Solutions
by Apni Kaksha
Class XII Board Exams (Target 100)

These notes have been verified by CBSE Science Toppers.

Previous 15 year questions have been integrated in the notes.
HOW TO STUDY THE NOTES?

Apni Kaksha

- Coloured and double sided print
- Revise the notes at least 3-4 time
- Write to revise | 10% rule
- Keep track of previous year qs
- See the marking scheme
Flow Chart Of Complete chapter: NCERT

SOLUTION

Formation of solution and its type
Solubility of gas in liquid
Henry Law
Vapour Pressure
Raoult's Law

Concentration Terms
- Mass percentage
- Volume Percentage
- Mole fraction
- Parts per million
- Molarity
- Molality

Types Of Solution
- Ideal Solution
  - Relative lowering of v.p.
  - Elevation of b.p.
  - Depression of freezing point
  - Osmosis and osmotic pressure
  - Reverse Osmosis
- Non-ideal Solution
  - Positive Deviation
  - Azeotrope
  - Negative Deviation
  - Azeotrope

ABNORMAL MOLECULAR MASS
Solutions

- Solutions are homogeneous mixtures of two or more than two components.
- Homogeneous mixture means composition and properties are uniform throughout the mixture.
- Generally, the component that is present in the largest quantity is known as Solvent.
- Components present in the solution other than solvent is known as Solute.

<table>
<thead>
<tr>
<th>Type of Solution</th>
<th>Solute</th>
<th>Solvent</th>
<th>Common Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gaseous Solutions</td>
<td>Gas</td>
<td>Gas</td>
<td>Mixture of oxygen and nitrogen gases</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td>Gas</td>
<td>Chloroform mixed with nitrogen gas</td>
</tr>
<tr>
<td></td>
<td>Solid</td>
<td>Gas</td>
<td>Camphor in nitrogen gas</td>
</tr>
<tr>
<td>Liquid Solutions</td>
<td>Gas</td>
<td>Liquid</td>
<td>Oxygen dissolved in water</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td>Liquid</td>
<td>Ethanol dissolved in water</td>
</tr>
<tr>
<td></td>
<td>Solid</td>
<td>Liquid</td>
<td>Glucose dissolved in water</td>
</tr>
<tr>
<td>Solid Solutions</td>
<td>Gas</td>
<td>Solid</td>
<td>Solution of hydrogen in palladium</td>
</tr>
<tr>
<td></td>
<td>Liquid</td>
<td>Solid</td>
<td>Amalgam of mercury with sodium</td>
</tr>
<tr>
<td></td>
<td>Solid</td>
<td>Solid</td>
<td>Copper dissolved in gold</td>
</tr>
</tbody>
</table>

Expressions for concentration of solution

- Mole fraction \( \left[ \frac{x}{X} \right] \) of a component = \( \frac{\text{No. of moles of component}}{\text{Total no. of moles of all components}} \)

- For a binary mixture (having component A and B), if the no. of moles of A and B are \( n_A \) and \( n_B \) respectively, then mole fraction of A will be \( x_A = \frac{n_A}{n_A + n_B} \).

\[
\text{mole fraction of } B = x_B = \frac{n_B}{n_A + n_B}
\]

- For binary mixture \( x_A + x_B = 1 \) [sum of all the mole fractions is unity]

Example: A mixture having two gaseous component \( \text{N}_2(g) \) and \( \text{O}_2(g) \) with no. of moles of 10 and 20 respectively. Then what is the mole fraction of both components?

\[
\begin{align*}
\text{Mole fraction of } \text{N}_2 &= \frac{n_{\text{N}_2}}{n_{\text{N}_2} + n_{\text{O}_2}} = 10 \frac{10}{10 + 20} = \frac{1}{3} \\
\text{Then } x_{\text{O}_2} &= 1 - \frac{1}{3} = \frac{2}{3}
\end{align*}
\]

And:

\[
\text{Mole fraction of } \text{N}_2 = \frac{n_{\text{N}_2}}{n_{\text{N}_2} + n_{\text{O}_2}} = \frac{10}{10 + 20} = \frac{1}{3}
\]

\[
\text{Then } x_{\text{O}_2} = 1 - \frac{1}{3} = \frac{2}{3}
\]
**Mass Percentage [W/W]**

\[
\text{Mass % of a Component} = \frac{\text{Mass of the Component in Solution}}{\text{Total mass of solution}} \times 100
\]

→ 10% glucose in water means 10 g of glucose is dissolved in 90 g of water resulting in 100 g solution.

**Volume Percentage [V/V]**

\[
\text{Volume % of a Component} = \frac{\text{Volume of the Component}}{\text{Total Volume of Solution}}
\]

→ 10% ethanol in water means that 10 ml of ethanol is dissolved in water such that total volume of solution is 100 ml.

**Mass by Volume Percentage [m/V]**

→ It is mass of solute dissolved in 100 ml of the solution.

**Parts per Million [ppm]**

→ Parts per million = \(\frac{\text{No. of parts of Component}}{\text{Total no. of parts of all components of the solution}} \times 10^6\)

→ Concentration in parts per million can also be expressed as mass to mass (W/W), volume to volume (V/V) and mass to volume (m/V).

→ \(\frac{\text{W}}{\text{V}}\) = \(\frac{\text{Weight of solute (g)}}{\text{Volume of solution (ml)}}\) \times 100  
   \(\text{Similarly; PPM (W/V)} = \frac{\text{Weight of solute (g)}}{\text{Volume of solution (ml)}} \times 10^6\)

→ 5.0 ppm O₂ is dissolved in sea → means 5.0 g of O₂ is dissolved in 10⁶ g of sea water.

→ The concentration of pollutants in water and atmosphere is expressed in terms of ppm.
Question: Calculate the mole fraction of ethylene glycol (C\textsubscript{2}H\textsubscript{6}O\textsubscript{2}) in a solution containing 20% of C\textsubscript{2}H\textsubscript{6}O\textsubscript{2} by mass.

Answer: 20% of C\textsubscript{2}H\textsubscript{6}O\textsubscript{2} means 20 g of C\textsubscript{2}H\textsubscript{6}O\textsubscript{2} is present in 100 g of water.

Molar mass of C\textsubscript{2}H\textsubscript{6}O\textsubscript{2} = 2 \times 12 + 1 \times 6 + 16 \times 2 = 62 g/mol.

Moles of C\textsubscript{2}H\textsubscript{6}O\textsubscript{2} = \frac{20 g}{62 g/mol} = 0.322 mol = n\textsubscript{glycol}

Moles of water = \frac{80 g}{18 g/mol} = 4.444 mol = n\textsubscript{water}

\[ \text{Mole fraction of glycol} = \frac{n\textsubscript{glycol}}{n\textsubscript{glycol} + n\textsubscript{water}} = \frac{0.322}{0.322 + 4.444} = 0.068 \]

Similarly, \[ \text{Mole fraction of water} = 1 - \text{Mole fraction of glycol} = 1 - 0.068 = 0.932 \]

vi) Molarity [M]:

- It is defined as the number of moles of solute dissolved in one litre of solution.

\[ \text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution (in litre)}} \]

- Unit: mol/litre [M]

- 0.25 M solution of NaOH means that 0.25 mol of NaOH has been dissolved in 1 litre.

- Calculate the molarity of a solution containing 5 g of NaOH in 450 ml solution?

Answer: moles of NaOH = \frac{5 g}{40 g/mol} = 0.125 mol, volume of solution in litre = \frac{450 ml}{1000 ml} = 0.45 L

Molarity = \frac{0.125 \text{ mol}}{0.45 L} = 0.278 \text{ mol L}^{-1} = 0.278 \text{ mol dm}^{-3}

1 litre = 1 dm\textsuperscript{3}

A solution of glucose in water is labelled as 10% by weight. What would be the modality of a solution? [Molar mass of glucose = 180 g/mol-1]

Answer: 10% glucose solution by weight means 10 g glucose is present in 100 g solution.

Then weight of water = 100 - 10 = 90 g

\[ \text{Modality} = \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}} = \frac{\left(\frac{10}{180}\right) \text{ mol}}{\left(\frac{90}{1000}\right) \text{ kg}} = 0.61 \text{ mol kg}^{-1} = 0.61 \text{ m} \]
Motality \( [\text{m}] \): It is defined as no. of moles of the solute per kg of solvent.

\[
\text{Motality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent (kg)}} \quad \text{unit} \rightarrow \frac{\text{mol}}{\text{Kg}}.
\]

1 m solution of KCl means that 1 mol of KCl (74.58 g) is dissolved in 1 kg of water.

Calculate motality of 25 g of ethanoic acid in 75 g of benzene!

**Answer:**

Molar mass \( = \text{CH}_3\text{-COOH} = 12 \times 2 + 1 \times 4 + 16 \times 2 = 60 \text{ g mol}^{-1} \)

\[
\text{Motality of CH}_3\text{COOH} = \frac{\text{Moles of CH}_3\text{COOH}}{\text{Kg of benzene}} = \frac{2.5/60}{75/1000} = 0.556 \text{ mol kg}^{-1}.
\]

Main advantage of motality over molarity: Motality does not change with change in temperature while, molarity decreases with rise in temperature. This is because volume depends on temperature (V=dT) but mass does not.

Relation between Density, Molarity, and Motality:

If \( d \) is density of solution, \( m \) is motality, and \( M \) is molarity, \( M_2 \) is molar mass of solute. Then

\[
\text{Motality } m = \frac{M \times 1000}{1000 \times d - M \times M_2} \quad \text{(No need to memorise this formula)}
\]

**Question:**

Calculate the motality of 9.81% w/w solution of \( \text{H}_2\text{SO}_4 \) if the density of the solution is 1.02 g ml\(^{-1}\)? Molar mass of \( \text{H}_2\text{SO}_4 \) \( \rightarrow \) 98 g mol\(^{-1}\)

**Answer:**

9.81% solution means 9.8 g of \( \text{H}_2\text{SO}_4 \) is present in 100 g of the solution.

Density of solution = 1.02 g ml\(^{-1}\), then Volume of solution = \( \frac{\text{Mass of Solution}}{\text{Density of Solution}} \)

\[
= \frac{100}{1.02} = 98.04 \text{ ml}
\]

Moles of \( \text{H}_2\text{SO}_4 = \frac{9.8}{98 \text{ g mol}^{-1}} = 0.1 \text{ mol} \)

Molarity = \( \frac{0.1 \text{ mol}}{0.098 \text{ l}} = 1.018 = 1.02 \text{ M} \)

**Question:**

A solution of glucose (molar mass = 180 g mol\(^{-1}\)) in water is labelled as 10% (mass). What would be the motality and molarity of the solution?

Density of solution \( \rightarrow \) 1.2 g ml\(^{-1}\)

**Answer:**

[Delhi 2014]
Answer:  
10. glucose solution (by mass) means that mass of glucose = 10g
\[ \text{mass of solution} = 100g \]
\[ \text{mass of solvent} = 90g \]

\[ \text{Molar mass of glucose} = \frac{160.3}{\text{mol}} \]

\[ \text{Density of solution} = 1.2 \text{ g ml}^{-1} \]
\[ \text{Volume of solution} = \frac{m}{d} = \frac{100 \text{ g}}{1.2 \text{ g ml}^{-1}} = \frac{1000 \text{ ml}}{12} = \frac{1}{12} \text{ litre} \]

\[ \text{Molarity} = \frac{\text{mole of glucose}}{\text{volume of solution (in L)}} = \frac{(10 \text{ g})}{12} = 0.667 \text{M} \]

\[ \text{Molarity} = \frac{\text{mole of glucose}}{\text{mass of solvent (in kg)}} = \frac{(10 \text{ g})}{90 \text{ g}} = 0.667 \text{m} \]

Solubility

- Solubility of a substance is its maximum amount that can be dissolved in a fixed amount of solvent.
- When a solid solute is added to solvent, some solute dissolves and its concentration increases in solution. This process is known as Dissolution.
- Some solute particles in solution collide with the solid solute particles and get separated out of solution. This process is known as Crystallisation.
- At point of equilibrium, no of solute particles going into solution will be equal to solute particles separating out. Solute + Solvent \( \Leftrightarrow \) Solution
- At this dynamic equilibrium concentration of solute in solution will remain constant at given temperature and pressure.
- Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a saturated solution.
- Unsaturated solution: A solution in which more solute can be dissolved.

Effect of temperature: If in a nearly saturated solution, the dissolution process is endothermic \( \Delta H > 0 \) then on \( T \) of temperature \( \Rightarrow \) solubility \( T \).

For exothermic \( \Delta H < 0 \) then on \( T \) of temperature \( \Rightarrow \) solubility \( \downarrow \).

Pressure does not have any significant effect on solubility of solids in liquids because solid and liquid both are incompressible.
Henry Law [Effect of pressure on solubility]:

"The solubility of a gas in a liquid at a given temperature is directly proportional to the pressure at which it is dissolved."

If we use mole fraction \( x \) of a gas in solution as a measure of its solubility, then

\[
\text{Partial pressure of a gas (}\ p \text{)} = k_H \cdot x
\]

Henry Law Constant:

(i) \( k_H \) is a function of the nature of a gas means that different gases have different \( k_H \) value.

(ii) Higher the value of \( k_H \) → lower is the solubility because at constant pressure \( k_H \propto \frac{1}{x} \).

(iii) Unit of \( k_H \) = Unit of pressure = atm \|

\( k_H \) is proportional to temperature. \([ k_H \propto T \text{ and } k_H \propto \frac{1}{x} \Rightarrow T \propto \frac{1}{x} \] means that solubility of a gas increases with decrease of temperature.

Due to above reason \( O_2 \) is getting more dissolve in cold water than in warm water. So, aquatic species are more comfortable in cold water than warm water.

Application of Henry's Law:

CAS 2011/2012 2011C 1M

Delhi 2011

CAS 2013/2014 2014C 1M

Delhi 2012A 2M

CAS 2019/2020 2019C 1M

CAS 2019/2020 2019C 1M

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

[ii] At higher altitudes, the partial pressure of oxygen is less than that at ground level. This leads to low concentration of oxygen in blood. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.
Question: The partial pressure of ethane over a saturated solution containing $6.56 \times 10^{-2}$ g of ethane is 1 bar. If solution contains $5.0 \times 10^{-2}$ g of ethane, then what will be the partial pressure of the gas?

Answer: According to Henry's Law:

(i) mass of ethane & partial pressure

$$m_1 = K_H \cdot p_1$$

$$6.56 \times 10^{-2} \text{ g} = K_H \cdot 1 \text{ bar}$$

(ii) $m_2 = K_H \cdot p_2$

Partial pressure of gas ($p_2$) = $\frac{m_2}{K_H} = \frac{5 \times 10^{-2} \text{ g}}{6.56 \times 10^{-2} \text{ g}} = 0.762 \text{ bar}$.

Answer: If N₂ gas is bubbled through water at 293 K, how many millimoles of N₂ gas would dissolve in 1L of water? Assume that N₂ exerts a partial pressure of 0.987 bar, given $K_H = 76.4 \text{ kbar}$ at 293 K.

Answer: According to Henry's Law:

$$p_{N_2} = K_H \cdot x_{N_2}$$

If n moles of N₂ are present in 1L or 1000 g of water, then moles of:

$$x_{N_2} = \frac{p_{N_2}}{K_H} = \frac{0.987 \text{ bar}}{76.4 \times 10^3 \text{ bar}} = 1.29 \times 10^{-5}$$

Water = $n_{\text{water}} = \frac{1000}{18} = 55.5 \text{ mol}$

Mole fraction of N₂:

$$\frac{n}{n_{\text{water}}} = \frac{h}{55.5} = 0.0019$$

Vapour pressure of liquid solutions.

Definition of vapour pressure: The partial pressure of vapours in equilibrium with pure solid or pure liquid at a given temperature.

At equilibrium: Rate of evaporation = Rate of condensation.

For example: $H_2O(\ell) \rightleftharpoons H_2O(\text{g})$

Equilibrium constant $K_p = \frac{p_{H_2O(\text{g})}}{p_{H_2O(\ell)}}$

For pure $H_2O(\ell): p_{H_2O(\text{g})} = 1$ then $K_p = p_{H_2O(\text{g})}$
For liquid \( \rightarrow \) vapours: Vapour pressure is an equilibrium constant. So it depends only on (a) Nature of liquid (b) Temperature of liquid.

If magnitude of intermolecular forces in the liquid is smaller then we observe high vapour pressure because loosely held molecules escape more easily into vapour phase.

**Boiling Point**: The temperature at which vapour pressure of a liquid is equal to external pressure.

A liquid having high vapour pressure boils at low temperature. \[ B.P. \propto \frac{1}{V.P.} \]

**Vapour pressure of liquid-liquid solutions**: -

**Raoult's Law**: For a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole fraction.

For a binary liquid-liquid solution

\[ p_1 = p_1^0 x_1 \]  
\[ p_2 = p_2^0 x_2 \]  

\[ p_1^0 \rightarrow \text{vapour pressure of pure liquid 1} \]

\[ p_2^0 \rightarrow \text{vapour pressure of pure liquid 2} \]

According to Dalton's law of partial pressures - : Total pressure over solution phase in the container will be the sum of the partial pressures of components of the solution.

\[ p_{total} = p_1 + p_2 = p_1^0 x_1 + p_2^0 x_2 \]

\[ p_{total} = (1-x_2) p_1 + p_2^0 x_2 = p_2^0 + (p_2^0 - p_1^0) x_2 \]

\[ y = mx + c \]

Linear graph between total V.P. and \( x_2 \).

For line II: \( p_{total} = p_2^0 \)

Initially \( x_1 = 0 \) \( \quad x_2 = 1 \)

\[ x_1 + x_2 = 1 \]
If \( y_1 \) and \( y_2 \) are the mole fractions of the liquid-1 and 2 respectively in the vapour phase then, using Dalton's law of partial pressures:

\[ p_1 = y_1 \cdot p_{\text{total}} \]

\[ p_2 = y_2 \cdot p_{\text{total}} \]

- At equilibrium, the vapour phase will be always rich in the component which is more volatile.

**Question:** The vapour pressure of pure liquids A and B are 450 mm and 700 mm of Hg respectively at 250 K. Find out the composition of the liquid mixture if total vapour pressure is 600 mm of Hg. Also, find the composition in vapour phase?

**Answer:**

\[ p_A = 450 \text{ mm of Hg} \quad p_B = 700 \text{ mm of Hg} \]

\[ p_T = 600 \text{ mm of Hg} \]

\[ x_A / x_B = y_A / y_B ? \]

\[ p_T = p_A^o + (p_A^o - p_B^o) x_A \quad \Rightarrow \quad 600 = 700 + (450 - 700) x_A \]

\[ \text{ mole fraction of A in liquid } x_A = \frac{100}{250} = 0.40 \]

\[ \text{ mole fraction of B in liquid phase } x_B = 1 - x_A = 1 - 0.40 = 0.60 \]

\[ p_A = x_A \cdot p_A^o = (0.40) (450) = 180 \text{ mm of Hg} \]

\[ p_B = x_B \cdot p_B^o = (0.60) (700) = 420 \text{ mm of Hg} \]

\[ p_A = y_A \cdot p_T \quad \Rightarrow \quad y_A = \text{ mole fraction of A in vapour phase} = \frac{p_A}{p_T} = \frac{180}{600} = 0.30 \]

\[ p_B = y_B \cdot p_T \quad \Rightarrow \quad y_B = \frac{p_B}{p_T} = \frac{420}{600} = 0.70 \]

**Note:** In above question: \( y_B > y_A \)

[So, vapour phase is more rich in component (B) \( \Rightarrow \) B is more volatile liquid than A.]

**Raoult's Law as a special case of Henry's Law**

According to Raoult's law, vapour pressure of volatile component \( p = x \cdot p^o \) in a given solution.

- In the solution of a gas in liquid, if one of the components is so volatile that it exists as a gas, it is directly proportional to mole fraction:

\[ p = k_m \cdot x \]

- Then its solubility

\[ \text{Henry's law} \]
When \( K_H \) becomes equal to \( p^o \), both are constant for a given liquid at constant temperature, then, Raoult's law become special case of Henry's law.

**Ideal and non-ideal solution:** Liquid-liquid solutions can be classified into ideal and non-ideal solutions on the basis of Raoult's law.

**Ideal Solution**

- The solutions which obey Raoult's law over entire range of concentration are known as ideal solution.
- \( p_a = x_a p^o \)
- \( p_b = x_b p^o \)

**Non-ideal Solution**

- When a solution does not obey Raoult's law over entire range of concentration, it is called non-ideal solution.
- \( p_a \neq x_a p^o \)
- \( p_b \neq x_b p^o \)

**Component A + Component B → Solution AB**

Forces of attraction between A-B are exactly same as A-A and B-B.

- \( f_{A-B} = f_{A-A} = f_{B-B} \)

**On mixing, there is no enthalpy and volume change**.
- \( \Delta H_{\text{mix}} = 0 \)
- \( \Delta V_{\text{mix}} = 0 \)

**Example:** n-Hexane and n-Heptane, Bromoethane and Chloroethane, Benzene and Toluene

**Two types of non-ideal solution:**

- Positive deviation from Raoult's law:- A-B interactions are weaker than A-A and B-B interactions. Due to this vapor pressure increases which results in positive deviation.
- **Example:** H2O and ethanol, H2O and CH3COOH, CH3 and CCL4.
\( \text{(P}_{\text{Total}} \text{)}_{\text{exp}} > (x_A p_A^0 + x_B p_B^0) \)

→ Liquid A + Liquid B → Solution A\(_B\)

\( \Delta H_{\text{mix}} = \Theta \text{ve} \)

\( \Delta V_{\text{mix}} = \Theta \text{ve} \)

**Example:**

\( H_2O + CH_3OH, \text{ Ethanol + Acetone} \)

\( H_2O + C_2H_5OH, \text{ C}_6H_6 + \text{ Acetone}, \text{ CH}_3 + \text{ CH}_4. \)

**ii) Negative Deviation from Raoult’s law:**

A-A interactions are stronger than A-B and B-B interactions. Due to this, vapour pressure decreases which results in negative deviation.

\( (P_{\text{Total}})_{\text{exp}} < x_A p_A^0 + x_B p_B^0 \)

\( \Delta H_{\text{mix}} = \Theta \text{ve} \) and \( \Delta V_{\text{mix}} = \Theta \text{ve} \)

**Example:**

\( H_2O + CH_3-\text{CH}_3 \)

\( H_2O + H-\text{CH}_3-\text{OH} \)

Phenol + Aniline

\( \text{CH}_3 + \text{ Acetone}. \) [CASE 2011]

\( \text{CASE 2010/11} \)

\( \text{Delhi 2010} \)

A solution of \( \text{CH}_3 \) \( \text{Cloroform} \) and \( \text{CH}_3-\text{CH}_3 \) \( \text{Acetone} \) shows \( \Theta \text{ve} \) deviation. Why?

In pure \( \text{CH}_3 \) and pure acetone, there is no hydrogen bonding, but after mixing, there is hydrogen bonding between hydrogen of \( \text{CH}_3 \) and oxygen of acetone. Due to strong interaction between solution molecules, vapour pressure decreases which results in \( \Theta \text{ve} \) deviation.

\( \alpha \)

Azeotropes: Binary mixtures having same composition in liquid and vapour phase and boil at a constant temperature. [ \( x_A = y_A \) and \( x_B = y_B \) ]

[CASE 2013]

[Delhi 2014/15]
Azeotropes can be separated into its components by fractional distillations.

There are two types of azeotropes.

1. Minimum boiling point azeotrope: The solution which show large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition. For example: \( \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \) [with 35% by volume of ethanol]"
For dilute solution \( n_2 \ll n_1 \)

\[
\frac{b^o - b}{b^o} = \frac{n_2}{n_1} = \frac{\left(\frac{M_2}{w_2}\right)}{\frac{M_1}{w_1}}
\]

Here \( w_1 \) and \( w_2 \) are the masses of solvent and solute respectively.

**Question:** A solution is prepared by dissolving 10 g of non-volatile solute in 200 g of water. It has a vapour pressure of 31.94 mm of Hg at 308 K. Calculate the molar mass of solute. \([\text{v.p. of pure water} = 32 \text{ mm of Hg}]\)

**Answer:**
\[
\begin{align*}
w_2 &= 10 \text{ g} \\
w_1 &= 200 \text{ g} \\
b^o &= 31.94 \text{ mm of Hg}
\end{align*}
\]
\[
M_2 = ? \\
M_1 &= 18 \text{ g} \\
b^o &= 32 \text{ mm of Hg}
\]

\[
\frac{b^o - b}{b^o} = \frac{n_2}{n_1} = \frac{(w_2/M_2)}{(w_1/M_1)} \quad \therefore \quad \frac{32 - 31.94}{32} = \frac{\left(\frac{10}{M_2}\right)}{\left(\frac{200}{10}\right)} \quad \text{Hence} \quad M_2 = 100 \text{ g/mol}
\]

**Elevation of boiling point:**

- As we know B.P. of a liquid is a temperature at which its v.p. becomes equal to the atmospheric pressure.

- The B.P. of a solution is always higher than the B.P. of pure solvent in which the solution is prepared. This is because v.p. of solution at a given temperature is found to be lower than v.p. of pure solvent at the same temperature.

- In a pure liquid, the entire surface is occupied by the molecules of liquid. If a non-volatile solute is added to pure liquid to give a solution, then surface has both solute and solvent molecules, so the fraction of surface covered by solvent molecules gets reduced, so the no. of solvent molecules escaping from surface is reduced. Thus the v.p. is also reduced. \([\text{Delhi 2014C]}\)
If $T_b^\circ$ is B.P. of pure solvent and $T_b$ is the B.P. of solution, then elevation in B.P. $\Delta T_b = T_b - T_b^\circ$

For dilute solutions $\Delta T_b \propto m$

$\Delta T_b = k_b \cdot m$

[Case 2012] 1

As unit of $m = \frac{\text{mol}}{\text{kg}}$, so, unit of $k_b = \text{K kg mol}^{-1}$.

If $W_2$ g of solute of molar mass $M_a$ is dissolved in $W_1$ g of solvent, then modality of solution $m = \frac{(W_2/M_a)}{(W_1/1000)} \text{ mol}$

Then, $\Delta T_b = k_b \cdot \frac{1000W_2}{M_a \cdot W_1}$

$M_2 = \frac{1000W_2 \cdot k_b}{\Delta T_b \cdot W_1}$

Questions:— 10 g of glucose (molar mass = 180 g mol$^{-1}$) is dissolved in 1 kg of water in a sauce pan. At what temperature will this solution boil?

(K$ b$ for water = 0.52 K kg mol$^{-1}$, B.P. of pure water = 373.15 K)

Answer: $W_1 = 1$ Kg = 1000 g $T_b^\circ = 373.15$

$W_2 = 10$ g $k_b = 0.52$ K kg mol$^{-1}$ $M_a = 180$ g mol$^{-1}$

$\Delta T_b = k_b \cdot m = k_b \cdot \frac{1000W_2}{M_a \cdot W_1} = 0.52 \times \frac{1000 \times 10}{180 \times 1000} = 0.052 K$

$\Delta T_b = T_b - T_b^\circ = T_b - 373.15 = 0.052 K$

$T_b = 373.15 + 0.052 = 373.202 K$

$T_b = 373.2 K$

[Case 2012]

[Delhi 2012/2010]

Question:— A solution of glycerol [C$ _3 $H$ _5 $O$ _3 $] in water was prepared by dissolving some glycerol in 500 g of water. This solution has a B.P. of 100.42°C, what mass of glycerol was dissolved to make this solution?

K$ b$ for water = 0.512 K kg mol$^{-1}$

[Case 2012] 3M

[Delhi 2012/2010]
Answer: \( M_2 = 92 \text{ g mol}^{-1} \quad W_1 = 500 \text{ g} \quad W_2 = ? \quad k_b = 0.512 \text{ K g mol}^{-1} \)

\[ \Delta T_b = T_b - T_b^o = 100.42 \text{ °C} - 100 \text{ °C} = 0.42 \text{ K} \]

\[ \Delta T_b = k_b \left( \frac{W_2}{M_2} \right) \times \left( \frac{1000}{W_1} \right) \Rightarrow 0.42 = 0.512 \left( \frac{W_2}{92} \right) \left( \frac{1000}{500} \right) \]

\[ W_2 = 37.73 \text{ g} = \text{mass of glucose dissolved} \]

**Depression of freezing point** - :

- The freezing point of a substance is the temperature at which v.p. of the substance in its liquid phase is equal to its v.p. in solid phase.
- When a non-volatile solute is added to a solvent, the freezing point of the solution is always lower than that of pure solvent, as v.p. of solvent decreases in presence of non-volatile solute. [Delhi 2013 c]

- This difference in freezing point is known as Depression in freezing point:
  \[ \Delta T_f = T_f^o - T_f \]

  Freezing point of pure solvent \quad Freezing point of solution.

- \[ \Delta T_f \propto m \]
  \[ \Delta T_f = k_f m \]

  \[ \Delta T_f = k_f \times \left( \frac{W_2 (M_2)}{W_1 1000} \right) \]

  \( k_f \rightarrow \text{Freezing Point Depression Constant} \)

  \( m \rightarrow \text{Molar Depression constant} \)

  \( c \rightarrow \text{Cryoscopic constant} \)

**Question:** Calculate the freezing point of a solution containing 60 g of glucose (molar mass = 180 g mol\(^{-1}\)) in 250 g of water. (\( k_f \) of water = 1.86 K g mol\(^{-1}\))

**Answer:**

\[ W_2 = 60 \text{ g} \quad M_2 = 180 \text{ g mol}^{-1} \quad W_1 = 250 \text{ g} \]

\[
\text{Molarity of solution} \Rightarrow m = \left( \frac{W_2}{M_2} \right) \times \frac{1000}{W_1} \quad \Rightarrow \quad \frac{60 \text{ g}}{180 \text{ g mol}^{-1}} \times \frac{1000}{250 \text{ g mol}^{-1}}
\]

\[ m = 1.33 \text{ mol l}^{-1} \]
\[ \Delta T_f = K_f \cdot m = 1.86 \times 1.33 = 2.47 \text{ K} \]

\[ T_f^\circ - T_f = 2.47 \text{ K} \quad \square \text{ Freezing point of pure water} = 273.15 \text{ K} = 0.0^\circ \text{C} \]

Freezing point of solution \( (T_f) \) = 273.15 - 2.47 = 270.68 K

**Question:** Calculate the mass of compound (molar mass = 256 g mol\(^{-1}\)) to be dissolved in 75 g of benzene to lower its freezing point by 0.48 K. \( (K_f = 5.12 \text{ K kg mol}^{-1}) \).

**Answer:**

\[ W_1 = 75 \text{ g} \quad \Delta T_f = 0.48 \text{ K} \quad M_a = 256 \text{ g mol}^{-1} \]

\[ K_f = 5.12 \text{ K kg mol}^{-1} \]

\[ \Rightarrow \Delta T_f = K_f \cdot m = \frac{K_f \cdot W_2 \cdot 1000}{W_1 \cdot M_a} \]

\[ 0.48 = \frac{5.12 \times W_2 \times 1000}{75 \times 256} \]

\[ W_2 = \text{mass of solute} = 1.0 \text{ g} \]

**Question:** A 101 solution (by mass) of sucrose in water has freezing point of 269.15 K. Calculate freezing point of 101 glucose in water. If freezing point of pure water is 273.15 K. \[ \text{[Given: molar mass of sucrose} = 342 \text{ g mol}^{-1} ; \text{molar mass of glucose} = 180 \text{ g mol}^{-1}] \]

**Answer:** 101 solution by mass means 10 g of sucrose dissolved in 90 g of water.

\[ W_2 = 10 \text{ g} \quad W_1 = 90 \text{ g} \quad M_a = 342 \text{ g mol}^{-1} \]

\[ \text{then molality} \ m = \frac{(W_2 \times M_a)}{(W_1 \times 1000)} = \frac{(10 \times 342)}{(90 \times 1000)} = 0.324 \text{ mol kg}^{-1} \]

\[ \Delta T_f = T_f^\circ - T_f = 273.15 - 269.15 = 4 \text{ K} \]

\[ \Rightarrow \Delta T_f = K_f \cdot m \quad \Rightarrow K_f = \frac{\Delta T_f}{m} = \frac{4}{0.324} \quad \square \text{Kf is constant (same) for solvent (water)} \]

For glucose solution:

\[ W_2 = 10 \text{ g} \quad W_1 = 90 \text{ g} \quad M_a = 180 \text{ g mol}^{-1} \]

\[ \Rightarrow \text{then molality} \ m = \frac{(10 \times 180)}{(90 \times 1000)} \]

\[ \Rightarrow \Delta T_f = K_f \cdot m \Rightarrow \left( \frac{4}{0.324} \right) \times 0.617 = 7.617 \text{ K} \]

Hence, freezing point of glucose solution = 273.15 - 7.617 = 265.53 K

\[ m = 0.617 \text{ mol kg}^{-1} \]
Osmosis and Osmotic Pressure: The process of flow of solvent molecules from a solution of lower concentration to a solution of higher concentration through a semipermeable membrane is known as Osmosis.

- The hydrostatic pressure which develops on account of osmosis is called Osmotic Pressure.

- The pressure which just stops the flow of solvent is called Osmotic Pressure of solution.

Osmotic Pressure & Molarity (\(\mathcal{N}\))

\[ \mathcal{N} = C \cdot RT = \frac{n_a}{V} \cdot RT \]

Here, \(V\) → volume of solution (in L), \(n_a\) → moles of solute (= \(\frac{W_2}{M_2}\))

\[ \mathcal{N} = \frac{(W_2/M_2)}{V} \cdot RT \]

\[ M_2 = \frac{W_2 \cdot RT}{\mathcal{N} \cdot V} \] → Osmotic pressure is used to determine molar masses of macromolecules like proteins, polymers.

**Question:** A solution prepared by dissolving 0.95 mg of a gene fragment in 35 ml of water has an osmotic pressure of 0.335 torr at 25°C. Assuming the gene fragment is non-electrolyte, determine its molar mass.

**Answer:**

\[ W_2 = 0.95 \text{ mg} = 0.95 \times 10^{-3} \text{ g} \]

\[ V = 35 \text{ ml} = \frac{35}{1000} \text{ L} \]

\[ T = 273 + 25 = 298 \text{ K} \]

\[ \mathcal{N} = 0.335 \text{ torr} = \frac{0.335}{760} \text{ atm} \]

\[ \mathcal{N} = C \cdot RT = \frac{(W_2/M_2)}{V} \cdot RT \] \[ \text{Then} \quad M_2 = \frac{W_2 \cdot RT}{\mathcal{N} \cdot V} = \frac{(0.95 \times 10^{-3})(0.082)(298)}{(0.335/760)(\frac{35}{1000})} \]

\[ M_2 = 1.417 \times 10^4 \text{ g mol}^{-1} \]

**Question:** At 300 K, 36 g of glucose (molar mass = 180 g mol\(^{-1}\)) present per litre in its solution has an osmotic pressure of 4.96 bar. If the osmotic pressure of another glucose solution is 1.52 bar at the same temperature, calculate the concentration of another solution.

[Similar question in 2018] [COSE 2011C]
The osmotic pressure associated with the fluid inside the blood cells is equivalent to that of 0.9% (m/v) NaCl solution, called normal saline solution and it is safe to inject intravenously.

If we place the cells in a solution containing more than 0.9% (m/v) NaCl, water will flow out of the cells and they would shrink. Such a solution is called hypertonic.

If the salt concentration is less than 0.9% (m/v), the solution is said to be hypotonic. In this case, water will flow into the cells if placed in this solution and they would swell.

Reverse Osmosis:

If a pressure larger than the osmotic pressure is applied to the solution side, then the pure solvent flows out of solution through semipermeable membrane. This phenomenon is called reverse osmosis [RO].

Reverse osmosis is used in desalination of sea water.
Important Q&A's

(i) The molecular masses of polymers are determined by osmotic pressure method and not by measuring other colligative properties. Give 2 reasons.

Answer:— The osmotic pressure method has the advantage over other colligative properties because:
1. Pressure measurement is around the room temperature and the molality of the solution is used instead of molality.
2. Its magnitude is large compared to other colligative properties even for very dilute solutions.

(ii) Outer hard shells of two eggs are removed. One of the egg is placed in pure water and the other egg is placed in saturated solution of NaCl. What will be observed and why?

Answer:— The egg placed in water will swell because the concentration of proteins is high inside the egg as compared to water. Therefore, water diffuses through semipermeable membrane of egg and egg swells.

→ The egg placed in NaCl solution will shrink due to osmosis, water will move out of the egg membrane, thereby shrinking the egg.

(iii) A 5% solution (by mass) of cane sugar (M_w = 342 g mol^{-1}) is isotonic with 0.877 M solution of substance X. Find the molecular weight of X.

Answer:—

\[ \text{W cane sugar} = 5\,\text{g} \]
\[ \text{M cane sugar} = 342\,\text{g mol}^{-1} \]
\[ M_x = ? \]

\[ \text{Isotonic means same osmotic pressure} \]
\[ \frac{\text{W cane sugar}}{\text{M cane sugar}} = \frac{\text{W_S}}{\text{M_S}} \]
\[ \Rightarrow \frac{5}{342} = \frac{0.877}{M_x} \]
\[ \Rightarrow (5 \times 342) = 0.877 \times M_x \]
\[ \Rightarrow M_x = 53.3\,\text{g mol}^{-1} \]

(iv) Out of 1M glucose and 2M glucose, which one has a higher boiling point and why?

2M glucose has higher B.P. because more the concentration, more is the elevation in boiling point.
Abnormal Molar Mass:— For the substances undergoing association or dissociation in solution, molecular mass determined from colligative properties is different [either lower or higher] from expected value.

This experimentally determined molar mass is known as abnormal molar mass.

Van't Hoff Factor:— It is the ratio of the experimental value of colligative property to the calculated value of the colligative property.

\[
\text{Van't Hoff Factor } [i] = \frac{\text{Normal Molar Mass}}{\text{Abnormal Molar Mass}}
\]

\[
= \frac{\text{Observed Experimental colligative property}}{\text{Calculated colligative property}}
\]

\[
= \frac{\text{Total no. of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociation}}
\]

For Example:—

1. \( \text{KCl} \rightarrow K^+ + Cl^- \quad i = 2 \)
2. \( \text{MgSO}_4 \rightarrow \text{Mg}^{2+} + \text{SO}_4^{2-} \quad i = 2 \)
3. \( \text{K}_2\text{SO}_4 \rightarrow 2K^+ + \text{SO}_4^{2-} \quad i = 3 \)
4. \( \text{CaCl}_2 \rightarrow \text{Ca}^{2+} + 2\text{Cl}^- \quad i = 2 \)
5. \( 2\text{C}_6\text{H}_5\text{COOH} \rightarrow (\text{C}_6\text{H}_5\text{COO})_2 \quad i = \frac{1}{2} \)

Dissociation:— Let the degree of dissociation is \( \alpha \) for \( A_xB_y \).

\( A_xB_y \rightarrow xA^{y+} + yB^{x-} \)

\( t = 0 : \quad c \quad 0 \quad 0 \)

\( t_{eq} : \quad c(1-\alpha) \quad xcd \quad ycd \)

\[ i = \frac{c [1 + (n-1)d]}{c} \]

Then; \( i = 1 + (n-1)d \)
Association:

\[ nA \rightarrow An \]
\[ \delta = 0 \quad C \quad 0 \]
\[ \delta_{eq} = C(1-\delta) \frac{C\beta}{n} \]

\[ i = C(1-\delta) + \frac{C\beta}{n} \]
\[ \Rightarrow \quad i = 1 + \left( \frac{1}{n} - 1 \right) \beta \]

**NOTE:** Modification in equations for Colligative properties.

1. **R.L.V.P. of solvent**
   \[ \frac{P^o - P}{P^o} = i \frac{n^2}{n} \]

2. **Elevation of B.P.**
   \[ \Delta T_b = i \Delta \theta \]

3. **Depression of freezing point**
   \[ \Delta T_f = i \Delta \theta \]

4. **Osmotic pressure of solution**
   \[ \pi = i \frac{n^2}{V} \]

**Question:** A 1 molar solution of trichloroacetic acid is heated to its B.P. The solution has B.P. 100.10°C. Determine Van't Hoff factor for COOH COOH. Kb (water) = 0.512 kg mol⁻¹

**Answer:**

\[ m = 1 \quad , \quad K_b = 0.512 \quad \text{K kg mol}^{-1} \quad , \quad T_b = 100.10^\circ \text{C} \]

\[ \Delta T_b = T_b - T_b^o = 100.10 - 100 = 0.10^\circ \text{C} \]

\[ T_b^o \quad (water) = 100^\circ \text{C} \]

\[ \Delta T_b = i \Delta \theta \]
\[ \Rightarrow \quad 0.10 = i \times 0.512 \times 1 \]
\[ \text{Then} \quad i = 0.19 \]

**Question:** Calculate the freezing point of an aqueous solution containing 10.5 g of magnesium bromide in 200 g of water, assuming complete dissociation of MgBr₂ [Molar mass of MgBr₂ = 104 g mol⁻¹, K_f (water) = 1.86 K kg mol⁻¹]

**Answer:**

\[ W_2 = 10.5 \quad g \quad , \quad W_1 = 200 \quad g \quad , \quad M_2 (MgBr₂) = 104 \quad g \quad \text{mol}^{-1} \quad , \quad K_f = 1.86 \quad \text{K kg mol}^{-1} \]

\[ \text{MgBr₂} \rightarrow \text{Mg}^{2+} + 2\text{Br}^- \quad : \quad i = 3 \]

\[ \Delta T_f = i \Delta \theta = i \Delta \theta \left[ \frac{W_2 \times 1000}{M_2 \times W_1} \right] = 3 \times 1.86 \left[ \frac{10.5 \times 1000}{104 \times 200} \right] = 1.592 \quad \text{K} \]

\[ \text{Freezing point of solution} = T_f^o - \Delta T_f = 273 \quad K - 1.592 \quad K = 271.408 \quad \text{K} \]

**Question:** Phenol associates in benzene to a certain extent to form a dimer. A solution containing 20 g of phenol in 1 kg of benzene has its freezing point lowered by 0.69 K. Calculate the fraction of phenol that has dimerised.

\[ K_f (benzene) = 5.1 \quad \text{K kg mol}^{-1} \]
Answer: \[ \Delta T_f = k_f \frac{M_2 \times 1000}{M_2 W_1} \]

\[ M_2 = \frac{5.1 \times 20 \times 1000}{(0.69) \times 1000} = 147.82 \text{ g mol}^{-1} \Rightarrow \text{Experimental molar mass} \]

Calculated molar mass of phenol \( [C_6H_5OH] = 6 \times 12 + 6 \times 1 + 16 = 94 \text{ g mol}^{-1} \)

\[ i = \frac{M_2 (\text{calculated})}{M_2 (\text{experimental})} = \frac{94}{147.82} = 0.635 \]

\[ \Rightarrow \beta = \frac{i - 1}{(\frac{1}{n} - 1)} = \frac{(0.635 - 1)}{\left(\frac{1}{2} - 1\right)} = 0.73 \Rightarrow \beta = 73 \% \]

Question: An aq. solution containing 12.48 g of \( Ba(OH)_2 \) in 1 kg of water at 373.0832 K. Calculate the degree of dissociation of \( Ba(OH)_2 \).

[Given, \( K_b (H_2O) = 0.52 \text{ K kg mol}^{-1} \), molar mass of \( Ba(OH)_2 = 208.34 \text{ g mol}^{-1} \) ]

Answer: \[ W_2 = 12.48 \text{ g} \quad W_1 = 1000 \text{ g} \quad T_b (\text{solution}) = 373.0832 \text{K} \]

\[ K_b (H_2O) = 0.52 \text{ K kg mol}^{-1} \quad M_2 = 208.34 \text{ g mol}^{-1} \]

\[ \Delta T_b = \frac{k_b W_2 \times 1000}{M_2 \times W_1} \]

\[ M_2 = \frac{k_b W_2 \times 1000}{\Delta T_b \times W_1} = \frac{(0.52) (12.48) \times 1000}{(0.0832) \times 1000} = 78 \text{ g mol}^{-1} = \text{Experimental molar mass} \]

\[ i = \frac{M_2 (\text{calculated})}{M_2 (\text{experimental})} = \frac{208.34}{78} = 2.67 \]

For \( Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^- \) : \( i = 1 + (n-1)d \)

\[ d = \frac{i - 1}{n - 1} = \frac{2.67 - 1}{3 - 1} = 0.835 \]

\[ d = 0.835 \% \]