

LESSON 3

SOLUBILITY AND ELECTROLYSIS

1. Solubility

- 1.1. **Solutions:** A homogeneous mixture of two or more substances is known as solution. The substance that is present in smaller quantity in the solution is the solute and that present in larger quantity is the solvent.



Types of solutions: It is possible to have different types of solutions from the three states of matter i.e., all three states of matter are soluble in one another.

Solvent	Solute	Example
Liquid	Solid	Solution of common salt in water
Liquid	Liquid	Alcohol in water
Liquid	Gas	Solution of CO ₂ in water – soda water
Solid	Solid	Brass – alloy of copper and zinc Sovereign – alloy of gold and copper
Gas	Gas	Air

Thus there can be many types of solutions such as solutions of solids in liquids other than water (i.e., non-aqueous solutions).

E.g., Dirt and grease in clothes dissolve in petrol (this is the basis for dry-cleaning of clothes); air is a solution of many gases – nitrogen, oxygen, carbon dioxide, water vapour, etc. Alloys are solutions; solutions of one metal in another; eg., brass – solution of zinc and copper. Soda water and chlorine water are examples of solutions of a gas in a liquid.

Dilute solution: A solution in which the amount of solute is quite small compared to the amount of solvent is called a dilute solution.

- 1.2. **Saturated, unsaturated and supersaturated solutions:** It can be seen that a given quantity of a solvent cannot dissolve an unlimited quantity of the solute.
- (a) **Unsaturated solution:** Let a little powdered potassium dichromate be added to some distilled water and the mixture stirred well. The substance dissolves and forms a clear orange coloured solution. If this solution can dissolve more of the solute, it is said to be unsaturated. Hence, an unsaturated solution is a solution which can dissolve more of the solute at a given temperature.

(b) **Saturated solution:** If the temperature is kept constant and more and more of salt is added to the solution and stirred, a stage will soon be reached when no more of the salt will dissolve. It can be seen that some of the salt settles at the bottom. The solution is then said to be saturated. Hence, a saturated solution is a solution which contains as much solute as it can dissolve at a particular temperature in the presence of undissolved solute.

(c) **Supersaturated solution:** Normally, when a saturated solution at a higher temperature is cooled to a lower temperature the excess solute that cannot be held in solution is deposited. Sometimes, however, the substance is not thrown out. Such a solution is said to be supersaturated (i.e. it is more than saturated). Supersaturated solutions are unstable. Addition of a small crystal of the solute (seeding) or even mere shaking will cause deposition of the extra solute from the solution.

i.g. When crystals of hypo ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) are carefully heated, they dissolve in the water of hydration forming a saturated solution. But when this solution is cooled, hypo is not deposited. Hence, the solution is supersaturated. However, when a small crystal of hypo is added to this solution or when the solution is shaken, the crystals get deposited.

1.3. Solubility

It is the weight in grams of substance which will dissolve in 100 gms. of the solvent to give a saturated solution at a particular temperature.

Factors which influence solubility:

1. Solubility depends upon the nature of the solute and solvent.

e.g. sodium chloride dissolves in water but sulphur is insoluble in water, it is soluble only in carbon disulphide.

2. Solubility depends on temperature: The higher the temperature the greater is the solubility. But there are some exceptions. Substance such as $\text{Ca}(\text{OH})_2$ have lower solubility at higher temperatures. In the case of solutions of gases in liquids also there is decrease in solubility with increase in temperature.

3. Solubility also depends on pressure particularly when gases are dissolved in a solvent.

e.g. the solubility of CO_2 in water increases with increase in pressure.

1.4. Determination of solubility at room temperature

Principle: A saturated solution of the substance (say sodium chloride) in water is first prepared. A known quantity of the solution is evaporated to dryness and from the weight of the residue; the amount of solute in 10 grams of water is calculated.

Procedure

- (a) Preparation of saturated solution of common salt at room temperature.

About 50 ml of distilled water is taken in a clean beaker. The common salt is powdered and added in small quantities to the water with frequent stirring till no more of the salt dissolves. This is indicated by some quantity of salt remaining undissolved at the bottom. The supernatant liquid is a saturated solution of common salt.

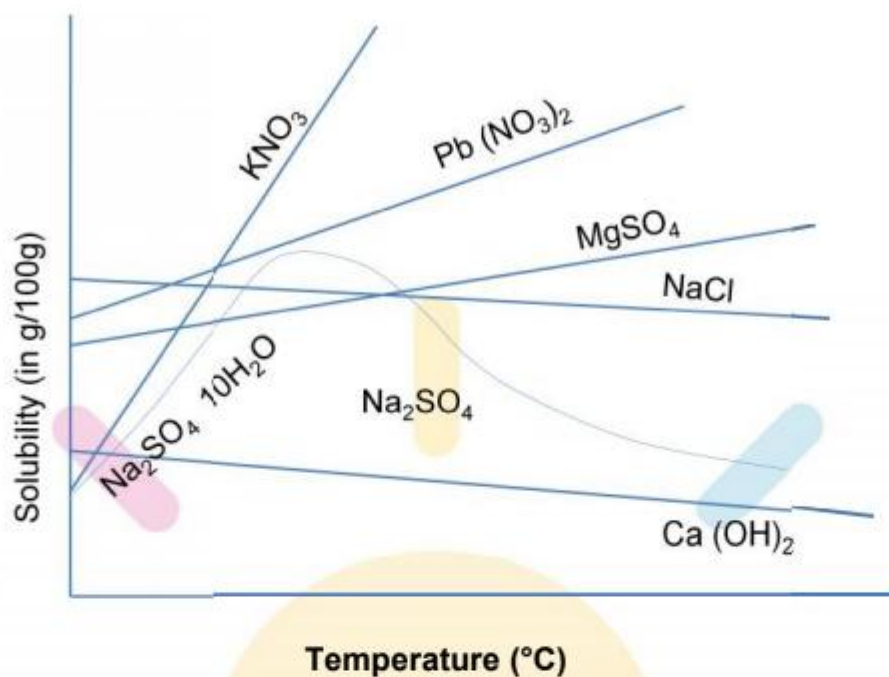
- (b) About 20 ml of the saturated solution is filtered into a dry and weighed china dish (w_1 gms). The dish is weighed with the solution (w_2 gms). It is then placed over a water bath and evaporated (without spurting) to dryness. When quite dry, the dish with the residue (the solute) is heated strongly over a sand bath to remove the last traces of water. The dish is cooled and weighed. To ensure complete removal of water, the process of heating, cooling and weighing is repeated till the last two weights are the same (w_3 gms). From the readings the solubility of common salt at room temperature is calculated.

Readings and calculations: Laboratory temperature 30°C .

Weight of china dish	= w_1 gms
Weight of china dish + saturated solution	= w_2 gms
Weight of china dish + solute	= w_3 gms
\therefore weight of solute	= $(w_3 - w_1)$ gms
\therefore weight of water in saturated solution	= $(w_2 - w_3)$ gms
\therefore $(w_2 - w_3)$ gms of water are saturated by $(w_3 - w_1)$ gms of solute	
\therefore 100 gms of water saturated by $\frac{w_3 - w_1}{w_2 - w_3} \times 100$ gms = S	
\therefore the solubility of the solid in water at 30°C is S gms.	

- 1.5. **Solubility Curves:** Saturated solutions of the substance at different temperatures are prepared by using hot water funnels to maintain the temperature during filtration and the solubilities at different temperatures are determined. The solubility curve is the graph obtained by plotting the solubility

against temperature. **Figure 1** gives the solubility curves of some substances in water. Solubility curves show



Temperature (°C)
Fig. 1

1. the change in the solubility of a substance with temperature
2. the different effects of temperature on solubility of different substances
 - (a) in most cases the change is gradual.
 - (b) in some cases (e.g. KNO_3), there is rapid increase.
 - (c) in cases like NaCl there is very little variation.
 - (d) in cases like $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ there are two curves, indicating transition of the crystalline state. The point at which the two curves meet is the transition temperature. For $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ it is 32.5°C and at his temperature the crystalline hydrate loses its water of hydration and becomes the anhydrous salt Na_2SO_4 .
 - (e) in a few cases [e.g. $\text{Ca}(\text{OH})_2$] the solubility decreases with increase in temperature.
3. The amount of the substance that can be deposited by cooling its saturated solution at a known higher temperature to a lower temperature can be known.

Example 1: A china dish weighs 53.6 gms and 43.12 gms with a saturated solution and solute respectively. If the weight of the empty china dish is 39.4 gms, calculate the solubility of the substance at room temperature.

Solution:

Weight of china dish	= 39.4 gms
Weight of china dish + saturated solution	= 53.6 gms
Weight of china dish + solute	= 43.12 gms
∴ weight of solute alone (43.12 – 39.4)	= 3.72 gms
∴ weight of water in saturated solution (53.6 – 43.12)	= 10.48 gms
∴ 10.48 gms of water are saturated by 3.72 gms of solid	
∴ 100 gms of water saturated by $\frac{3.72 \times 100}{10.48}$	= 35.5 gms
∴ the solubility of the solid at the room temperature is 35.5 gms.	

1.6. Strengths of solutions: Expression of concentrations of solutions.

Concentration of a solution means the amount of solute present in a definite weight or volume of solution. There are various methods of expressing concentrations of solutions. Some of them are

- (i) **Percentage of strength:** It is the number of grams of solute present in 100 gms of the solution. E.g. a 10% solution of glucose in water contains 10 gms of glucose in 100 gms of solution
- (ii) **Strength in Molarity (M):** A solution containing 1 gram molecular weight of the solute dissolved in **1 litre of the solution** is called a **molar (M) solution**.

Molarity is thus the number of moles of solute present in 1 litre of the solution.

$$\text{Number of moles} = \frac{W}{M} = \frac{\text{weight in grams per litre}}{\text{gram molecular weight}}$$

i.g. 1 M solution of sodium hydroxide (Molecular weight 40) will contain 40 g of NaOH in 1 litre of the solution.

- (iii) **Strength in Molality (m):** A solution containing 1 g molecular weight of the solute dissolved in **1000 g of the solvent** is called **molal (m) solution**.

Example 1: Let W_2 g of solute of molecular weight m_2 be dissolved in W_1 g of solvent.

Then W_1 g of solvent contains $\frac{W_2}{M_2}$ moles of solute

\therefore 1000 g of solvent contains $\frac{W_2}{M_2} \times \frac{1000}{W_1} = \text{moles} = m$

\therefore molality of the solution = m

(iv) **Strength in Normality (N):** A solution containing 1 g equivalent weight of the solute dissolved in 1 litre of the solution is called a normal (N) solution.

$$\therefore \text{normality} = \frac{\text{weight in grams per litre}}{\text{gram equivalent weight}} = \frac{W}{E \cdot V} \times 1000$$

Where W = Weight of the substance, E = Equivalent weight, V = Volume of the solvent in ml.

Example 2: What is the molarity of a solution of H_2SO_4 which contains 0.98 g of H_2SO_4 in 500 c.c. of solution?

Solution: Molecular weight of $\text{H}_2\text{SO}_4 = 98$

98 g of H_2SO_4 dissolved in 1000 c.c of solution gives 1 M solution

\therefore 0.98 g of H_2SO_4 dissolved in 1000 c.c of $\frac{M}{98} \times 0.98 = 0.01M$

\therefore 0.98 g of H_2SO_4 dissolved in 500 c.c. of $\frac{0.01 \times 1000}{500} = 0.02M$

Example 3: The molarity of a solution of NaOH is 0.0125 M. What is the weight of NaOH in 400 ml of the solution?

Solution: Molecular weight of $\text{NaOH} = 23 + 16 + 1 = 40$

$$\text{Molarity} = \frac{\text{weight in grams per litre}}{\text{gram molecular weight}}$$

\therefore weight in g in 1000 ml = Molarity \times molecular weight
= $0.0125 \times 40 = 0.5$ g

\therefore weight of NaOH in 400 ml = $400 \times 0.00125 = 0.2$ g

Example 4: A Solution of acetic acid (molecular weight 60) containing 80.8 g of the acid per litre of solution has a density of 1.0097 g/ml. Calculate the molality of the solution.

Solution

$$\begin{aligned} \text{Weight of 1000 ml of solution} &= \text{Volume} \times \text{Density} \\ &= 1000 \times 1.0097 \\ &= 1009.7 \text{ g} \end{aligned}$$

Weight of acetic acid in the solution = 80.8 g

\therefore weigh of water in the solution = $(1009.7 - 80.8) = 928.9$ g

The number of moles of acetic acid in 928.9 g of water = $\frac{80.8}{60} = 1.34$

\therefore the number of moles of acetic acid in 1000 g of water = $\frac{1.34}{928.9} \times 1000 = 1.443$

Molality of acetic acid solution = **1.443 m**

2. ELECTROLYSIS

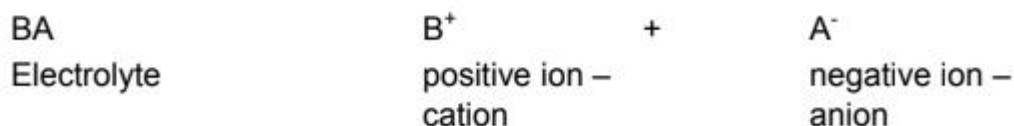
2.1. Electric Current and Substances: Substances behave differently towards electric current; some allow the current to pass through them while some do not. Substances which allow the passage of current are called conductors; those which do not allow the passage of current are non-conductors or insulators. Conductors are classified as

- (i) Metallic conductors
- (ii) Electrolytic conductors

(i) **Metallic conductors:** They do not undergo any change when current passes through them except that they get warmed up during the flow of current. The flow of current in metallic conductors is through electrons. Most metals are good conductors of electricity. E.g. lighting of electric bulb

(ii) **Electrolytic conductors or Electrolytes:** They are aqueous solutions or substances in the fused state which allow the passage of current. They undergo chemical change and get decomposed. These substances are called **electrolytes**. E.g. electrolysis of water produces hydrogen and oxygen.

2.2. Electrolysis: The process of decomposition of an electrolyte into its component ions by the passage of current through the electrolyte is called **electrolysis**. The vessel in which electrolysis takes place is called the electrolytic cell. The points at which the current enters and leaves the solution are called the electrodes; anode is the positive electrode and cathode is the negative electrode. During electrolysis, the electrolyte decomposes into its ions.



The positive ion (cation) moves towards the cathode where it gets its positive charge neutralized by the negative charge on the cathode and appears as neutral atom. Similarly, the negative ion (anion) moves towards the anode and gets discharged at the electrode as the neutral atom or radical.

E.g. the products of electrolysis of a solution of sodium chloride are sodium at the cathode and chlorine at the anode.

In some cases the products of electrolysis may react further with water or with the electrode and give rise to secondary reactions.

2.3. Theory of Ionisation: Postulates of Arrhenius theory of Electrolytic Dissociation.

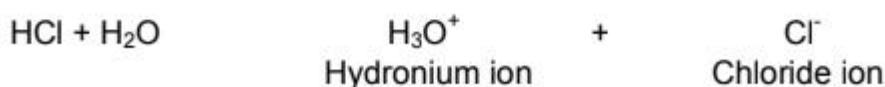
1. Acids, bases and salts in aqueous solution yield two types of charged particles called ions – cation (positive) and anion (negative).
2. When an electrolyte is put into water, it dissociates to greater or smaller extent into its component ions. At any given temperature, the undissociated molecules of the electrolyte are in equilibrium with the ions.
3. Dilution increases ionization and at infinite dilution almost all electrolytes are completely ionized.
4. The movement of ions through the solution constitutes the electric current through the electrolyte.
5. The properties of the electrolytes in solution are the properties of the ions.

E.g. acid properties are due to H^+ ions; basic properties due to OH^- ions and blue colour of copper sulphate solution is due to Cu^{2+} ions, etc.

2.4. Strong and Weak Electrolytes: All electrolytes do not conduct electricity to the same extent.

E.g. 0.1 M HCl has a very high conductance whereas, 0.1 M acetic acid has a relatively low conductance.

It may therefore be inferred that there are more ions in 0.1 M HCl than in 0.1 M acetic acid. HCl is said to be a strong electrolyte, while acetic acid is a weak electrolyte. When HCl is dissolved in water, the following reaction takes place:



The reaction is reversible but almost all the HCl molecules are converted into hydronium and chloride ions. Hence, HCl is a strong electrolyte.

When acetic acid is dissolved in water, hydronium and acetate ions are produced:



H_3O^+ and CH_3COO^- recombine to give back acetic acid and water. The forward reaction i.e. formation of hydronium ion and acetate ion proceeds to a very small extent producing only a very few ions. Hence, a solution of acetic acid is a weak electrolyte.

		Strong Electrolytes	Weak electrolytes
1.	Ionisation	Ionise to a large extent (ie.) almost completely ionized)	Ionise only to a small extent in aqueous solution
2.	Conductance	Have high conductance	Have low conductance
3.	Examples	Mineral (strong) acids HCl, H_2SO_4 and HNO_3 . Strong bases NaOH, KOH and all salts	Organic (weak) acids oxalic, acetic, etc. weak bases NH_4OH , Na_2CO_3 and water

- 2.5. Degree of Ionisation or Degree of Dissociation (α):** It is the fraction of 1 mole of an electrolyte that has dissociated under the given conditions. Strong electrolytes have a high degree of ionisation e.g. 0.1 M HCl may have $\alpha = 0.99$ (i.e. it is 99% dissociated). Weak electrolytes have a low degree of ionisation E.g. 0.1M acetic acid solution may have $\alpha = 0.02$ (i.e. it is only about 2% dissociated).

X-ray studies of crystals have revealed that salts contain ions even in the solid state. When a salt is placed in water, the inter-ionic attractive forces are weakened and the ions get separated. They are now free to move and they conduct electricity. (it is to be noted that in the solid state the ions are not mobile and so they do not conduct electricity.)

$$\alpha = \frac{A_c}{A_\infty} \quad \text{where } A_c \text{ is the conductance of the solution at a}$$

Particular concentration 'c' and A_∞ is the conductance At infinite dilution i.e. when all the molecules are dissociated.

$$= \frac{\text{Number of ions in solution}}{\text{Total number of ions produced by complete dissociation}}$$

This is true only for weak electrolytes. In the case of strong electrolytes which are almost completely ionised in aqueous solution, this ratio is called **conductance ratio**.

Factors which affect the value of α : The value of degree of ionization α depends upon

1. The nature of solute, 2. The nature of solvent. 3. Temperature and 4. Dilution.

2.6. Applications of Electrolysis:

1. In the extraction of metals such as sodium, potassium, calcium and magnesium by the electrolysis of their fused chlorides; and of aluminium by the electrolysis of pure Al_2O_3 dissolved in molten cryolite.
2. In the refining of metals such as copper and silver; the impure metal is made the anode and a thin strip of the pure metal forms the cathode. Generally the electrolyte is an acidic solution of a salt of the metal; e.g. in the electrolytic refining of copper, the electrolyte is CuSO_4 + dilute H_2SO_4 . On passing a current the impure metal at the anode dissolves and very pure metal is deposited on the cathode.
3. In electroplating; the deposition of metals by electrolysis is of great technical importance. Electro-deposition may be done for decorative purposes such as silver-plating of tableware; for engineering purposes as in chromium plating on the surface of special tools.

Printing surfaces for books and textiles are prepared by copper plating.

4. In the manufacture of certain compounds like NaOH , KOH , KClO_3 , etc.

