**Dev Academy**
**Yamunanagar (Haryana)**

# Solutions

## Class 12

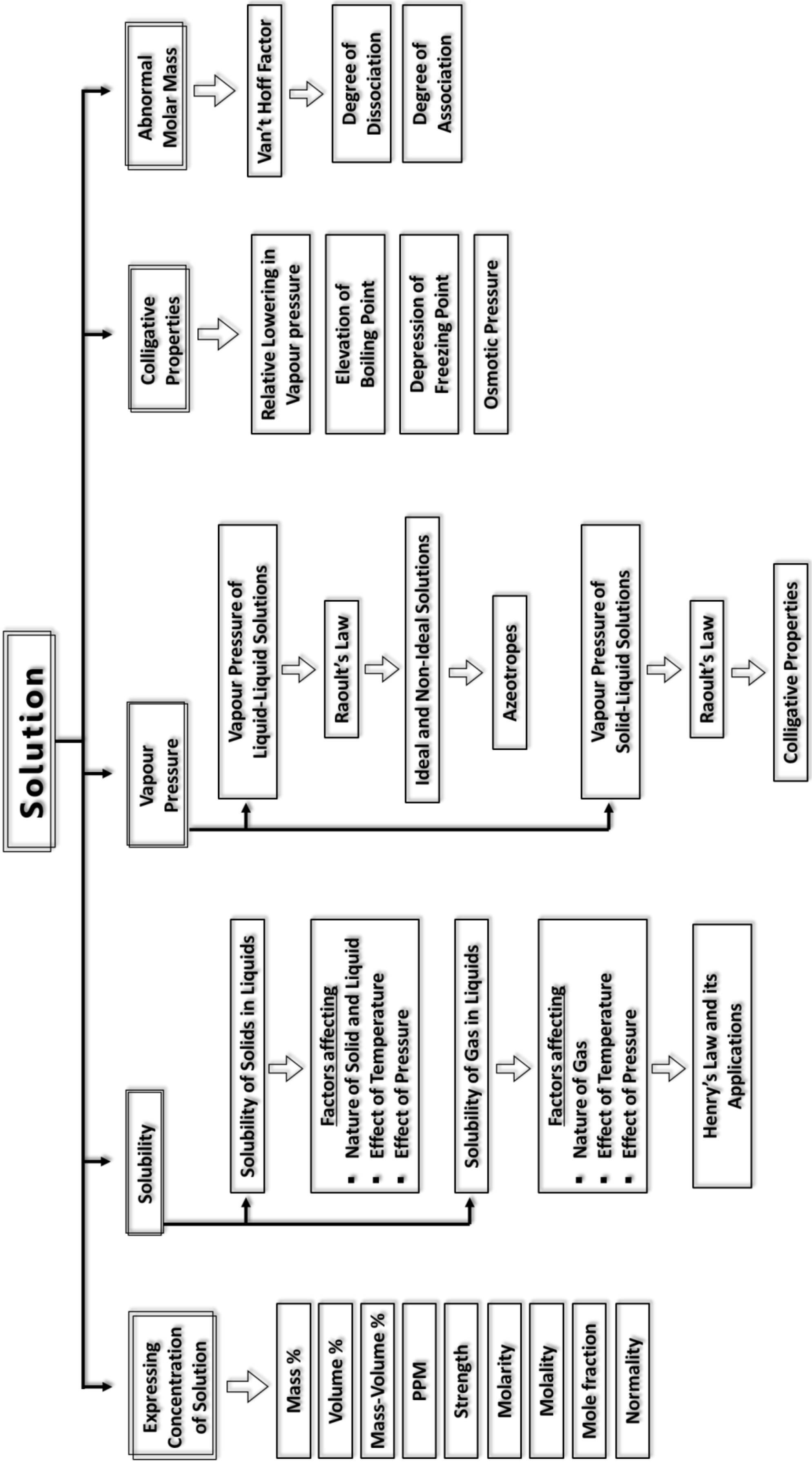
**Detailed Notes**

# CHEMISTRY

By
**Mr. Hardev Singh Antal**

**Website:** devacademy.click
**Email id:** support@devacademy.click

**Ph.: 7404044544**


Solution
Expressing Concentration of Solution
Mass %
Volume %
Mass-Volume %
PPM
Strength
Molarity
Molality
Mole fraction
Normality
Solubility
Solubility of Solids in Liquids
Factors affecting
▪ Nature of Solid and Liquid
▪ Effect of Temperature
▪ Effect of Pressure
Solubility of Gas in Liquids
Factors affecting
▪ Nature of Gas
▪ Effect of Temperature
▪ Effect of Pressure
Henry's Law and its Applications
Vapour Pressure
Vapour Pressure of Liquid-Liquid Solutions
Raoult's Law
Ideal and Non-Ideal Solutions
Azeotropes
Vapour Pressure of Solid-Liquid Solutions
Raoult's Law
Colligative Properties
Colligative Properties
Relative Lowering in Vapour pressure
Elevation of Boiling Point
Depression of Freezing Point
Osmotic Pressure
Abnormal Molar Mass
Van't Hoff Factor
Degree of Dissociation
Degree of Association

# INDEX

## Introduction

- A solution is a homogeneous mixture of two or more non-reacting substances where the composition is uniform throughout.
- Depending on the number of components, a solution can be:
  - **Binary solution** – Two components
  - **Ternary solution** – Three components
  - **Quaternary solution** – Four components
- The components of binary solution are generally referred to as solute and solvent.
  - **Solvent:** The component present in a larger quantity and determines the physical state of the solution.
  - **Solute:** The component present in a smaller quantity.
- Saturated and Unsaturated solutions:
  - **Saturated Solution:** A solution that holds the maximum amount of solute at a specific temperature and pressure. Any additional solute will not dissolve and remains undissolved.
  - **Unsaturated Solution:** A solution that contains less than the maximum amount of solute, meaning more solute can still dissolve until it reaches saturation.
- Aqueous and non-aqueous solution:
  - **Aqueous Solution:** A solution in which water is the solvent.
  - **Non-Aqueous Solution:** A solution where the solvent is a substance other than water. Examples of Non-Aqueous Solvents:
    - Organic solvents: Ethanol, acetone, benzene
    - Inorganic solvents: Liquid ammonia, carbon disulfide, liquid sulfur dioxide

## Types of Solution Based on Physical State

- **Solid Solution:**

| Type of Solid Solution | Solute | Solvent | Examples |
|---|---|---|---|
| **Solid in Solid** | Solid | Solid | - Alloys (Brass, German silver, Bronze) |
| **Liquid in Solid** | Liquid | Solid | - Hydrated salts<br>- Mercury amalgam with sodium |
| **Gas in Solid** | Gas | Solid | - Gases dissolved in minerals<br>- Gases adsorbed on metal surfaces (occlusion) |

  - **Brass**: Composed of copper (60-90%) and zinc (10-40%).
  - **German Silver**: Composed of copper (60%), zinc (20%), and nickel (20%).
  - **Bronze**: Composed of copper (80-90%) and tin (10-20%).

- **Liquid Solution:**

| Type of Liquid Solution | Solute | Solvent | Examples |
|---|---|---|---|
| **Solid in Liquid** | Solid | Liquid | - Salt dissolved in water<br>- Sugar dissolved in water |
| **Liquid in Liquid** | Liquid | Liquid | - Alcohol in water<br>- Formic acid in water |
| **Gas in Liquid** | Gas | Liquid | - Oxygen dissolved in water<br>- Carbonated beverages ($CO_2$ in water) |

- **Gaseous Solution:**

| Type of Gaseous Solution | Solute | Solvent | Examples |
|---|---|---|---|
| **Solid in Gas** | Solid | Gas | - Camphor in nitrogen gas<br>- Iodine vapours in air |
| **Liquid in Gas** | Liquid | Gas | - Humidity in air<br>- Chloroform in nitrogen gas |
| **Gas in Gas** | Gas | Gas | - Air (a mixture of gases)<br>- Oxygen and nitrogen mixture |

## Expressing Concentration of Solutions

The concentration of a solution is defined as the amount of solute present in a given quantity of solvent or solution. It is expressed in various ways, as discussed below:

- Mass Percentage (w/w)
- Volume Percentage (v/v)
- Mass by Volume Percentage (w/v)
- Parts per Million (ppm)
- Strength (g/L)
- Molarity (mol/L)
- Molality (mol/kg)
- Mole Fraction (mol/mol)
- Normality (gm.eq/L)

**Key Note:**

**Temperature-Dependent Quantities**
Volume-based concentrations (Volume %, Mass/Volume %, Strength, Molarity, Normality) change with temperature due to expansion or contraction of liquids.

**Temperature-Independent Quantities**
Mass and mole-based concentrations (Mass %, Mole Fraction, Molality) remain unchanged with temperature.

## 1. Mass Percentage (w/w)

- Represents the mass of solute in **100 gm** of solution.
- **Formula:**

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

Where: $W_{sol}$ = Mass of solution
$W_B$ = Mass of solute
$W_A$ = Mass of solvent

**Key Note:**
Commercial bleaching sol$^n$ is 3.62 mass% aq. sol$^n$ of sodium hypochlorite (NaOCl).

## 2. Volume Percentage (v/v)

- Represents the volume of solute in **100 mL** of solution.
- **Formula:**

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

Where:

$V_B$ = Volume of solute
$V_A$ = Volume of solvent
$V_{sol}$ = Volume of solution

**Key Note:**
35 % (v/v) aqueous solution of ethylene glycol, an antifreeze, is used in cars for cooling engine. At this concentration the antifreeze lowers the freezing point of water to 255.4 K (-17.6 ˚C)

## 3. Mass-Volume Percentage (w/v)

- Represents the mass of solute in **100 mL** of solution.
- **Formula:**

$$\text{Mass-Volume \% of solute} = \frac{\text{Mass of solute} \times 100}{\text{Total volume of solution}} = \frac{W_B \times 100}{V_{sol}} = \frac{W_B \times 100 \times D_{sol}}{W_{sol}}$$

Where:

$$D_{sol} = \text{Density of solution} = \frac{W_{sol}}{V_{sol}}$$

## 4. Parts per Million (ppm)

- Represents the mass or volume of solute per **one million ($10^6$)** parts of solution.
- **Formula:**
  - **For mass (w/w):** $\text{ppm of solute} = \frac{\text{Mass of solute} \times 10^6}{\text{Total Mass of solution}} = \frac{W_B \times 10^6}{W_{sol}}$
  - **For volume (v/v):** $\text{ppm of solute} = \frac{\text{Volume of solute} \times 10^6}{\text{Total Volume of solution}} = \frac{V_B \times 10^6}{V_{sol}}$
- **Note:**
  - 1 ppm of fluoride ions in water prevents tooth decay, while 1.5 ppm causes the tooth to become mottled and high concentrations of fluoride ions can be poisonous (for example: Sodium fluoride is used in rat poison.)
  - Chlorine levels up to 4 ppm are considered safe in drinking water.

### Numerical Based on mass%, volume%, mass by volume%, and ppm

**Problem 1.:**
A litre of sea water (about 1030 gm) contains $6 \times 10^{-3}$ gm of dissolved oxygen. Calculate the mass% and ppm of dissolved oxygen.
**Answer.:**

Given Values: $W_{sol}$ = 1030 gm , $W_{oxygen} = 6 \times 10^{-3}$ gm

$$\text{Calculate mass\% of oxygen} = \frac{W_{oxygen} \times 100}{W_{sol}} = \frac{6 \times 10^{-3} \times 100}{1030} = 5.8 \times 10^{-4}\ \%$$

Calculate ppm of oxygen = Mass% of $O_2 \times 10^4 = 5.8 \times 10^{-4} \times 10^4 =$ **5.8 ppm**

**Problem 2.:**
A litre of public supply water contains $3 \times 10^{-3}$ g of chlorine. Calculate the mass % and ppm of chlorine.
**Answer.:**

Given Values: $W_{chlorine} = 3 \times 10^{-3}$ gm , $V_{sol} = 1L = 1000$ ml ,

Assuming, $D_{sol} \approx D_{water} = 1$ gm/ml ,

$\therefore W_{sol} = D_{sol} \times V_{sol} = 1$ gm/ml × 1000 ml = 1000 gm

Calculate mass% of $Cl_2 = \frac{W_{chlorine} \times 100}{W_{sol}} = \frac{3 \times 10^{-3} \times 100}{1000} = 3 \times 10^{-4}$ %

Calculate ppm of $Cl_2$ = Mass% of $Cl_2 \times 10^4 = 3 \times 10^{-4} \times 10^4 =$ **3 ppm**

**Problem 3.:**
Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile ($CH_3CN$) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of $CH_3CN$.
**Answer.:**

Given Values: $W_{Aspirin} = 6.5$ gm , $W_{Acetonitrile} = 450$ gm ,

$\therefore W_{sol} = 6.5gm + 450gm = 456.5$ gm

Calculate mass% of Aspirin $= \frac{W_{Aspirin} \times 100}{W_{sol}} = \frac{6.5 \times 100}{456.5} =$ **1.42 %**

**Problem 4.:**
Calculate the percentage composition in terms of mass of a solution obtained by mixing 300 g of a 25 % and 400 g of a 40 % solution by mass.
**Answer.:**

Given Values: Weight of solute in solution-1 $= \frac{300 \times 25}{100} = 75$ gm

Weight of solute in solution-2 $= \frac{400 \times 40}{100} = 160$ gm

After mixing both solutions,
Total weight of solute = 75 + 160 = 235 gm
Total weight of solution = 300 + 400 = 700 gm

Calculate mass% of solute $= \frac{W_{solute} \times 100}{W_{solution}} = \frac{235 \times 100}{700} = 33.57\%$

Calculate mass% of solvent = 100 – mass% of solute = 100 – 33.57 = **66.43%**

**Problem 5.:**
If 16 g of oxalic acid is dissolved in 750 ml of solution, what is the mass % of oxalic acid in solution ? (Density of solution is 1.05 g cm$^{-3}$)
**Answer.:**

Given Values: $W_B = 16$ gm , $V_{sol} = 750$ ml , $D_{sol} = 1.05$ gm/cc

Calculate : mass% of oxalic acid $= \frac{W_B \times 100}{W_{sol}}$ [As we know, $W_{sol} = V_{sol} \times D_{sol}$]

$$\text{Mass\% of oxalic acid} = \frac{W_B \times 100}{V_{sol} \times D_{sol}} = \frac{16 \times 100}{750 \times 1.05} = \mathbf{2.03\%}$$

## 5. Strength (gm/L)

- Represents the mass of solute per **liter** of the solution.
- **Formula:**

$$\text{Strength } (\mathbf{S}) = \frac{\text{Mass of the solute in grams}}{\text{Volume of solution in litres}} = \frac{W_B}{V_{\text{sol in L}}} = \frac{W_B \times 1000}{V_{\text{sol in ml}}} = \frac{W_B \times 1000 \times D_{sol}}{W_{sol}}$$

$$\text{Strength } (\mathbf{S}) = \text{Mass \% of solute} \times 10 \times D_{sol}$$

## 6. Molarity (M) – (mol/L)

- Represents the number of moles of solute per **liter** volume of the solution.
- **Formula:**

$$\text{Molarity } (\mathbf{M}) = \frac{\text{Number of moles of solute}}{\text{Volume of the solution in Litres}} = \frac{n_B}{V_{\text{sol in L}}} = \frac{n_B \times 1000}{V_{\text{sol in mL}}}$$

$$\boxed{\text{Moles of solute } (n_B) = \frac{\text{Weight of solute}}{\text{Molecular mass of solute}} = \frac{W_B}{M_B}}$$

$$\text{Molarity } (\mathbf{M}) = \frac{W_B \times 1000}{M_B \times V_{\text{sol in mL}}} = \frac{\text{Strength}}{M_B} = \frac{\text{Mass\% of solute} \times 10 \times D_{sol}}{M_B}$$

## 7. Molality (m) – (mol/kg)

- Represents the number of moles of solute per **kilogram** of the solvent.
- **Formula:**

$$\text{Molality } (\mathbf{m}) = \frac{\text{Number of moles of solute}}{\text{Weight of the solvent in Kg}} = \frac{n_B}{W_{\text{A in Kg}}} = \frac{n_B \times 1000}{W_{\text{A in g}}} = \frac{W_B \times 1000}{M_B \times W_{\text{A in g}}}$$

$$= \frac{W_B \times 1000}{M_B \times (W_{sol} - W_B)} = \frac{W_B \times 1000}{M_B \times ((D_{sol} \times V_{sol}) - W_B)}$$

## 8. Mole fraction (χ : Chi) - (mol/mol)

- Represents the ratio of moles of component to the total moles in the solution.
- **Formula:**
  - **For solute 'B':** Mole fraction of B ($\chi_B$) $= \frac{\text{Moles of B}}{\text{Moles of solution}} = \frac{n_B}{n_{sol}} = \frac{n_B}{n_A + n_B}$
  - **For solvent 'A':** Mole fraction of A ($\chi_A$) $= \frac{\text{Moles of A}}{\text{Moles of solution}} = \frac{n_A}{n_{sol}} = \frac{n_A}{n_A + n_B}$
  - The sum of mole fraction of all components in solution is always equal to 1.

$$\chi_A + \chi_B = 1$$

  - So that: $\chi_A = 1 - \chi_B$ or $\chi_B = 1 - \chi_A$

## 9. Normality (N) – (gm.eq./L)

- Represents the number of **gram-equivalents** of the solute per **liter** of the solution.
- **Formula:**

$$\text{Normality } (\mathbf{N}) = \frac{\text{Gram equivalent weight of solute}}{\text{Volume of solution in Litre}} = \frac{\text{gm eq.wt}_B}{V_{sol} \text{ in L}} = \frac{\text{gm eq.wt}_B \times 1000}{V_{sol} \text{ in mL}}$$

$$\boxed{\text{Gram equivalent weight of solute} = \frac{\text{Weight of solute in gm}}{\text{Equivalent mass of solute}} = \frac{W_B}{\text{Eq.wt.}_B}}$$

$$\text{Normality } (\mathbf{N}) = \frac{W_B \times 1000}{\text{Eq.wt.}_B \times V_{\text{Sol in mL}}} \qquad \boxed{\text{Eq.wt. of B} = \frac{M_B}{\text{n\_factor}}}$$

$$\text{Normality } (\mathbf{N}) = \frac{W_B \times 1000 \times \text{n\_factor}}{M_B \times V_{\text{Sol in mL}}} = \text{Molarity} \times \text{n\_factor}$$

- **How to determine *n_factor* ?**
  - **For Acids:** Number of $H^+$ ions.
  - **For Base:** Number of $OH^{-1}$ ions.
  - **For Salts:** Total charge of cations or anions per molecule.
  - **For Redox agents:** Number of electrons gained/lost.

---

### Important Points to Remember

- **Dilution Formula:**
  - **Molarity:** $M_1V_1 = M_2V_2$
  - **Normality** $N_1V_1 = N_2V_2$
- **Mixture Formula:**
  - **Molarity** $M_{mixture} = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2}$ or $\frac{M_1 V_1 + M_2 V_2 \dots + M_n V_n}{V_1 + V_2 \dots + V_n}$
  - **Normality** $N_{mixture} = \frac{N_1 V_1 + N_2 V_2}{V_1 + V_2}$ or $\frac{N_1 V_1 + N_2 V_2 \dots + N_n V_n}{V_1 + V_2 \dots + V_n}$
- **Molarity Equation for reacting components:** $\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$
- **Relationship between Molarity and Molality:**
  - $\text{Molality} = \frac{\text{Molarity} \times 1000}{(\text{density} \times 1000) - (\text{Molarity} \times M_B)}$
  - $\text{Molarity} = \frac{\text{Molality} \times 1000 \times \text{density}}{1000 + (\text{Molality} \times M_B)}$

---

### Practice Problems

**Problem 1.:**
2.46 gm of NaOH is dissolved in water and the solution is made to 250 mL in the volumetric flask. Calculate the molarity of the solution.

**Answer:**

- Given Values: Solute = NaOH , $M_B = 40$ , $W_B = 2.46$ gm , $V_{sol} = 250$ mL

- Formula Used: Molarity $(\mathbf{M}) = \frac{W_B \times 1000}{M_B \times V_{\text{sol in mL}}}$
- Calculations: Molarity $(\mathbf{M}) = \frac{2.46 \times 1000}{40 \times 250} = \frac{2.46}{10} = \mathbf{0.246\ mol/L}$

**Problem 2.:**
Calculate the molality of a solution containing 20.7 gm of $K_2CO_3$ dissolved in 500 mL of the solution (assuming density of solution = 1.05 g/ml).
**Answer:**

- Given Values: Solute = $K_2CO_3$ , $M_B$ = 138 , $W_B$ = 20.7 gm , $V_{sol}$ = 500 mL, $D_{sol}$ = 1.05 gm/mL.
- Formula Used: Molality $(\mathbf{m}) = \frac{W_B \times 1000}{M_B \times W_{A\text{ in g}}} = \frac{W_B \times 1000}{M_B \times ((D_{sol} \times V_{sol}) - W_B)}$
- Calculations:

$$\text{Molality } (\mathbf{m}) = \frac{20.7 \times 1000}{138 \times ((1.05 \times 500) - 20.7)} = \frac{20.7 \times 1000}{138 \times 504.3} = \frac{20700}{69593.4} = \mathbf{0.297\ mol/Kg}$$

**Problem 3.:**
Battery acid is 4.27 M $H_2SO_4$ and has density of 1.25 g/ml. What is the molality of $H_2SO_4$ in solution?
**Answer:**

- Given Values: Solute = $H_2SO_4$ , $M_B$ = 98 , $D_{sol}$ = 1.25 gm/mL , Molarity = 4.27 mol/L
- Formula Used: Molality $= \frac{\text{Molarity} \times 1000}{(\text{density} \times 1000) - (\text{Molarity} \times M_B)}$
- Calculations: Molality $= \frac{4.27 \times 1000}{(1.25 \times 1000) - (4.27 \times 98)}$ = **5.135 mol/Kg**

## Exercises

**Q 1.** A litre of sea water (about 1030 gm) contains $6\times10^{-3}$ gm of dissolved oxygen. Calculate the mass % and ppm of dissolved oxygen.

**Q 2.** Calculate the percentage composition in terms of mass of a solution obtained by mixing 300 gm of 25% and 400 gm of 40% solution by mass.

**Q 3.** Calculate the molarity of a solution of $CaCl_2$ if on chemical analysis it is found that 500 mL of $CaCl_2$ solution contain $1.505 \times 10^{23}$ $Cl^-$ ions.

**Q 4.** 100 ml of a solution containing 5 g of NaOH are mixed with 200 ml of M/5 NaOH solution. Calculate the molarity of the resulting solution.

**Q 5.** The density of a 2.05 M acetic acid in water is 1.02 g/ml. Calculate the molality of the solution.

**Q 6.** Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in a solution containing 20% of $C_2H_6O_2$ by mass.

**Q 7.** 2.82 gm of glucose is dissolved in 30 gm of water. Calculate (a) molality (b) mole fraction of glucose and water.

**Q 8.** A solution is 25% water, 25% ethanol, and 50% acetic acid by mass. Calculate the mole fraction of each component.

**Q 9.** A solution of glucose in water is labelled as 10 % (w/w). The density of the solution is 1.20 g/ml. Calculate the (a) molality (b) molarity and (c) mole fraction of each component in solution.

**Q 10.** A sugar syrup of weight 214.2 gm contains 34.2 gm of sugar ($C_{12}H_{22}O_{11}$). Calculate: (a) Molal concentration (b) mole fraction of sugar in solution.

**Q 11.** A commercially available sample of sulphuric acid is 15% $H_2SO_4$ by weight (density = 1.10 g/mL). Calculate (a) molarity (b) normality (c) molality.

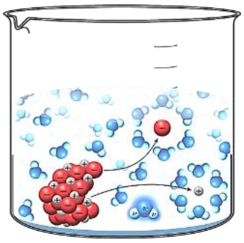
**Q 12.** Concentrated sulphuric acid has a density 1.9 gm/mL and is 99% $H_2SO_4$ by mass. Calculate the molarity of sulphuric acid.

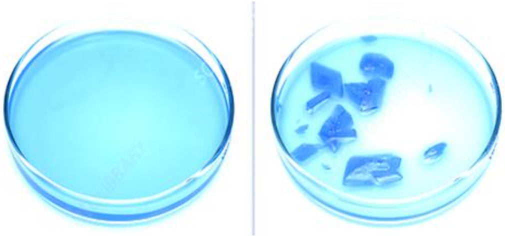
## Solubility of Solids in Liquids

Solubility and dissolution are closely related concepts in chemistry:

- **Dissolution** is the process in which a solute dissolve in a solvent to form a solution. It involves breaking intermolecular bonds in the solute and forming new bonds between solute and solvent molecules.
    - Example: When salt (solute) dissolves in water (solvent), the salt ions separate and bond with the polar water molecules.
- **Saturation & Crystallization**:
    - As dissolution proceeds, the concentration of solute in the solution increases.
    - At a certain point, no more solute dissolves at a given temperature - this is called a **saturated solution**.
    - Any additional solute beyond this point remains undissolved and forms **crystals** through **crystallization**.

$$\text{Solvent} + \text{Solute} \xrightleftharpoons[\text{Crystallisation}]{\text{Dissolution}} \text{Solution}$$





- 
    - Dissolution and crystallization occur at equal rates in a saturated solution, keeping the solute concentration constant under fixed conditions of **temperature and pressure**.
- **Solubility** is the maximum amount of solute (in grams) that can dissolve in 100g of solvent at a given temperature and pressure.

## Factors Affecting the Solubility of Solids in Liquids

### (a) Nature of Solute and Solvent

- **Polarity**: "Like dissolves like" – polar solutes dissolve in polar solvents, and nonpolar solutes dissolve in nonpolar solvents. Higher the value of dielectric constant indicates stronger solvent polarity (e.g., Water = 80, Benzene = 2.3).
  Example: Water (polar) dissolves sugar (polar) but not iodine (nonpolar).
- **Intermolecular Forces**: Stronger solute-solvent attractions increase solubility.
    - **Ionic Compounds** dissolve in $H_2O$ if hydration enthalpy is greater than lattice enthalpy.
      Example: **$MgSO_4$ (high solubility) vs. $BaSO_4$ (low solubility)** due to differences in hydration and lattice enthalpies.

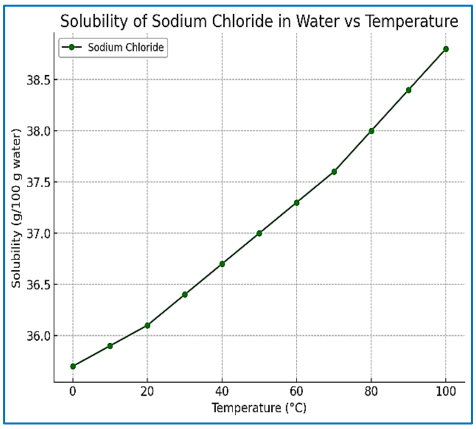
## (b) Effect of Temperature

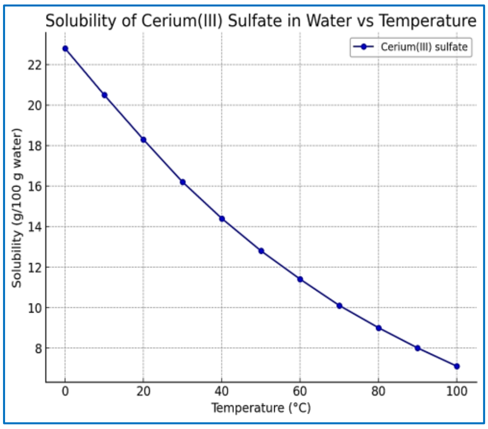
- **Solubility Increases with Temperature**:
  The solubility of most of substances (i.e., $NaNO_3$, $NH_4Cl$, KCl, $AgNO_3$, NaCl, KI, and sugar etc.) increases with rise in temperature.
  This is because the dissolution process for these substances is endothermic ($\Delta_{sol}\mathbf{H} > 0$).

  $$\text{Solvent + Solute + Heat} \rightleftharpoons \text{Solution} \qquad (\mathbf{\Delta H = +ve})$$

- **Solubility Decreases with Temperature**:
  The solubility of some substances (i.e., $Ce_2(SO_4)_3$, $Li_2SO_4$, etc.) decreases with rise in temperature.
  This is because the dissolution process for these substances is exothermic ($\Delta_{sol}\mathbf{H} < 0$).

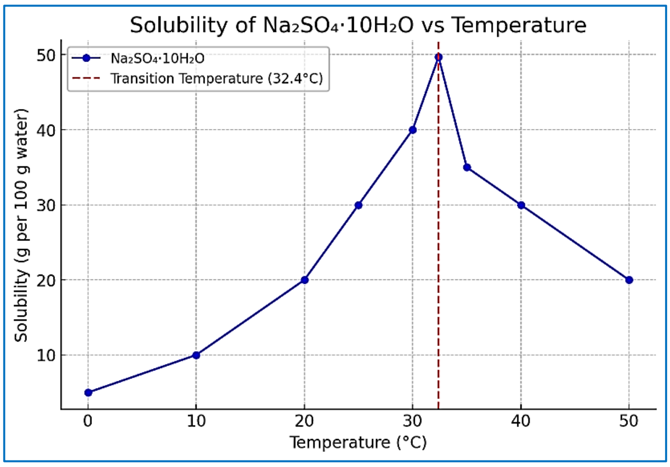
  $$\text{Solvent + Solute} \rightleftharpoons \text{Solution + Heat} \qquad (\mathbf{\Delta H = -ve})$$





- **Solubility Show Irregular Behavior with Temperature**:
  Some compounds (e.g., $Na_2SO_4{\cdot}10H_2O$ and $CaCl_2{\cdot}6H_2O$) show irregular trends due to polymorphic transformations.
  Example:
  The solubility of **$Na_2SO_4{\cdot}10H_2O$ (Glauber's salt)** increases up to 32.4 ˚C and then decreases as the temperature is further raised. The temperature at which solubility starts to decrease is called the transition temperature. This decrease occurs due to the change from one solid form to another. Below the transition temperature, only hydrated $Na_2SO_4{\cdot}10H_2O$ exists, while above this temperature, anhydrous $Na_2SO_4$ exists.

$$\underset{\text{Hydrated salt}}{\mathbf{Na_2SO_4{\cdot}10H_2O}} \underset{\text{Below 32.4 ˚C}}{\overset{\text{Above 32.4 ˚C}}{\rightleftarrows}} \underset{\text{Anhydrous salt}}{\mathbf{Na_2SO_4}}$$



### (c) Effect of Pressure

- Solids and liquids are incompressible, so pressure changes hardly affect solubility.
- However, there are exceptions to this general rule. Some systems may exhibit a slight increase in solubility with increasing pressure, especially if the dissolution process is associated with a decrease in volume. This phenomenon is more commonly observed in systems involving compressible solvents.

## Solubility of Gases in Liquids

- Almost all gases dissolve in water to different extents.
- Oxygen dissolves in water, supporting aquatic life. At STP (273K, 1 atm), oxygen's solubility is **8.26 mg/L**, but it changes with temperature and pressure.
- HCl gas is highly soluble in water and forms hydrochloric acid. It can dissolve in any proportion.
- The **solubility of a gas in a liquid** can be defined as the maximum amount of gas that can dissolve per liter of the solvent at standard temperature and pressure (STP), resulting in the formation of a homogeneous mixture.

## Factors Affecting the Solubility of Gases in Liquids

### (a) Nature of the Gas and the Solvent

- **Chemical Reactivity & Ionization:**
    - Gases that react chemically or form ions in water dissolve more readily.
    - Examples: $H_2$, $O_2$, and $N_2$ dissolve in very small amounts, whereas $SO_2$, $H_2S$, HCl, and $NH_3$ are highly soluble.
- **Critical Temperature & Liquefaction:**
    - Gases that are easily liquefied (having higher critical temperatures) tend to be more soluble.
    - When a gas's temperature approaches or exceeds its critical temperature, its kinetic energy increases, making it less compressible and harder to dissolve.
- **Polarity of Gas & Solvent:**
    - Polar gases dissolve more in polar solvents due to dipole-dipole interactions or hydrogen bonding.
    - Examples: $NH_3$ and $H_2S$ dissolve better in water, whereas $O_2$, $N_2$, and $CO_2$ are more soluble in ethyl alcohol than in water.
- **Size & Shape of Gas Molecules:**
    - Smaller gas molecules dissolve more easily as they can fit between solvent molecules.
    - Example: Oxygen ($O_2$) and Carbon Dioxide ($CO_2$) have relatively small molecular sizes and dissolve readily in liquids.

### (b) Effect of Temperature:

The solubility of gases generally decreases with an increase in temperature due to:

- **Thermodynamic Factor:**
    - Dissolving a gas in a liquid is an exothermic process (releases heat).
    - According to Le-Chatelier's Principle, increasing temperature shifts equilibrium backward, reducing solubility.
    - **Equation:** $\text{Gas} + \text{Liquid} \rightleftharpoons \text{Dissolved Gas}_{\text{(Solution)}}$ $(\Delta H < 0)$

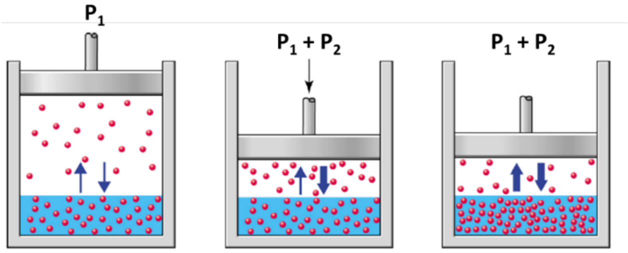
- **Kinetic Energy Effect:**
    - Higher temperatures increase the kinetic energy of gas molecules, making them move faster and escape from the liquid, reducing solubility.
- **Intermolecular Forces:**
    - Weaker intermolecular forces at higher temperatures make it easier for gas molecules to leave the liquid phase.

### Note

- Aquatic animals are more comfortable in cold water than in hot water because cold water holds more dissolved oxygen than warm water.

## (c) Effect of Pressure

- The solubility of gases increases with an increase in pressure.
- To understand this, consider a gas in dynamic equilibrium with a solution.
- When the pressure over the solution is increased, the number of gas molecules per unit volume above the solution also increases.
- As a result, more gas molecules dissolve in the solution until a new equilibrium is established, thereby increasing the solubility of the gas.



Initial Equilibrium Increased Pressure New Equilibrium

- **William Henry** gave quantitative relationship between the solubility of a gas in a solvent and the pressure of a gas on a solution, known as Henry's law.

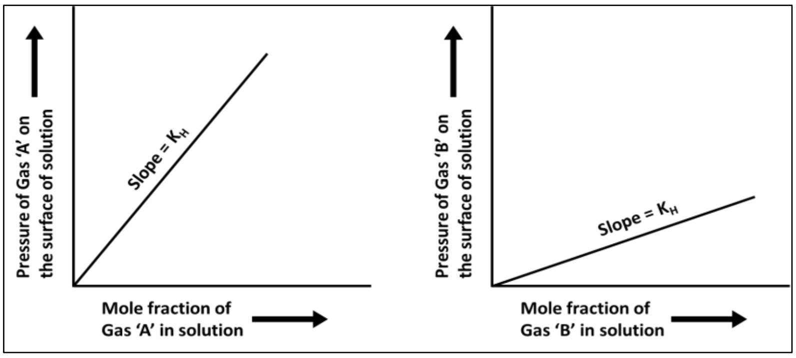
### According to Henry's Law

The solubility of a gas in a liquid at a particular temperature is directly proportional to the pressure of the gas over the solution at equilibrium.

**Alternatively,**

The partial pressure of a gas over a liquid solution is directly proportional to its mole fraction in the solution at equilibrium.

$$P_{gas} \propto \chi_{gas}$$
$$P_{gas} = \mathrm{K_H} \cdot \chi_{gas}$$



- **Mathematical Derivation:**
    - Starting with: $P_{gas} = K_H \cdot \chi_{gas}$
    - We know that: $\chi_{gas} = \frac{n_{gas}}{n_{solution}} = \frac{n_{gas}}{n_{solvent} + n_{gas}}$
    - Assuming that, $n_{solvent} \ggg n_{gas}$ ,we approximate: $n_{solvent} + n_{gas} \approx n_{solvent}$
    - So that, $\chi_{gas} \approx \frac{n_{gas}}{n_{solvent}}$
    - Now, converting moles into mass: $n_{gas} = \frac{W_{gas}}{M_{gas}}$ , $n_{solvent} = \frac{W_{solvent}}{M_{solvent}}$
    - Substitute these into the expression: $\chi_{gas} \approx \frac{\frac{W_{gas}}{M_{gas}}}{\frac{W_{solvent}}{M_{solvent}}} = \frac{W_{gas} \times M_{solvent}}{M_{gas} \times W_{solvent}}$
    - Now, plug into Henry's law Equation: $P_{gas} = K_H \cdot \frac{W_{gas} \times M_{solvent}}{M_{gas} \times W_{solvent}}$

- **Properties of Henry's Constant ($K_H$)**
    - **$K_H$ is specific to each gas:**
      The value of Henry's constant depends on the nature of the gas. Different gases have different $K_H$ values at the same temperature.
    - **Solubility is inversely related to $K_H$:**
      A higher value of $K_H$ indicates lower solubility of the gas in the liquid.
    - **Temperature dependence:**
      The value of $K_H$ increases with an increase in temperature, meaning gases become less soluble at higher temperatures.

- **Applications of Henry's law:**
    - **In the Production of Carbonated Beverages:**
        - $CO_2$ is dissolved in beverages like soda, beer etc. under high pressure.
        - According to Henry's Law, increasing pressure increases gas solubility.
        - When bottle is opened, pressure decreases, and $CO_2$ escapes, forming bubbles.

- **In Deep Sea Diving (Scuba Diving):**
  - Scuba divers breathe compressed air, which contains nitrogen.
  - At greater depths, the high pressure causes more nitrogen to dissolve in the blood (as per Henry's Law).
  - During ascent, the pressure drops rapidly, and nitrogen comes out of blood forming bubbles in the blood vessels.
  - These bubbles restrict blood flow and can even burst or blocks capillaries, which cause painful and dangerous condition called **"the bends"** or **decompression sickness.**
  - To prevent this, divers use air mixtures diluted with **helium** gas (less soluble and non-toxic). A typical mixture may include: 11.7% He, 56.2% $N_2$, 32.1% $O_2$.

- **At High Altitudes:**
  - Atmospheric pressure is lower at high altitudes.
  - This results in lower oxygen partial pressure, and thus, less $O_2$ dissolves in blood.
  - It leads to a condition called **anoxia**, where tissues receive insufficient oxygen. Climbers may feel dizzy, weak, or mentally disoriented due to lack of oxygen.
  - To **avoid anoxia** at high altitudes, climbers and travelers take pressurize supplemental oxygen cylinder.

- **Limitations of Henry's law:**
    - The law fails if the solution is non-ideal.
    - The law fails at very high pressures because gases no longer behave ideally under such conditions.
    - The temperature should not be too low or too high, as extreme temperatures can affect gas–liquid interactions, making the law less reliable.
    - The gas should not be highly soluble in the solvent.
    - The gas should not chemically react (e.g., HCl in water), dissociate (e.g., $NH_3$), or associate in the solvent.

---

### Numerical Based on Henry's Law

**Problem 1.:**
If $N_2$ gas is bubbled through water at 293 K, how many milli moles of $N_2$ gas would dissolve in 1 litre of water. Assume that $N_2$ exerts a partial pressure of 0.987 bar. The $K_H$ for $N_2$ at 293 K is 76.48 k bar.
**Answer:**

- Given values: $P_{N_2}$ = 0.987 bar , $K_H$ = 76.48 k bar = 76480 bar , $M_{H_2O}$ = 18
  $V_{solvent(H_2O)}$ = 1 Litre or 1000 ml ($D_{H_2O}$ = 1 gm/ml)
- Formula used: $n_{gas} = \frac{P_{gas} \times W_A}{K_H \times M_A} = \frac{P_{gas} \times (D_A \times V_A)}{K_H \times M_A}$
- Calculations:
  $$n_{gas} = \frac{0.987 \text{ bar} \times (1 \text{ gm/ml} \times 1000 \text{ ml})}{76480 \text{ bar} \times 18 \text{ gm/mol}} = 7.16 \times 10^{-4} \text{ mol}$$
- Now Milli moles of $N_2$ = $7.16 \times 10^{-4} \times 10^3 = 7.16 \times 10^{-1}$ m mol **or 0.716 m mol**

---

**Problem 2.:**
At what partial pressure, oxygen will have solubility of 0.05 g $L^{-1}$ in water at 293 K? Henry's constant ($K_H$) for $O_2$ in water at 293 K is 34.36 k bar. Assume the density of the solution to be same as that of the solvent.
**Answer:**

- Given values: $K_H$ = 34.36 k bar = $34.36 \times 10^3$ bar , $M_{H_2O}$ = 18 , $M_{O_2}$ = 32
  Solubility of gas = 0.05 g/L [i.e. 0.05 gm of $O_2$ in 1 L of solution]
  $W_{O_2}$ = 0.05 gm , $V_{sol}$ = 1 L or 1000 ml , $D_{sol} \approx D_{H_2O}$ = 1 gm/ml
- Formula used: $P_{gas} = K_H \times \frac{W_{gas} \times M_A}{M_{gas} \times (D_A \times V_A)}$
- Calculations: $P_{gas} = \frac{34.36 \times 10^3 \times 0.05 \times 18}{32 \times (1 \times 1000)}$ **= 0.966 bar**

---

**Problem 3.:**
Air contain $O_2$ and $N_2$ in the ratio of 1 : 4. Calculate the ratio of solubilities in term of mole fraction of $O_2$ and $N_2$ dissolved in water at atmospheric pressure and room temperature at which Henry's constant for $O_2$ and $N_2$ are $3.30 \times 10^7$ torr and $6.60 \times 10^7$ torr respectively.

**Answer:**

- At 1 bar pressure,
  Partial pressure of $O_2$ ($P_{O_2}$) $= \frac{1}{5} \times 1$ bar $= 0.2$ bar
  Partial pressure of $N_2$ ($P_{N_2}$) $= \frac{4}{5} \times 1$ bar $= 0.8$ bar
- Applying Henry's law $P_{O_2} = K_H(O_2) \times \chi_{O_2}$ or $\chi_{O_2} = \frac{P_{O_2}}{K_H\,(O_2)}$

  $P_{N_2} = K_H(N_2) \times \chi_{N_2}$ or $\chi_{N_2} = \frac{P_{N_2}}{K_H\,(N_2)}$
- $\frac{\chi_{O_2}}{\chi_{N_2}} = \frac{P_{O_2}}{K_H\,(O_2)} \times \frac{K_H\,(N_2)}{P_{N_2}} = \frac{P_{O_2}}{P_{N_2}} \times \frac{K_H\,(N_2)}{K_H\,(O_2)} = \frac{0.2\ bar}{0.8\ bar} \times \frac{6.60 \times 10^7\ torr}{3.30 \times 10^7\ torr} = \frac{1}{2}$

$$\boldsymbol{\chi_{O_2} : \chi_{N_2} = 1 : 2}$$

---

**Problem 4.:**
$H_2S$, a toxic gas with rotten egg like smell, is used for qualitative analysis. If the solubility of $H_2S$ in water at STP is 0.195 m, calculate Henry's law constant.

**Answer:**

- Solubility of $H_2S$ gas = 0.195 m = 0.195 mole in 1 kg of the solvent (water)

  1 kg of the solvent (water) = 1000 g $= \frac{1000\text{ g}}{18\text{ gm/mol}} =$ 55.55 moles
- Mole fraction of $H_2S$ gas in the solution ($\chi$) $= \frac{0.195}{0.195 + 55.55} = \frac{0.195}{55.745} = 0.0035$

  Pressure at STP = 0.987 bar
- Applying Henry's law, $P_{H_2S} = K_H \times \chi_{H_2S}$

  $K_H = \frac{P_{H_2S}}{\chi_{H_2S}} = \frac{0.987\ bar}{0.0035} =$ **282 bar**

---

**Problem 5.:**
Henry's law constant for $CO_2$ in water is $1.67 \times 10^8$ Pa at 298 K. Calculate the quantity of $CO_2$ in 500 mL of soda water when packed under 2.5 atm $CO_2$ pressure at 298 K.

**Answer:**

- $K_H = 1.67 \times 10^8$ Pa , $P_{CO_2} = 2.5$ atm $= 2.5 \times 101325$ Pa
- Applying Henry's law: $P_{CO_2} = K_H \times x_{CO_2}$

  $x_{CO_2} = \frac{P_{CO_2}}{K_H} = \frac{2.5 \times 101325\text{ Pa}}{1.67 \times 10^8\text{ Pa}} = 1.517 \times 10^{-3}$, i.e. $\frac{n_{CO_2}}{n_{H_2O} + n_{CO_2}} \approx \frac{n_{CO_2}}{n_{H_2O}} = 1.517 \times 10^{-3}$

  [ For 500 mL of soda water, water present ≈ 500 mL = 500 g $= \frac{500}{18} =$ 27.78 moles ]

  $\frac{n_{CO_2}}{27.78} = 1.517 \times 10^{-3}$ or $n_{CO_2} = \mathbf{42.14 \times 10^{-3}}$ **mole**

  Weight = moles × molecular wt. $= 42.14 \times 10^{-3} \times 44$ g = **1.854 g**

---

## Exercises

**Q 1.** If nitrogen gas is bubbled through water at 293 K, how many milliliters (at STP) of nitrogen would dissolve in a litter of water? Given that the partial pressure of nitrogen is equal to 742.5 torr and $K_H$ for nitrogen is $5.75 \times 10^7$ torr.

**Q 2.** The Henry's law constant for the solubility of nitrogen gas in water at 298 K is $1 \times 10^5$ atm. The mole fraction of nitrogen in air is 0.8. What is the number of moles of nitrogen from the air dissolved in 10 moles of water at 298 K and 5 atm pressure?

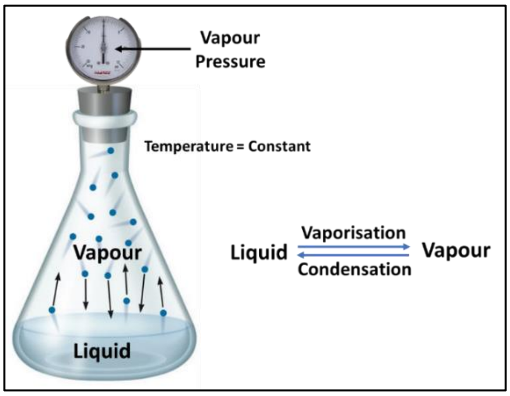
**Q 3.** The solubility of pure nitrogen gas at 25 ˚C and 1 atm is $6.8 \times 10^{-4}$ mole/L. What is the concentration of nitrogen dissolved in water under atmospheric conditions? The partial pressure of nitrogen gas in atmosphere is 0.78 atm.

**Q 4.** If solubility of any gas in the liquid at 1 bar pressure is 0.05 mole/L. What will be its solubility at 3 bar pressure, keeping the temperature constant?

**Q 5.** What is the ratio of the solubilities of nitrogen and oxygen in water at 373 K, given that $K_H (N_2) = 12.6 \times 10^4$ atm and $K_H (O_2) = 7.01 \times 10^4$ atm. Assume that pressure 'P' $(N_2) = 0.80$ atm and pressure 'P' $(O_2) = 0.20$ atm.

## Vapour Pressure of Liquids

- When a liquid is allowed to evaporate in a closed vessel, a portion of the liquid converts into vapour and fills the available space. The level of the liquid decreases due to this process, which is known as **vaporisation**.
- Some vapour molecules collide with the surface of the liquid and return to the liquid phase. This reverse process is known as **condensation**.
- Eventually, a stage is reached where the **rate of evaporation becomes equal to the rate of condensation**. At this point, a dynamic equilibrium is established between the liquid and vapour phases.
- The **pressure exerted by the vapour molecules** at this equilibrium, at a given temperature, is called the **vapour pressure** of the liquid.



- **Factors Affecting Vapour Pressure:**
    - **Nature of the Liquid**
        - Liquids with **weaker intermolecular forces** exhibit **higher vapour pressure**, as more molecules can escape into the vapour phase.
        - **Example:** Dimethyl ether and ethyl alcohol have higher vapour pressure than water due to weaker intermolecular forces compared to water.

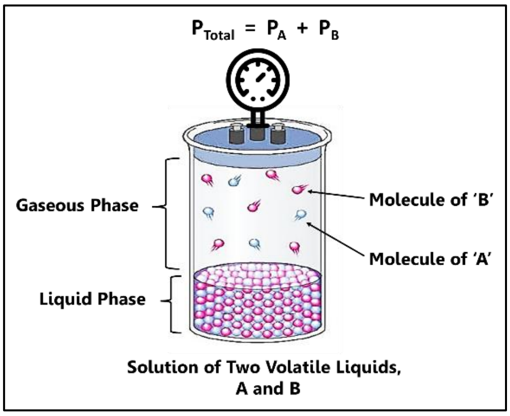
- **Temperature**
    - Vapour pressure **increases with temperature**.
    - This is because, at higher temperatures, **more molecules possess greater kinetic energy** and can more easily overcome intermolecular forces to escape into the vapour phase, resulting in higher vapour pressure.

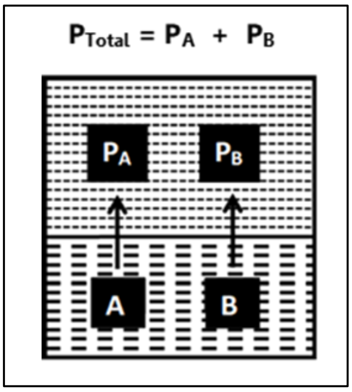
## Vapour Pressure of Liquid-Liquid Solutions

When a **binary solution** of two **volatile liquids**, A and B, is placed in a closed vessel, both components evaporate. Eventually, an equilibrium is established between liquid and vapour phases.

- **Dalton's Law of Partial Pressures:**
    - According to Dalton's law, the **total vapour pressure** ($P_{Total}$) in the container is the **sum of the partial vapour pressures** of both components:

$$P_{Total} = P_A + P_B$$



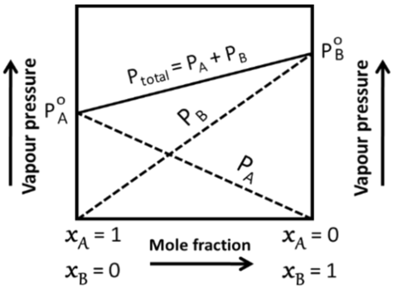


- **Raoult's Law:**
    - Raoult's law states that **the partial vapour pressure** of each volatile component is directly proportional to **its mole fraction in the solution**:

$$P_A \propto \chi_A \quad \text{and} \quad P_A = P_A^{\circ} \cdot \chi_A$$

$$P_B \propto \chi_B \quad \text{and} \quad P_B = P_B^{\circ} \cdot \chi_B$$

- Where:
    - **$P_A$ and $P_B$ :** Partial vapour pressures of components A and B in solution.
    - **$P_A^{\circ}$ and $P_B^{\circ}$ :** Vapour pressures of pure components in A and B.
    - **$\chi_A$ and $\chi_B$ :** Mole fractions of components A and B in liquid phase of the solution



- **Total Vapour Pressure of the Solution:**

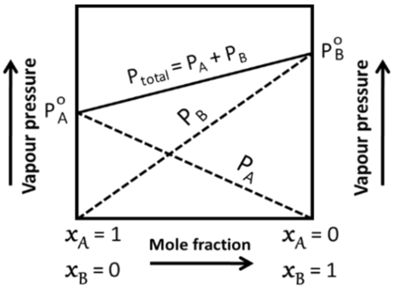
  Substituting the Raoult's law expression into Dalton's law:

  - $\mathbf{P_{Total}} = [P_A^\circ \cdot \chi_A] + [P_B^\circ \cdot \chi_B]$

    Since $\chi_A + \chi_B = 1$, we can also write: $\chi_A = 1 - \chi_B$
  - $\mathbf{P_{Total}} = [P_A^\circ (1 - \chi_B)] + [P_B^\circ \cdot \chi_B]$

    $= P_A^\circ - P_A^\circ \cdot \chi_B + P_B^\circ \cdot \chi_B$

    $= \mathbf{P_A^\circ + (P_B^\circ - P_A^\circ)\chi_B}$



This equation shows that the vapour pressure varies linearly with the mole fraction of component B (more volatile component).

- **Vapour Phase Composition:**

  The composition of the vapour phase at equilibrium can be calculated using partial pressures:

  - Mole fraction of component 'A' in vapour phase:

$$\mathbf{Y_A} = \frac{P_A}{P_A + P_B} = \frac{P_A}{P_{Total}}$$

  - Mole fraction of component 'B' in vapour phase:

$$\mathbf{Y_B} = \frac{P_B}{P_A + P_B} = \frac{P_B}{P_{Total}}$$

- **Konowaloff's Rule:**

  At a fixed temperature, the more volatile component (with higher vapour pressure**)** will have a higher mole fraction in the vapour phase than in the liquid phase.

- **Raoult's Law as a Special Case of Henry's Law:**

  If we compare the equations for Raoult's law and Henry's law**:**

  - **Henry's Law:** $P_{gas} = K_H \cdot \chi_{gas}$

    (Where '$P_{gas}$' is the partial pressure of the gas, '$K_H$' is Henry's law constant, and $\chi_{gas}$ is the mole fraction of the gas in solution)
  - **Raoult's Law**: $\mathbf{P_A} = \mathbf{P_A^\circ \cdot \chi_A}$

    (Where $P_A$ is the partial pressure of the volatile component 'A', $P_A^\circ$ is its vapour pressure in pure state, and $\chi_A$ is its mole fraction in the solution)

  It can be seen that the partial pressure of a component is directly proportional to its mole fraction in the solution in both laws. The only difference lies in the proportionality constant:

    - In Henry's law, it is $K_H$ (experimentally determined)
    - In Raoult's law, it is $P_A^\circ$ (vapour pressure of the pure component)

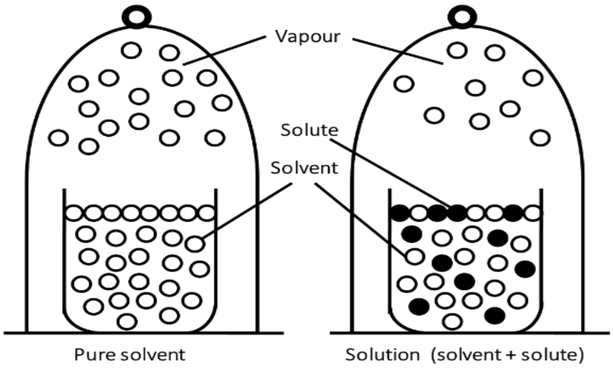
  Thus, Raoult's law can be considered a special case of Henry's law where the solute is a volatile liquid instead of a gas.
  Moreover, it is observed that: If the solute obeys Henry's law, the solvent obeys Raoult's law.

## Vapour Pressure of Solid-Liquid Solutions

- When the solute is **non-volatile**, only the solvent molecules are present in the vapour phase. Therefore, the vapour pressure of the solution is due to the **solvent only**.
- However, it is observed that the vapour pressure of a solution is **less than that of the pure solvent**.

### Explanation:

- Evaporation is a surface phenomenon, and the vapour pressure depends on the ability of solvent molecules to escape from the surface into the vapour phase.
- In a solution:
  - Some of the surface area is occupied by non-volatile solute particles.
  - This reduces the number of solvent molecules available at surface to escape into vapour phase.
  - As a result, fewer solvent molecules escape, and the vapour pressure decreases.
  - Therefore, the lowering of vapour pressure depends on the amount (concentration) of non-volatile solute present. Higher the solute concentration → Lower the vapour pressure

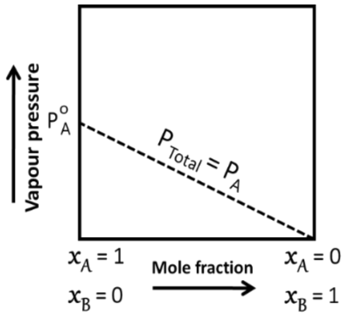


- **Mathematical Representation:**
  - Since only the solvent contributes to the total vapour pressure of solution: $\mathbf{P_{Total} = P_A}$
  - According to Raoult's law: $\mathbf{P_A = P_A^\circ \cdot \chi_A}$
    - Where:
      - $P_A$ : Partial vapour pressure of solvent in solution
      - $P_A^\circ$ : Vapour pressure of pure solvent
      - $\chi_A$ : Mole fraction of solvent in the solution
  - Since, $\chi_A = 1 - \chi_B$ , we get: $\mathbf{P_A = P_A^\circ (1 - \chi_B)}$
  - Now simplifying:

$$\mathbf{P_A = P_A^\circ - P_A^\circ \chi_B}$$

$$\mathbf{P_A^\circ \chi_B = P_A^\circ - P_A = \Delta P_A}$$

$$\chi_B = \frac{\mathbf{P_A^\circ - P_A}}{\mathbf{P_A^\circ}} = \frac{\mathbf{\Delta P_A}}{\mathbf{P_A^\circ}}$$



  - In this expression, [ $\mathbf{P_A^\circ - P_A = \Delta P_A}$ ] , represents the lowering of vapour pressure.
  - While, $\chi_B = \frac{\mathbf{P_A^\circ - P_A}}{\mathbf{P_A^\circ}}$ , represents the relative lowering of vapour pressure.

- **Hence, the expression can be stated as follows:**
  The relative lowering of vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution at a given temperature.

### Numerical Based on Vapour Pressure

**Problem 1.:**
The vapour pressure of ethyl alcohol at 298 K is 40 mmHg. Its mole fraction in a solution with methyl alcohol is 0.80. What is its vapour pressure in solution if the mixture obeys Raoult's law?
**Answer:**

According to Raoult's law $P_A = P_A^\circ . \chi_A$
Vapour pressure of pure ethyl alcohol ($P_A^\circ$) = 40 mmHg
Mole fraction of ethyl alcohol ($\chi_A$) = 0.80
Partial vapour pressure of ethyl alcohol ($P_A$) = 40 × 0.80 = **32 mmHg**

**Problem 2.:**
The vapour pressure of chloroform ($CHCl_3$) and dichloromethane ($CH_2Cl_2$) at 298 K are 200 mmHg and 415 mmHg respectively.

(i) Calculate the vapour pressure of the solution prepared by mixing 25.5 g of $CHCl_3$ and 40 g of $CH_2Cl_2$ at 298 K
(ii) Mole fraction of each component in vapour phase.

**Answer:**

**i) Vapour pressure of the solution :** $P_{Total} = P_A + P_B$

- According to Raoult's law; $P_A (CH_2Cl_2) = P_A^\circ . \chi_A$ and $P_B (CHCl_3) = P_B^\circ . \chi_B$
- Calculate the mole fraction of chloroform and dichloromethane:

$M_{CH_2Cl_2}$ = 85 g/mol  $W_{CH_2Cl_2}$ = 40 g  $n_{CH_2Cl_2} = \frac{W_{CH_2Cl_2}}{M_{CH_2Cl_2}} = \frac{40\text{ g}}{85\text{ g/mol}} = 0.47\text{ mol}$

$M_{CHCl_3}$ = 119.5 g/mol  $W_{CHCl_3}$ = 25.5 g  $n_{CHCl_3} = \frac{W_{CHCl_3}}{M_{CHCl_3}} = \frac{25.5\text{ g}}{119.5\text{ g/mol}} = 0.213\text{ mol}$

Total number of moles in solution = 0.47 + 0.213 = 0.683 mol

$$\chi_{CH_2Cl_2} = \frac{n_{CH_2Cl_2}}{n_{solution}} = \frac{0.47\text{ mol}}{0.683\text{ mol}} = \mathbf{0.688}$$

$$\chi_{CHCl_3} = 1 - \chi_{CH_2Cl_2} = 1 - 0.688 = \mathbf{0.312}$$

- Now, the total vapour pressure of the solution: $P_{Total} = P_A + P_B$

$P_A (CH_2Cl_2) = P_A^\circ . \chi_A$ = 415 × 0.688 = 285.5 mmHg
$P_B (CHCl_3) = P_B^\circ . \chi_B$ = 200 × 0.312 = 62.4 mmHg
$P_{Total} = P_A + P_B$ = 285.5 + 62.5 = 347.9 mmHg

**ii) Mole fraction in vapour phase**

$$Y_A (CH_2Cl_2) = \frac{P_A}{P_{Total}} = \frac{285.5}{347.9} = 0.82 \quad , \quad Y_B (CHCl_3) = \frac{P_B}{P_{Total}} = \frac{62.4}{347.9} = 0.18$$

## Exercises

**Q 1.** The vapour pressure of a pure liquid A is 40 mmHg at 310 K. The vapour pressure of this liquid in solution with liquid B is .32 mmHg Calculate the mole fraction of A in the solution if the mixture obeys Raoult's law.

**Q 2.** The vapour pressure of benzene and toluene at 298 K are 75 mmHg and 22 mmHg respectively. 23.4 g of benzene and 64.4 g of toluene are mixed. If the two forms an ideal solution, calculate the mole fraction of benzene in the vapour phase assuming that vapours are in equilibrium with the liquid mixture at this temperature.

**Q 3.** The vapour pressure of ethyl acetate and ethyl propionate are 72.8 and 27.7 mmHg respectively. A solution is prepared by mixing 25 g of ethyl acetate and 50 g of ethyl propionate. Assuming the solution to be ideal, Calculate the vapour pressure of the solution.

**Q 4.** Benzene and toluene form nearly ideal solution. At certain temperature, the vapour pressure of the pure benzene is 150 mmHg and of pure toluene is 50 mmHg. For this temperature, calculate the vapour pressure of solution containing equal weights of two substances. Also calculate their composition in the vapour phase.

**Q 5.** At 298 K, the vapour pressure of pure benzene is 0.256 bar and vapour pressure of pure toluene is 0.925 bar. If the mole fraction of benzene in solution is 0.40, find the total vapour pressure of solution. Also find the mole fraction of toluene in vapour phase.

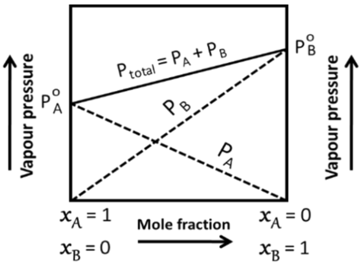
**Q 6.** The vapour pressure of pure liquids A and B are 450 and 700 mmHg respectively, at 350 K. Find out the composition of the mixture if total vapour pressure is 600 mmHg. Also find the composition of the vapour phase.

## Ideal and Non-ideal Solutions

### Ideal Solution

- An **ideal solution** is a solution that **obeys Raoult's law** *at all temperatures and concentrations* of its components.
- **Characteristics of Ideal Solutions:**
  - **Obedience to Raoult's Law:**
    - The partial vapour pressure of each component in the solution is directly proportional to its mole fraction.
    - Mathematically:

$$P_A \propto \chi_A \quad \text{and} \quad \mathbf{P_A = P^{\circ}_A \cdot \chi_A}$$
$$P_B \propto \chi_B \quad \text{and} \quad \mathbf{P_B = P^{\circ}_B \cdot \chi_B}$$



  - **Similar Intermolecular Forces:**
    - The intermolecular attractions between unlike molecules (A–B) (solvent-solute) are nearly equal to those between like molecules (A–A or B–B) (solvent-solvent or solute-solute)

  - **No Enthalpy Change on Mixing:** **[ $\Delta H_{mixing} = 0$ ]**
    - The heat evolved or absorbed during mixing is zero.
  - **No Volume Change on Mixing:** **[ $\Delta V_{mixing} = 0$ ]**
    - The total volume of the solution is equal to the sum of the individual volumes of the components.
  - **Similar Molecular Size and Nature:**
    - Ideal solutions are typically formed when the constituent components are chemically and structurally similar in size and polarity.

- **Examples of Ideal Solutions**
  - **Benzene + Toluene** -
    Both are non-polar aromatic hydrocarbons with almost similar structures.
  - **n-Hexane + n-Heptane** -
    Straight-chain alkanes with nearly identical molecular sizes.
  - **Ethyl chloride + Ethyl bromide**
    Halogen derivatives of ethane with comparable polarity.
  - **Chlorobenzene + Bromobenzene** -
    Halogenated benzenes with very similar physical and chemical properties.

## Non-Ideal Solution

- Non-ideal solutions are those that **do not obey Raoult's law** under all conditions of temperature and concentration.

- **Characteristics of non-ideal solutions:**
  - **Do not obey Raoult's law:**
    The partial vapour pressures of the components deviate from Raoult's law:

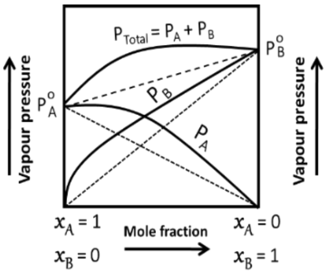
$$P_A \neq P^{\circ}_{A} \cdot \chi_A$$
$$P_B \neq P^{\circ}_{B} \cdot \chi_B$$

  - **Dissimilar Molecular Properties:**
    - They are formed by mixing two components that differ in molecular size, polarity, or intermolecular forces.
    - The intermolecular attractions between unlike molecules (A–B) are significantly different from those between like molecules (A–A or B–B).
  - **Enthalpy Change on Mixing:** **[ $\Delta H_{mixing} \neq 0$ ]**
    - Heat is either absorbed or evolved during mixing.
  - **Volume Change on Mixing:** **[ $\Delta H_{mixing} \neq 0$ ]**
    - Volume of the solution changes after mixing.

- **Types of Non-ideal Solutions:**
  - Non-ideal solution showing **positive deviations** from Raoult's law.
  - Non-ideal solution showing **negative deviations** from Raoult's law.

## Non-ideal solutions showing positive deviations from Raoult's law

- A non-ideal solution showing positive deviation from Raoult's law is one where the **partial vapour pressure of each component is higher** than expected.
- This happens because the intermolecular forces between unlike molecules (A–B) are **weaker** than those between like molecules (A–A or B–B).



- **Characteristics:**
  - **Excess Vapour Pressure:**
    - The partial vapour pressure of each component is **greater than predicted** by Raoult's law.

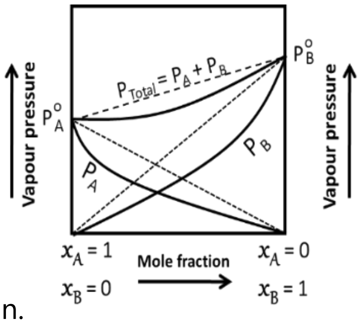
$$P_A > P^{\circ}_{A} \cdot \chi_A$$
$$P_B > P^{\circ}_{B} \cdot \chi_B$$

    - This leads to a higher total vapour pressure for the solution.
  - **Weaker intermolecular force:**
    - Intermolecular attractions between unlike molecules (A–B) are **weaker** than those between like molecules (A–A or B–B).
    - This allows molecules to escape more easily into the vapour phase
  - **Positive Enthalpy Change on Mixing:** **[ $\Delta H_{mixing} > 0$ ]**
    - Heat is absorbed during mixing
  - **Positive Volume Change on Mixing:** **[ $\Delta V_{mixing} > 0$ ]**
    - Volume increases when components are mixed due to looser packing of dissimilar molecules.
  - **Lower boiling point:**
    - These solutions generally have lower boiling points than either of the pure components
    - Some form **minimum boiling azeotropes**.

- **Examples:**
  - **Acetone + Carbon Disulphide** -
    Polar acetone and non-polar carbon disulphide have weak A–B interactions due to polarity difference.
  - **Acetone + Benzene**
    Weak interactions between polar acetone and non-polar benzene lead to increased vapour pressure.
  - **Acetone + Ethanol (Ethyl Alcohol)** -
    Hydrogen bonding in pure ethanol is disrupted by acetone, weakening intermolecular forces.
  - **Ethanol + Water**
    Strong hydrogen bonding in pure water and ethanol is weakened upon mixing, increasing vapour escape.
  - **Methanol + Water**
    Similar to ethanol + water; hydrogen bonding weakens in the mixture causing positive deviation.

## Non-ideal solutions showing negative deviations from Raoult's law

- A non-ideal solution showing negative deviation from Raoult's law is one where the **partial vapour pressure of each component is lower** than expected.
- This happens because the intermolecular forces between unlike molecules (A–B) are **stronger** than those between like molecules (A–A or B–B).



- **Characteristics:**
  - **Lower Vapour Pressure:**
    - The partial vapour pressure of each component is **lower than predicted** by Raoult's law.

      $$P_A < P^\circ_A \cdot \chi_A$$

      $$P_B < P^\circ_B \cdot \chi_B$$

    - This leads to a lesser total vapour pressure for the solution.
  - **Stronger intermolecular force:**
    - Intermolecular attractions between unlike molecules (A–B) are **stronger** than those between like molecules (A–A or B–B).
    - This stronger interaction reduces the tendency of molecules to escape into the vapour phase.
  - **Negative Enthalpy Change on Mixing:** **[ $\Delta H_{mixing} < 0$ ]**
    - Heat is released when components are mixed
  - **Negative Volume Change on Mixing:** **[ $\Delta V_{mixing} < 0$ ]**
    - Total volume contracts upon mixing due to strong interaction between A-B.
  - **Higher boiling point:**
    - Due to lower vapour pressure, boiling occurs at a higher temperature.
    - Some form **maximum boiling azeotropes**

---

- **Examples:**
  - **Chloroform + Acetone** -
    Strong hydrogen bonding between chloroform and acetone molecules lowers vapour pressure
  - **Chloroform + Benzene**
    Strong dipole-induced dipole interactions cause stronger A–B forces
  - **Chloroform + Diethyl Ether**
    Intermolecular hydrogen bonding results in lower-than-expected vapour pressure
  - **Phenol + Aniline** -
    Strong hydrogen bonding between the –OH group of phenol and the $-NH_2$ group of aniline.
  - **Acetone + Aniline**
    Hydrogen bonding between polar acetone and aniline molecules strengthens A–B interactions.
  - **Hydrochloric Acid (HCl) + Water**
    Ion-dipole interactions between $H^+/Cl^-$ ions and water are very strong, reducing vapour pressure significantly.

---

# Solution

## Ideal Solutions

- Obeys Raoult's Law.
  $P_A = P_A^{\circ} \cdot \chi_A$
- Similar Molecular properties like size, polarity, or intermolecular forces
- $\Delta H_{mixing} = 0$
- $\Delta V_{mixing} = 0$

## Non-Ideal Solutions

- Do not obey Raoult's Law.
  $P_A \neq P_A^{\circ} \cdot \chi_A$
- Dissimilar Molecular properties like size, polarity, or intermolecular forces
- $\Delta H_{mixing} \neq 0$
- $\Delta V_{mixing} \neq 0$

### Showing Positive Deviation from Raoult's Law

- Partial vapour pressure is greater than expected.
  $P_A > P_A^{\circ} \cdot \chi_A$
- The intermolecular attractions between unlike molecules (A–B) are weaker than those between like molecules (A–A or B–B).
- Heat is absorbed on mixing
  $\Delta H_{mixing} > 0$
- Volume increases on mixing.
  $\Delta V_{mixing} > 0$
- These solutions tends to form minimum boiling Azeotropes

### Showing Negative Deviation from Raoult's Law

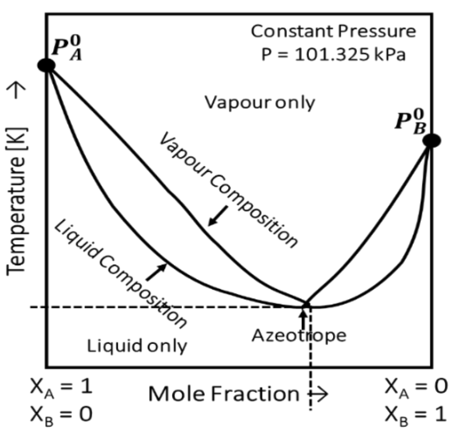
- Partial vapour pressure is lower than expected.
  $P_A < P_A^{\circ} \cdot \chi_A$
- The intermolecular attractions between unlike molecules (A–B) are stronger from those between like molecules (A–A or B–B).
- Heat is evolved on mixing.
  $\Delta H_{mixing} < 0$
- Volume decreases on mixing.
  $\Delta V_{mixing} < 0$
- These solutions tends to form maximum boiling Azeotropes

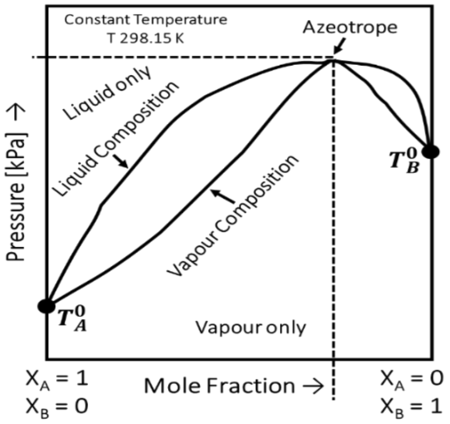
## Azeotropes

- **Azeotropes** are binary mixtures that have the **same composition in both the liquid and vapour phase**, and they **boil at a constant temperature**.
- Because of this unique property, **the components of an azeotrope cannot be separated by fractional distillation**.
- There are **two types** of azeotropes based on their boiling behaviour:
  - Minimum boiling azeotropes (Positive Azeotropes)
  - Maximum boiling azeotropes (Negative Azeotropes)

## Minimum Boiling Azeotropes (Positive Azeotropes)

- An azeotrope whose **boiling point is lower** than that of either of the pure components.
- This occurs in **non-ideal solutions showing positive deviation** from Raoult's law.
- At a certain intermediate composition, the **vapour pressure is maximum** and the **boiling point is minimum**. At this point, the solution behaves like a **minimum boiling azeotrope**.

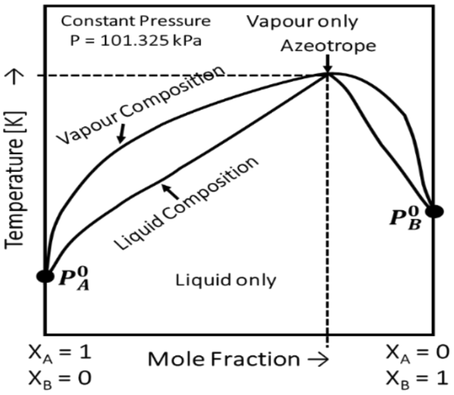


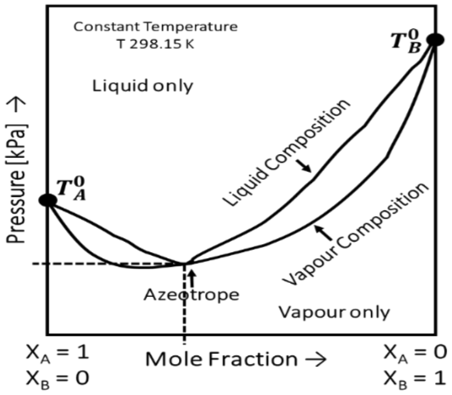


- **Example:**
  - **Ethanol + Water (95.4% Ethanol)**
    Boils at 351.15 K (78.0°C), which is lower than the boiling point of either pure ethanol or pure water.

## Maximum Boiling Azeotropes (Negative Azeotropes)

- An azeotrope whose **boiling point is higher** than that of either of the pure components.
- This occurs in **non-ideal solutions showing negative deviation** from Raoult's law.
- At a specific composition, the **vapour pressure is minimum** and the **boiling point is maximum**. At this point, the solution behaves like a **maximum boiling azeotrope**.





- **Example:**
  - **Nitric Acid + Water (68% Nitric Acid)**
    Boils at 393.5 K (120.35°C), which is higher than the boiling point of either pure nitric acid or water.

## Exercises

**Q 1.** Vapour pressure of chloroform ($CHCl_3$) and dichloromethane ($CH_2Cl_2$) at 298 K are 200 mmHg and 415 mmHg respectively. Calculate the (a) Vapour pressure of the solution prepared by mixing 25.5 g of $CHCl_3$ and 40 g of $CH_2Cl_2$ at 298 K and (b) Mole fraction of each component in vapour phase.

**Q 2.** In ideal solution of a non-volatile solute 'B' in solvent 'A' in 2 : 5 molar ratio and has vapour pressure 250 mmHg. If another solution in ratio 3 : 4 prepared, then calculate vapour pressure above this solution.

**Q 3.** The vapour pressure of an aqueous solution of glucose is 750 mmHg at 373 K. Calculate the molality and mole fraction of glucose.

**Q 4.** Methanol and ethanol form nearly an ideal solution. If the vapour pressure of pure methanol and pure ethanol at 350 K are $8.1 \times 10^4$ and $4.5 \times 10^4$ $Nm^{-2}$ respectively, calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour phase if the solution contains 64 gm of methanol and 46 gm of ethanol at this temperature.

**Q 5.** The vapour pressure of a dilute aqueous solution of glucose is 750 mmHg at 373 K. Calculate the mole fraction of solute if the vapour pressure of pure water is 760 mmHg at 373 K.

**Q 6.** Equal moles of benzene and toluene are mixed. The vapour pressure of benzene and toluene in the pure state are 700 and 600 mmHg respectively. Calculate the mole fraction of benzene in vapour state.

**Q 7.** Two liquids 'X' and 'Y' on mixing form an ideal solution. The vapour pressure of the solution containing 3 moles of 'X' and 1 mole of 'Y' is 550 mmHg. But when 4 moles of 'X' and 1 mole of 'Y' are mixed, the vapour pressure of solution thus formed is 560 mmHg. What will be the vapour pressure of the pure 'X' and pure 'Y' at this temperature.

**Q 8.** Vapour pressure of $CH_3Cl$ and $CH_2Cl_2$ are 540 mmHg and 402 mmHg respectively. 101 gm of $CH_3Cl$ and 85 grams of $CH_2Cl_2$ are mixed together. Determine: (a) the vapour pressure at which the solution starts boiling (b) Molar ratio of solute versus solvent in vapour phase in equilibrium with solution.

**Q 9.** The vapour pressure of ethyl acetate and ethyl propionate are 72.8 and 27.7 mmHg respectively. A solution is prepared by mixing 25 g of ethyl acetate and 50 g of ethyl propionate. Assuming the solution to be ideal, Calculate the vapour pressure of the solution.

## Colligative Properties

- Colligative properties are those properties of ideal solutions that **depend only on the number of solute particles** present in the solution, and **not on the nature of the solute** itself.

- **Major Colligative Properties are:**
  - Relative Lowering of Vapour Pressure
  - Elevation of Boiling Point
  - Depression of Freezing Point
  - Osmotic Pressure

## Relative Lowering of Vapour Pressure

- When a **non-volatile solute** is added to a **volatile solvent**, the **vapour pressure of the solvent decreases**.
- This is because solute particles occupy space at the surface and reduce the number of solvent molecules escaping into the vapour phase.
- The extent of vapour pressure lowering depends **only on the number of solute particles (i.e., concentration)** and **not on their chemical nature** — a defining feature of colligative properties.

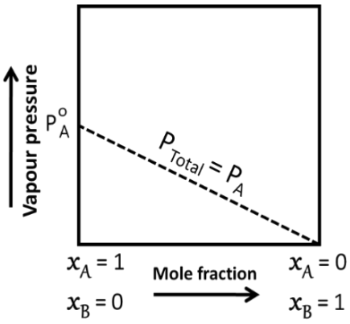
- **Mathematical Expression:**
  - Since only the solvent contributes to the total vapour pressure of solution: $\mathbf{P_{Total} = P_A}$
  - Let:

    $\mathbf{P_A}$ = Vapour pressure of solvent in solution or Total pressure of the solution.
    $P^\circ_A$ = Vapour pressures of pure solvent.
    $\chi_A$ = Mole fraction of solvent
    $\chi_B$ = Mole fractions of solute

  - According to Raoult's law: $\mathbf{P_A = P^\circ_A \cdot \chi_A}$
  - Since, $\chi_A = 1 - \chi_B$ , we get: $\mathbf{P_A = P^\circ_A (1 - \chi_B)}$
  - Now simplifying: $\mathbf{P_A = P^\circ_A - P^\circ_A \chi_B}$

$$\mathbf{P^\circ_A \chi_B = P^\circ_A - P_A = \Delta P_A}$$

$$\chi_B = \frac{\mathbf{P^\circ_A - P_A}}{\mathbf{P^\circ_A}} = \frac{\mathbf{\Delta P_A}}{\mathbf{P^\circ_A}}$$



  - In this expression, [ $\mathbf{P^\circ_A - P_A = \Delta P_A}$ ] , represents the lowering of vapour pressure.
  - While, $\chi_B = \frac{\mathbf{P^\circ_A - P_A}}{\mathbf{P^\circ_A}}$ , represents the relative lowering of vapour pressure.

- **Determination of Molar Mass from Relative Lowering of Vapour Pressure:**
  - From the previous relation:

$$\frac{\mathbf{P^\circ_A - P_A}}{\mathbf{P^\circ_A}} = \chi_B = \frac{n_B}{n_A + n_B}$$

  - For dilute solutions, where $n_A \gg n_B$ , we approximate: $n_A + n_B = n_A$
  - So, $\chi_B \approx \frac{n_B}{n_A}$
  - Now, expressing number of moles as: $n_A = \frac{W_A}{M_A}$ and $n_B = \frac{W_B}{M_B}$
  - Substitute: $\chi_B \approx \frac{\mathbf{W_B \times M_A}}{\mathbf{M_B \times W_A}}$
    - $\frac{\mathbf{P^\circ_A - P_A}}{\mathbf{P^\circ_A}} = \frac{\mathbf{\Delta P_A}}{\mathbf{P^\circ_A}} = \chi_B = \frac{\mathbf{W_B \times M_A}}{\mathbf{M_B \times W_A}}$ or $\frac{\mathbf{\Delta P_A}}{\mathbf{P^\circ_A}} = \frac{\mathbf{W_B \times M_A}}{\mathbf{M_B \times W_A}}$

- Solving for $M_B$ (molar mass of solute): $$M_B = \frac{W_B \times M_A \times P_A^\circ}{\Delta P_A \times W_A}$$

- **Key Points Recap:**
    - Relative lowering of vapour pressure is a direct measure of solute concentration.
    - It enables **experimental determination of molar mass** of unknown solutes.
    - This property is especially useful for **non-volatile** solutes in **dilute solutions**.

## Exercises

**Q 1.** Vapour pressure of water at 293 K is 17.51 mm. Lowering of vapour pressure of a sugar solution is 0.0614 mm. Calculate (i) Relative lowering of vapour pressure (ii) Mole fraction of water (iii) Vapour pressure of the solution.

**Q 2.** The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile and non-electrolyte solid weighing 0.5 g is added to 39.0 g of benzene (molar mass 78 g/mol). The vapour pressure of the solution then is 0.845 bar. What is the molar mass of the solid substance?

**Q 3.** The vapour pressure of 2.1 % of an aqueous solution of non-electrolyte at 373 K is 755 mm. Calculate the molar mass of solute. (Consider that vapour pressure of water at 373 K is 760.

**Q 4.** 20 g of solute was added to 100 g of water at 25 ˚C. The vapour pressure of water and that of the solution were 23.76 mmHg and 22.41 mmHg respectively at that temperature. Calculate the relative molecular mass of the solute.

**Q 5.** Why is the vapour pressure of an aqueous solution of glucose lower than that of water?

**Q 6.** How much urea ($NH_2CONH_2$) must be dissolved in 50 gm of water so that the vapour pressure at room temperature is reduced by 25% ? Also calculate the molarity of the solution obtained.

## Elevation of Boiling Point

- **Boiling Point:**
  The boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure.

  **Example:**

  Water boils at 373 K (100°C) because at this temperature, its vapour pressure is 1.013 bar (or 760 mmHg), which is equal to 1 atm pressure.

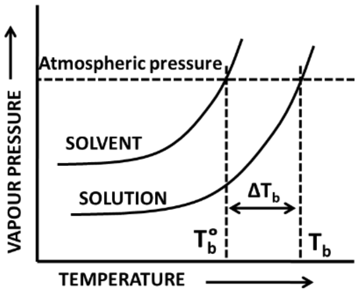
- **Elevation in boiling point ($\Delta T_b$):**
  When a non-volatile solute is dissolved in a volatile solvent, the boiling point of the solution increases compared to that of the pure solvent.

$$\Delta T_b = T_b - T_b^\circ$$

Where:

$T_b$ = Temperature of boiling of solution

$T_b^\circ$ = Temperature of boiling of pure solvent



- **Why does a solution boil at a higher temperature than the pure solvent?**
  Because the vapour pressure of the solution is lower than that of the pure solvent, more heat is required to raise the vapour pressure of the solution to match the atmospheric pressure. As a result, the solution boils at a higher temperature than the pure solvent.

- The extent of elevation in boiling point ($\Delta T_b$) depends on the molal concentration (m) of the non-volatile solute present in the solution.

$$\Delta \mathbf{T_b} \propto \mathbf{m}$$

$$\Delta \mathbf{T_b} = \mathbf{K_b} \times \mathbf{m}$$

Where:

$\Delta \mathbf{T_b}$ = Elevation in Boiling point
$\mathbf{m}$ = Molality of the solution
$\mathbf{K_b}$ = molal elevation constant (ebullioscopic constant)

| **Solvent** | **$K_b$ (K Kg/mol)** |
|---|---|
| $H_2O$ | 0.52 |
| $C_6H_6$ | 2.53 |
| $C_2H_5OH$ | 1.20 |

- **If molality = 1 mol/kg**, then $\Delta \mathbf{T_b} = \mathbf{K_b}$
  So, $K_b$ is defined as the elevation in boiling point produced by 1 mole of solute in 1 kg of solvent.

- **Calculation of Molar Mass from Boiling Point Elevation:**
  - We know: $\Delta T_b = K_b \times m$
  - And molality: $m = \dfrac{W_B \times 1000}{M_B \times W_{A\ \text{in g}}}$
  - Substitute in the equation: $\Delta \mathbf{T_b} = \mathbf{K_b} \times \dfrac{\mathbf{W_B \times 1000}}{\mathbf{M_B \times W_{A\ in\ g}}}$
  - Solve for $M_B$ (molar mass of solute): $\mathbf{M_B} = \dfrac{\mathbf{K_b \times W_B \times 1000}}{\mathbf{\Delta T_b \times W_{A\ in\ g}}}$

- **Key Points Recap:**
  - Boiling point of a solution is higher than that of the pure solvent.
  - Used to determine molar mass of unknown solutes using known values of $K_b$ , solvent mass, and temperature rise.

---

## Exercises

**Q 1.** The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute. $K_b$ for benzene is 2.53 K kg/mol.

**Q 2.** 18 g of glucose, $C_6H_{12}O_6$, is dissolved in 1 kg of water. At what temperature will the water boil at 1.013 bar pressure? $K_b$ for water is 0.52 K kg/mol.

**Q 3.** A solution of glycerol ($C_3H_8O_3$), in water was prepared by dissolving some glycerol in 500 g of water. This solution has a boiling point of 100.42 ˚C. What mass of glycerol was dissolved to make the solution? $K_b$ for water = 0.52 K kg/mol.

**Q 4.** The solution of 2.5 gm of a non-volatile substance in 100 gm of benzene boiled at a temperature 0.42 ˚C higher than the boiling point of pure benzene. Calculate molar mass of the substance. (Given $K_b$ of benzene is 2.67 K/molal)

**Q 5.** A solution of urea (molar mass = 60 gm/mole) boils at 100.18 ˚C at the atmospheric pressure. If $K_f$ and $K_b$ for water are 1.86 and 0.512 ˚C/molal respectively, calculate freezing point of the solution.

**Q 6.** The boiling point of pure acetone is 56.38 ˚C. When 0.71 gram of a compound is dissolved in 10 gm of acetone, there is elevation of 56.88 ˚C in boiling point. What is the molar mass of the compound? Given, $K_b$ of acetone is 1.72 K kg $mole^{-1}$.

## Depression of Freezing Point

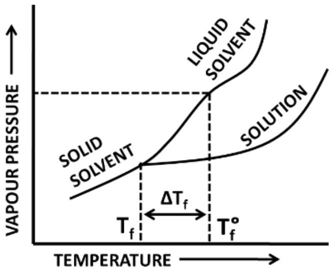
- **Freezing Point:**
  Freezing point of a substance is the temperature at which its solid and liquid phases exist in equilibrium — i.e., both have the same vapour pressure.
- **Depression in freezing point ($\Delta T_f$):**
  When a non-volatile solute is dissolved in a volatile solvent, the freezing point of the solution decreases compared to that of the pure solvent.

$$\Delta T_f = T_f^{\circ} - T_f$$

Where:

$T_f$ = Temperature of freezing of solution

$T_f^{\circ}$ = Temperature of freezing of pure solvent



- **Why is freezing point of a solution lower than that of a pure solvent?**
  The vapour pressure of a solution is lower than that of the pure solvent. Therefore, the solution must be cooled more (to a lower temperature) so that its vapour pressure equals that of the solid phase — leading to depression in freezing point.

- The extent of depression in freezing point ($\Delta T_f$) depends upon the molal concentration (m) of the non-volatile solute present in the solution.

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

Where:

$\Delta T_f$ = Depression in Freezing point

**m** = Molality of the solution

$K_f$ = molal depression constant (cryoscopic constant)

| Solvent | $K_f$ (K Kg/mol) |
|---|---|
| $H_2O$ | 1.86 |
| $C_6H_6$ | 5.12 |
| $C_2H_5OH$ | 1.99 |

- **If molality = 1 mol/kg**, then $\Delta T_f = K_f$
  So, $K_f$ is defined as the depression in freezing point produced by 1 mole of solute in 1 kg of solvent.

- **Calculation of Molar Mass from Depression in Freezing Point:**
  - We know: $\Delta T_f = K_f \times m$
  - And molality: $m = \frac{W_B \times 1000}{M_B \times W_{A\ in\ g}}$
  - Substitute in the equation: $\Delta T_f = K_f \times \frac{W_B \times 1000}{M_B \times W_{A\ in\ g}}$

- Solve for $M_B$ (molar mass of solute): $$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_{A\ in\ g}}$$

- **Applications of Depression in Freezing Point:**
  - **Antifreeze in Car Radiators**
    - Ethylene glycol (called antifreeze) is added to water to lower its freezing point, preventing freezing in cold climates.
    - This allows cars and buses to operate smoothly even in sub-zero temperatures.
    - **Note:**
      - Ethylene glycol is not just an **antifreeze** (used to lower the freezing point in winter), but also acts as a **coolant** and helps **raise the boiling point** of water in the radiator.
      - Due to high temperature in summer, engine heat can cause water to boil. Boiling water can lead to radiator damage or engine overheating. Ethylene glycol raises the boiling point of the coolant mixture, helping the engine run safely at higher temperatures.

  - **Melting Ice on Roads**
    - Common salt (NaCl) or calcium chloride ($CaCl_2$) is spread over icy roads.
    - These salts lower the freezing point of ice, making it melt faster and preventing accumulation.

## Exercises

**Q 1.** A solution containing 34.2 g of cane-sugar ($C_{12}H_{22}O_{11}$) dissolved in 500 $cm^3$ of water froze at -0.374 ˚C. Calculate the $K_b$ of water.

**Q 2.** 1.00 g of non-electrolyte solute dissolved in 50 g of benzene lowered the freezing point of benzene by 0.40 K. $K_f$ of benzene is 5.12 K kg/mol. Find Molar mass of solute.

**Q 3.** 45 g of ethylene glycol ($C_2H_6O_2$) is mixed with 600 g water. Calculate: (a) freezing point of depression (b) freezing point of solution. ($K_f$ for $H_2O$ = 1.86 K kg/mol)

**Q 4.** Calculate the temperature at which a solution containing 54 g of glucose in 250 g of water will freeze. ($K_f$ for water = 1.86 K kg/mol)

**Q 5.** 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 ˚C to -10.0 ˚C. ($K_f$ for $H_2O$ is 1.86 K kg/mol).

**Q 6.** What is the relationship between $\Delta T_f$ and $\Delta T_b$ of a solution?

**Q 7.** 1 gm of a non-electrolyte solute (molar mass 250 gm/mole) was dissolved in 51.2 gm of benzene. If the freezing point depression constant, $K_f$ of benzene is 5.12 K kg mole$^{-1}$, then, calculate the freezing point of benzene.

**Q 8.** The normal freezing point of nitrobenzene ($C_6H_5NO_2$) is 278.82 K. A 0.25 molal solution of a certain solute in nitrobenzene causes a freezing point depression of 2 ˚C. Calculate the value of $K_f$ for Nitrobenzene.

**Q 9.** Is it advisable to use ethylene glycol in car radiators during summer ?

**Q 10.** A solution of sucrose (molar mass = 342 gm/mole) is prepared by dissolving 68.4 gm in 1000 gm of water. What is the freezing point and boiling point of solution? ($K_f$ for water is 1.86 K/m and $K_b$ for water is 0.52 K/m).

---

### Calculation of molal depression constant from enthalpy of fusion :

- Formula Used: $\mathbf{K_f} = \dfrac{R \times (T_f^o)^2}{1000 \times l_f}$
- As we know: $l_f = \dfrac{\Delta_{fus}H}{M_A}$
- Substituting: $\mathbf{K_f} = \dfrac{R \times (T_f^o)^2 \times M_A}{1000 \times \Delta_{fus}H}$

Where:

**R** = Gas constant
$\mathbf{M_A}$ = Molar mass of solvent.
$T_f^o$ = Freezing point of pure solvent in Kelvin
$l_f$ = Latent heat of fusion per gram of solvent,
$\Delta_{fus}\mathbf{H}$ = Enthalpy of fusion per mole of solvent.

R = 8.134 J K$^{-1}$ mol$^{-1}$ if $l_f$ or $\Delta_{fus}H$ are in joules
R = 2 cal deg$^{-1}$ mol$^{-1}$ if $l_f$ or $\Delta_{fus}H$ are in calories

---

### Calculation of molal elevation constant from enthalpy of vaporization :

- Formula Used: $\mathbf{K_b} = \dfrac{R \times (T_b^o)^2}{1000 \times l_b}$
- As we know: $l_b = \dfrac{\Delta_{vap}H}{M_A}$
- Substituting: $\mathbf{K_b} = \dfrac{R \times (T_b^o)^2 \times M_A}{1000 \times \Delta_{vap}H}$

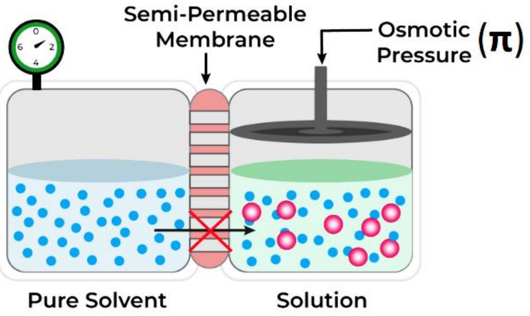
Where:

**R** = Gas constant
$\mathbf{M_A}$ = Molar mass of solvent.
$T_b^o$ = Boiling point of pure solvent in Kelvin
$l_b$ = Latent heat of vaporisation per gram of solvent,
$\Delta_{vap}\mathbf{H}$ = Enthalpy of vaporisation per mole of solvent.

R = 8.134 J K$^{-1}$ mol$^{-1}$ if $l_b$ or $\Delta_{vap}H$ are in joules
R = 2 cal deg$^{-1}$ mol$^{-1}$ if $l_b$ or $\Delta_{vap}H$ are in calories

## Osmotic Pressure

- **Osmosis and Diffusion:**
    - **Diffusion** is a spontaneous movement of both solute and solvent from higher concentration to lower concentration.
    - **Osmosis** is a spontaneous movement of solvent only through a semi-permeable membrane from higher to lower concentration.
- **Demonstration of Osmosis:**
    - **Exosmosis**: Grapes placed in concentrated NaCl solution shrink because water moves out (solvent concentration is higher in grape sap).
    - **Endosmosis**: Kismis placed in pure water swells up because water moves in (solvent concentration is higher outside).
- **Semi-Permeable Membranes:**
  A membrane that allows only solvent molecules to pass through but not solute particles.
    - **Natural:** Plant/animal cell membranes
    - **Artificial:** Parchment paper, cellophane, copper ferrocyanide
- **Osmotic Pressure:**
    - The additional pressure that must be applied on a solution to prevent the inward flow of solvent through a semi-permeable membrane.
    - It is denoted by **π**.



    - **Mathematical Expression:**
        - Osmotic pressure is directly proportional to molar concentration (C) of the solute and absolute temperature (T).

$$\pi \propto CT$$
$$\pi = CRT$$

Where:

**R** = Gas constant

**C** = Molar concentration = $\frac{\text{Number of moles of solute}}{\text{Volume of solution in L}} = \frac{n}{V}$

**T** = Temperature in Kelvin

- Substituting C = $\frac{n}{V}$ , We get: $\pi = \frac{n}{V}RT$ or $\pi V = nRT$
- This is known as Van't Hoff Equation for dilute solutions.

- **Determination of Molecular Mass Using Osmotic Pressure:**
  - From Van't Hoff's equation: $\pi V = nRT$
  - Where, '**n**' is number of moles of solute = $\frac{\text{Weight of solute}}{\text{Molar mass of solute}} = \frac{W_B}{M_B}$
  - Substituting: $\pi V = \frac{W_B \cdot R \cdot T}{M_B}$ or $\pi = \frac{W_B \cdot R \cdot T}{M_B \cdot V}$

    Where:

    $W_B$ = Weight of solute in gm
    $M_B$ = Molar mass of solute (gm/mole)
    **V** = Volume of solution in **Litre**.
  - If volume is in **mL**, multiply by 1000: $\pi = \frac{W_B \cdot R \cdot T \cdot 1000}{M_B \cdot V}$
  - Rearranging to find molar mass: $M_B = \frac{W_B \cdot R \cdot T \cdot 1000}{\pi \cdot V}$

- **Reverse Osmosis (RO):**
  If a pressure greater than the osmotic pressure is applied on a solution, the solvent flows from the solution into the pure solvent through a semi-permeable membrane. This is called Reverse Osmosis.

- **Types of Solutions Based on Osmotic Pressure:**

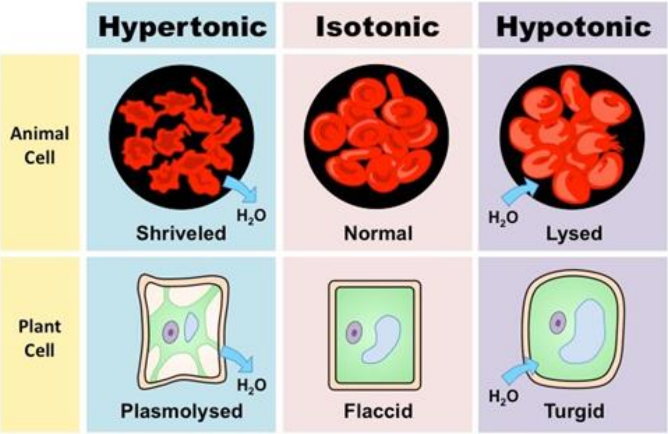
| Type | Osmotic Pressure | Solute Concentration |
|---|---|---|
| **Hypertonic** | Higher than comparison solution | More solute |
| **Hypotonic** | Lower than comparison solution | Less solute |
| **Isotonic** | Equal to comparison solution | Equal solute |

- **Biological Importance of Osmosis:**
  - Water absorption by plant roots.
  - Movement of water across animal cells.
  - Bursting of RBCs in water.
  - Opening/closing of stomata in plants.
  - Preservation and pickling of raw mangoes.
  - Revival of wilted flowers in fresh water

- **Effect of Osmosis on RBCs:**
  - When RBCs are placed in **hypotonic solution**, having salt concentration less than 0.9 %, they will start swell up due to endosmosis.
  - When RBCs are placed in **hypertonic solution**, having salt concentration more than 0.9 %, they will start shrink due to exosmosis.
  - When RBCs are placed in **isotonic solution**, having salt concentration 0.9 %, the cell never swell and nor shrink because no osmosis takes place.

| Solution Type | Salt Concentration | Effect on RBCs | Reason |
|---|---|---|---|
| Hypotonic | < 0.9% | Swells (Endosmosis) | Water enters |
| Hypertonic | > 0.9% | Shrinks (Exosmosis) | Water exits |
| Isotonic | = 0.9% | No change | No net osmosis |

- **Effect of Osmosis on Plant Cell (Turgid and Plasmolysed Cell):**
  - **Turgid Cell:**
    - When a plant cell is placed in hypotonic solution, water enters the cell through endosmosis, the cell begins to swell. As a result, the **cell wall exerts a pressure** to resist further entry of water. This opposing pressure is known as Turgor Pressure, and the cell is called a Turgid Cell.
  - **Plasmolysed Cell:**
    - When a turgid plant cell is placed in hypertonic solution, water leaves the cell through exosmosis, the cell begins to shrink. The **protoplasm detaches** from the cell wall and becomes small and spherical in shape. This process is called Plasmolysis (or Crenation in animal cells), and the cell is known as a Plasmolysed Cell.



- **Osmosis-Based Phenomena:**
  - **Edema:** Tissue swelling from excess salt due to water retention.
  - **Pickled Mango:** Water moves out from mango cells in salt**.**
  - **Wilted Flower:** Water flows into cells in fresh water, reviving the flower

- **Direction of Osmosis:**
    - From high solvent concentration → low solvent concentration
    - From low solute concentration → high solute concentration
    - From dilute solution → concentrated solution
    - From low osmotic pressure → high osmotic pressure

## Exercises

**Q 1.** 200 $cm^3$ of an aqueous $sol^n$ of protein contains 1.26 g of protein. Osmotic pressure of this solution at 300 K is found to be $2.57 \times 10^{-3}$ bar. Calculate molecular mass of protein.

**Q 2.** 10 g of a substance were dissolved in water and solution was made up to 250 $cm^3$. Osmotic pressure of solution was found to be $8 \times 10^5$ $Nm^{-2}$ at 288 K. Find molar mass of solute.

**Q 3.** A solution prepared by dissolving 8.95 mg of a gene fragment in 35.0 mL of water has an osmotic pressure of 0.335 torr at 25 ˚C. Assuming that the gene fragment is a non-electrolyte, calculate its molar mass.

**Q 4.** 4% NaOH solution (w/v) and 6% urea solution (w/v) are equimolar but not isotonic. Explain.

**Q 5.** 3% solution of glucose is isotonic with 1% solution of a non-volatile non electrolyte substance. The molecular mass of the substance would be:

**Q 6.** One litre of aqueous solution of sucrose (molar mass = 342 gm/mole) weighing 1015 gm is found to record an osmotic pressure of 4.82 atm at 298 K. What is the molality of the solution?

**Q 7.** A solution containing 10 gm per $dm^3$ of urea (molar mass = 60 gm/mole) is isotonic with a 5% solution of a non-volatile and non-electrolyte solute. Calculate the molecular mass of the solute.

**Q 8.** 100 mg of a protein was dissolved in just enough water to make 10 mL of the solution. If the solution has an osmotic pressure of 13.3 mmHg at 25 ˚C, what is the molar mass of the protein? ($R = 0.0821$ L atm $mole^{-1}$ $K^{-1}$)

**Methods used for the measurement of different colligative properties are:**

- Relative lowering in vapour pressure – Ostwald and Walker method
- Elevation in Boiling point – Landsberger method
- Depression in Freezing point – Beckmann method
- Osmotic pressure – Berkeley and Hartley method OR Morse and Frazer method

## Abnormal Molecular Masses and Van't Hoff Factor

When the molecular mass of a substance, determined using any one of the colligative properties, found to be differ from the theoretically expected value, then the substance is said to exhibit an abnormal molecular mass.

- **Causes of Abnormal Molecular Mass:**
    - **Dissociation** of solute in solution
    - **Association** of solute in solution
    - **Non-ideal** behavior of the solution

- **Van't Hoff factor (i):**
  - To calculate the extent of association or dissociation, Van't Hoff introduced a correction factor 'i' called Van't Hoff factor.
  - It is defined as the **ratio** of the **experimental value** of the colligative property to the **calculated value** of the colligative property.

$$i = \frac{\text{Observed (Experimental) colligative property}}{\text{Calculated (Normal) colligative property}} = \frac{C_O}{C_C}$$

  - Since colligative property is **inversely proportional to molecular mass**, it can also be written as:

$$i = \frac{\text{Calculated (Normal) Molecular mass}}{\text{Observed (Experimental) Molecular mass}} = \frac{M_C}{M_O}$$

- **Interpretation of Van't Hoff factor (i):**

| Value of i | Interpretation | Number of Particles in Solution |
|---|---|---|
| $i = 1$ | No association or dissociation | Remain Unchanged |
| $i > 1$ | Dissociation occurs | Increases |
| $i < 1$ | Association occurs | Decrease |

- **Modified Expressions of Colligative Properties with Van't Hoff Factor (i)**
  - Relative Lowering in Vapour pressure: $\frac{\Delta P_A}{P^\circ_A} = i\,\chi_B$
  - Elevation in Boiling point: $\Delta T_b = i \times K_b \times m$
  - Depression in Freezing point: $\Delta T_f = i \times K_f \times m$
  - Osmotic pressure: $\pi = i\,\frac{W_B \times R \times T \times 1000}{M_B \times V}$

## Degree of Dissociation (∝)

- Consider that, 'A' molecules dissociate in solvent to give '$n$' number of ions.

$$\underbrace{A}\longrightarrow \underbrace{bB + cC + dD + \ldots\ldots} \qquad \therefore \text{ number of ions} = b + c + d = n$$

Initial conc. : 1 0 moles
Final conc. : $1-\alpha$ $n \propto$ moles

- Observed colligative property = $1 - \alpha + n\,\alpha$ = $1 + (n-1)\propto$
- Calculated colligative property = 1 (as 1 mole of solute 'A' was taken)

- Van't Hoff factor '$i$' $= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}} = \frac{1 + (n-1)\propto}{1}$
- By solving further: $i = 1 + (n-1)\propto$

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

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

- As we know that, '$i$' $= \frac{\text{Calculated Molecular mass}}{\text{Observed Molecular mass}} = \frac{M_C}{M_O}$
- Substituting: $\propto = \frac{i-1}{n-1} = \frac{\frac{M_C}{M_O} - 1}{n-1} = \frac{\frac{M_C - M_O}{M_O}}{n-1} = \frac{M_C - M_O}{M_O\,(n-1)}$

Where:

**n =** Number of ions given by solute in the solution
**$M_C$ =** Calculated molar mass of the solute.
**$M_O$ =** Observed molar mass of the solute.
$\propto$ = Degree of dissociation.
**$i$** = Van't Hoff factor.

## Degree of Association ($\propto$)

- In some cases, molecules of the solute 'A' associate to form large associated molecule '$A_n$'.
- Consider that, '**n**' number of solute '**A**' molecules associate to form associated molecule **$A_n$**.

$$\underbrace{nA} \rightleftharpoons \underbrace{A_n}$$

| | | | |
|---|---|---|---|
| Initial conc. : | 1 | 0 | moles |
| Final conc. : | $1 - \alpha$ | $\frac{\propto}{n}$ | moles |

- Hence, total number of moles in solution $= (1 - \propto) + \frac{\propto}{n}$ (observed colligative property)
- And, total number of moles of solute was taken = 1 (calculated colligative property)
- Van't Hoff factor '$i$' $= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}} = \frac{(1-\propto) + \frac{\propto}{n}}{1}$
- By solving Further: '$i$' $= 1 - \propto + \frac{\propto}{n}$

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

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

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

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

- As we know that, ‘$i$’ $= \frac{\text{Calculated Molecular mass}}{\text{Observed Molecular mass}} = \frac{M_C}{M_O}$
- Substituting: $\propto = \left(1 - \frac{M_C}{M_O}\right)\frac{n}{n-1} = \left(\frac{M_O - M_C}{M_O}\right)\frac{n}{n-1}$

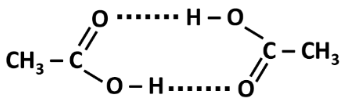
Where:

**n =** Number of molecules present in association.
**$M_C$ =** Calculated molar mass of the solute.
**$M_O$ =** Observed molar mass of the solute.
$\propto$ = Degree of association.
**$i$** = Van’t Hoff factor.

## Dimerization of Ethanoic Acid

- Ethanoic acid ($CH_3COOH$) molecules tend to dimerise in benzene or other non-polar solvents due to hydrogen bonding between two molecules.
- This association typically occurs in solvents with a low dielectric constant, where polar interactions are minimized, favoring molecular aggregation.
- Due to dimerization, two molecules combine to form one dimer, which reduces the number of particles in the solution.

$$2\ CH_3 - COOH \rightleftharpoons (CH_3COOH)_2$$



## Exercises

**Q 1.** 0.5 gm KCl was dissolved in 100 gm water and the solution originally at 20 °C, froze at –0.24 °C. Calculate the percentage ionization of salt. $K_f$ for water = 1.86 K Kg mol$^{-1}$.

**Q 2.** 0.6 mL of acetic acid having density of 1.06 gm/ml is dissolved in 1 Litre of water. The depression in freezing point observed for this strength of the acid was 0.0205 °C. Calculate the Van’t Hoff factor and the dissociation constant of the acid. $K_f$ for water = 1.86 K Kg mol$^{-1}$.

**Q 3.** Depression in freezing point of 0.10 molal solution of HF is –0.201 °C. Calculate percentage degree of dissociation of HF. $K_f$ for $H_2O$ = 1.86 K Kg mol$^{-1}$.

**Q 4.** Calculate the freezing point depression expected for 0.0711 molal aqueous solution of $Na_2SO_4$. If this solution freezes at –0.32 °C, what would be the value of Van’t Hoff factor? $K_f$ for water = 1.86 K Kg mol$^{-1}$.

**Q 5.** Calculate the boiling point of a solution prepared by adding 15 gm of NaCl to 250 gm of water ($K_b$ for water = 0.52 K Kg $mol^{-1}$).

## NCERT : Intext Questions

1. Calculate the mass percentage of benzene ($C_6H_6$) and carbon tetrachloride ($CCl_4$) if 22 g of benzene is dissolved in 122 g of carbon tetrachloride.
2. Calculate the mole fraction of benzene in solution containing 30% by mass in carbon tetrachloride.
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.
4. Calculate the mass of urea ($NH_2CONH_2$) required in making 2.5 kg of 0.25 molal aqueous solution.
5. Calculate (a) molality (b) molarity and (c) mole fraction of KI if the density of 20% (mass/mass) aqueous KI is 1.202 g $mL^{-1}$.
6. Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in a solution containing 20% of $C_2H_6O_2$ by mass.
7. Calculate the molarity of a solution containing 5 g of NaOH in 450 mL solution.
8. Calculate molality of 2.5 g of ethanoic acid ($CH_3COOH$) in 75 g of benzene.
9. $H_2S$, 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 m, calculate Henry's law constant.
10. Henry's law constant for $CO_2$ in water is 1.67x108 Pa at 298 K. Calculate the quantity of $CO_2$ in 500 mL of soda water when packed under 2.5 atm $CO_2$ pressure at 298 K.
11. If $N_2$ gas is bubbled through water at 293 K, how many millimoles of $N_2$ gas would dissolve in 1 litre of water? Assume that $N_2$ exerts a partial pressure of 0.987 bar. Given that Henry's law constant for $N_2$ at 293 K is 76.48 *k* bar.
12. Vapour pressure of chloroform ($CHCl_3$) and dichloromethane ($CH_2Cl_2$) at 298 K are 200 mm Hg and 415 mm Hg respectively. (i) Calculate the vapour pressure of the solution prepared by mixing 25.5 g of $CHCl_3$ and 40 g of $CH_2Cl_2$ at 298 K and, (ii) mole fractions of each component in vapour phase.
13. The vapour pressure of pure liquids A and B are 450 and 700 mmHg respectively, at 350 K . Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.
14. The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.5 g when added to 39.0 g of benzene (molar mass 78 g $mol^{-1}$). Vapour pressure of the solution, then, is 0.845 bar. What is the molar mass of the solid substance?
15. 18 g of glucose, $C_6H_{12}O_6$, is dissolved in 1 kg of water in a sauce-pan. At what temperature will water boil at 1.013 bar? $K_b$ for water is 0.52 K kg $mol^{-1}$.
16. The boiling point of benzene is 353.23 K. When 1.80 g of a non-volatile solute was dissolved in 90 g of benzene, the boiling point is raised to 354.11 K. Calculate the molar mass of the solute. $K_b$ for benzene is 2.53 K kg $mol^{-1}$.
17. 45 g of ethylene glycol ($C_2H_6O_2$) is mixed with 600 g of water. Calculate (a) the freezing point depression and (b) the freezing point of the solution.
18. 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.
19. 200 $cm^3$ of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be $2.57 \times 10^{-3}$ bar. Calculate the molar mass of the protein.
20. 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 and its relative lowering.

21. Boiling point of water at 750 mm Hg is 99.63°C. How much sucrose is to be added to 500 g of water such that it boils at 100°C.
22. Calculate the mass of ascorbic acid (Vitamin C, $C_6H_8O_6$) to be dissolved in 75 g of acetic acid to lower its melting point by 1.5°C. $K_f$ = 3.9 K kg mol$^{-1}$.
23. Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185,000 in 450 mL of water at 37°C.
24. 2 g of benzoic acid (C6H5COOH) dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant for benzene is 4.9 K kg mol$^{-1}$. What is the percentage association of acid if it forms dimer in solution?
25. 0.6 mL of acetic acid ($CH_3COOH$), having density 1.06 g mL$^{-1}$, is dissolved in 1 litre of water. The depression in freezing point observed for this strength of acid was 0.0205°C. Calculate the van't Hoff factor and the dissociation constant of acid.

## NCERT : Exercise Questions

1. Define the term solution. How many types of solutions are formed? Write briefly about each type with an example.
2. Give an example of a solid solution in which the solute is a gas.
3. Define the following terms: (i) Mole fraction (ii) Molality (iii) Molarity (iv) Mass percentage.
4. Concentrated nitric acid used in laboratory work is 68% nitric acid by mass in aqueous solution. What should be the molarity of such a sample of the acid if the density of the solution is 1.504 g mL$^{-1}$?
5. A solution of glucose in water is labelled as 10% w/w, what would be the molality and mole fraction of each component in the solution? If the density of solution is 1.2 g mL$^{-1}$, then what shall be the molarity of the solution?
6. How many mL of 0.1 M HCl are required to react completely with 1 g mixture of $Na_2CO_3$ and $NaHCO_3$ containing equimolar amounts of both?
7. A solution is obtained by mixing 300 g of 25% solution and 400 g of 40% solution by mass. Calculate the mass percentage of the resulting solution.
8. An antifreeze solution is prepared from 222.6 g of ethylene glycol ($C_2H_6O_2$) and 200 g of water. Calculate the molality of the solution. If the density of the solution is 1.072 g mL$^{-1}$, then what shall be the molarity of the solution?
9. A sample of drinking water was found to be severely contaminated with chloroform ($CHCl_3$) supposed to be a carcinogen. The level of contamination was 15 ppm (by mass): (i) express this in percent by mass (ii) determine the molality of chloroform in the water sample.
10. What role does the molecular interaction play in a solution of alcohol and water?
11. Why do gases always tend to be less soluble in liquids as the temperature is raised?
12. State Henry's law and mention some important applications.
13. The partial pressure of ethane over a solution containing $6.56 \times 10^{-3}$ g of ethane is 1 bar. If the solution contains $5.00 \times 10^{-2}$ g of ethane, then what shall be the partial pressure of the gas?
14. What is meant by positive and negative deviations from Raoult's law and how is the sign of $\Delta_{mix}H$ related to positive and negative deviations from Raoult's law?
15. An aqueous solution of 2% non-volatile solute exerts a pressure of 1.004 bar at the normal boiling point of the solvent. What is the molar mass of the solute?
16. Heptane and octane form an ideal solution. At 373 *K*, the vapour pressures of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35 g of octane?

17. The vapour pressure of water is 12.3 kPa at 300 K. Calculate vapour pressure of 1 molal solution of a non-volatile solute in it.
18. Calculate the mass of a non-volatile solute (molar mass 40 g mol$^{-1}$) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.
19. A solution containing 30 g of non-volatile solute exactly in 90 g of water has a vapour pressure of 2.8 kPa at 298 K. Further, 18 g of water is then added to the solution and the new vapour pressure becomes 2.9 kPa at 298 K. Calculate: (i) molar mass of the solute (ii) vapour pressure of water at 298 K.
20. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K. Calculate the freezing point of 5% glucose in water if freezing point of pure water is 273.15 K.
21. Two elements A and B form compounds having formula $AB_2$ and $AB_4$. When dissolved in 20 g of benzene ($C_6H_6$), 1 g of $AB_2$ lowers the freezing point by 2.3 K whereas 1.0 g of $AB_4$ lowers it by 1.3 K. The molar depression constant for benzene is 5.1 K kg mol$^{-1}$. Calculate atomic masses of A and B.
22. At 300 K, 36 g of glucose present in a litre of its solution has an osmotic pressure of 4.98 bar. If the osmotic pressure of the solution is 1.52 bars at the same temperature, what would be its concentration?
23. Suggest the most important type of intermolecular attractive interaction in the following pairs.
    - (i) n-hexane and n-octane
    - (ii) $I_2$ and $CCl_4$
    - (iii) $NaClO_4$ and water
    - (iv) methanol and acetone
    - (v) acetonitrile ($CH_3CN$) and acetone ($C_3H_6O$).
24. Based on solute-solvent interactions, arrange the following in order of increasing solubility in n-octane and explain. Cyclohexane, KCl, $CH_3OH$, $CH_3CN$.
25. Amongst the following compounds, identify which are insoluble, partially soluble and highly soluble in water? (i) phenol (ii) toluene (iii) formic acid (iv) ethylene glycol (v) chloroform (vi) pentanol.
26. If the density of some lake water is 1.25g mL$^{-1}$ and contains 92 g of $Na^+$ ions per kg of water, calculate the molarity of $Na^+$ ions in the lake.
27. If the solubility product of CuS is $6 \times 10^{-16}$, calculate the maximum molarity of CuS in aqueous solution.
28. Calculate the mass percentage of aspirin ($C_9H_8O_4$) in acetonitrile ($CH_3CN$) when 6.5 g of $C_9H_8O_4$ is dissolved in 450 g of $CH_3CN$.
29. Nalorphene ($C_{19}H_{21}NO_3$), similar to morphine, is used to combat withdrawal symptoms in narcotic users. Dose of nalorphene generally given is 1.5 mg. Calculate the mass of $1.5 \times 10^{-3}$ molal aqueous solution required for the above dose.
30. Calculate the amount of benzoic acid ($C_6H_5COOH$) required for preparing 250 mL of 0.15 M solution in methanol.
31. The depression in freezing point of water observed for the same amount of acetic acid, trichloroacetic acid and trifluoroacetic acid increases in the order given above. Explain briefly.
32. Calculate the depression in the freezing point of water when 10 g of $CH_3CH_2CH(Cl)COOH$ is added to 250 g of water. $Ka = 1.4 \times 10^{-3}$, $K_f = 1.86$ K kg mol$^{-1}$.
33. 19.5 g of $CH_2(F)COOH$ is dissolved in 500 g of water. The depression in the freezing point of water observed is 1.00 C. Calculate the van't Hoff factor and dissociation constant of fluoroacetic acid.
34. Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g of water.
35. Henry's law constant for the molality of methane in benzene at 298 K is $4.27 \times 10^5$ mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.
36. 100 g of liquid A (molar mass 140 g mol$^{-1}$) was dissolved in 1000 g of liquid B (molar mass 180 g mol$^{-1}$). The vapour pressure of pure liquid B was found to be 500 torr. Calculate the vapour pressure of pure liquid A and its vapour pressure in the solution if the total vapour pressure of the solution is 475 Torr.

37. Vapour pressures of pure acetone and chloroform at 328 *K* are 741.8 mm Hg and 632.8 mm Hg respectively. Assuming that they form ideal solution over the entire range of composition, plot $P_{total}$, $P_{chloroform}$, and $P_{acetone}$ as a function of $\chi_{acetone}$. The experimental data observed for different compositions of mixture is:

| $100 \times x_{acetone}$ | 0 | 11.8 | 23.4 | 36.0 | 50.8 | 58.2 | 64.5 | 72.1 |
|---|---|---|---|---|---|---|---|---|
| $p_{acetone}$ /mm Hg | 0 | 54.9 | 110.1 | 202.4 | 322.7 | 405.9 | 454.1 | 521.1 |
| $p_{chloroform}$ /mm Hg | 632.8 | 548.1 | 469.4 | 359.7 | 257.7 | 193.6 | 161.2 | 120.7 |

Plot this data also on the same graph paper. Indicate whether it has positive deviation or negative deviation from the ideal solution.

38. Benzene and toluene form ideal solution over the entire range of composition. The vapour pressure of pure benzene and toluene at 300 *K* are 50.71 mm Hg and 32.06 mm Hg respectively. Calculate the mole fraction of benzene in vapour phase if 80 g of benzene is mixed with 100 g of toluene.

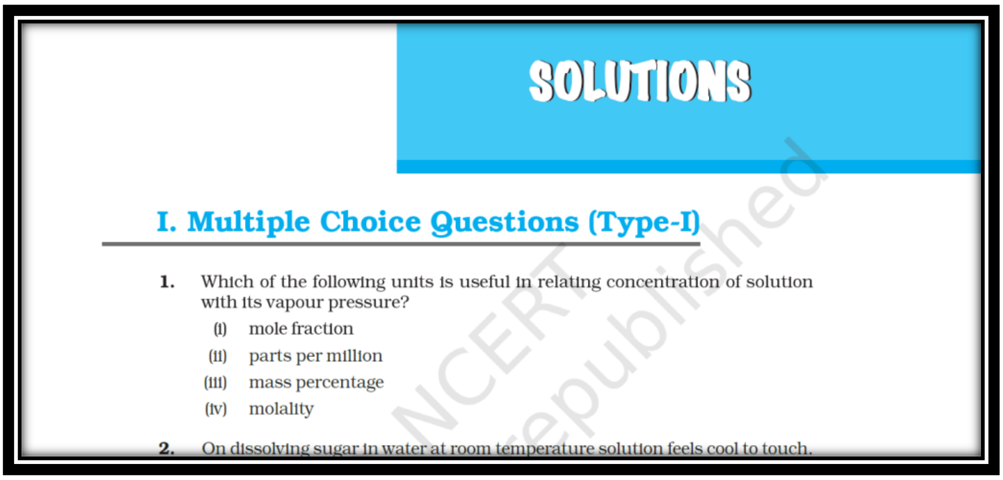
39. The air is a mixture of a number of gases. The major components are oxygen and nitrogen with approximate proportion of 20% is to 79% by volume at 298 *K*. The water is in equilibrium with air at a pressure of 10 atm. At 298 *K* if the Henry's law constants for oxygen and nitrogen at 298 *K* are $3.30 \times 10^7$ mm and $6.51 \times 10^7$ mm respectively, calculate the composition of these gases in water.

40. Determine the amount of $CaCl_2$ ($i = 2.47$) dissolved in 2.5 litre of water such that its osmotic pressure is 0.75 atm at 27° C.

41. Determine the osmotic pressure of a solution prepared by dissolving 25 mg of $K_2SO_4$ in 2 litre of water at 25° C, assuming that it is completely dissociated.

## NCERT : Examplar

Click on the link below to download the pdf :
https://ncert.nic.in/pdf/publication/exemplarproblem/classXII/chemistry/leep502.pdf



SOLUTIONS

I. Multiple Choice Questions (Type-I)

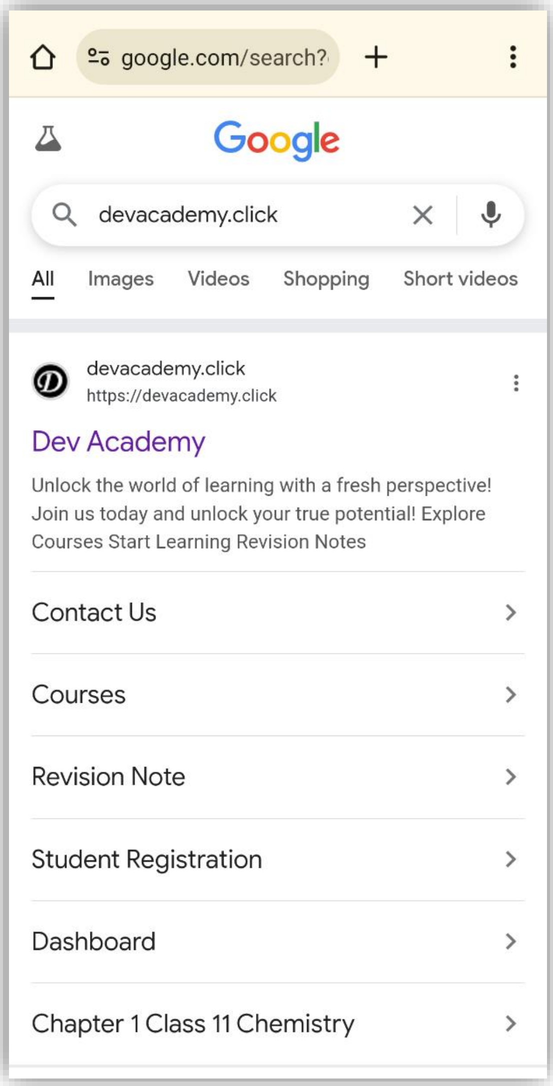
1. Which of the following units is useful in relating concentration of solution with its vapour pressure?
   (i) mole fraction
   (ii) parts per million
   (iii) mass percentage
   (iv) molality

2. On dissolving sugar in water at room temperature solution feels cool to touch.

Scan QR Code

Click on the link to visit our website:
[https://devacademy.click/](https://devacademy.click/)

**Scan QR Code**



devacademy.click
https://devacademy.click

Dev Academy

Unlock the world of learning with a fresh perspective! Join us today and unlock your true potential! Explore Courses Start Learning Revision Notes

- Contact Us
- Courses
- Revision Note
- Student Registration
- Dashboard
- Chapter 1 Class 11 Chemistry

## Follow us on social media

YouTube

WhatsApp

Instagram