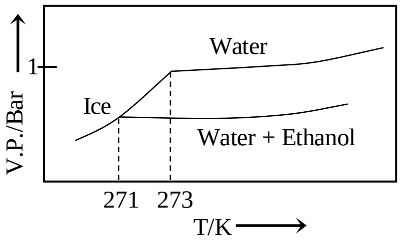
(a)



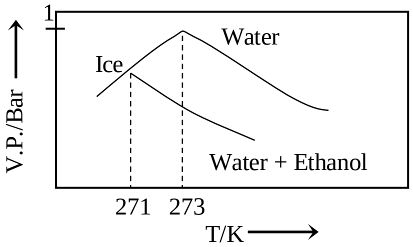
(b)



(c)



(d)



28. Calculate the molality of a solution the contains 51.2 g of naphthalene ($C_{10}H_8$) in 500 mL of carbon tetrachloride. The density of CCl_4 is 1.60 g/mL :

(a) 0.250 m
(b) 0.500 m
(c) 0.750 m
(d) 0.840 m
(e) 1.69 m

29. The vapour pressure of acetone at 20^{0}C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20^{0}C, its vapour pressure was 183 torr. The molar mass (g/mol) of the substance is:

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

30. Which solution will have least vapour pressure:
(a) 0.1 M $BaCl_2$
(b) 0.1 M urea
(c) 0.1 M Na_2SO_4
(d) 0.1 M Na_3PO_4

31. 5% (mass / volume) aqueous NaCl solution & 5% (mass / volume) aqueous KCl solution are:
(a) Isotonic
(b) Isomolar
(c) Equimolal
(d) None of these

32. One mole each of urea, glucose & sodium chloride were dissolved in one litre of water. Equal osmotic pressure will be produced by solutions of:
(a) urea & glucose
(b) sodium chloride & urea
(c) glucose & sodium chloride
(d) none of these

33. Which aqueous solution has minimum freezing point?
(a) 0.01 M NaCl
(b) 0.005 M C_2H_5OH
(c) 0.005 M MgI_2
(d) 0.005 M $MgSO_4$

34. The value of K_f for water is 1.86^0, calculated from glucose solution. The value of K_f for water calculated for NaCl solution will be:
(a) = 1.86
(b) < 1.86
(c) > 1.86
(d) Zero

35. K_f for water is 1.86 K kg mol^{-1}. If your automobile radiator holds 1.0 kg of water, how many grams of ethylene glycol must you add to get the freezing point of the solution lowered to -2.8^0C?
(a) 93 g
(b) 39 g
(c) 27 g
(d) 72 g

36. The freezing point of a solution prepared from 1.25 g of non-electrolyte & 20 g of water is 271.9 K. If molar depression constant is 1.86 K/mol then molar mass of the solute will be:
(a) 105.7
(b) 106.7
(c) 115.3
(d) 93.9

37. Ethylene glycol is used as an antifreeze in a cold climate. Mass of ethylene glycol which should be added to 4 kg of water to prevent it from freezing at – 6^0C will be:
Given: (K_f for water = 1.86 K kg mol^{-1} and molar mass of ethylene glycol = 62 g/mol)
(a) 804.32 g
(b) 204.30 g
(c) 400.00 g
(d) 304.60 g

38. In cold countries, ethylene glycol is added to water in the radiators of car during winters. It results in:
(a) lowering in boiling point
(b) reducing viscosity
(c) reducing specific heat
(d) lowering in freezing point

39. Azeotropes mixture of HCl and water has:
(a) 84% HCl
(b) 22.4% HCl
(c) 63% HCl
(d) 20.4% HCl

40. Pick out the combination which show positive deviations from Raoult's law:
(a) $C_2H_5OH + CCl_4$
(b) $H_2O + CH_3CH_2CH_2OH$
(c) $C_2H_5OH + CHCl_3$
(d) All are correct

41. Latent heat of fusion and vaporization of water are 80 cal/g & 540 cal/g respectively. If boiling point of an aqueous solution is 100.1^0C, then is its freezing point:
(a) -0.181^0C
(b) -0.521^0C
(c) -362^0C
(d) -1.52^0C

42. The vapour pressure of pure benzene at a certain temperature is 640 mm of Hg. A non-volatile non-electrolyte solid weighting 2.175 g is added 39.0 g of benzene. The vapour pressure of the solution is 600 mm of Hg. The molecular mass of solid substance is:
(a) 40.5
(b) 65.25
(c) 36
(d) 72

43. 18 g glucose ($C_6H_{12}O_6$) is added to 178.2 g water. The vapour pressure of water for this aqueous solution at 100^0C is:
(a) 759 torr
(b) 7.60 torr
(c) 76.0 torr
(d) 752.40 torr

44. The vapour pressure of two pure liquids (A) and (B) are 100 and 80 torr respectively. The total pressure of solution obtained by mixing 2 mole of (A) and 3 mole of (B) would be:
(a) 120 torr
(b) 36 torr
(c) 88 torr
(d) 180 torr

45. Equimolar solutions of two non-electrolytes in the same solvent have:
(a) same boiling point but different freezing point
(b) same freezing point but different boiling point
(c) same boiling point & same freezing point
(d) different boiling point & different freezing point

46. At 27^{0}C, 36 g of glucose per litre has an osmotic pressure of 4.92 atm. If the osmotic pressure of solution is 1.5 atm at the same temperature, the concentration of solution is:
(a) 0.01 M
(b) 0.052 M
(c) 0.061 M
(d)0.031 M

47. Osmotic pressure of 40% (mass/volume) urea solution is 1.64 atm and that of 3.42% (mass/volume) cane-sugar is 2.46 atm. When equal volumes of the above two solutions are mixed, the osmotic pressure of the resulting solution is:
(a) 1.64 atm
(b) 2.46 atm
(c) 4.10 atm
(d) 2.05 atm

48. Blood cells retain their normal shapes in solutions which are:
(a) isotonic to blood
(b) hypotonic to blood
(c) hypertonic to blood
(d) equinormal to blood

49. The natural semi-permeable membrane is:
(a) gelatinous $Cu_2[Fe(CN)_6]$
(b) gelatinous $Ca_3(PO_4)_2$
(c) plant cell
(d) phenol layer

50. A 5.2 molal aqueous solution of methyl alcohol, CH_3OH, is supplied. What is the mole fraction of methyl alcohol in the solution?
(a) 0.100
(b) 0.190
(c) 0.086
(d) 0.050

Multiple Choice Questions Answers

1. Ans: (c) Semi-molal $= \frac{1}{2}m$

$d = 1.02\ g/mL$

1 Kg of water contains $\frac{1}{2}$ mole of NaOH i.e., 20g

Mass of solution = $1000 + 20 = 1020g$

Volume of solution $= \frac{1020}{1.02} = 1000mL = 1L$

$M = \frac{\frac{1}{2}}{1} = \frac{1}{2};$

$X_{NaOH} = \frac{\frac{1}{2}}{\frac{1}{2} + \frac{1000}{18}} = \frac{9}{1009}$

$\%w/w = \frac{20}{1020} \times 100 = 2\%$

$\%w/v = \frac{20}{1000} \times 100 = 2\%$

2. Ans: (c) $P_A^0 . X_{A_{(LP)}} = P_M . X'_{A_{(VP)}}$

$P_A^0 \times \frac{30}{100} = P_M \times \frac{60}{100}$; $P_B^0 \times \frac{70}{100} = P_M \times \frac{40}{100}$

$\therefore \frac{P_A^0}{P_B^0} \times \frac{30}{70} = \frac{60}{40}$

$\therefore \frac{P_A^0}{P_B^0} = \frac{60 \times 70}{30 \times 40} = 3.5$

3. Ans: (c) Since, molar depression constant,

$K_f = 1.86K\ kg\ mol^{-1}$

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

Given that, $w = 1.9g,\ W = 128g,$

$\Delta T_f = 0 — 0.35 = 0.35K \quad \therefore 0.35 = \frac{1000 \times 1.86 \times 1.9}{M \times 128}$

$M = 78.88$

4. Ans: (d) Osmotic rise in terms of mm of Hg = $\frac{38}{13.6}$

Now, $\pi = CRT; \frac{38}{13.6} \times \frac{1}{760} = \left(\frac{\frac{1.9}{M}}{200} \times 1000\right) \times 0.0821 \times 300$

$M = 63644\ g/m$

5. Ans: (b) $\therefore \frac{P^0 - P_s}{P_s} = \frac{w \times M}{m \times W}$

$\therefore Molality = \frac{w}{m \times W} \times 1000 = \frac{P^0 \times P_s}{P_s \times M} = 1000$

$= \frac{639.7 - 631.9}{631.9 \times 78} \times 1000 = 0.158\ mol/kg$

6. Ans: (a) $\pi_{th} = \frac{n}{V}RT = \frac{7.6}{119} \times \frac{1}{1.25} \times 0.0821 \times 300$

$\pi_{th} = 1.258\ atm$ & $\pi_{exp.} = 1.804\ atm$

$\therefore i = \frac{\pi_{exp.}}{\pi_{th}} = \frac{1.804}{1.258} = 1.4$

7. Ans: (a) According to Henry's law, $x_{N_2} \times K_H = P_{N_2}$ (P_{N_2} = Partial pressure of N_2).

Given, total pressure = 5 atm, mole fraction of N_2 = 0.8

∴ Partial pressure of N_2 = $0.8 \times 5 = 4$

$x_{N_2} \times 1 \times 10^5 = 4 \quad \Rightarrow x_{N_2} = 4 \times 10^{-5}$

No. of moles H_2O, $n_{H_2O} = 10$

No. of moles of N_2, $n_{N_2} = ?$

$\frac{n_{N_2}}{n_{N_2} + n_{H_2O}} = x_{N_2} \qquad \Rightarrow \frac{n_{N_2}}{10 + n_{N_2}} = 4 \times 10^{-5} \qquad \Rightarrow n_{N_2} = 4 \times 10^{-4}$

$\therefore n_{N_2} \ll\ll\ll 10$

8. Ans: (c) $\pi V = nRT$

Using the given data, $\pi_1 = 4.92$ atm, $\pi_2 = 1.5$ atm

$C_1 = \frac{36}{180 \times 1}$, $C_2 = ?$ $\left(\because C = \frac{w}{M \times V}\right)$

$\pi_1 V_1 = n_1 RT_1$; $\pi_2 V_2 = n_2 RT_2$

$\frac{\pi_1}{\pi_2} = \frac{n_1}{V_1} \times \frac{V_2}{n_2} = \frac{C_1}{C_2}$

$\therefore \frac{4.92}{1.5} = \frac{36}{180 \times C_2} \Rightarrow C_2 = 0.061\ mol/L$

9. Ans: (b)

10. Ans: (a)

11. Ans: (b) $m = KP$

$\text{In } M = In\ P + In\ K$; $\log m = \log P + \log K$

Comparing with $y = mx + c$ we get graph given in option (b).

12. Ans: (a) $\frac{P^0 - P_s}{P_s} = \frac{w \times M}{m \times W}$

$\therefore \frac{100 - 98.88}{98.88} = \frac{w \times 78}{m \times W}$

Or, Molality $\left(\frac{w \times 1000}{m \times W}\right) = \frac{1.12 \times 1000}{78 \times 98.88} = 0.1452\ m$

13. Ans: (d)

14. Ans: (d)

15. Ans: (b)

16. Ans: (a)

17. Ans: (a)

18. Ans: (c) Osmosis will occur, i.e., solvent will move from dilute solution (low osmotic pressure) to concentrated solution (higher osmotic pressure).

19. Ans: (a) Mass of 3M NaCl solution $= density \times volume = 1.25 \frac{g}{cc} \times 1000\ cc = 1250g$

Molar mass of NaCl = 58.5 g/mol

⇒ Mass of 3 moles of NaCl = $3 \times 58.5 = 175.5g$

So, mass of solvent in 3M NaCl solution $= 1250 - 175.5 = 1074.5g$

Molality of solution = $\frac{No.of\ moles\ of\ NaCl}{Mass\ of\ solvent\ in\ kg} = \frac{3}{1074.5} \times 1000 = 2.79\ molal$

20. Ans: (a) $m = \frac{1000M}{1000d - MM_B}$

$= \frac{1000 \times 4}{(1000 \times 1.6) - (4 \times 40)}$

$= \frac{4000}{1600 - 160}$

$= \frac{4000}{1440} = 2.77\ mol\ kg^{-1}$

21. Ans: (b) $P_{total} = 0.4 \times 80 + 0.6 \times 120 = 104$

$P_A + P_B < P_A^0 X_A + P_B^0 X_B$

Thus, solution shows negative deviation & for negative deviation $\Delta H_{mix} < 0$.

22. Ans: (a)

23. Ans: (d) Molarity $= \frac{1000md}{1000 + mM_B}$

$= \frac{1000 \times 2 \times 1.2}{1000 + 2 \times 100} = \frac{2400}{1000 + 200} = \frac{2400}{1200} = 2M$

24. Ans: (c)

25. Ans: (b) Whatever be the volume of pure water, its molarity is fixed,

$1000mL\ H_2O = 1000g$

$= \frac{1000}{18} mol = 55.56 mol$

26. Ans: (b) Depression in freezing point, $\Delta T_f = i, K_f m$

Less the value of *i*, Higher the value of freezing point

For (2) i = 1 (min)

27. Ans: (b)

28. Ans: (b) Given, Volume of CCl_4 = 500 mL

Density of CCl_4 = 1.60 g/mL

∴ Mass of solvent CCl_4 (W_A) = 500×1.60 = 800g

Mass of solute $C_{10}H_8$ (W_B) = 51.2 g

Now, molality = $\frac{W_B \times 1000}{M_B \times W_A\ (in\ g)} = \frac{51.2 \times 1000}{128 \times 800} = 0.500\ m$

29. Ans: (d) Given, $P^0 = 185$ torr, w = 1.2 g, W = 100 g, p = 183 torr, M = $M_{CH_3COCH_3} = 58$ g/mol

$$\frac{P^0 - P_S}{P_S} = \frac{w \times M}{m \times W}$$

$$\therefore \frac{185 - 183}{185} = \frac{1.2 \times 58}{m \times 100}$$

Or, $m = \left(\frac{1.2 \times 58 \times 185}{2 \times 100}\right) = 64.38\ \approx 64\ g/mol$

30. Ans: (d)

31. Ans: (d)

32. Ans: (a) Both urea & glucose are non-electrolytes; NaCl being electrolyte ionises.

33. Ans: (a) Colligative property ∝ $\frac{w}{m \times V}(1 - \alpha + x\alpha + y\alpha)$

Colligative property ∝ C× $(1 - \alpha + x\alpha + y\alpha)$

For solute A_xB_y; α is degree of ionisation.

Colligative properties are osmotic pressure, lowering in vapour pressure, elevation in boiling point, depression in freezing point

34. Ans: (a)

35. Ans: (a) K_f = 1.86 K kg mol^{-1}

$\Delta T_f = 0 - (-2.8) = 2.8^0$C

Mass of solvent = 1.0 kg

Mass of solute = ?

Molecular mass of solute = 62

$\Delta T_f = K_f\ m$

$$m = \frac{\frac{Weight\ of\ solute}{Molecular\ mass\ of\ solute}}{Mass\ of\ solvent\ (g)} \times 1000$$

$$m = \frac{\frac{w}{62}}{1000} \times 1000 = \frac{w}{62}$$

$\Delta T_f = K_f\ m$

$2.8 = 1.86 \times \frac{w}{62}$

$w = \frac{62 \times 2.8}{1.86} = 93\ g$

36. Ans: (a)

37. Ans: (a) $\Delta T_f = K_f\ m = K_f \times \frac{w \times 1000}{m \times W}$

$w = ?, W = 4 \times 10^3\ g, m = 62$

$\Delta T_f = 0 — 6 = 6$

$w = \frac{6 \times 62 \times 4 \times 10^3}{1000 \times 1.86} = 800g$

38. Ans: (d) Addition of glycol lowers the freezing point of water and thus glycol water mixture is used as antifreeze in cars radiator.

39. Ans: (d) Azeotropic mixture of HCl contains 20.4% HCl.

40. Ans: (d)

41. Ans: (c) For an aqueous solution,

$\Delta T_b = K'_b\, m$ .... (i)

$\Delta T_f = K'_f\, m$ .... (ii)

Dividing equation (i) and (ii)

$$\frac{\Delta T_b}{\Delta T_f} = \frac{K'_b}{K'_f} = \frac{RT_b^2}{1000\times l_v}\times\frac{1000\times l_f}{RT_f^2} =$$

$$\frac{\Delta T_b}{\Delta T_f} = \frac{\Delta T_b^2\times l_f}{\Delta T_f^2\times l_v} \text{ .... (iii)}$$

Given, $T_b = 100 + 273 = 373K$

$T_f = 0 + 273 = 273K$

$l_f = 80\ cal/g$

$l_v = 540\ cal/g$

Using the values in equation (iii)

$$\frac{0.1}{\Delta T_f} = \frac{373\times373\times80}{273\times273\times540}$$

$\Delta T_f = 0.362$

$T_f = 0.0 - 0.362 = -0.362^0C$

42. Ans: (b) According to Raoult's law,

$$\frac{P^0 - P_s}{P_s} = \frac{w\times M}{m\times W}$$

Using the given data, p^0 = 640 mm, p_s = 600 mm, w = 2.175 g, W = 39.0 g, M = 78

$$\therefore \frac{640\times600}{600} = \frac{2.175\times78}{m\times W}$$

$m = 65.25$

43. Ans: (d) $\frac{P^0-P_s}{P_s} = \frac{n}{N} = \frac{18\times18}{180\times178.2} = 0.01$

$\therefore \frac{760-P_s}{P_s} = 0.01$ [$P^0 = 760$ torr at boiling point of H_2O]

$p_s = 752.47$ torr

44. Ans: (c)

45. Ans: (c) $\Delta T_f = K_f\, m$

$\Delta T_b = K_b\, m$

Thus, ΔT_f and ΔT_b for different non-electrolytes is same as K_f and K_b are constant.

46. Ans: (c) $\pi V = nST$

Using the given data, $\pi_1 = 4.92$ atm, $\pi_2 = 1.5$ atm

$C = \frac{w}{m\times V}$ [For C_1 w = 36, m = 180, V = 1]; [C_2 = ?]

$C_1 = \frac{36}{180\times1}$

$\pi_1 V_1 = n_1 S T_1$

$\pi_1 V_1 = n_1 S T_1$

$\frac{\pi_1}{\pi_2} = \frac{n_1}{V_1}\times\frac{V_2}{n_2}\times\frac{C_1}{C_2}$ [If $T_1 = T_2$]

$\therefore \frac{4.92}{1.5} = \frac{36}{180\times C_2}$

$C_2 = .061\ mol/L$

47. Ans: (d)

48. Ans: (a)

49. Ans: (c)

50. Ans: (c) Mole fraction of solute = $\frac{n}{N+n}$

n = number of moles of solute (methyl alcohol), N = number of moles of solvent (water)

Given, n = 5.2, N = $\frac{1000}{18} = 55.55$

∴ Mole fraction = $\frac{5.2}{5.2+55.55} = 0.086$