

SOLUTIONS

- A solution is a homogenous mixture of two (or more) chemically non reacting substances which can be varied within certain limits.
- When the solution is composed of only two chemical substances it is termed a binary solution. Solution is composed of solvent and solute. Solvent is that component in large amount and in same physical state as that of the resulting solution. Component present in smaller amount is called solute.
- The constituent of solution cannot be separated by filtration settling or centrifugal action. All solutions are characterized by
 - (i) Homogeneity
 - (ii) Absence of settling
 - (iii) The molecular or ionic state of sub-division of the components.

TYPE OF SOLUTIONS

| Sr.No | SOLUTE | SOLVENT | EXAMPLES |
|-------|--------|---------|-------------------------------|
| 1 | Gas | Gas | Air |
| 2 | Liquid | Gas | Humidity in air |
| 3 | Solid | Gas | Camphor in N ₂ gas |
| 4 | Gas | Liquid | Aerated drink |
| 5 | Liquid | Liquid | Alcohol in water |
| 6 | Solid | Liquid | Salt in water |
| 7 | Gas | Solid | Dissolved gases in mixture |
| 8 | Liquid | Solid | Amalgams |
| 9 | Solid | Solid | Alloys |

CONCENTRATION OF SOLUTION

1. Molarity

$$M = \frac{\text{Number of moles of solute}}{\text{Volume of solution (in litre)}}$$
$$M = \frac{W \times 1000}{M_0 \times V}$$

W : Wight of solute in grams
M₀ : Molecular mass of solute
V: Volume of solution in ml

2. Normality

$$M = \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution (in litre)}}$$
$$M = \frac{W \times 1000}{Eq \times V}$$

W : Wight of solute in grams
Eq : Equivalent weight of solute
V: Volume of solution in ml

Equivalent weight of solute

$$Eq = \frac{\text{molecular mass of solute}}{\text{Acidity, Basicity, charge on compound, change in oxidationstate}}$$

Acidity : Number replaceable -OH group in basic compound

Example: NaOH : number of -OH groups 1, Thus Acidity = 1

Ca(OH)₂ : Number of -OH groups 2, Acidity = 2

Al(OH)₃ : Number of -OH groups 3, Acidity = 3

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Basicity of acid is defined as the no of ionizable hydrogen (H^+) ions present in one molecule of an acid.

Example: HCl , HNO_3 , CH_3COOH : H^+ ions are 1, thus Basicity is 1,

H_2SO_3 : H^+ ions are 2, thus Basicity is 2,

Oxalic acid : H^+ ions are 2, thus Basicity is 2

Charge: Na^+ thus take charge as 1

Ca^{++} thus take charge as 2

SO_4^{-2} thus take charge as 2

Change is oxidation state:

Example $KMnO_4$

Basic medium : Change in oxidation state of $Mn = +1$

Acidic medium : Change in oxidation state of $Mn = +5$

Neutral medium : Change in oxidation state of $Mn = +3$

3. Molality

$$m = \frac{\text{moles of solute}}{\text{Weight of solvent in Kg}}$$
$$m = \frac{W \times 1000}{M_0 \times W_s}$$

W : Wight of solute in grams

M_0 : Molecular mass of solute

M_s : Weight of solvent in grams

4. Formality

In case of ionic compounds like $NaCl$, formality is used in place of molarity

$$F = \frac{\text{weight of solute}}{\text{Formula weight} \times \text{Volume if solution in ml}}$$

Formula weight : Example $NaCl = 23 + 35.5 = 58.5$

5. Mass percentage

$$m\% = \frac{\text{weight of solute} \times 1000}{\text{weight of solution}}$$

6. Volume percentage

$$V\% = \frac{\text{volume of solute} \times 1000}{\text{volume of solution}}$$

7. Strength

Strength of a solution may be defined as weight of solute in gram present per litre of the solution. It is expressed as gram/litre

8. Mole fraction

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

N = Number of moles of solvent; n = number of moles of solute

Sum of mole fraction of binary solution (one solute and one solvent) is 1

9. Parts per million (ppm)

$$ppm = \frac{\text{mass of component}}{\text{total mass of solution}} \times 10^6$$

This concentration term is used for very dilute concentration.

- When one substance (the solute) dissolves in another (the solvent), particles of the solute disperse throughout the solvent molecules the ease with which a solute particles replaces a solvent molecules depends on relative strength of three types of interactions

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- (i) Solvent – Solvent interaction
- (ii) Solute – Solute interaction
- (iii) Solute – solvent interaction

It involves three stages

Step I : Involves the separation of solvent molecules (ΔH_1)

Step II: Separation of solute molecules (ΔH_2)

Step III: Solute and solvent molecules mix (ΔH_3)

The heat of solution

$$\Delta H_{\text{solution}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

- If the solute – Solvent attraction is stronger than Solvent – Solvent and Solute –Solute interaction, the solution process will be favorable i.e. its exothermic ($\Delta H_{\text{solution}} < 0$)
- If the solute –solvent interaction is weaker than solvent –solvent and solute –solute interaction then the process is endothermic and solute still dissolves in solvent because along with energy factor, entropy factor plays a major role
- Dissolution of a substance in a solvent is associated with a free energy change , ΔG . If ΔG is negative, the process is spontaneous and substance dissolve on its own. If ΔG is positive the process is non-spontaneous and substance does not dissolve
 $\Delta G = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}}$
- “Like dissolve like “. Polar compound dissolve in polar solvent whereas non-polar compounds dissolve in non-polar solvent

SOLUTIONS OF GASES IN LIQUIDS

- The solubility of a gas in liquid is expressed in terms of absorption coefficient. It is defined as the volume of the gas in ml that can be dissolved by 1ml of liquid solvent at the temperature of the experiment at one atmospheric pressure.
- The following factors affect the solubility of gases in liquids
 - (i) Nature of the gas and solvent.
Chemical similarity between the gas and solvent leads to higher solubility of gas in solvent.
Eg. H_2 , N_2 , O_2 etc are less soluble in water than CO_2 , NH_3 , HCl etc. because later gases react with the solvent.
 - (ii) Effect of temperature
The solubility of most of the gases in liquids decreases with increase of temperature as the dissolution is an exothermic process
Change in entropy i.e. ΔS is negative for dissolution of gas in a liquid, it means ΔH has to be negative (exothermic), so that the process becomes spontaneous.
 $\Delta G = -ve$
 - (iii) Effect of pressure
Effect of pressure on solubility of a gas in a liquid is given by Henry’s Law which states that the solubility of gas in a liquid at a particular temperature is directly proportional to the pressure of gas in equilibrium with the liquid at that temperature
Mole fraction \propto partial pressure of gas (P)
 $X = K_H P$; K_H – Henry constant

Henry’s law holds good if the following conditions are fulfilled

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- a) The pressure is not too high
- b) The temperature is not very low
- c) The gas does not chemically combine with the solvent.

Applications of Henry's law

- a) Carbonated beverages: Effect of pressure on solubility of gas, is used in producing carbonated beverages like soft drinks, beer etc. these are bottled under carbon dioxide pressure greater than 1atm
- b) Deep sea diving
The solubility of gases increases with increasing pressure. The deep sea divers who breath compressed air must be concerned about the solubility of gases in their blood. The scuba divers must ascend gases from being released rapidly from blood and other body fluids. The bubbles of nitrogen and other gases affect nerve impulses and give rise to the decompression sickness or the bends which is painful and can be fatal. Deep sea divers substitute helium from nitrogen in the air that they breathe because helium has a much lower solubility in biological fluids than nitrogen. Generally the scuba divers use the air tank filled with 11.7% helium, 56.2% nitrogen and 32.1% oxygen
- c) High altitude sickness
At high altitudes, partial pressure of oxygen is low, therefore concentration of dissolved oxygen in the blood and tissues of the people diving there is also low. At low concentration of oxygen in blood, the people suffer from anoxia i.e. people suffer from weakness and inability to think properly.

SOLUTIONS OF LIQUIDS IN LIQUIDS

When two liquids are mixed, the mixture may be of following types

- (i) The two liquids do not mix but form separate layer. These are termed as immiscible. Ex: water and benzene
- (ii) The two liquids may be partially miscible Eg. Water and ether
- (iii) The two liquids dissolve in each other in all proportions. These are said to be miscible

SOLUTIONS OF SOLID IN A LIQUID

- Solubility of a solid in a liquid can be defined as the amount of solid (solute) in grams dissolved in 100 gm of the liquid (solvent) to form a saturated solutions at a given temperature.
- Factors affecting the solubility of a solid in a liquid
 - (i) Nature of solute and solvent : Ionic solids dissolve in polar solvents like water and non-ionic or covalent compounds dissolve readily in non-polar solvent " Like dissolves like" rule
 - (ii) Temperature: The solubility increases continuously with increase of temperature if the dissolution process is endothermic Eg. NaNO_3 , KNO_3 , NaCl
If the dissolution process is exothermic then solubility decreases with increase of temperature Eg Li_2CO_3 , $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$

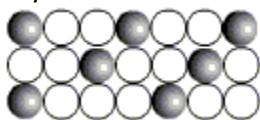
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SOLID SOLUTIONS

Solid solutions are homogeneous mixture of two or more solid components

Solid solutions are of two types

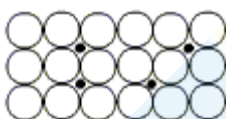
- (i) Substitution solid solutions : Solid elements, which are quite similar in atomic size, can mutually substitute one another in crystal lattices. This gives solid solutions and smooth alloys Eg. Silver and copper alloy



substitutional solid solution

● solute ○ solvent

- (ii) Interstitial solid solutions: In this type of solid solutions smaller atoms are accommodated in the voids or interstices of the solid have bigger atoms. Transition elements have a very strong tendency to combine with atoms of relatively small size to form interstitial compounds eg. Carbides and hydrides. Tungsten carbides and hydrides. Tungsten carbide (WC) is a very hard substance used for cutting and grinding.



Interstitial solid solution

○ solvent • solute

VAPOUR PRESSURE

- The pressure exerted by vapours over the liquid surface at equilibrium is called vapour pressure of the liquid
- Factors affecting vapour pressure of liquid are
 1. Nature of liquid: Weaker the intermolecular forces, greater is the amount of vapour because molecules can leave the liquid easily and can come to the vapour phase easily. Eg. Ether have lighter vapour pressure as compared to alcohol
 2. Temperature: For a particular liquid, higher the temperature, more will be the vapour pressure. The reason for this is the increase in the kinetic energy of molecules to leave the surface of the liquid easily to come to the vapour stateEffect of temperature on vapour pressure of a liquid is given by Clausius – Clapeyron equation

$$\ln \frac{P_2}{P_1} = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

ΔH : Enthalpy of vapourisation

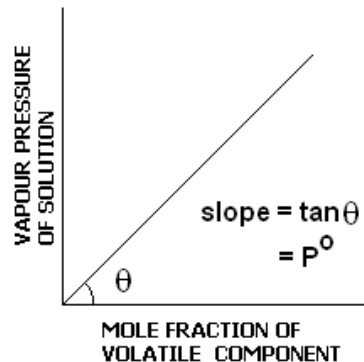
VAPOUR PRESSURE OF SOLUTION

- If solute is non volatile solid or liquid, the vapour pressure of solution is equal to partial vapour pressure of solvent in the solution.
- If solute is volatile solid or liquid the vapour pressure will be equal to the sum of partial vapour pressure of solute and that of solvent.

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RAOULT'S LAW

- For any solution, the partial vapour pressure of each volatile components in the solution is directly proportional to its mole fraction



RAOULT'S LAW FOR VOLATILE SOLUTES

- For volatile solute it states that " Partial vapour pressure of any components of solution at given temperature is equal to its mole fraction and its vapour pressure in pure state.
- For binary solutions of A and B

$$P_A = P_A^0 X_A \text{ and } P_B = P_B^0 X_B$$

$$\begin{aligned} P_{\text{TOTAL}} &= P_A + P_B \\ &= P_A^0 X_A + P_B^0 X_B \\ &= P_A^0 (1 - X_B) + P_B^0 X_B \\ &= P_A^0 + (P_B^0 - P_A^0) X_B \end{aligned}$$

RAOULTS LAW FOR NON-VOLATILE SOLUTE

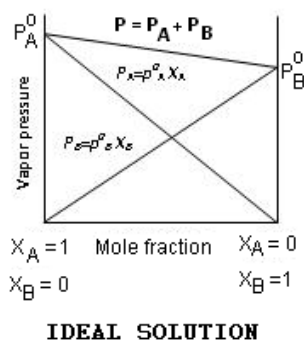
For non-volatile solute, vapour pressure of solution is equal to mole fraction of solvent

$$P_{\text{SOLVENT}} = P^0 X_{\text{SOLVANT}}$$

- Raoult's law is special case of Henry's law
If we compare the solute with the gas dissolved in liquid then in the above expression it can be seen that K_H is just replaced by P^0

IDEAL AND NON-IDEAL SOLUTIONS

1. IDEAL SOLUTIONS



A solution is said to be ideal which obey's Raoult's law in the entire concentration range and at all temperature

An Ideal Solution should have following characteristics

- It should obey Raoult's law
- $\Delta H_{\text{MIXING}} = 0$, i.e. no heat should be absorbed or evolved during mixing
- $\Delta V_{\text{MIXING}} = 0$, i.e. no expansion or contraction on mixing

Examples: Ethyl bromide and ethyl chloride, n-hexane and n-heptane, Benzene and toluene

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2. NON-IDEAL SOLUTION

The solutions which do not obey Raoult's law are called non-ideal solution

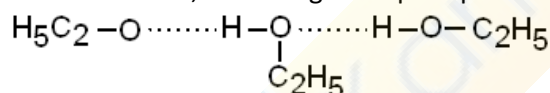
i. Non – ideal solution showing positive deviation

$$P_A > P_A^0 X_A; \quad P_B > P_B^0 X_B$$

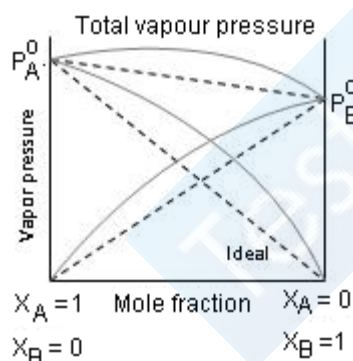
$$\Delta H_{\text{MIXING}} = \text{Positive}; \quad \Delta V_{\text{MIXING}} = \text{Positive}$$

Such solution shows positive deviation from Raoult's law. The observed vapour pressure of each component and total vapour pressure of the solution is greater than the expected from Raoult's law, thus boiling point of such solution is found to be less than the calculated value, this is because the new interactions are weaker than those in the pure components i.e. A-B interactions are weaker than A-A interactions and B-B interactions

Cyclohexane and ethanol. In ethanol, the molecules are held together by hydrogen bonding when cyclohexane is added to ethanol, the molecules of cyclohexane tend to occupy the space between ethanol molecules due to which some hydrogen bonds are broken down. So that intermolecular interactions between cyclohexane and ethanol are reduced and hence, shows higher vapour pressure



Some examples of non-ideal solutions showing positive deviations are acetone + ethyl alcohol, water + ethyl alcohol, CCl₄ + CHCl₃, acetone + carbon disulphide, acetone + benzene



Positive deviation

ii. Non – ideal solutions showing negative deviation

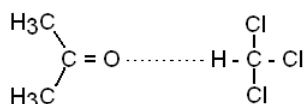
$$P_A < P_A^0 X_A; \quad P_B < P_B^0 X_B$$

$$\Delta H_{\text{MIXING}} = \text{Negative}; \quad \Delta V_{\text{MIXING}} = \text{Negative}$$

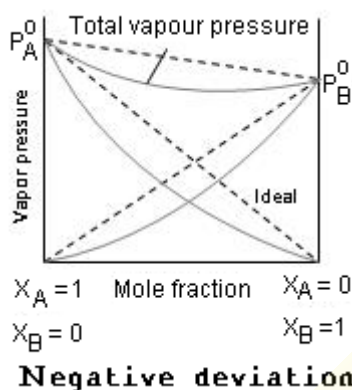
Solutions of above type shows negative deviations from Raoult's law. The observed vapour pressure of each component and total vapour pressure of the solution is lower than expected from Raoult's law, thus boiling point of such solution is found to be higher than the calculated values this is because the new interactions are stronger than those in pure components i.e. A – B interactions and B – B interactions

When acetone and chloroform are mixed together a hydrogen bond is formed between them which increases intermolecular interactions between them and hence decreases the vapour pressure

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Some example of non-ideal solutions showing negative deviation are Acetone + aniline , HCl + water, HNO₃ + water; water + H₂SO₄ , acetone + chloroform , Nitric acid + Chloroform; Benzene + chloroform, Pyridine + glacial acetic acid



AZOTROPIC MIXTURE

A mixture of two real miscible liquids having a definite composition which boils at constant temperature without undergoing any change in composition is called as azeotropic mixture or constant boiling mixture or azeotrope

Azeotropic mixture cannot be separated into their constituent by fractional distillation

MINIMUM BOILING AZEOTROPES

These are the mixture of two liquids whose boiling point is less than either of the two pure component. They are formed by non-ideal solutions showing positive deviations

Eg ethanol – 95.5% (B.P. 351.3K) + water -4.5% (B.P. 373K) mixture boiling at 351.15 K

Ethanol – 6.8% (B.P. 351.3 K) + chloroform - 93.2% (B.P. 334.2K) mixture boiling at 332.3K

MAXIMUM BOILING AZEOTROPES

These are the mixtures of two liquids whose boiling points is less than either of the two pure components. They are formed by no-ideal solutions showing negative deviations

Eg NH₃ – 68% (B.P. 359K) + Water -32% (B.P. 373K) mixture boiling at 393.5K

H₂O – 43% (B.P. 373K) + HI -57% (B.P. 293K) mixture boiling at 400K

COLLIGATIVE PROPERTIES

The properties of dilute solutions which depends only on number of particles of solute present in the solution and not on their nature are called colligative properties

Colligative properties are

1. Relative lowering of vapour pressure
2. Osmotic pressure

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3. Elevation in boiling point
4. Depression in freezing point

RELATIVE LOWERING OF VAPOUR PRESSURE

- Vapour pressure of a solvent in the solution is less than that of pure solvent
- According to Raoult's law, the vapour pressure of the solvent (P_1) in an ideal solution is given by $P_1 = x_1 P_1^0$; x_1 = mole fraction of solvent

Reduction in vapour pressure of solvent (ΔP_1)

$$\begin{aligned}\Delta P_1 &= P_1^0 - P_1 \\ &= P_1^0 - P_1^0 x_1 \\ &= P_1^0 (1 - x_1)\end{aligned}$$

Mole fraction of solute $x_2 = (1 - x_1)$

$$\Delta P_1 = x_2 P_1^0$$

- In a solution containing several non-volatile solutes, the lowering of the vapour pressure depends on the sum of mole fraction of different solutes

$$\Delta P_1 = x_2 P_1^0$$

$$\frac{\Delta P_1}{P_1^0} = \frac{P_1^0 - P_1}{P_1^0} = x_2$$

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{n}{n + N}$$

N: number of moles of solvent ; n = number of moles of solute

For dilute solution $n \ll N$

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{n}{N}$$

$$\frac{P_1^0 - P_1}{P_1^0} = \frac{w_2 \times M_1}{w_1 \times M_2}$$

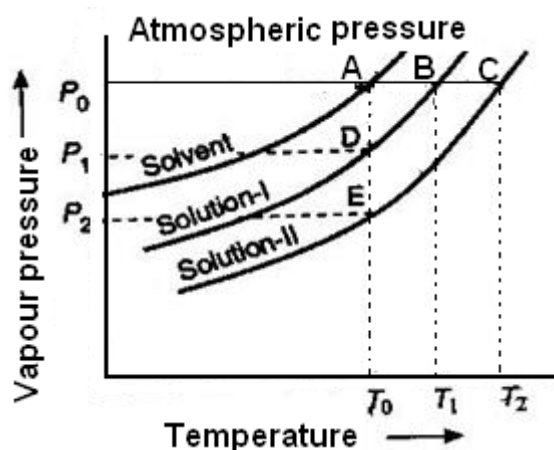
w_1 = mass of solvent ; M_1 : Molar mass of solvent

w_2 = mass of solute ; M_2 mass of solute

ELEVATION IN BOILING POINT (EBULLIOSCOPY)

- The boiling point of a liquid is the temperature at which its vapour pressure is equal to the atmospheric pressure.
- The vapour pressure of a liquid is lowered when a non-volatile solute is added to it. Hence, at the higher temperature of solution, than solvent , vapour pressure of solution equal the atmospheric pressure .
- Elevation in boiling point ΔT = Boiling point of solution – Boiling point of pure solvent
- The curves of the solutions always lie below the curve of the pure solvent. The line P_0C represents the atmospheric pressure. T_0 , T_1 and T_2 represents the boiling points of pure solvent, solution I and solution II at temperature T_0 are P_1 and P_2 respectively.

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Assuming that the solutions are very dilute, these curves may be approximately taken as straight lines near the boiling point. Thus $\triangle ACE$ and $\triangle ABD$ are similar

$$\frac{AC}{AB} = \frac{AE}{AD}$$

$$\frac{T_2 - T_0}{T_1 - T_0} = \frac{P_0 - P_2}{P_0 - P_1}$$

$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

$$\Delta T \propto \Delta P$$

From Raoult's law

$$\Delta P \propto \frac{w_B}{m_B \times w_A} \quad w_B = \text{weight of solute, } m_B = \text{molecular weight of solute, } w_A = \text{weight of solvent}$$

$$\Delta P \propto m \quad (\text{molality of the solution})$$

OR

$$\Delta T \propto \frac{w_B}{m_B \times w_A}$$

$$\Delta T \propto m \quad (\text{molality of the solution})$$

$$\Delta T = K_b m \quad (K_b = \text{molal elevation constant or ebullioscope constant})$$

- Molal elevation constant be defined as the elevation in boiling point when the molality of solution is unity

$$\Delta T = K_b \times \frac{w_B}{w_A \times m_B} \times 1000$$

Here formula for K_b

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

R = gas constant, T_b : Boiling point of solvent in Kelvin, L_v = latent heat of vapourisation of solvent in calories per gram

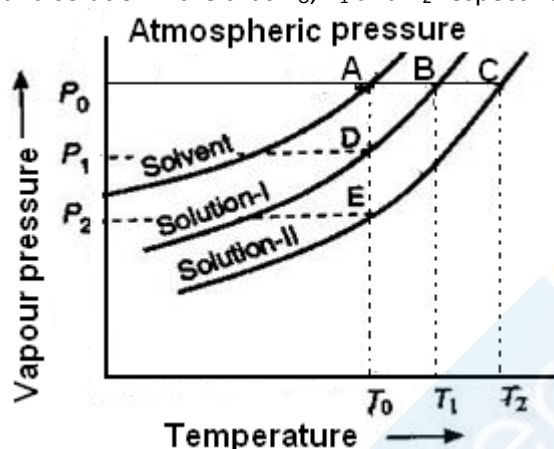
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DEPRESSION IN FREEZING POINT (CRYOSCOPY)

- Freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to vapour pressure of the corresponding solid
- Since, the addition of a non-volatile solute always lowers the vapour pressure of a solvent therefore, it will be in equilibrium with solid phase at a lower pressure and hence at a lower temperature. The difference between the freezing points of a pure solvent and its solution is called depression in freezing point.

Depression in freezing point $\Delta T =$ freezing point of the solvent – freezing point of the solution.

- This can be better understood by plotting a graph of vapour pressure against temperature for a pure solvent and two solutions solution I and solution II. CFB is a curve for the solid solvent. The solvent, solution I, solution II respectively. The vapour pressure at temperatures and solution II are thus P_0 , P_1 and P_2 respectively.



- For very dilute solutions, the curves FD and CE is also nearly a straight line. The ΔBEC and ΔBDF are similar so,

$$\frac{EC}{DF} = \frac{BE}{BD}$$

$$\frac{T_0 - T_2}{T_0 - T_1} = \frac{P_0 - P_2}{P_0 - P_1}$$

$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta P_2}{\Delta P_1}$$

$$\Delta T \propto \Delta P$$

From Raoult's law

$$\Delta P \propto \frac{w_B}{m_B \times w_A} \quad w_B = \text{weight of solute, } m_B = \text{molecular weight of solute, } w_A = \text{weight of solvent}$$

$$\Delta P \propto m \quad (\text{molality of the solution})$$

OR

$$\Delta T \propto \frac{w_B}{m_B \times w_A}$$

$$\Delta T \propto m \quad (\text{molality of the solution})$$

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- (i) The depression in freezing point of a solvent is directly proportional to molal concentration of solution
- (ii) Equimolal quantities of different substances dissolved in the same quantity of solvent bring out the same depression in freezing point of the solvent under ideal conditions. So, depression in freezing point is a colligative property.

$$\Delta T \propto m$$

$$\Delta T = K_f m \quad (K_f = \text{molal depression constant or cryoscopic constant})$$

- Molal depression constant, K_f may be defined as depression in freezing point of a solvent when one mole of a solute is dissolved in 1000 g of the solvent. It is expressed as K_{f1000}

$$\Delta T = K_f \times \frac{w_B}{w_A \times m_B} \times 1000$$

Here formula for K_f

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

R = gas constant, T_f : Freezing point of solvent in Kelvin, L_f = latent heat of fusion of solvent in calories per gram

Ebullioscope and Cryoscopic methods are effective to determine molecular weight when:

- (i) Solutions are dilute. Solutions obey Raoult's law
- (ii) The solute is non-volatile
- (iii) There is no association of solute molecules in the solution
- (iv) Solute does not form a solid solution with solvent in frozen state, i.e., only solvent separates in solid state on freezing the solution

OSMOTIC PRESSURE

- The phenomenon of the passage of pure solvent from a region of lower concentration of solution to a region of higher concentration of solution through a semi-permeable membrane is called osmosis.
- The driving force of osmosis is known as osmotic pressure. It is the difference in the pressure between the solution and the solvent system or it is the excess pressure which must be applied to a solution in order to prevent flow of solvent into the solution through the semi-permeable membrane. Once osmosis is completed the pressure exerted on the semi-permeable membrane is same.

Osmotic pressure

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

π = Osmotic pressure

V = Volume of solution

n = number of molecules of solute = w_B/m_B

R = Gas constant

T = Temperature

C = concentration

w_B = weight of solute

M_B = molecular weight of solute

$$\pi = \frac{w_B}{m_B V} RT$$

- When height is involved $\pi = hdg$ here h = height; d = density; g = gravitational acceleration
- The two solutions having same osmotic pressure and hence same molar concentration at the same temperature are called isotonic or iso-osmotic solutions

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For isotonic solutions, at constant temperature

$$\frac{n_1}{v_1} = \frac{n_2}{v_2}$$

If one of the solution is of lower osmotic pressure, it is called hypotonic solution with respect to more concentrated solution.

The more concentrated solution with higher osmotic pressure is known as hypertonic solution with respect to dilute solution

- When the pressure applied on the solution is more than osmotic pressure then solvent will start flowing from the solution to the solvent through semi-permeable membrane. This process is called reverse osmosis. It is used in the desalination of water.

VAN'T HOFF FACTOR

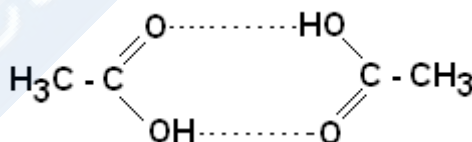
- Colligative properties depend upon the number of particles of the solute in the solution. In some cases, where the solute undergoes association or dissociation in solution, abnormal results for molecular masses are obtained.
- Van't Hoff Factor (i)
Van't Hoff, in order to account for extent of association or dissociation of solute in solution introduced a factor " i " known as the van't Hoff factor. It is defined as the ratio of experimental value of colligative property to the calculated value of that colligative property

$$i = \frac{\text{observed colligative property (actual)}}{\text{theoretical colligative property (expected)}}$$

$$i = \frac{\text{Calculated molecular mass } (M_C)}{\text{observed (experimental) molecular mass } (M_O)}$$

$$i = \frac{\text{Number of molecules actually present}}{\text{Number of molecules expected to be present}}$$

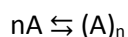
- Association
There are many organic solutes which in non-aqueous solutions undergo associated, that is two or more molecules of solute associate to form a one bigger molecule. Thus, the number of effective molecules decreases and consequently the colligative property become less than expected value which depend upon the number of solute molecules. Example : acetic acid in benzene and chloroacetic acid in naphthalene



- Degree of association α

$$\alpha = \frac{\text{Number of molecules associated}}{\text{Total number of molecules taken}}$$

Suppose n simple molecules combine to form an associated molecules



initial concentration 1 0

Final concentration 1- α α/n

Total number of effective moles after dissociation = 1 - α + α/n

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

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

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

Here $i = \frac{\text{Calculated molecular mass } (M_C)}{\text{observed (experimental) molecular mass } (M_O)}$

SOLUTIONS

$$\alpha = \frac{M_0 - M_c}{M_0} \frac{n}{n-1}$$

$M_0 > M_c$

Thus $i < 1$

Observed colligative property < Calculated value

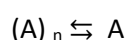
- Dissociation

Inorganic acids, bases and salts in aqueous solutions undergo dissociation that is, the molecules break down into ions. In such cases, the number of effective particles increases and value of colligative property becomes higher than expected one (which depends upon number of solute particles

- Degree of dissociation α

$$\alpha = \frac{\text{Number of molecules dissociated}}{\text{Total number of molecules taken}}$$

Consider a molecule of an electrolyte dissolved in a solvent dissociated to give n ions



initial concentration 1 0

Final concentration 1- α n α

Total number of effective moles after dissociation = 1 - α + n α

$i = 1 - \alpha + n\alpha$

= 1 - α (n - 1)

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

$$i = \frac{M_c}{M_0}$$

$$\alpha = \frac{M_c - M_0}{M_0} \frac{1}{n-1}$$

$M_c > M_0$: $i > 1$

Observed colligative property > Calculated value of colligative property

1. Relative lowering of vapour pressure

$$\frac{P_1^0 - P_s}{P_1^0} = iX_2$$

X_2 = mole fraction of solute

2. Osmotic pressure $\pi = i CRT$

3. Elevation in boiling point $\Delta T_b = i \times K_b \times \text{molality}$

4. Depression in freezing point $\Delta T_f = i \times K_f \times \text{molality}$

SOLVED NUMARICAL

Q1) The mole fraction of methanol in an aqueous is 0.02 and its density is 0.994 g/ml. Determine the molarity of the solution.

Solution:

Let volume of solution be 1 L . From density of solution weight of solution = 994 gm

N = Number of moles of water (solvent) ; n = number of moles of solute (methanol)

Molecular weight of methanol = 32; molecular weight of water = 18

Now 994 = n(32) + N(18) --- eq(1)

From the formula of mole fraction $X = \frac{n}{n+N}$

SOLUTIONS

$$\therefore n = \frac{XN}{1-X} \dots \dots \dots eq(1)$$

Substituting value of n in equation 1

$$994 = \left(\frac{XN}{1-X} \right) 32 + 18N$$

$$994 = \left(\frac{0.02}{1-0.02} \right) 32N + 18N$$

$$994 = (0.65 + 18) N$$

$$N = 53.29$$

Substituting value of N in equation 2 we get n = 1.08

According to definition of molarity volume is taken 1 litre therefore molarity = 1.08

Q2) 100g water contains 1.0 g urea and 2.0 g sucrose at 298 K. The vapour pressure of water at 298K is 0.03167 bar. Determine the vapour pressure of the solution.

Solution :

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

$$\frac{\Delta P}{P^0} = \frac{n_2}{n_1}$$

$$\frac{\Delta P}{0.03167} = \frac{\frac{1}{60} + \frac{2}{242}}{\frac{100}{18}}$$

$$\Delta P = 0.00014$$

$$P^0 - P_s = \Delta P$$

$$P_s = P^0 - \Delta P$$

$$P_s = 0.03167 - 0.00014 = 0.03153 \text{ bar}$$

Q3) The boiling point of a solution of 0.105g of substance in 15.84 g of ether was found to be 0.1°C higher than that of pure ether. What is molecular weight of solute? Given: $K_b(\text{ether}) = 21.6 \text{ K mole}^{-1}$ per 100 g.

Solution

$$\Delta T_b = 0.1^\circ\text{C}$$

$$m = \frac{w \times 1000}{M_0 \times W} = \frac{0.105 \times 1000}{M_0 \times 15.84}$$

$$\Delta T_b = K_b \times m$$

K_b is for 100g, must be converted for 1000g. Therefore value of ΔT_b will be 21.6/10

SOLUTIONS

$$0.1 = \frac{21.6}{10} \times \frac{0.105 \times 1000}{M_0 \times 15.84}$$

$$M_0 = 143.18 \text{ gm/mol}$$

Q4) Calculate the mole fraction, molal and molar concentration of a solution containing 20% acetic acid by mass in water, if the density of the solution at 20°C is 1.026 g cm⁻³.

Solution:



Initial concentration 1 0 0

Final concentration (1-α) α α

Now $i = 1 - \alpha + 2\alpha$

$$= 1 + \alpha$$

Now

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

$$\frac{750 - 740}{750} = i \frac{0.5}{55.55}$$

$$i = 1.482$$

$$1 + \alpha = 1.482$$

$$\alpha = 0.482$$

$$\% \text{ dissociation} = 48.2\%$$

Q5) Calculate the amount of ice that will separate out on cooling a solution containing 50g of ethylene glycol in 200g water to -9.3°C. Given K_f for water = 1.86 K mol⁻¹kg

Solution:

$$\Delta T_f = K_f \times m$$

$$m = 9.3 / 1.86$$

For the formula of molality

$$\frac{50 \times 1000}{62 \times W} = \frac{9.3}{1.86}$$

$$W = 161.29$$

$$\text{Weight of water converted in to ice} = 200 - 161.29 = 38.71 \text{ g}$$

Q6) A solution contains 0.011 kg of barium nitrate in 0.1 kg of water boils at 100.46°C. Calculate the degree of ionization of salt. Given $K_b(\text{water}) = 0.52 \text{ K kg mol}^{-1}$

$$\Delta T_b = i \times K_b \times m$$

SOLUTIONS

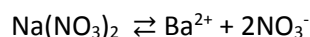
$$i = \frac{\Delta T_b}{K_b \times m}$$

Molecular weight of barium nitrate = 261, weight of solvent = 0.1, weight of solute 11, molality

$$m = \frac{11}{261 \times 0.1}$$

Thus

$$i = \frac{0.46 \times 261 \times 0.1}{0.52 \times 11} = 2.098$$



Final concentration 1 α 2α

$$i = (1 - \alpha) + 3\alpha = 1 + 2\alpha$$

$$2.098 = 1 + 2\alpha$$

$$\alpha = 0.55$$

Q7) if boiling point of an aqueous solution is 100.1°C , what is its freezing point? Given latent heat of fusion and vaporization of water are 80 cal g^{-1} and 540 cal g^{-1} respectively

Solution

$$K_f = \frac{RT_0^2}{1000L_f} = \frac{2 \times (273)^2}{1000 \times 80} = 1.8632$$

$$K_b = \frac{RT_0^2}{1000L_v} = \frac{2 \times (273)^2}{1000 \times 540} = 0.5153$$

$$\Delta T_b = K_b \times m$$

$$0.1 = 0.5153 \times m$$

Therefore $m = 0.194 \text{ mol/kg}$

$$\Delta T_f = K_f \times m$$

$$\Delta T_f = 1.8632 \times 0.194 = 0.361^\circ\text{C}$$

Freezing point of pure water is 0° ,

Therefore freezing point of solution = $0 - 0.361 = -0.361^\circ\text{C}$

Q8) Find the molarity and molality of a 15% solution of H_2SO_4 (density $\text{H}_2\text{SO}_4 = 1.020 \text{ g/cc}$)

Solution:

15% solution of H_2SO_4 means 15g of H_2SO_4 have been dissolved in 100 g of solution i.e.

Weight of $\text{H}_2\text{SO}_4 = 15 \text{ g}$ and weight of water = 85

SOLUTIONS

Molarity

Volume of solution = mass/density = 100/1.02 = 98.04 ml

$$M = \frac{W \times 1000}{M_0 \times V} = \frac{15 \times 1000}{98 \times 100} = 1.56M$$

Molality

$$m = \frac{W \times 1000}{M_0 \times \text{mass of solvent}} = \frac{15 \times 1000}{98 \times 85} = 1.8m$$

Q9) A 500g tooth paste sample has 0.2g fluoride concentration. What is the concentration of fluorine in terms of ppm level?

Solution

$$ppm = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 = \frac{0.2}{500} \times 10^6 = 400ppm$$

Q10) The vapour pressure of pure benzene and toluene at 40°C are 184.0 torr and 59.0 torr respectively. Calculate the partial pressures of benzene and toluene, the total vapour pressure of the solution and mole fraction of benzene in the vapour phase above the solution, if mole fraction of benzene in solution is 0.40. Assume that the solution is ideal

Solution: subscript B denote Benzene and T denote Toluene

In Solution $X_B = 0.40$ and Hence $X_T = 0.6$

$$P_B = X_B P_B^0 = 0.40 \times 184.0 = 73.6 \text{ torr}$$

$$P_T = X_T P_T^0 = 0.6 \times 59.0 = 35.4 \text{ torr}$$

$$P_{TOTAL} = P_B + P_T = 73.6 + 35.4 = 109.0 \text{ torr}$$

$$X_B = \frac{P_B}{P_{TOTAL}} = \frac{73.6}{109} = 0.675$$

Q10) The vapour pressure of benzene and toluene are 75 mmHg and 22mmHg respectively. 23.4g of benzene and 64.4 g of toluene are mixed. If the two form an ideal solution, calculate the mole fraction of benzene in the vapour phase if the vapours are in equilibrium with the liquid mixture at the same temperature.

Solution

$$\text{Number of moles of benzene } n_B = 23.4 / 78 = 0.3$$

$$\text{Number of moles of toluene } n_T = 64.4 / 92 = 0.7$$

Mole fraction of Benzene

$$X_B = \frac{0.3}{0.3 + 0.7} = 0.3$$

Then mole fraction of toluene $X_T = 1 - 0.3 = 0.7$

$$P_{TOTAL} = P_{benzen} + P_{toluene}$$

SOLUTIONS

$$= 75 \times 0.3 + 22 \times 0.7 = 37.9$$

Mole fraction of benzene in vapour phase = $P_{\text{benzene}} / P_{\text{TOTAL}}$

$$= \frac{75 \times 0.3}{37.9} = 0.59$$

Q11) Vapour pressure of a pure liquid A is 10.0 torr at 270°C. the vapour pressure is lowered to 9.0 torr on dissolving one gram of B in 20g of A. If molar mass of A is 200 then calculate molar mass of B

Solution

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A}$$

$$\frac{10 - 9}{9} = \frac{w_B}{M_B} \times \frac{M_A}{w_A} = \frac{1}{M_B} \times \frac{200}{20}$$

$$M_B = 100$$

Q12) Calculate the molecular weight of glycerine if its solution containing 10.2 g of glycerine per litre is isotonic with solution of glucose.

Solution:

For being isotonic

$$\pi_{\text{glycerine}} = \pi_{\text{glucose}}$$

$$\frac{n_1}{V_1} RT = \frac{n_2}{V_2} RT$$

Number of moles = weight/molecular weight,

2% solution means 2 gram glucose in 100g solution, density of water = 1g/cm³

$$\frac{W_{\text{glycerine}}}{M_{\text{glycerine}}} \times \frac{1}{V_1} = \frac{W_{\text{glucose}}}{M_{\text{glucose}}} \times \frac{1}{V_2}$$

$$\frac{10.2}{M_{\text{glycerine}}} \times \frac{1}{1000} = \frac{2}{180} \times \frac{1}{100}$$

$$M_{\text{glycerine}} = 91.8$$

Q13) A 5% aqueous solution by mass of a volatile solute boils at 100.15°C. Calculate the molar mass of the solute $K_b = 0.52 \text{ K Kg mol}^{-1}$

Solution

Normal boiling point of water = 100°C

∴ Increase in boiling point of water = 100.15 - 100 = 0.15°C

The solution contains 5% by mass of the solute that is 5 g solute in 100 g of solvent

∴ Mass of solvent = 100 - 5 = 95g

From the formula for elevation in boiling point

SOLUTIONS

$$\Delta T = K_b \times \frac{w_B}{w_A \times m_B} \times 1000$$

$$m_B = K_b \times \frac{w_B}{w_A \times \Delta T} \times 1000$$

$$m_B = 0.52 \times \frac{5}{95 \times 0.15} \times 1000 = 21.6$$

Q14) What weight of glycerol have to be added in 500g of water in order to lower its freezing point by 20°C? $K_f = 1.86^\circ\text{C}$

Solution

From the formula for depression in freezing point

$$\Delta T = K_f \times \frac{w_B}{w_A \times m_B} \times 1000$$

Molecular weight of glycerol m_B is 92

$$w_B = \frac{\Delta T \times w_A \times m_B}{K_f \times 1000} = \frac{20 \times 92 \times 500}{1.86 \times 1000} = 495g$$

Q15) In 100g of naphthalene, 2.423 g of S was dissolved. Melting point of naphthalene = 80.1°C. $\Delta T_f = 0.661^\circ\text{C}$ $L_f = 35.7$ cal/g of naphthalene. Determine the molecular formula of sulphur added

Solution

From the formula

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

And formula for depression in freezing point

$$\Delta T_f = K_f \times \frac{w_B}{w_A \times m_B} \times 1000$$

$$\Delta T_f = \frac{RT_f^2}{1000L_f} \times \frac{w_B}{w_A \times m_B} \times 1000$$

$$m_B = \frac{RT_f^2}{1000L_f} \times \frac{w_B}{w_A \times \Delta T_f} \times 1000$$

$$m_B = \frac{2 \times (353.1)^2}{1000 \times 35.7} \times \frac{2.423}{0.661 \times 100} \times 1000 = 256$$

(value of R taken as 2 in calories)

If molecular formula of S is S_x then

$$x = 256/32 = 8$$

Thus substance is S_8

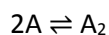
SOLUTIONS

Q16) The freezing point of a solution of acetic acid (mole fraction = 0.02) in benzene 277.4 K. Acetic acid exists partly as dimer $2A \rightleftharpoons A_2$. Calculate equilibrium constant for dimerisation. Freezing point of benzene is 278.4K and K_f for benzene is 5 K kg mol^{-1}

Solution

Let acetic acid = A, Benzene = B

Assume α part of A forms dimer



$1-\alpha$ $\alpha/2$ moles after dimer is formed

$$l = (1-\alpha) + \alpha/2 = 1 - \alpha/2 \text{ ---- eq(1)}$$

Mole fraction of A = $X_A = 0.02$

Mole fraction of B = $X_B = 1 - 0.02 = 0.98$

Molality of A in B

$$m = \frac{X_A \times 1000}{X_B \times M_B} = \frac{0.02 \times 1000}{0.98 \times 78} = 0.262 \text{ mol kg}^{-1}$$

(Molecular weight of benzene = 78)

Since $\Delta T_f = K_f \times i \times \text{molality}$

$$278.4 - 277.4 = 5 \times i \times 0.262$$

$$i = 0.763$$

Thus from equation 1

$$0.763 = 1 - \alpha/2$$

$$A = 0.48$$

Hence the molality of A after dimer is formed = $(1-\alpha) \times \text{initial molality}$

$$= (1 - 0.48) \times 0.262 = 0.13624$$

And the molality of A_2 after dimer is formed = $(\alpha/2) \times \text{molality} = 0.24 \times 0.262 = 0.06288$

The equilibrium constant

$$K_{eq} = \frac{[A_2]}{[A_1]^2} = \frac{0.06288}{(0.13624)^2} = 3.39 \text{ kg mol}^{-1}$$

Q17) A solution of monobasic acid ($3 \times 10^{-2} \text{ m}$) has a freezing point depression of 0.06°C . Calculate pK_a for the acid [Molar depression constant 1.86°C/m for water]

Solution

We know that $\Delta T_f = K_f \times i \times \text{molality}$

$$0.06 = 1.86 \times i \times 3 \times 10^{-2}$$

$$i = 1.07526$$

Let acid is MH



Initial concentration C 0 0

Final concentration $C(1-\alpha)$ $C\alpha$ $C\alpha$

SOLUTIONS

$$K_a = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = C\alpha^2$$

Now

$$i = \frac{\text{total moles after dissociation}}{\text{initial mole}}$$

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

$$\alpha = i - 1 = 1.07526 - 1 = 0.07526$$

$$K_a = 1.6992 \times 10^{-4}$$

$$pK_a = -\log K_a = -\log(1.6992 \times 10^{-4})$$

$$pK_a = +3.769$$

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