SEMESTER–I (Period–I)

1
TOPIC

Solution and Solubility

C11CH1

Learning Objectives

Upon completion of this topic, learners will:

- Discuss the types of Solution
- Distinguish between dilute and concentrated solutions
- Analyze stock solution
- Analyze various concentration units
- Describe the colligative properties of solutions
- Discuss colloids
- Discuss factors affecting solubility
- Discuss the general principles of solubility
- Analyze the solubility curves
- Discuss the solubility of ionic substances and
- Apply the solubility table to determine the quantitative analysis of a solution.

1.1. SOLUTION

A solution is a homogeneous mixture of two or more pure substances. Solution retains the properties of both solvent and solute even if the solution is homogeneous.

Example: When salt is dissolved in water, it makes a homogeneous mixture called solution.

1. **Soda Water** is a solution of carbondioxide dissolved in water
2. **Tincture of Iodine** is a solution of iodine in ethyle alcohol
3. **Liquor ammonia** is a solution of ammonia dissolved in water.

A solution is made up of two components: *i.e.*, a solute and a solvent. Solvent is the component of solution present in larger amount and its physical state is same as that of the resulting solution.

Table 1.1. Different Types of Solutions

Type of Solution	*Solvent*	*Examples*
Gaseous Solutions	*Gas*	
• Solid in gas		Sublimation of solid in gas; camphor vapours in N_2 gas.
• Liquid in gas		Water vapours in air (mist).
• Gas in gas		Mixture of gases, air.
Liquid Solutions	*Liquid*	
• Solid in liquid		Salt in water, sucrose in water.
• Liquid in liquid		Alcohol in water, mixture of miscible liquids.
• Gas in liquid		Aerated drinks, CO_2 in water.
Solid Solutions	*Solid*	
• Solid in solid		Alloys; homogeneous mixture of two or more metals.
• Liquid in solid		Mercury in zinc, mercury in gold.
• Gas in solid		Adsorption of gases on metals, solution of hydrogen in palladium.

Homogeneous solution: Homogeneous solutions are solutions with uniform composition and properties throughout the solution. **For example:** Solution of sugar in water, solution of salt in water, a cap of tea, etc. In a homogeneous mixture all components of solution exist in same state.

Heterogeneous solution: Heterogeneous solutions are solutions with non uniform composition and properties throughout the solution. **Example:** A solution of oil in water is heterogeneous as concentration of oil and water remains different at different points in solution and same way properties of solution remain different at different point in the solution.

1.2. TYPES OF SOLUTION ON THE BASIS OF CONCENTRATION

On the basis of concentration (the amount of solute present in the given quantity of solution), solutions are classified into three types:

(*a*) Saturated solutions
(*b*) Unsaturated solutions
(*c*) Supersaturated solutions

Saturated Solutions

Saturated solution is a solution that has dissolved as much solute as it is possible to dissolve for a given amount of solvent and temperature. No more solute can be dissolved in given amount of solvent at that temperature. **Example:** Take 100 ml water at room temperature and keep on dissolving salt (NaCl) into it. A stage will come when salt will stop dissolving. At this stage when no further salt can be dissolved the solution is called saturated solution. If we add more solvent or increase the temperature then more solute can be dissolved.

Unsaturated Solutions

A solution that still can dissolved more solute into it for a given amount of solvent and temperature is known as unsaturated solution. Example: Take 100 ml of water and start dissolving salt (NaCl) into it. Salt will keep dissolving into it. Till salt will keep dissolving into water at the constant temperature, the solution is unsaturated solution. The moment salt stops dissolving into water, the solution becomes saturated solution.

Supersaturated Solutions

The solution that contain more solute than required to prepare a saturated solution. When we heat saturated solution and then add some solute it results into super saturated solution. Excess dissolved solute crystallizes if we cool the supersaturated solution and add few crystals of solute. Hence supersaturated solution is a solution that contains more than the average solvent that can be dissolved at a given temperature. The excess dissolved solute can be recrystalised by inserting some solute crystals which work as **seed crystals**.

Solubility: The maximum amount of solute that can be dissolved in 100 g of solvent at a given temperature is known as solubility of that solute. **For example:** 36 g of salt (NaCl) can be dissolved in 100 g of water at 20°C. Hence the solubility of NaCl is 36 g in water at 20°C.

Effect of temperature on solubility: We have observed that a maximum of 36 g NaCl can be dissolved in 100 g of water at 20°C. Now increase the temperature of solution to 25°C we see that more NaCl can be dissolved. It is evident that solution has now become unsaturated on increasing temperature. Hence, *the solubility of solute in a solvent increases on increasing temperature.* Now if we cool down this solution to 20°C again the excess NaCl which was dissolved on increasing temperature will deposit in solid crystalline form. In case of gases solubility decreases with increase of temperature.

1.3. DILUTE AND CONCENTRATED SOLUTIONS

Dilute solution: A solution that contain relatively small amount of solute dissolved in given amount of solution, is known as dilute solution. There is a scope for more solute to be dissolved in dilute solution to make it concentrated.

Concentrated solution: A solution that contain relatively more amount of solute dissolved in given amount of solution, is known as concentrated solution.

The terms dilute and concentrated do not tell any quantitative information but they are used to compare solutions. Dilute solution can become the concentrated solution if we add more solute to the solution. Concentrated solution can become dilute solution if we add more solvent to the solution.

1.4. CONCENTRATION OF SOLUTIONS

Concentration of solution means describing its composition. Qualitatively it can be described by using the word *dilute* for solutions having very small quantity of solute and the word *concentrated* for solutions having large quantity of solute. However, this kind of description is inadequate and leads to confusion. Therefore, quantitative description which is more appropriate is used. Quantitatively, concentration of a solution refers to *the amount of solute present in the given quantity of solution or solvent.* The concentration of the solution may be expressed in any of the following ways:

1. Mass Percentage (% mass)

Mass percentage may be defined as the *number of parts by mass of solute per hundred parts by mass of solution.* **For example:** a 5% (aqueous) solution of sugar by mass means that per 100 g of solution contain 5 g of sugar.

Let W_B be the mass of solute (B) and W_A be the mass of solvent (A), then

$$\text{Mass percentage of B} = \frac{W_B}{W_A + W_B} \times 100 \qquad \text{...(1.1)}$$

2. Volume Percentage (% volume)

This mode of concentration is used in case of solutions when *solutes* and *solvents* both are *liquids*. Volume percentage may be defined as *the number of parts by volume of solute per hundred parts by volume of solution*. **For example:** a 25% solution of ethyl alcohol (by volume) means that 100 cm^3 of the solution contain 25 cm^3 of ethyl alcohol and 75 cm^3 of water.

Let V_A and V_B be the volumes of component A and B, then

Volume percentage of B

$$= \frac{V_B}{V_A + V_B} \times 100 \qquad \text{...(1.2)}$$

Mass-Volume Percentage (W/V)

The concentration of the solution is also expressed in terms of mass-volume percentage. *It is the mass of the solute present in 100 cm^3 of the solution.* **For example:** 20% (W/V) solution of NaOH means that 100 cm^3 of the solution contains 20 g of NaOH.

3. Parts Per Million (ppm)

When a solute is present in very minute amounts, its concentration is expressed in parts per million. It may be defined as *the number of parts by mass of solute per million parts by mass of the solution*. It is abbreviated as ppm.

$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6.$$

$$\text{ppm} = \frac{W_B}{W_A + W_B} \times 10^6 \qquad \text{...(1.3)}$$

This mode of concentration is generally used to express very low concentrations such as hardness of water or concentration of Cl_2 in public supply of potable water.

4. Normality (N)

Normality of a solution is defined as *the number of gram-equivalents of the solute present per litre or per cubic decimeter of the solution. It may* *also be expressed in terms of milliequivalents of solute present in one mililitre of solution.* It is represented by N.

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

Gram-equivalents of solute (B) represents the ratio of its mass in gram (W_B) to its equivalent mass (E_B). Also, the ratio of the mass of solute in gram (W_B) to the volume of the solution in litre (V_L) represents the **strength** of the solution. Thus,

$$\text{Normality (N)} = \frac{W_B(g)}{E_B \times V_{(L)}}$$

or $$\frac{\text{strength of solution (gL}^{-1}\text{)}}{E_B}$$

or $$\frac{W_B(g) \times 1000}{E_B \times V_{(mL)}} \qquad \text{...(1.4)}$$

A solution having normality equal to unity is called a *normal solution.* Such a solution contains one gram equivalent of solute per litre of solution.

5. Molarity (M)

Molarity of a solution is defined as *the number of gram mole of the solute present per litre or per cubic decimeter of the solution.* It may also be expressed in terms of millimol of solute present per mililitre of solution. It is represented by M.

$$\text{Molarity (M)} = \frac{\text{Moles of solute}}{\text{Volume of solution in litres}}$$

$$= \frac{\text{Mass of solute in gram}}{\text{Molar mass of solute} \times \text{Volume of solution (L)}}$$

Now, moles of the solute (n_B) represents the ratio of mass of solute in gram (W_B) to its molar mass (M_B). Thus, molarity can be represented by the expressions.

$$M = \frac{n_B}{V_{(L)}} \quad \text{or} \quad \frac{W_B(g)}{M_B \times V_{(L)}}$$

or $$\frac{\text{Strength (gL}^{-1}\text{)}}{M_B} \quad \text{or} \quad \frac{W_B(g) \times 1000}{M_B \times V_{(mL)}} \qquad \text{...(1.5)}$$

A solution having molarity equal to unity is called ***molar solution***. Such a solution contains one mole of solute per litre of solution. The solutions having concentration equal to *0.5 M, 0.1 M* and *0.01 M* are called *semimolar, decimolar* and *centimolar* solutions respectively. Molarity is expressed in units of ***mol L^{-1}*** or ***mol dm^{-3}***. It may be noted that *both normality as well as molarity of a solution change with change in temperature*.

6. Molality (m)

Molality of a solution may be defined as *the number of gram mole of the solute present per kilogram (1000 g) of the solvent*. It is represented by *m*.

$$= \frac{\text{Mole of solute}}{\text{Mass of solvent (kg)}}$$

$$= \frac{\text{Mass of solute (g)}}{\text{(Molar mass of solute)} \times \text{(Mass of solvent (kg))}}$$

or $$m = \frac{n_B}{W_A(\text{kg})} \text{ or } \frac{W_B(\text{g})}{M_B \times W_A\ (\text{kg})}$$

or $$\frac{W_B(\text{g}) \times 1000}{M_B \times W_A\ (\text{g})} \qquad ...(1.6)$$

A solution containing one mole of solute per 1000 g of solvent has molality equal to unity and is called a ***molal solution***. Molality is expressed in units of moles per kilogram ***(mol kg^{-1})***. The *molality of a solution does not change with change in temperature.*

1.5. COLLIGATIVE PROPERTIES OF SOLUTIONS

Dilute solutions of non-volatile solutes exhibit a certain set of properties which are independent of the identity of the solute and their values depend on the molar concentration of the solute in the solution. These properties are collectively called *colligative properties*. ***Colligative properties*** may, thus, be defined as *properties of dilute solutions of non-volatile solutes whose value depend upon the concentration of solute particles in the solution but not on the individual identity of the solute.* Various colligative properties are:

(*i*) Relative lowering of vapour pressure

(*ii*) Elevation of boiling point

(*iii*) Depression of freezing point

(*iv*) Osmotic pressure.

Relative Lowering of Vapour Pressure ($\Delta p/p_A^\circ$)

We have studied that for a solution of non-volatile solute the relative lowering of vapour pressure is equal to the mole fraction of the solute. This holds true even for dilute non-ideal solutions because when the concentration of solute is low, the solutions behave as ideal solutions:

$$\frac{\Delta p}{p_A^o} = x_B$$

where, $\Delta p = p_A^\circ - p_A$ = lowering of vapour pressure

p_A° = vapour pressure of pure solvent

x_B = mole fraction of solute.

Relative lowering of vapour pressure depends upon relative number of solute and solvent molecules but does not depend upon their nature and hence, it is a colligative property.

Determination of Molar Mass of Solute from Relative Lowering of Vapour Pressure. Molar mass of non-volatile substance can be determined from relative lowering of vapour pressure. A known mass (W_B) of the solute is dissolved in a known mass (W_A) of solvent to prepare a dilute solution and relative lowering of vapour pressure is determined experimentally. Knowing the molar mass (M_A) of the solvent, molar mass (M_B) of the solute can be determined as shown under:

$$n_A = \frac{W_A}{M_A};\ n_B = \frac{W_B}{M_B}$$

$$x_B = \frac{n_B}{n_A + n_B} = \frac{W_B/M_B}{W_A/M_A + W_B/M_B}$$

Relative lowering of vapour pressure is given by

$$\frac{\Delta p}{p_A^o} = \frac{p_A^o - p_A}{p_A^o} = x_B = \frac{W_B/M_B}{W_A/M_A + W_B/M_B}$$

For dilute solutions $W_B/M_B << W_A/M_A$ and hence in the above expression W_B/M_B may be neglected in the denominator as compared with W_A/M_A.

$$\therefore \qquad \frac{p_A^o - p_A}{p_A^o} = \frac{W_B/M_B}{W_A/M_A} = \frac{W_B}{M_B} \cdot \frac{M_A}{W_A}$$

$$= \frac{W_B M_A}{M_B W_A} - \frac{P_A^o - P_B^o}{P_A^o}$$

or $$M_B = \frac{W_B \,.\, M_A}{W_A}\left(\frac{p_A^o}{p_A^o - p_A}\right)$$

or $$M_B = \frac{W_B\ M_A}{W_A\ (\Delta p/p_A^o)} \qquad \text{...(1.7)}$$

In these expressions, all the parameters except M_B are known and hence, M_B can be calculated.

Example 1.1. *The vapour pressure of 2% aqueous solution of a non-volatile substance X at 373 K is 755 torr. Calculate the molar mass of the solute. Vapour pressure of pure water at 373 K is 760 torr.*

Solution. Here,

Mass of the solvent $W_A = 100 - 2 = 98$ g

Mass of the solute $W_B = 2$ g

Molar mass of solvent $(M_A) = 18$ g mol^{-1}

Molar mass of solute $(M_B) = ?$

Vapour pressure of pure water $(p_A^o) = 760$ torr

Vapour pressure of solution $(p_A) = 755$ torr.

Now, for dilute solutions, $M_B = \frac{W_B\ M_A}{W_A}\left(\frac{p_A^o}{p_A^o - p_A}\right)$

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

$$= \frac{2 \times 18 \times 760}{98 \times 5} = \mathbf{55.8\ g\ mol^{-1}.}$$

Elevation in Boiling Point

We know that dissolution of non volatile solute in a liquid causes lowering of its vapour pressure. This further results in elevation of boiling point as explained below.

The **boiling point** *of a liquid may be defined as the temperature at which its vapour pressure becomes equal to atmospheric pressure.* The effect of addition of a **non-volatile** solute on the boiling point is shown in Fig. 1.1. The variation of vapour pressures of pure liquid and its solution containing non-volatile solute with temperature are represented by the curves AB and CD respectively. It is evident from the plot that at each temperature the vapour pressure of solution is lower than that of the pure solvent and thus, the vapour pressure curve for the solution runs below that of the pure solvent. At temperature T_0, the vapour pressure of the pure solvent becomes equal to the atmospheric pressure. Therefore, T_0 is the boiling point of the pure solvent. The vapour pressure of the solution at T_0 is much less than the atmospheric pressure and therefore, it is necessary to heat the solution to a higher temperature, say T_1, so that its vapour pressure becomes equal to the atmospheric pressure. Hence, T_1 is the boiling point of the solution. Thus, it is clear that the solution boils at a temperature higher than the pure solvent. Evidently, $T_1 - T_0$ (or ΔT_b) is the **elevation in boiling point.** Since magnitude of ΔT_b depends on the lowering of vapour pressure (Δp). Thus,

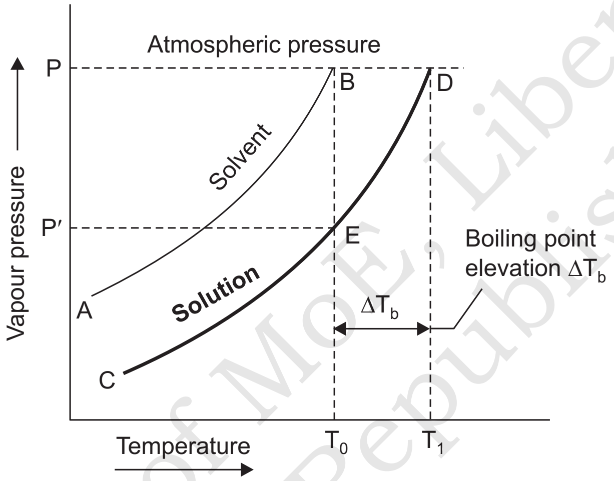


Fig. 1.1. Vapour pressure curves explaining elevation of boiling point.

$$\Delta T_b \propto \Delta p$$

According to Raoult's law, $\Delta p \propto x_B$

$$\therefore \quad \Delta T_b \propto x_B$$

or

$$\Delta T_b = kx_B = k\frac{n_B}{n_A + n_B}$$

$$= k\frac{W_B/M_B}{W_A/M_A + W_B/M_B}$$

For dilute solutions $\frac{W_B}{M_B} << \frac{W_A}{M_A}$ and hence, $\frac{W_B}{M_B}$ may be neglected in denominator as compared to W_A/M_A.

$$\therefore \quad \Delta T_b = k\,\frac{W_B/M_B}{W_A/M_A} = k\,\frac{n_B}{W_A}\,M_A \qquad \left[\because \frac{W_B}{M_B} = n_B\right]$$

If W_A is the mass of solvent in kg, then $\frac{n_B}{W_A}$ is equal to molality (m) of the solution

$$\Delta T_b = kM_A\,m$$

Here k and M_A are constants for a given solvent, and hence their product, *i.e.*, kM_A is replaced by another constant K_b.

$$\Delta T_b = K_b\,m \qquad \text{...(1.8)}$$

where K_b is called boiling point-elevation constant or molal elevation constant or molal ebullioscopic constant of the solvent.

As is clear from Eq. (1.8), *elevation in boiling point depends upon the relative number of moles of solute and solvent but does not depend upon nature of solute,* **so it is a colligative property.**

Determination of Molar Mass of an Unknown Non-volatile Compound from Elevation of Boiling Point

To calculate the molar mass of an unknown non-volatile compound a known mass (say W_B g) of it is dissolved in a known mass (say W_A g) of some suitable solvent and elevation in its boiling point (ΔT_b) is determined. Let M_B be the molar mass of the compound. Then

Molality of solution,

$$m = \frac{W_B}{M_B}\,\frac{1000}{W_A}$$

We know, $\Delta T_b = K_b \times m = K_b \cdot \frac{W_B}{W_A} \cdot \frac{1000}{M_B}$

$$M_B = \frac{K_b \times W_B \times 1000}{W_A \times \Delta T_b} \qquad \text{...(1.9)}$$

Knowing K_b, W_B, W_A and ΔT_b, the molar mass of the compound can be calculated from the above relation.

The method of determining the molar mass of a substance by the study of elevation in boiling point is known as **ebullioscopic method.**

Example 1.2. *Dissolution of 10 g of a non-volatile solute in 100 g of benzene raises its boiling point by 1°. Calculate the molar mass of solute. (K_b for benzene 2.53 Km^{-1})*

Solution. Mass of solute (W_B) = 10 g

Mass of solvent (W_A) = 100 g

Elevation in boiling point ΔT_b = 1°

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

or

$$M_B = K_b \frac{W_B}{W_A} \frac{1000}{\Delta T_b} = \frac{2.53 \times 10 \times 1000}{100 \times 1}$$

$$= \mathbf{253\ g\ mol^{-1}}.$$

Depression in Freezing Point

Freezing point of a substance is the temperature at which solid and liquid phases of the substance coexist. It is defined as the *temperature at which its solid and liquid phases have the same vapour pressure.*

The freezing point of a pure liquid is fixed. Now, if a non-volatile solute is dissolved in the pure liquid to constitute a solution, there occurs a lowering in the freezing point. *The freezing point of solution refers to the temperature at which the vapour pressure of the solvent in two phases, i.e., liquid solvent and solid solvent is the same.* Since, the vapour pressure of solvent in solution is lowered, it becomes equal to that of the solid solvent at a lower temperature (Fig. 1.2).

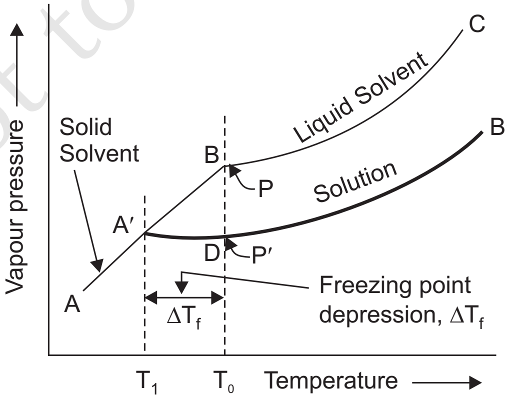


Fig. 1.2. Depression of freezing point.

Here AB, BC and A′B′ are the vapour pressure curves of solid solvent (ice), liquid solvent (water) and solution containing non-volatile solute respectively.

Evidently the freezing point of the pure solvent is the temperature corresponding to the point B (T_0 K) and that of the solution is the temperature corresponding to the point A′ (T_1 K). Clearly, ($T_0 - T_1$) K or ΔT_f is the freezing point depression. The magnitude of ΔT_f is determined by lowering of vapour pressure (Δp), which is directly proportional to the mole fraction of the solute. Thus,

$$\Delta T_f \propto \Delta p \text{ and } \Delta p \propto x_B$$

$$\therefore \quad \Delta T_f = kx_B = k\,\frac{n_B}{n_A + n_B}$$

$$= k\,\frac{W_B/M_B}{W_A/M_A + W_B/M_B}$$

For dilute solution, $\frac{W_B}{M_B} << \frac{W_A}{M_A}$ and hence, $\frac{W_B}{M_B}$ may be neglected in denominator as compared to W_A/M_A.

$$\therefore \quad \Delta T_f = k\,\frac{W_B/M_B}{W_A/M_A} = k\,\frac{n_B}{W_A}\,M_A$$

If W_A is the mass of solvent in kg, then $\frac{n_B}{W_A}$ is equal to molality (m) of the solution

$$\Delta T_f = kM_A m \qquad (k.M_A = K_f)$$

$$\therefore \quad \Delta T_f = K_f\, m \qquad \text{...(1.10)}$$

where K_f is called Freezing point depression constant or molal depression constant or cryoscopic constant of the solvent.

As is clear from Eq. (1.10), *depression in freezing point depends upon relative number of moles of solute and solvent but does not depend upon nature of solute, so it is a* ***colligative property.*** It may be noted that freezing point is not a colligative property. It is ΔT_f which is colligative property.

When molality (m) of the solution is unity, Eq. (1.10) becomes

$$\Delta T_f = K_f$$

Hence, **molal depression constant** may be defined as the *depression in freezing point when one mole of non-volatile solute is dissolved per* *kilogram (1000 g) of solvent.* The **units** of K_f are **K kg mol^{-1}.** Also the value of K_f for 100 g of solvent will be ten times the value of molal depression constant.

K_f is related to molar enthalpy of fusion of solvent as:

$$K_f = \frac{M_A \, RT_f^{\,2}}{\Delta_{fus}H \times 1000} \qquad \text{...(1.11)}$$

where, M_A = Molar mass of solvent

R = Universal gas constant

T_f = Freezing point of pure solvent

$\Delta_{fus}H$ = Enthalpy of fusion of solid solvent.

Determination of Molar Mass of an Unknown Non-volatile Compound from Depression in Freezing Point. To determine the molar mass of an unknown non-volatile compound a known mass (say W_B g) of it is dissolved in a known mass (say W_A g) of some suitable solvent and depression in its freezing point (ΔT_f) is determined. Let M_B be the molar mass of the compound. Then,

Molality of the solution, $m = \frac{W_B}{M_B} \frac{1000}{W_A}$

We know

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

$$M_B = \frac{K_f \times W_B \times 1000}{W_A \times \Delta T_f} \qquad \text{...(1.12)}$$

Knowing K_f, W_B, W_A and ΔT_f, the molar mass of the compound can be calculated from the above relation.

The method of determining molecular mass of a substance by the study of depression in freezing point is called **cryoscopic method.**

Example 1.3. *100 g of the solution contains 5 g of urea (NH_2CONH_2) and 10 g of glucose ($C_6H_{12}O_6$). What will be the freezing point of the solution. K_f for water is 1.86 K kg mol^{-1}.*

Solution. Mass of solution = 100 g

Mass of urea = 5 g

Mass of glucose = 10 g

Mass of water (W_A) = 100 – (5 + 10) = 85 g

Moles of urea = $\frac{5\text{ (g)}}{60\text{ (g mol}^{-1})}$ = 0.083 mol

Moles of glucose = $\frac{10\text{ (g)}}{180\text{ (g mol}^{-1})}$ = 0.055 mol

Total moles of solute (n_B) = 0.083 + 0.055
= 0.138 mol

Total molality of solution (m) = $\frac{0.138\text{ (mol)}}{85 \times 10^{-3}\text{ (kg)}}$
= 1.62 mol kg^{-1}

$$\Delta T_f = K_f \times m$$
$$= 1.86\text{ (K kg mol}^{-1}) \times 1.62\text{ (mol kg}^{-1})$$
$$= 3.01\text{ K}$$

Freezing point of solution = 273 – 3.01
= **269.69 K** or **– 3.01°C**.

Concept of Osmotic Pressure

In order to understand concept of osmotic pressure, take a thistle funnel covered with semi-permeable membrane and put $CuSO_4$ solution in it. Now place this funnel in a beaker containing pure water. It is observed that water flows from beaker into the funnel (Fig. 1.3). As a result of this solvent flow, the level of solution in funnel starts rising. After sometime the level of solution in the thistle funnel becomes constant indicating that process of osmosis has stopped.

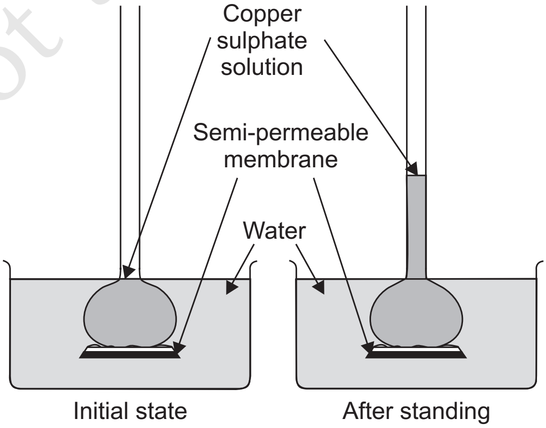


Fig. 1.3. Osmosis.

At this stage hydrostatic pressure of the column is sufficient to stop inward flow of solvent into solution. *The excess hydrostatic pressure which builds up as a result of osmosis is called* ***osmotic pressure.***

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

The osmotic pressure can also be defined in another way. In order to understand this, let us consider the phenomenon of osmosis in a special type of apparatus as shown in Fig. 1.4.

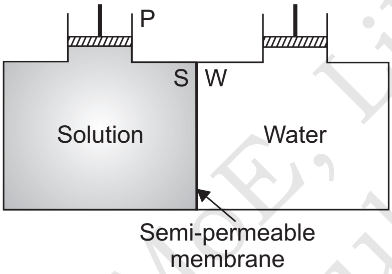


Fig. 1.4. Definition of osmotic pressure.

The apparatus consists of a chamber divided into two water-tight compartments (S and W) by a semi-permeable membrane and fitted with the water-tight pistons. On putting the solution in compartment S and water in the compartment W, the piston P will be displaced upwards due to the movement of water from W to S. To stop this movement of water, we have to apply mechanical pressure on solution side. The pressure just sufficient to stop osmosis will be the osmotic pressure.

Thus, the **osmotic pressure** may also be defined as the *excess pressure that must be applied to the solution side to prevent the passage of solvent into it through a semi-permeable membrane.*

The osmotic pressure is a colligative property

For a given solvent the osmotic pressure depends only upon the molar concentration of solute but does not depend upon its nature. Osmotic pressure is related to the number of moles of the solute by the following relation:

$$\pi \mathbf{V} = \mathbf{nRT} \qquad \ldots(1.13)$$

or

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

$$\pi = \mathbf{CRT} \qquad \text{...(1.14)}$$

C = Conc. in mol L^{-1}

R = Gas constant (bar LK^{-1} mol^{-1})

T = Temperature (K) n = mol of solute

V = Volume of soln. (L)

Eqn. (1.14) is called **Van't Hoff's solution equation.**

Relationship of Osmotic Pressure with Other Colligative Properties

Osmotic pressure (π) is related to relative *lowering of vapour pressure* *($\Delta p/p_A^\circ$), elevation of boiling point (ΔT_b)* and *depression freezing point* *(ΔT_f)* according to the following relations.

(*i*) π and $\frac{\Delta p}{p_A^o}$ $$\pi = \left(\frac{\Delta p}{p_A^o}\right) \times \frac{dRT}{M_A} \qquad \text{...(1.15)}$$

(*ii*) π and ΔT_b $$\pi = \Delta T_b \times \frac{dRT}{1000 \times K_b} \qquad \text{...(1.16)}$$

(*iii*) π and ΔT_f $$\pi = \Delta T_f \times \frac{dRT}{1000 \times K_f} \qquad \text{...(1.17)}$$

In the above relations,

- π = Osmotic pressure,
- d = Density of solution at temperature T
- R = Universal gas constant,
- M_B = Molar mass of solute
- K_b = Molal elevation constant of solvent,
- K_f = Molal depression constant of solvent.

Determination of Osmotic Pressure

There are several methods for the determination of osmotic pressure. The most simple and preferred method is Berkley and Hartley's method which is being described here.

Berkley and Hartley's Method. This method involves the measurement of external pressure which is just sufficient to prevent the entry of solvent into solution through a semi-permeable membrane. This pressure is equal to the osmotic pressure of the solution.

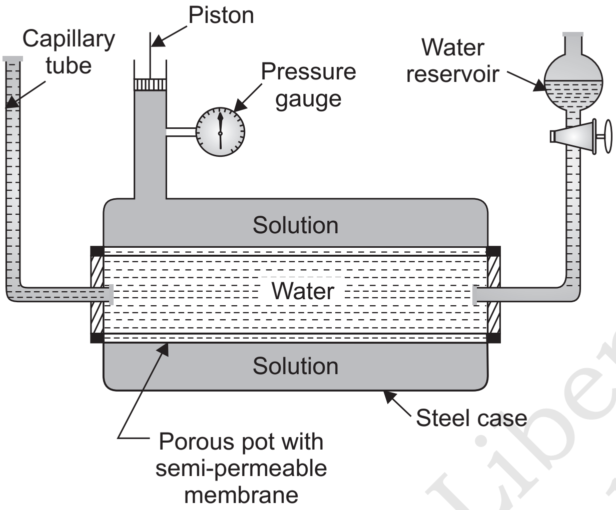


Fig. 1.5. Determination of osmotic pressure.

The apparatus consists of a strong vessel made up of steel into which a porous pot is fitted. The walls of the porous pot are coated with a semi-permeable membrane of copper ferrocyanide. The porous pot is fitted with a capillary tube on one side and water reservoir on the other. The steel vessel is fitted with a piston and pressure gauge as shown in Fig. 1.5.

Water and solution are taken in the porous pot and steel vessel respectively. Due to osmosis, water tends to move into steel vessel from the porous pot through the membrane. It is indicated by the fall in water level in the capillary tube. This flow of water is stopped by applying the pressure on the solution with the help of the piston, so that the level of water in the capillary tube does not change. The pressure so applied is equal to the osmotic pressure and can be measured from the pressure gauge.

Example 1.4. *Calculate the osmotic pressure of a solution containing 3.42 g of sucrose per litre at 400 K. Molar mass of sucrose is 342 g* mol^{-1}. $R = 0.083$ *bar L* mol^{-1} K^{-1}.

Solution. We know that $\pi = \frac{n_B}{V} RT$

Mass of solute (M_B) = 3.42 g

Molar mass of source = 342 g mol^{-1}

Moles of solute (n_B) = $\frac{3.42\ (g)}{342\ (g\ mol^{-1})}$ = 0.01 mol

Volume of solution (V) = 1 litre

$$T = 400\ \text{K}$$

$$\pi = \frac{n_B RT}{V}$$

$$= \frac{0.01\ (\text{mol}) \times 0.083\ (\text{L bar mol}^{-1}\ \text{K}^{-1}) \times 400\ (\text{K})}{1\ (\text{L})}$$

$$= \mathbf{0.332\ bar.}$$

Abnormal Molar Masses

In the previous section, we have studied the colligative properties of dilute solutions and their relationship with the molar masses of the solutes. The different relations between colligative properties and molar mass are applicable only to the solutions of *non-electrolytes* and are based on the following assumptions:

(*a*) *The solution is dilute, so that Raoult's Law is obeyed.*

(*b*) *The molecular state of solutes remains unchanged, i.e., they neither undergo dissociation nor association in solution.*

When we measure the colligative properties of electrolytic solutions or the solutions where above assumptions are not valid, we find discrepencies between the observed and the calculated values of colligative properties.

Consequently, the molar masses of such solutes as determined from the experimentally measured values of the colligative properties differ widely from their actual molar masses. Such substances, therefore, are said to exhibit **abnormal molar masses** in solutions.

The anomalies in molar masses are primarily due to:

(*i*) *Association of solute molecules* or

(*ii*) *Dissociation of solute particles in solutions.*

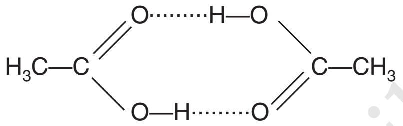
(*i*) **Association of solute molecules.** Certain solutes undergo association in their solutions.

Association involves the combination of two or more molecules of solute to form a single entity. For example, combination of n molecules of solute **A** results in single associated entity as $\mathbf{(A)}_n$. This eventually leads to a **decrease** in the number of molecular species in the solution thereby decreasing the magnitude of colligative property.

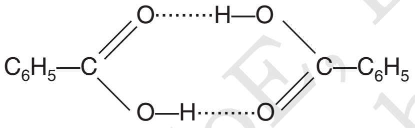
$$\text{Molar mass of solute} \propto \frac{1}{\text{Colligative property}}$$

As colligative properties and molar mass are inversely related to each other, the experimental values of molar masses in such cases are **higher** than the normal values for unassociated solutes.

For example, ethanoic acid dissolved in benzene shows a molar mass of 120 $g\ mol^{-1}$ (normal molar mass is 60 g mol^{-1}). Similarly, benzoic acid dissolved in benzene is found to have molar mass double of its normal molar mass. This is explained by the fact, that both acetic acid and benzoic acid form ***dimers*** in solution due to hydrogen bonding.



Acetic acid



Benzoic acid

(*ii*) **Dissociation of solute molecules.** Electrolytes like acids, bases and salts dissociate in aqueous solutions to form two or more ionic particles. Therefore, the number of particles, in solutions of such substances, increases. Accordingly, such solutions exhibit **higher** values of colligative properties. Since, colligative properties are inversely related to molar masses, therefore, molar masses of such substances as calculated from colligative properties will be **less** than their normal values.

For example, KCl dissociates into K^+ and Cl^- ions when dissolved in water. So the number of solute particles in its solution would be double the number of particles if no dissociation had taken place. Hence, it is expected to have molar mass (on the basis of colligative properties) equal to half of its normal molar mass, *i.e.*, $\frac{74.5}{2}$ or 37.25 g mol^{-1}. However, the molar mass of KCl is found to be 40.3 g mol^{-1} by studies of depression in freezing point. The difference in the two values is due to the fact that there are strong attractive forces present in the oppositely charged ions of the strong electrolyte in solution. These electrical forces hold together a number of the ion pairs. Thus, such electrolytes are incompletely dissociated and the number of the ions formed in solution is not exactly the double but is somewhat less. Consequently, there is difference in the values of molar masses.

1.6. COLLOIDAL SOLUTIONS OR COLLOIDS

A ***colloid*** *is a solution in which size of solute particles lies between 1 nm to 100 nm.* Thus, solute particles in colloids are bigger than the solute particles in true solutions but smaller than the particles in suspensions. Milk, gum solution, blood, milk-cream, ink, smoke, mist, boot-polish are some common examples of colloidal solutions.

It may be noted that a colloidal solution is heterogeneous in nature and always consists of at least two phases: *the dispersed phase* and the *dispersion medium.*

(*a*) **Dispersed phase.** *It is the component present in small proportion and consists of particles of colloidal dimensions (1 nm to 100 nm).*

(*b*) **Dispersion medium.** *The solvent like medium in which colloidal particles are dispersed is called dispersion medium.* In a colloidal solution of sulphur in water, sulphur particles constitute disperse phase and water constitutes dispersion medium.

The two phases, namely dispersed and dispersion can be solid, liquid or a gas. Thus, different types of colloidal solutions are possible depending upon the physical states of the two phases (Table 1.2).

Table 1.2. Types of colloidal solutions.

Dispersed Phase	*Dispersion Medium*	*Type*	*Examples*
Liquid	Gas	Aerosol	Mist, fog, clouds, insecticide sprays,
Solid	Gas	Aerosol	Smoke, dust-storm, automobile exhaust
Gas	Liquid	Foam	Soap lather, whipped cream
Liquid	Liquid	Emulsion	Milk, cod liver oil, face-cream
Solid	Liquid	Sol	Gold sol, starch sol, muddy water, Milk of magnesia.
Gas	Solid	Solid foam	Foam rubber, pumice stone, sponge
Liquid	Solid	Gel	Cheese, butter, jelly, shoe-polish
Solid	Solid	Solid sol	Coloured gem stone, some alloys, milky glass.

The colloidal solutions having fluid-like appearance are called ***sols.*** The dispersion medium in sols is generally liquid. Colloids are sometimes given specific names depending upon the nature of the dispersion medium. Some common examples are as follows:

Dispersion Medium	*Name of Colloids*
Water	Hydrosols
Alcohol	Alcosols
Benzene	Benzosols
Gases	Aerosols

Properties of Colloidal Solutions

1. **Heterogeneous Nature.** A colloidal solution is heterogeneous in nature. It consists of two phases: *dispersed phase* and *dispersion medium.*
2. **Filtrability**. The size of the colloidal particles is less than the pores of a filter paper. Therefore, they easily pass through a filter paper. Colloidal particles, however, cannot pass through the parchment paper or an animal membrane or ultra-filter.
3. **Tyndall Effect.** When a strong beam of light is passed through a colloidal solution placed in dark place, the path of the beam gets illuminated by a bluish light (Fig. 1.6). This phenomenon is called **Tyndall effect.** The phenomenon is due to the scattering of light by the colloidal particles.

   The same phenomenon is noticed when a beam of sunlight enters a dark room through a small slit, due to scattering of light by dust particles in the air.

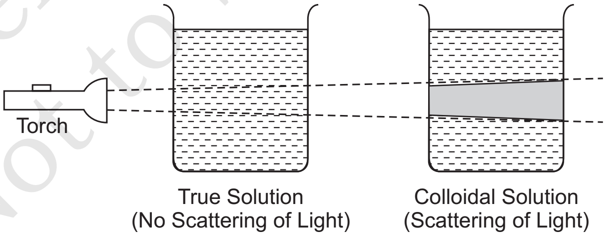


Fig. 1.6. Tyndall effect.

4. **Visibility.** Colloidal particles are too small to be seen by the naked eye. They, however, scatter light and become visible when viewed through an **ultramicroscope.**
5. **Brownian Movement.** When colloidal particles are seen under an ultramicroscope, the particles are found to be in constant motion in zig-zag path in all possible directions (Fig. 1.7). *This*

zig-zag motion of colloidal particles is called **Brownian movement.** The movement of the particles is due to the collisions with the molecules of the dispersion medium.

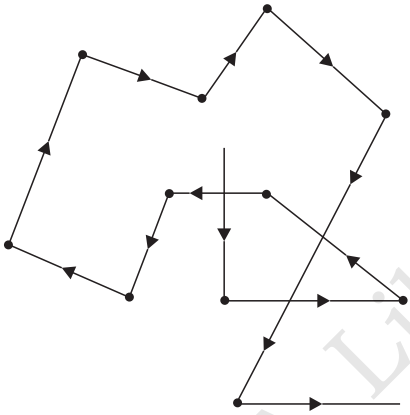


Fig. 1.7. Brownian movement.

6. **Diffusion.** Colloidal particles diffuse from a region of higher concentration to that of lower concentration. However, because of their bigger size colloidal particles move slowly and hence diffuse at slower rate.
7. **Sedimentation or Settling.** Under the influence of gravity, the solute particles tend to settle down very slowly. This rate of settling down or sedimentation can be accelerated by the use of high speed centrifuge called *ultra-centrifuge*.

A comparison between suspension, colloidal solution and true solution has been given in Table 1.3.

Table 1.3. Distinction between true solutions, colloidal solutions and suspensions.

Name of the Property	*True Solutions*	*Colloidal Solutions*	*Suspensions*
1. **Size of particles**	The solute particle in true solutions are molecules having diameter less than 1 nm	The particle size in colloidal solution lies in the range 1 nm to 100 nm.	The size of the particles in case of suspension is greater than 100 nm.

2. Visibility or appearance	The solute particles are invisible to the naked eye as well as under the most powerful microscope.	The solute particles are invisible to the naked eye but their scattering effect can be viewed with the help of a microscope.	The solute particles are visible even to the naked eye or can be seen with the help of a microscope.
3. Settling	The solute particles in the true solution do not settle.	The solute particles in the colloidal solution can be made to settle by centrifugation.	The solute particles in the suspension settle under gravity.
4. Filterability	The solute particles in the true solution diffuse rapidly, pass through a parchment membrane as well as filter paper.	The solute particles in the colloidal solution do not pass through a parchment membrane, but pass through a filter paper.	The solute particles in the suspension cannot pass through a parchment membrane or a filter paper.
5. Tyndall effect	True solution does not show Tyndall effect.	Colloidal solution shows Tyndall effect.	Suspension may or may not show Tyndall effect.
6. Brownian movement	True solution does not show Brownian movement.	Colloidal solution shows Brownian movement.	Suspension may show Brownian movement.

1.7. SOLUBILITY

It is commonly observed that some substances dissolve in water quite appreciably while there are many others which either dissolve to a smaller extent or do not dissolve at all. The extent to which a substance dissolve in a specified amount of solvent is expressed in terms of solubility. In general, solubility is defined as the amount of solute that can be dissolved in 100 gram of the solvent at the given conditions.

Another common way of expressing solubility of a substance at a given temperature *is maximum quantity of solute in moles (or gram) that can dissolve in solvent to form 1* dm^3 *of solution*. The units of solubility are ***mol*** $\boldsymbol{dm^{-3}}$ *or* ***g*** $\boldsymbol{dm^{-3}}$ or ***g per 100 g*** *of solvent*. The solubility of gases in water is also expressed in terms of its *mole fraction*. Solubility depends on nature of solute, and solvent as well as the conditions of temperature and pressure. Let us study the effect of these factors on solutions of solids and gases in liquids.

Solubility of Solid in liquid

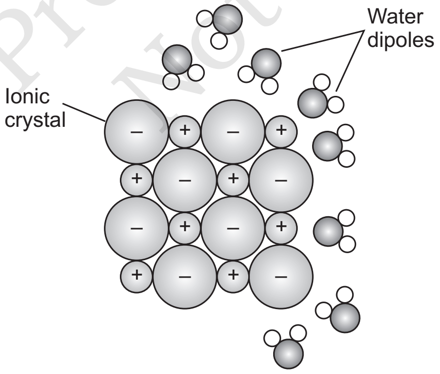
When a solid solute is added to solvent, dissolution of solute occurs. The solute particles go into solution and acquire random movement. The concentration of the solution gradually increases as more and more solute dissolves. The dissolved solute particles also collide with solid solute and some of them separate out of solution and get deposited there. This process is called *crystallisation.* Soon a stage is reached when the two opposite processes; *dissolution* and *crystallisation* occur at the same rate and a state of dynamic equilibrium is established.

$$\textit{Solid solute} + \textit{Solvent} \rightleftharpoons \textit{Solution}$$

At this stage, the concentration of solution becomes constant at the given conditions because the number of solute particles going into solution will be equal to number of solute particles separating out of solution. Such a solution at which no more solute can be dissolved at the given conditions of temperature and pressure is called **saturated solution,** and the amount of solute dissolved in a given amount of solvent is called solubility. The solubility of solids is generally is expressed as the *amount of solid that can be dissolved in 100 grams of the solvent at a given temperature.* In fact, solubility refers to concentration of solute in a **saturated solution** at given temperature.

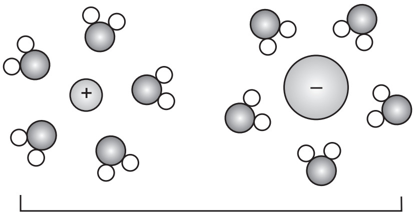
Cause of Solubility of Solids in Liquids

Dissolution of **ionic solids** in liquids occurs due to **ion-dipole** interactions. In order to understand it let us consider the dissolution of **ionic solids** in **water.** The attractive forces within the ionic solids are *interionic attractions.* When an ionic solid is dissolved in water, the cations and anions of the solid get attracted by the opposite ends



Hydration of ionic crystal

Fig. 1.8.



Hydrated ions

Fig. 1.9.

of water dipoles (Fig. 1.8). If ion-dipole attractive forces are stronger enough to overcome the interionic attraction, the ions are pulled out of crystal lattice and they pass into solution. In the solution, the ions behave as independent entities, but they remain surrounded by the envelop of water dipoles and are called hydrated ions (Fig. 1.9). This process is referred to as hydration of ions. ***Molecular solids*** do not ionise. Their dissolution in water involves the formation of *hydrogen-bonds* with water molecules.

In general, the energy required to break apart 1 mol of crystal lattice is called lattice energy and is represented by $\Delta_L H$. The energy released during hydration of particles furnished by one mole of solid is called hydration energy and is represented by $\Delta_{Hyd.}H$. It may be noted that $\Delta_L H$ is +ve while $\Delta_{Hyd.}H$ is –ve.

The net enthalpy change occurring during dissolution of 1 mol of solid ($\Delta_{sol.}H$) is given by the expression

$$\Delta_{Sol}H = \Delta_L H + \Delta_{Hyd}H$$

- If $\Delta_{Hyd}H \geq \Delta_L H$; Dissolution occurs with $\Delta_{Sol}H < 0$.
- If $\Delta_{Hyd}H$ is marginally < than $\Delta_L H$ even then dissolution takes place and $\Delta_{Sol}H > 0$.
- If $\Delta_L H$ is too large to be compensated by $\Delta_{Hyd}H$ then dissolution does not takes place.

Factors Affecting Solubility of Solids

The solubility of a solid solute in liquid depends on following factors.

(*i*) **Nature of solute.** Dissolution of solid solutes in liquids can be summed up in a phrase **"like dissolves like".** This means that, polar solutes dissolve in polar solvents and non-polar solutes dissolve in non-polar solvents. For example, ionic substances such as NaCl, KCl, KNO_3, etc., have larger solubilities in polar solvents like water but they have poor solubilities in non-polar solvents like CCl_4, CS_2, etc. On the other hand, non-polar solids such as I_2, S_8, etc., are more soluble in non-polar solvents like CCl_4, CS_2 but they are almost insoluble in polar solvents like water.

(*ii*) **Temperature.** Temperature has a marked effect on the solubility of a solid in liquid. The solubility may increase or decrease with the rise in temperature depending upon the value of $\Delta_{sol}H$. Let us recall, that saturated solution represents equilibrium between undissolved solute and dissolved solute

$$\textit{Solute} + \textit{Solvent} \rightleftharpoons \textit{Solution};\ \Delta_{Sol}H = \pm x.$$

(*a*) If the value of $\Delta_{\text{Sol}}H < 0$; *i.e.,* the solution process is **exothermic,** then according to Le-chatelier's principle, the increase of temperature will push the solution equilibrium in the backward direction (endothermic side). In other words, the solubility of such solutes **decreases** with rise in temperature. Some examples are, Li_2SO_4, Na_2SO_4, etc.

(*b*) If $\Delta_{\text{Sol}}H > 0$; *i.e.,* solution process is **endothermic**, then, increase of temperature will push the solution equilibrium in the forward direction (exothermic side). In other words, the solubility of such solutes **increases** with the rise in temperature. Some examples of such solutes are KCl, KNO_3, $NaNO_3$, etc.

1.8. SOLUBILITY CURVES

The plots of solubility of solids *vs* temperature are referred to as **solubility curves.** The various ionic substances can be divided into three categories on the basis of effect of temperature on solubility.

(*i*) ***Solids whose solubility increase continuously and gradually with rise in temperature.*** This happens in case of solids whose $\Delta_{\text{Sol}}H$ is > 0. Some examples are NaCl, KCl, $NaClO_3$, $Pb(NO_3)_2$, $AgNO_3$ etc. It is commonly observed that certain substances and hydrated salts.

(*ii*) ***Solids whose solubility decrease gradually with rise in temperature.*** This happens in case of solids whose $\Delta_{\text{Sol}}H < 0$. Li_2SO_4 and anhydrous salts like $CuSO_4$, Na_2SO_4 are common examples of this category.

(*iii*) ***Solids whose solubility does not increase or decrease regularly or continuously.*** This happens if a substances undergoes a change from one polymorphic form to another at particular temperature. For example, dissolution of $Na_2SO_4.10H_2O$ is endothermic but dissolution of Na_2SO_4 is exothermic. The conversion of $Na_2SO_4.10H_2O$ to Na_2SO_4 occurs at 34°C. Thus solubility of $Na_2SO_4.10H_2O$ increases with the rise in temperature till 34°C and thereafter it starts decreasing. The temperature at which this reversal of solubility occurs is often called **transition temperature.** The solubility curves of some substances are shown in Fig. 1.10.

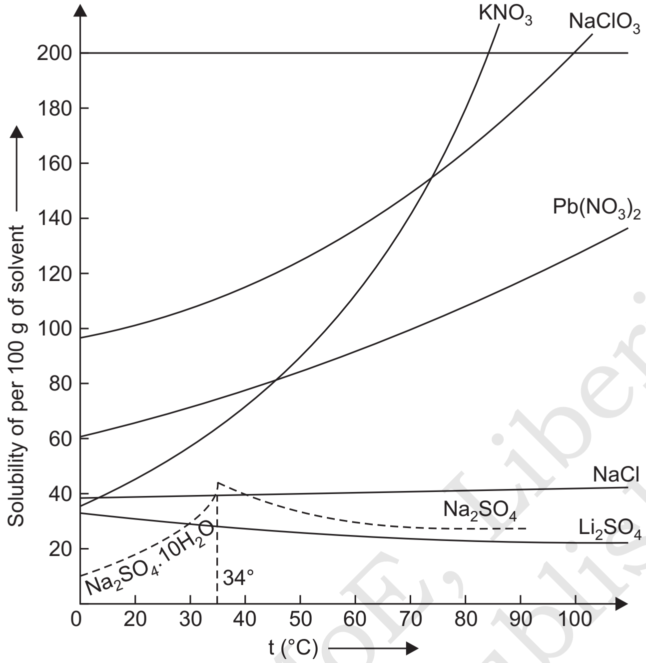


Fig. 1.10. Solubility curves of some substances.

Remember

With the increase in temperature the solubility of a solute

- increases if its dissolution process is endothermic.
- decreases if its dissolution process is exothermic.

Solubility of Gases in Liquids

When a gas is passed through the liquid solvent, the gas particles dissolve in liquid. The concentration of the solution gradually increases till the equilibrium point is reached and a *saturated solution* is obtained. At this stage the gas particles entering the solution phase and those escaping out of the solution surface have the same rate. The amount of gas present in a given amount of solvent at this saturation state is referred to as solubility of gas at the given conditions. The solubility of gases, however, is generally expressed either in *terms of number of mol of a gas that can dissolve per litre of the solvent at the given conditions* **(mol L^{-1})** or *more conveniently, in terms of mole fraction of the gas* **(x_B).**

Factors Affecting the Solubility of Gases

The following factors affect the solubilities of gases in liquids:

(*i*) **The nature of gas and the nature of solvent.** Different gases dissolve to a different extent even in the same solvent and same gas has different solubilities in different solvents. **For example,** non-polar gases like O_2, N_2, etc., are very less soluble in water whereas gases like HCl, SO_2, NH_3, CO_2, etc., are highly soluble in water because they undergo chemical reaction with water molecules.

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$$

$$SO_2(g) + H_2O(l) \rightleftharpoons HSO_3^-\ (aq) + H^+\ (aq)$$

$$CO_2(g) + H_2O(l) \rightleftharpoons HCO_3^-\ (aq) + H^+\ (aq)$$

These highly soluble gases in water do not dissolve in non-polar solvents like benzene, carbon tetrachloride, etc., because of their inability to react with these solvents.

(*ii*) **Effect of temperature.** *The solubilities of most of gases in water diminish with the rise in temperature.* **For example,** the amount of O_2 dissolved in water at 298 K is about one half of that at 273 K.

Dissolution of gases in liquids involves decrease in *molecular disorder.* Therefore, their dissolution in liquids is favoured by negative value of $\Delta_{sol}H$. This means that gases generally dissolve in liquids with the evolution of heat. The solution equilibrium can be represented as.

$$\textit{Gas + Liquid solvent} \rightleftharpoons \textit{Solution};\ \Delta H = -ve$$

Applying Le-Chatelier's principle on the above equilibrium, it can be explained that increase in temperature would push the equilibrium towards endothermic side *i.e.,* toward backward direction thereby decreasing the solubility of a gas.

The quantitative effect of temperature on the solubility of gases can be described by the expression similar to *Clapeyron's equation.*

$$\log \frac{C_2}{C_1} = \frac{\Delta_{Sol}H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

C_1 and C_2 are concentrations of solution at temperature T_1 and T_2 respectively and $\Delta_{Sol}H$ is enthalpy of dissolution of the gas. It may be noted that some gases do exhibit reverse trends with respect to some organic solvents.

(*iii*) **Effect of pressure.** Unlike solids and liquids, the solubility of gases vary appreciably with variation in pressure. This can be illustrated as follows. Consider a system as shown in Fig. 1.11 (*a*). Lower part is a solution and upper part is a gas at temperature T and pressure p_1. Assume the system to be in dynamic equilibrium. When the pressure is increased to p_2 by compressing the gas. The number of particles per unit volume over the solution will increase. This will result in the increase of rate at which the gas particles are striking the surface of solution to enter it, thereby, causing increase in the solubility of gas till new equilibrium is attained. Thus, increasing the pressure of gas above the solution increases its solubility.

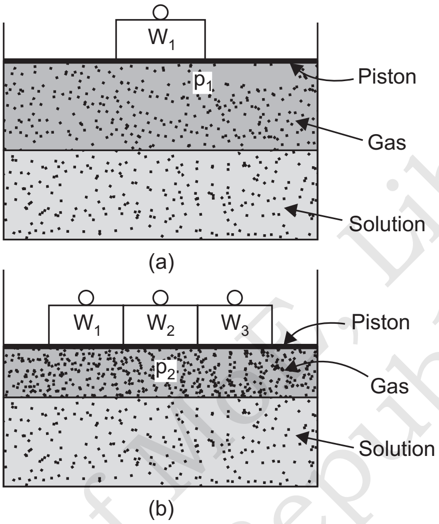


Fig. 1.11. Effect of pressure on solubility of gas pressure increases ($p_2 > p_1$), solubility also increases.

Henrys' Law

In 1805, an English Chemist William Henry gave an important generalisation called ***Henry's law*** on the basis of series of observations about the quantitative effect of pressure on the solubility of gases. The law states that ***the solubility of a gas at a given temperature is directly proportional to the pressure*** at which ***it is dissolved.***

If we take mole fraction of gas (x_B) at a given temperature as a measure of its solubility and p is the partial pressure of the gas in equilibrium with the solution, then according to Henry's law,

$$x_B \propto p \quad \text{or} \quad p \propto x_B \quad \text{or} \quad p = K_H \, . \, x_B \qquad ...(1.18)$$

where $\mathbf{K_H}$ is constant of proportionality and is called **Henry law constant.**

Solubility and Crystallization

We know that solubility of a solution increases on increase of temperature and more and more solute can be dissolved in a solvent by heating the solution. A stage comes when the solution becomes supersaturated solution. When this supersaturated solution is cooled crystallization of solute particles occurred. The small crystals may dissolve easily but at later stage will be formed due to crystallization because they will have lower solubility and the solution will be supersaturated with respect to the larger crystals. The solubility curve helps to select a suitable crystallization process. *e.g.* evaporative crystallization or cooling. Hence the knowledge of solubility is helpful for selection and design of crystallization process.

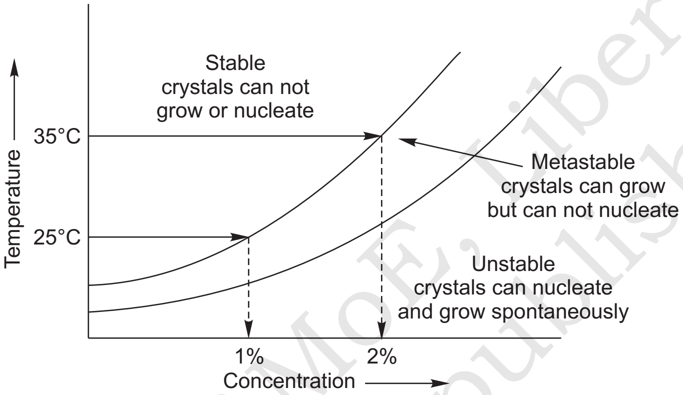


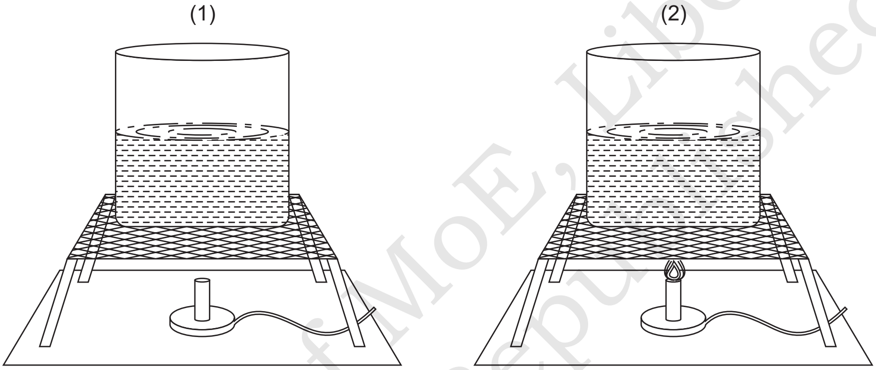
Fig. 1.12.

The concentration at which crystallization starts spontaneously even in the absence of heterogeneous nuclei, is called super solubility limit. Heterogeneous nuclei may be any foreign matter, dust or even scratches on the wall. Metastable region in the diagram is the area lying between solubility and super solubility concentrations. In meta states region crystals will form but spontaneous nucleation will not occur.

In the above graph we see that solute has an equilibrium solubility of 1% at 25°C and 2% at 35°C. A clean 2% solution cooled from 35°C to 25°C will still appear to be stable because there will be no crystals to grow. However the introduction of any nuclei would cause a rapid precipitation of half of the material from solution. Hence we do not normally use heat, ultrasound, or high sheer when measuring solubilities and we would usually ensure that there are nucleation sites present in the vessel.

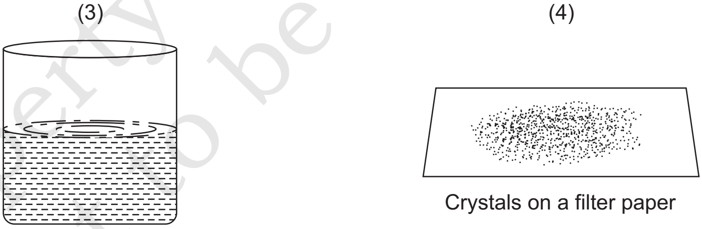
Crystallization and Recrystallization

Crystallization: When we prepare a solution by dissolving a solid substance into a liquid constantly stirring it, the solid substance dissolved in the liquid. When we keep on dissolving more and more substance in the liquid a stage comes when solid stops dissolving in the liquid. This solution is called saturated solution and the stage is called saturation point. This solution is then heated in an open container. The solvent molecules start evaporating leaving behind the solute molecules. Now cool the solution, crystals of solute start accumulating on the surface of the solution. Crystals are collected and dried. The solute which remains undissolved is separated by the process of **filteration**. If solution is cooled slowly large size crystals are formed. If solution is cooled rapidly small size crystals are formed. Hence it can be said that size of crystals depend upon the rate of cooling of the solution.



Solute is dissolved in solvent

Solution is heated to evaporate solvent



Cooling of hot solution
formation of crystals

Crystals on a filter paper

Fig. 1.13.

Hence crystallization can be defined as solidification of a liquid substance into a highly structured solid whose atoms and molecules are placed in a well defined three dimensional crystal lattice.

A smallest unit of a crystal is known as unit cell. A crystal is made up of hundreds of unit cell depending upon the size of crystal. During crystallization those unit cells get attached in all directions to form crystals of different shapes which results in great variation in shape, size and colour of crystals.

Types of crystallization: Crystallization is classified into three types depending upon the method of formation of crystals.

1. **Evaporative crystallization:** The crystallization in which crystals are formed by heating the solution which contain the solvent and soluble component. This method is used to form crystals of inorganic salts and sucrose etc. In evaporative crystallization, the crystallization is extracted from evaporation of solvent.

2. **Cooling crystallization:** In cooling crystallization super saturated solution is cooled to a temperature which is below equilibrium solubility. When solution is cooled to temperature below equilibrium solubility, it forms crystals.

3. **Reactive crystallization or precipitation:** This is the crystallization where crystals are formed from a solute which is formed when its reactants react. As the reaction process to form solute is quick hence reactive crystallization is faster than any other type of crystallization.

Uses of crystallization: Crystallization is used in laboratories to purify substances and can be merged to advance imaging methods to understand the nature of substances crystallized.

Recrystallization: Recrystallization is a technique of purification in which crystalline product is separated from impurities by dissolving it in a suitable solvent, and crystallised again to produce pure crystals. It is the most important method of purification of solid organic compounds. In Recrystallization substance to be purified is dissolved in minimum amount of solvent in which substance is more soluble at high temperature than at low temperature. The hot solution is then filtered to remove impurities. Then the filterate is allowed to cool when crystals of pure substances are obtained.

Crystals are filtered and again dissolve for recrystallization. Rapid cooling produces tiny but pure crystals while slow cooling produces larger but impure crystals. The solution left after the separation of crystals after recrystallization, is known as mother-Liquor. It is evaporated again and then cooled to obtain fresh lot of crystals of pure substance which are further subject to recrystallization.

Process of Recrystallization: The process of recrystallization involves three steps.

1. **Selection of suitable solvent:** For recrystallization the suitable solvent is to be selected which does not dissolve or dissolve a very small amount of substance in cold but dissolve more quantity of solute on boiling or heating. If no solvent seems good enough for recrystallization, a combination of two or more solvents can be used. Polar solutes are

soluble in polar substances while non polar solutes are soluble in non polar solvents. Impurities present in the substance should either be completely soluble or completely insoluble in the solvent.

2. **Drying of recrystallized substance:** Recrystallized substance is dried pressing it between several layers of filter paper or putting it onto fresh filter paper or by heating over a waterbath or in an electric oven. The safer and reliable method of drying is the use of vaccume discicator. Recrystallised substance is dried by putting it in vaccum descicator form many hours so that traces of solvent is dried up and dried recycled substance is left.

3. **Decolourisation of undesirable colour:** Sometimes recycled substance may have some undesirable colour which affect the appearance and sometimes properties of recycled substance. Such impurities are removed by boiling the substance in a solution containing finely powdered animal charcoal for 15–30 minutes then filtering the hot solution. Animal charcoal absorbs coloured impurities and pure decolourised substance crystallises out from the filterate on cooling.

Recrystallization temperature: When temperature of solution rises upto one third to half of the melting point, the mobility of atoms increases and recrystallization occurs.

1.9. SOLUBILITY AND IONIC SUBSTANCES

When soluble salts dissolve in water the ions in the solid separate and disperse uniformly throughout solution. This process of changing of a substance into ions is known as dissociation, which is a physical change. When NaCl is added to water, H^+ of polar water molecules is attracted to the negative chloride ions and OH^- ions of polar water are attracted to the positive sodium ions. The water molecules surround individual Na^+ and Cl^- ions, reducing the strong forces that bind the ions together and letting them move off into solution as solvated ions.

A compound is termed as soluble if it dissolves in water and compound is termed insoluble if it does not dissolve in water. Actually insoluble compounds also dissolve in water upto some extent (*i.e.*, less than 0.01 m).

In case of insoluble salts, the strong interionic forces that bind the ions in the solid are stronger than the ion dipole forces between individual ions and water molecules. In such case ions do not separate and remain intact. Hence most of the compound remain undissolve in water. Silver chloride (AgCl) is the example of an insoluble salt. The water molecules can not over cone the strong interionic forces that bind the Ag^+ and Cl^- ions together, hence silver nitrate remains undissolved in water.

The solubility of ionic compounds is affected by following factors:

1. **Solute solvent interaction:** Strong solute-solvent interaction increases solubility of ionic compounds. Ionic compounds are most soluble in polar solvents like water because the ions of solute are strongly attracted to the polar solvent molecules.

2. **Common ion effect:** Ionic compounds are less soluble in solvents which have common ions. For example, $CaSO_4$ is slightly soluble in water. If water contains calcium ions or sulphate ions, the solubility of $CaSO_4$ in water decreases.

Temperature: Solubility of ionic compounds increases on increasing the temperature.

Degree of Dissociation. It is defined as *the fraction of total number of molecules which dissociate into simpler molecules or ions.*

In order to calculate the degree of dissociation let us suppose that each molecule of a substance on dissociation gives ***m*** particles and that α is the degree of dissociation. Then *for each mole of the substance dissolved.*

Number of moles dissociated = α

Number of moles left undissociated = $1 - \alpha$

Number of moles of particles formed by dissociation = $m\alpha$

Total number of particles at equilibrium = $(1 - \alpha) + m\alpha$

Van't Hoff 's factor

or
$$i = \frac{\text{Moles of particles after dissociation}}{\text{Moles of particles before dissociation}}$$

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

or
$$\alpha = \frac{i-1}{m-1}$$

Since,
$$i = M_n/M_o$$

$\therefore$
$$\alpha = \frac{(M_n / M_o) - 1}{m-1}$$

or
$$\alpha = \frac{M_n - M_o}{M_o\,(m-1)} \qquad \begin{pmatrix} M_n = \text{normal molar mass} \\ M_o = \text{observed molar mass} \end{pmatrix}$$

The expressions can be put together as

$$\alpha = \frac{i-1}{m-1} \quad \text{or} \quad \alpha = \frac{M_n - M_o}{M_o\,(m-1)} \qquad ...(1.19)$$

For the electrolytes of the type AB, such as NaCl, KCl etc., the number of particles in solution *i.e.*, $m = 2$.

$$\therefore \qquad \alpha = i - 1.$$

Similarly, for the electrolytes of the type AB_2, like $CaCl_2$, the value of $m = 3$ and hence,

$$\alpha = \frac{i-1}{2}$$

Van't Hoff's factor and concentration of electrolytic solution

As the concentration of electrolytic, solution **decreases**, the extent of ionisation and also the number of particles in solution **increases.** As a result the value of ***i*** also increases and it becomes maximum as degree of dissociation approaches unity. The van't Hoff factor (*i*) for some electrolytes at different molalities are given in Table 1.4.

Table 1.4. Values of Van't Hoff factor, *i*, for some electrolytes at different concentrations

Salt	*Values of i*			*i for* $\alpha = 1$
	0.1 m	*0.01 m*	*0.0001 m*	
NaCl	1.87	1.94	1.97	2.0
KCl	1.85	1.94	1.98	2.0
$MgSO_4$	1.21	1.53	1.82	2.0
K_2SO_4	2.32	2.70	2.84	3.0

Example 1.5. *0.5 g of KCl was dissolved in 100 g of water and the solution originally at 20°C froze at –0.24°C. Calculate the percentage ionisation of the salt.* K_f *for water is 1.86 K kg* mol^{-1}.

Solution. Mass of KCl (W_B) = 0.5 g

Mass of water (W_A) = 100 g

$$\Delta T_f = 0 - (-0.24) = 0.24°$$

Molar mass of KCl (M_o) is given as

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

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

$$= 38.75 \text{ g mol}^{-1}$$

Normal molar mass of KCl $M_n = 39 + 35.5$

$$= 74.5 \text{ g mol}^{-1}$$

Van't Hoff factor i is given by

$$i = \frac{M_n}{M_o} = \frac{74.5}{38.75} = 1.92$$

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

If α is degree of dissociation

$$\alpha_{\text{diss}} = \frac{i-1}{m-1} = \frac{1.92-1}{2-1} = 0.92$$

Percentage dissociation = 0.92 × 100 = **92%**.

1.10. PRECIPITATION AND QUANTITATIVE ANALYSIS

When in a chemical reaction two ionic compounds in an aquous solution combine and react to form an insoluble salt the substance is called **precipitate** and the reaction is called **precipitation reaction** or **simply precipitation**. It is the process of turning a liquid into a solid by turning the liquid into an insoluble form or super saturating the solution.

Precipitation is a major part of water cycle because it brings the deposit of fresh water on earth. Precipitation can be divided into three categories depending upon the form such as:

- **Liquid water:** In liquid form precipitation occurs in the form of **Drizzle** and **rain**.
- **Freezing of liquid water:** When liquid water (Drizzle or rain) come in contact with the airmass at the subfreezing temperature it becomes **Freezing Drizzle** or **Freezing rain**.
- **Ice:** The frozen form of precipitated water includes **snow, ice needles, hail, Graupel, sleet.** Condensation of water vapours in air mass causes precipitation. Precipitation is a chemical reaction for example sodium chloride solution and silver nitrate solutions are mixed with each other, they react and form white silver chloride in the form of precipitate.

Precipitation decreases on increasing the temperature. When we increase the temperature of a solution, the solubility of ionic compounds increases hence precipitate formation decreases.

Heat of precipitation: The change in energy when one mole of precipitate is formed from its constituents, is known as heat of precipitation.

Types of precipitation

There are three types of precipitation depending upon the method by which air masses are lifted to higher altitudes.

1. **Cyclonic precipitation:** Cyclone is the region of low pressure having circular wind motion. When moist air mass rushes to this region because of difference in pressure, the precipitation is called cyclonic precipitation.

2. **Convective precipitation:** Moist air above the land area gets heated up because of sun's heat. This hot air rises up. When it reached a height it cools and precipitates in the form of showers of various intensity.

3. **Orographic precipitation:** Moving moist air mass when strike barriers like mountains, they rise up and cause condensation and precipitation. This type of precipitation is more on windward side of the barrier, in comparison to the leeward side of barrier.

Quantitative Analysis

Quantitative analysis is the determination of amount or percentage of one or more constituents chemicals present in a sample. The amount is expressed as a number with appropriate units. Various methods are used for quantitative analysis, which are broadly classified as chemical or physical depending upon which physical property is used in the process.

Chemical Methods of Quantitative Analysis

1. Gravimetric analysis
2. Volumetric analysis or Titrimetric analysis
3. Combustion analysis
4. Innert gas fusion

Physical Methods of Quantitative Analysis

1. **Gravimetric Analysis:** Here the sample is weighed and then constituents are separated or isolated through chemical reaction. The desired substance may be isolated by various means such as filteration

and centrifuge. The weight of the separated substance is then compared to the original sample substance.

2. **Volumetric Analysis or Titrimetric Analysis:** In titration neutralization reactions between acids and bases are used for quantitative calculation of the required solute or solvent. Titration is used to analyse the portion of an analyte solute to its solvent.

3. **Combustion analysis:** Imperical and molecular formula of hydrocarbons are generally analysed by combustion analysis. When any hydrocarbon is put to combustion, the product forms are always carbondioxide and water. Carbondioxide and water are then separated, and isolated by using adsorbant materials that are weighed before and after the reaction. Then proportion of hydrogen and carbon are calculated.

4. **Innert Gas Fusions:** Innert gas fusion is the process used for quantitative analysis of gases in ferrous and non ferrous materials where gases like hydrogen, nitrogen and oxygen are physically and chemically adsorbed by the material and later then removed and taken away from fusion area by an innert carrier gas.

Example 1.6. 0.24 g of solid iodine is dissolved in 100 ml of water at 25°C. The solubility of iodine is 0.03 g/100 ml of water at 25°C. How much iodine in grams, should precipitate out of the solution.

Solution: Mass of iodine = 0.024 g.

Volume of water = 200 ml at 25°C

Solubility of iodine = 0.03 g/100 ml water at 25°C

Mass (undissolved iodine)

= Mass (total iodine) – Mass (dissolved iodine).

Mass (Total iodine) in 100 ml water = $\frac{0.24}{200}\times 100$

= 0.12 g/100 ml at 25°C

Mass (dissolved iodine) = 0.03 g/100 ml at 25°C

Mass (undissolved iodine) = (0.12) – (0.03).

Mass of precipitated iodine

= 0.09 gms/100 ml water at 25°C

SUMMARY

- **Solution:** A homogeneous mixture of two or more substances whose concentration can be varied within certain limits.
- **Saturated Solution:** A solution which cannot dissolve any more of the solute at a particular temperature.
- **Solubility:** The maximum amount of the solute that can be dissolved in 100 g of the solvent at a given temperature.
- **Super Saturated Solution:** A solution in which the amount of solute present in 100 g of the solvent at a particular temperature is more than its normal solubility at that temperature.
- **Henry's Law:** The solubility of a gas in a liquid at a given temperature is directly proportional to the pressure at which it is dissolved.
- **Normality:** Number of gram-equivalents of solute in one litre of solution.
- **Molality:** Number of moles of solute in one kilogram of solvent.
- **Mole Fraction:** Ratio of number of moles of a component to total number of moles.
- **Raoult's Law:** The vapour pressure of a solution is equal to the product of the mole fraction of the solvent and its vapour pressure in pure state.
- **Azeotrope:** The mixture of liquids which boils at constant temperature like pure liquid and has same composition of components in liquid as well as vapour phase.
- **Colligative Properties:** The properties of the solution which are independent of nature of solute but depend upon the concentration of solute particles.
- **Molal Depression Constant:** The depression in the freezing point when the molality of the solution is unity. It is also called molal cryoscopic constant.
- **Osmotic Pressure:** The excess pressure that must be applied to the solution side to prevent the passage of solvent into it through semi-permeable membrane.
- **Van't Hoff Factor (*i*):** It is the ratio of normal molecular mass to observed molecular mass or the ratio of observed colligative property to normal colligative property.

EVALUATION

I. Multiple Choice Questions

1. Which of the following is the cause of low concentration of oxygen in the blood and tissues of people living at high altitude ?

(a) high atmospheric pressure

(b) low atmospheric pressure

(c) low temperature

(d) both low temperature and high atmospheric pressure.

2. Which of the following aqueous solutions should have the highest boiling point?

(a) 1.0 M KOH

(b) 1.0 M K_2SO_4

(c) 1.0 M NH_4NO_3

(d) 1.0 M KNO_3.

3. An raw mango placed in a concentrated salt solution to prepare pickle, shrivels because

(a) it gains water due to osmosis.

(b) it loses water due to reverse osmosis.

(c) it gains water due to reverse osmosis.

(d) it loses water due to osmosis.

4. In comparison to a 0.01 M aqueous solution of urea, the depression in freezing point of a 0.01 M $MgCl_2$ solution is

(a) the same

(b) about twice

(c) about three times

(d) about six times

5. The values of van't Hoff factor for KBr, KCl and K_2SO_4 are respectively:

(a) 2, 2, 3

(b) 2, 3, 2

(c) 1, 2, 2

(d) 1, 1, 1

6. Which of the following statements is incorrect?

(a) The osmotic pressure of a solution is given by the equation $\pi = CRT$ (where C is the molarity of the solution).

(b) Two different solutions of sucrose of same molarity prepared in different solvents will have the same depression in freezing point.

(c) Decreasing order of osmotic pressure for 0.01 M aqueous solutions of calcium chloride, sodium chloride, acetic acid and urea is

$CaCl_2 > NaCl > CH_3COOH > (NH_2)_2\,CO$.

(d) According to Raoult's law, the vapour pressure exerted by a volatile component of a solution is directly proportional to its mole fraction in the solution.

7. While relating concentration of solution to its vapour pressure? Which mode of concentration is useful?
   - (a) molality
   - (b) parts per million
   - (c) mass percentage
   - (d) mole fraction

8. On dissolving ammonium chloride in water at room temperature, the solution feels cool to touch. Under which of the following cases dissolution of the salt will be most rapid?
   - (a) Salt crystals in cold water.
   - (b) Salt crystals in hot water.
   - (c) Powdered salt in cold water.
   - (d) Powdered salt in hot water.

9. Which of the following statements is false?
   - (a) Atmospheric pressure and osmotic pressure are expressed in the same units.
   - (b) In reverse osmosis, solvent molecules move through a semipermeable membrane from a region of lower concentration of solute to a region of higher concentration.
   - (c) The value of molal depression constant depends on nature of solvent.
   - (d) Relative lowering of vapour pressure, is a dimensionless quantity.

10. 4L of 0.02 M aqueous solution of barium chloride was diluted by adding one litre of water. The molarity of the resultant solution is
   - (a) 0.004 mol^{-1} (b) 8×10^{-3} mol^{-1}
   - (c) 0.016 mol^{-1} (d) 0.012 mol^{-1}

II. Fill in the Blanks

Complete the following sentences by supplying appropriate words:

(i) Molality of the solution is number of moles of the solute in each .... kg of ....

(ii) If molarity of oxalic acid solution is M/2 then its normality will be ....

(iii) Concentrated solutions which can be diluted are known as .... solutions.

(iv) The amount of solute in grams present per dm^3 of solution is known as ....

(v) Amount of water to be added to 200 cm^3 of 1 M HCl to make it exactly 0.2 M HCl is ....

III. Matching Type Questions

Match the items of Column I to those of Column II.

Column I	Column II
A. Ratio of moles of solute to volumes of solution in dm^3	(*p*) Mole fraction of solute
B. A solution whose osmotic pressure is smaller than that of	(*q*) Depression in point freezing another
C. The product of cryoscopic constant of solvent and molality of solution	(*r*) Molarity
D. Ratio of moles of the solutes to the total moles of solute and solvent	(*s*) Hypertonic solution
E. Ratio of lowering of vapour pressure to the vapour pressure of pure solvent	(*t*) Relative lowering of vapour pressure

IV. Descriptive Questions

1. Which colligative property is preferred for molar mass determination of polymers or macromolecular substances and why?
2. What care is generally taken during intravenous injection and why?
3. Which out of 1 molar and 1 molal aqueous solution is more concentrated and why?
4. Why is freezing point depression of 0.1 M sodium chloride solution is nearly twice that of 0.1 M glucose solution?
5. Why do we have feeling of weakness or discomfort in breathing at high altitudes?
6. Sodium sulphate decahydrate gets dehydrated at 34.2°C. If dissolution of hydrated salt is endothermic while that of anhydrous salt is exothermic. What is the effect of temperature on the solubility of $Na_2SO_4.10H_2O$?
7. 0.5 M aqueous solution of sodium chloride show higher value of osmotic pressure than 0.5 M glucose solution at the same temperature. Why?

V. Numerical Questions

1. 5.00 g of a substance with molar mass 200 g mol^{-1} have been dissolved in 50 g of a solvent with molar mass 60 g mol^{-1} and vapour pressure 400 m bar. Find the vapour pressure of the solutions. (**Ans.** 388.35 m bar)
2. 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 solute. Kb for benzene is = 2.53 kg mol^{-1}. (**Ans.** 57.5 g mol^{-1})