CHEMISTRY

Grade 11

Student Textbook

CONTENTS

CHEMISTRY11

Semester–I

Semester–II

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

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

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

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

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.

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

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

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

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

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*** $\boldsymbol{L^{-1}}$ or ***mol*** $\boldsymbol{dm^{-3}}$**.** 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 $$\frac{W_B(\text{g}) \times 1000}{M_B \times W_A\ (\text{g})} \qquad \ldots(1.6)$$

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*** $\boldsymbol{kg^{-1}}$***)***. 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, $M_B = \dfrac{W_B\, M_A}{W_A}\left(\dfrac{p_A^o}{p_A^o - p_A}\right)$

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

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

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,

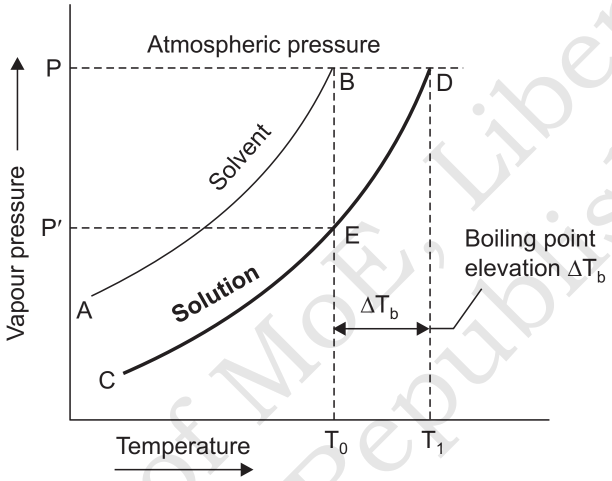


Fig. 1.1. Vapour pressure curves explaining elevation of boiling point.

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

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.

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

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

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

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).

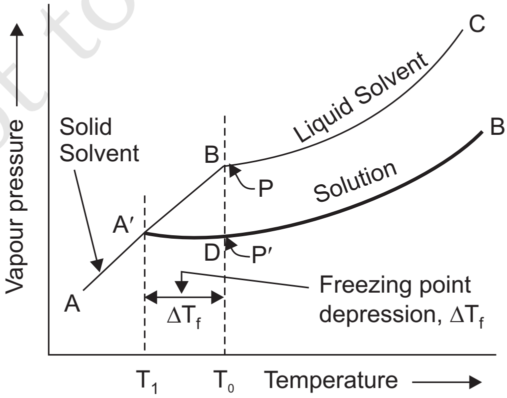


Fig. 1.2. Depression of freezing point.

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:

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

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

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

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

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

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

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

$$\text{Total moles of solute } (n_B) = 0.083 + 0.055$$
$$= 0.138\ \text{mol}$$

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

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

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.

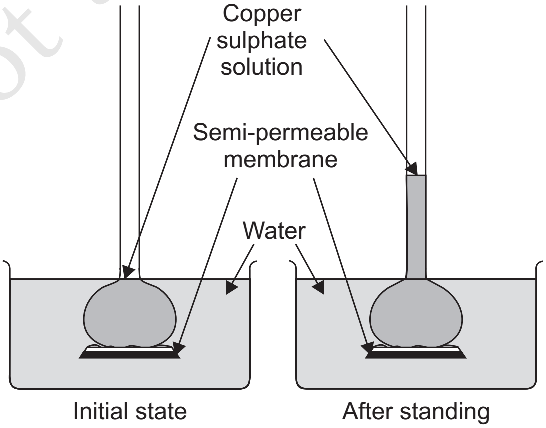


Fig. 1.3. Osmosis.

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.

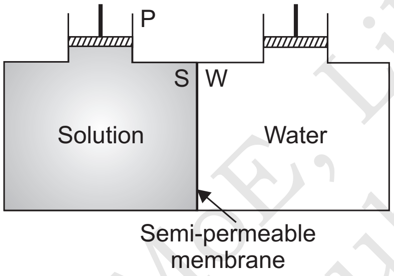


Fig. 1.4. Definition of osmotic pressure.

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

$$\pi = \frac{n}{\mathrm{V}}\,\mathrm{RT}$$

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

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 $\frac{\Delta p}{p_A^o}$ $\pi = \left(\frac{\Delta p}{p_A^o}\right) \times \frac{dRT}{M_A}$ ...(1.15)

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

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

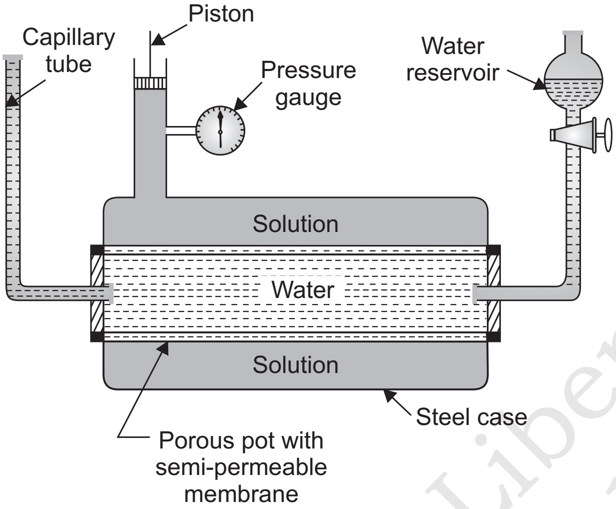


Fig. 1.5. Determination of osmotic pressure.

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

$$T = 400\ K$$

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

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

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

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.*

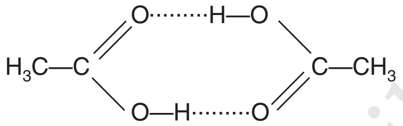
(*i*) **Association of solute molecules.** Certain solutes undergo association in their solutions.

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.

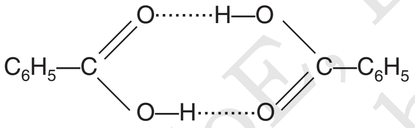
$$\text{Molar mass of solute} \propto \frac{1}{\text{Colligative property}}$$

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.

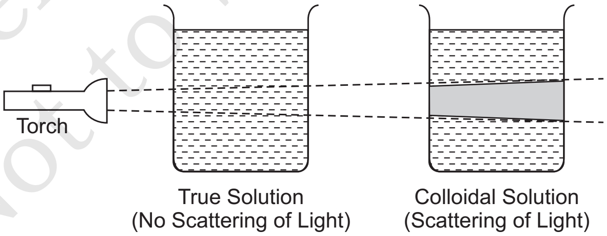


Fig. 1.6. Tyndall effect.

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.

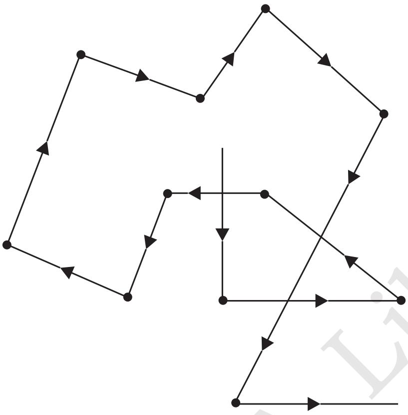


Fig. 1.7. Brownian movement.

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

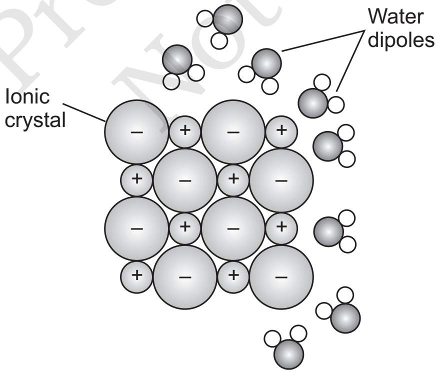
When a solid solute is added to solvent, dissolution of solute occurs. The solute particles go into solution and acquire random movement. The concentration of the solution gradually increases as more and more solute dissolves. The dissolved solute particles also collide with solid solute and some of 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.

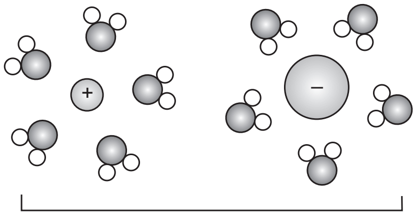
Cause of Solubility of Solids in Liquids

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

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

(*a*) If the value of $\Delta_{Sol}H < 0$; *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 $\Delta_{Sol}H > 0$; *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 $\Delta_{Sol}H$ 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 $\Delta_{Sol}H < 0$. 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.

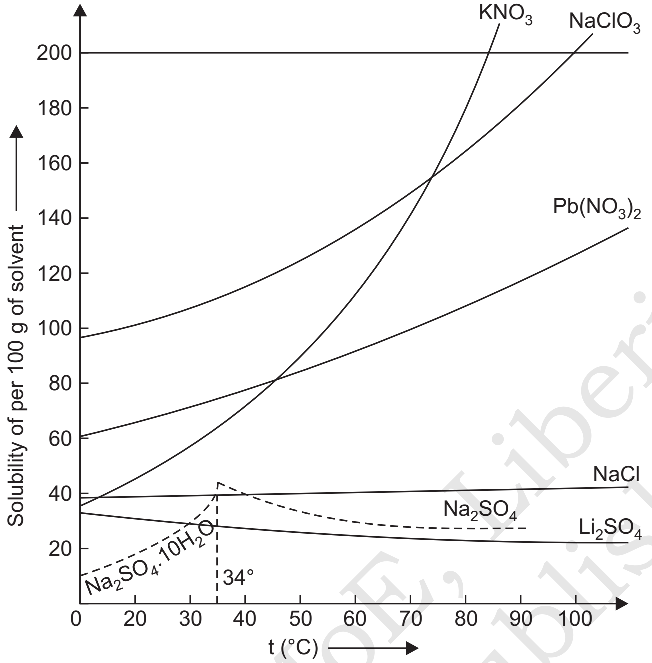


Fig. 1.10. Solubility curves of some substances.

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.*

$$\log \frac{C_2}{C_1} = \frac{\Delta_{Sol}H}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

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.

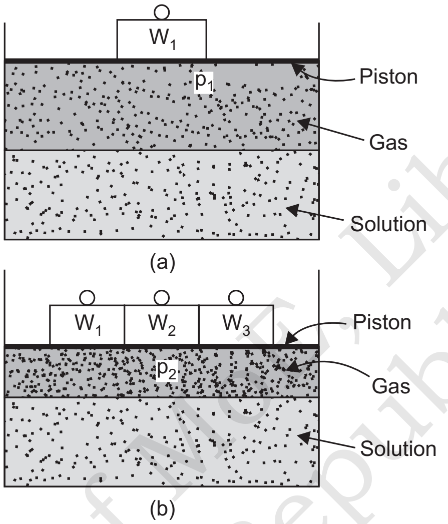


Fig. 1.11. Effect of pressure on solubility of gas pressure increases ($p_2 > p_1$), solubility also increases.

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,

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

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.

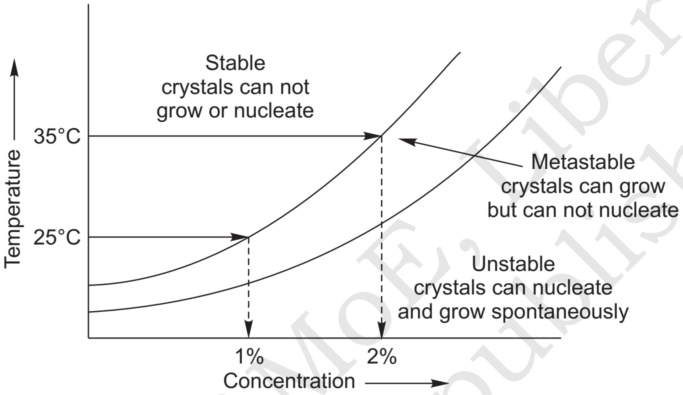


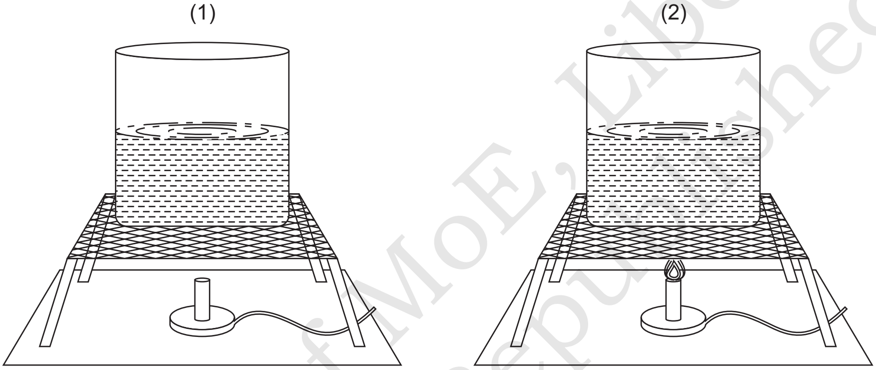
Fig. 1.12.

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.

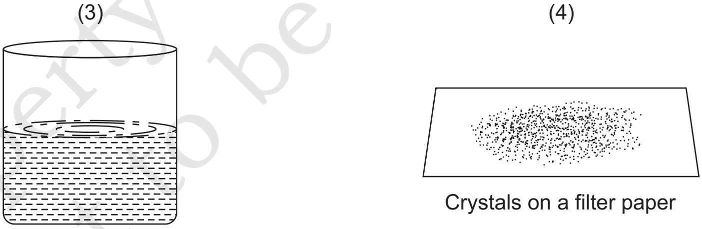
Crystallization and Recrystallization

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,
$$i = M_n/M_o$$

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

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

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

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 α = 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) $8 \times 10^{-3} \text{ mol}^{-1}$
(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})

SEMESTER–I (Period–II)

2

TOPIC

Kinetic Theory of Gases

C11CH2

Learning Objectives

Upon completion of this topic, learners will:

- Describe the concept of pressure
- Explain and apply Boyles, Charles', Gay-Lussac's, Avogadro's to observations of gas behavior
- Perform calculations using the Ideal Gas Equation
- Apply the concept of the gas laws to gas phase reactions and perform stoichiometric calculations using gas properties, masses, moles, limiting reagents and percent yield
- Describe the relationship between partial pressure and the total pressure as described in Dalton's Law of partial pressure
- Apply the ideas of Kinetic Molecular Theory to a variety of gas phenomena
- Discuss the Root Mean Square Velocity as it relates to gas particles
- Discuss effusion and diffusion in relation to Graham's Law
- Explain the general principles of the hard sphere model and the van der Waal's Model of gas and
- Discuss the concept of chemistry in the atmosphere.

Out of three states of matter, i.e., solid, liquid and gases, the gaseous state is simplest one. Kinetic energy of molecules in gases is more in comparison to that of solids and liquids. Molecules in gases have more thermal energy hence move almost like free entities. Gases have no fixed volume and shape, have very low density hence are highly compressible. Gases exert pressure, on the walls of container, that is equal in all directions. Gases have quality of diffusion hence mix evenly and uniformly.

Experimental studies show that gases behaviour follow some relative patterns among their measurable properties like **mass**, **volume**, **pressure**, and **temperature**. These relationships between measurable properties of gases are known as **gas laws**.

2.1. PRESSURE

Gases exert outward force on the walls of the container in which they are enclosed. The outward force experienced by the walls is due to bombardment of gas molecules on the walls. This *outward force per unit area of the walls* is termed as **gas pressure.**

Units of Gas Pressure

Pressure is force per unit area

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} \quad \ldots(i)$$

By definition,

$$\begin{aligned}\text{Force} &= \text{Mass} \times \text{Acceleration}\\ &= \frac{\text{Mass} \times \text{Velocity}}{\text{Time}} = \frac{\text{Mass} \times \text{Distance}}{\text{Time} \times \text{Time}}\\ &= \frac{\text{kg} \times \text{m}}{\text{s} \times \text{s}}\end{aligned}$$

Thus, SI unit of force is $kg\ ms^{-2}$ which is called *newton* (**N**)

$$1\ \text{N} = 1\ \text{kg ms}^{-2}$$

Putting SI units of force (N) and area (m^2) we get SI unit of pressure as N/m^2 or $\mathbf{Nm^{-2}}$. This SI unit of pressure is called *pascal* (**Pa**) in the honour of French mathematician and physicist *Blaise Pascal*

$$1\ \text{Pa} = 1\ \text{N m}^{-2}$$

Now, 1000 Pa = 1 kilo pascal abbriviated as **kPa.**

For gases, this unit of pressure is very small. Hence pressure is generally expressed in terms of bigger unit named as **bar.** One bar represents 100 kilo pascal. Thus

$$1\ \text{bar} = 100\ \text{kPa} = 10^5\ \text{Pa}$$

It may be noted that the older unit of pressure of the gases was *atmosphere* which was abbreviated as **atm.** The relationship between these units is given as follows:

$$1\ \text{atm} = 1.01325\ \text{bar} = 1.01325 \times 10^5\ \text{Pa}$$

or $$1\ \text{bar} = 0.987\ \text{atm} = 10^5\ \text{Pa}$$

Measurement of Gas Pressure

The pressures other than atmospheric pressure are measured by device is called **manometer.**

There are two types of manometer *open end* and *closed end* manometers

(*a*) **Open end manometer.** It consists of U tube partially filled with mercury. One limb of the tube is shorter than the other. The shorter limb is connected to the vessel containing the gas where as the longer limb is open as shown in Fig. 2.1. The mercury in the longer tube is subjected to the atmospheric pressure while mercury in the shorter tube is subjected to the pressure of the gas.

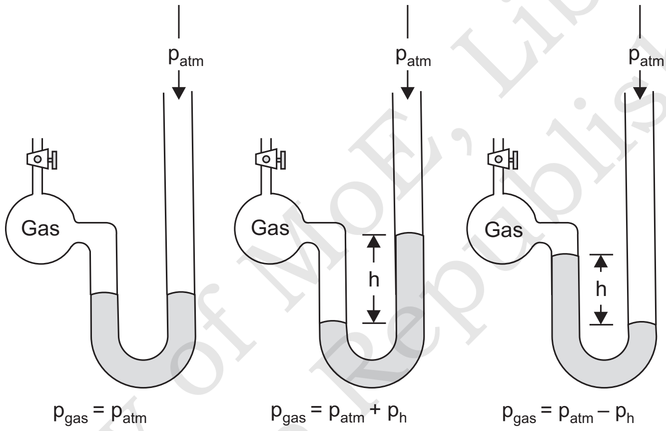


Fig 2.1. Measurement of gas pressure.

There are three possibilities described as follows:

(*i*) If the level of Hg in the two limbs is same, then

Gas pressure (p_{gas}) = *atmospheric pressure* (p_{atm})

(*ii*) If the level of Hg in the longer limb is higher, then

Gas pressure (p_{gas})

$= p_{atm}$ + (*difference between the two levels*)

$= p_{atm} + p_h$

(*iii*) If the level of Hg in the shorter limb is higher, then

Gas pressure (p_{gas})

$= P_{atm}$ – (*difference between the two levels*)

$= P_{atm} - p_h$.

(*b*) **Closed end manometer.** This is generally used to measure low gas pressures. It also consists of U-tube with one limb shorter than the other and partially filled with mercury as shown in Fig. 2.2. The space above mercury on the closed end is completely evacuated. The shorter limb is connected to the vessel containing gas. The gas exerts pressure on the mercury in the shorter limb and forces its level down.

Gas pressure (p_{gas})

$$= [\textit{Difference in the Hg level in two limbs}]$$

or $p_{gas} = p_h$

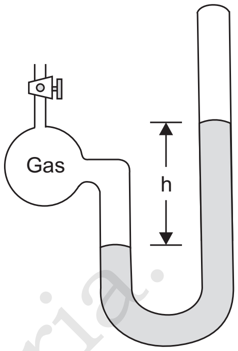


Fig. 2.2. Closed end manometer

It may be noted that **open end manometer** is better suited for measuring pressures **equal to or greater** than atmospheric pressure. On the other hand, **closed end manometer** is suited to measure pressures **below atmospheric pressure.**

2.2. GAS LAWS

Physical properties of gases like volume change with the change in temperature and pressure. The relationships between physical properties of gas as outcome of researches are formulated as gas laws. Some of the gas laws are Boyle's Law, Charles' Law, Gay Lussac's Law, Avogadro's Law and Dalton's Law.

BOYLE'S LAW—Pressure-Volume Relationship

This law describes the ***pressure-volume*** relationship of gases at constant temperature. It was given by Anglo-Irish scientist Robert Boyle (1662) and is known after his name as **Boyle's law**. The law states that:

The volume of a fixed mass of a gas is inversely proportional to its pressure at constant temperature.

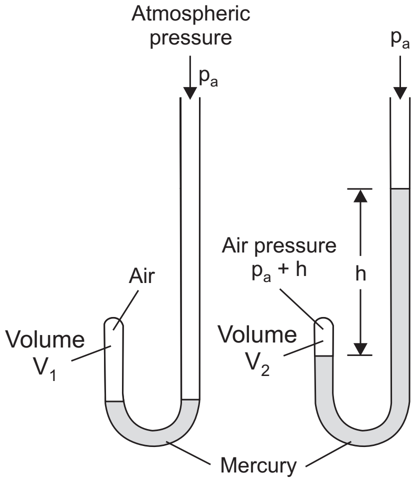


Fig. 2.3

The law can be demonstrated by the simple experiment as described below. Take a J shape tube as shown in Fig. 2.3. Tube is partially filled with mercury. Pressure is now increased by putting more mercury into the open limb. The volume of air enclosed in the space above mercury in shorter limb is noted each time. It is found that as pressure increases, the volume of enclosed air gradually decreases from V_1 to V_2.

Mathematical Interpretation of the Law

Mathematically, the law may be expressed as:

$$V \propto \frac{1}{p} \qquad \text{(\textit{Temperature and mass constant})}$$

or $$V = k_1 \frac{1}{p} \quad \text{where } k_1 \text{ is constant of proportionality}$$

or $$PV = k_1 = \text{constant.}$$

The value of the constant k_1 depends upon *amount of the gas*, *temperature of the gas* and the *units* in which P and V are expressed.

Thus, another statement of Boyle's law may be given as follows:

For a given amount of the gas, the product of pressure and volume is constant at constant temperature.

Let V_1 be the volume of a given mass of the gas having pressure p_1 at temperature T. Now if the pressure is changed to p_2 at the same temperature, let the volume changes to V_2. The quantitative relationship between the four variables p_1, V_1, p_2 and V_2 is:

$$\boldsymbol{p_1 V_1 = p_2 V_2} \quad \text{or} \quad \boldsymbol{\frac{p_1}{p_2} = \frac{V_2}{V_1}} \qquad \text{(\textit{T and n constant})}$$

The **experimental verification** of the law can be carried out by measuring the values of volumes of a given mass of a gas at different pressures keeping the temperature constant. In each case the product pV is found to be constant. The values of pressures and volumes of fixed mass (0.09 mol) of N_2 at constant temperature, 300 K are given in Table 2.1.

Table 2.1. Effect of Pressure on Volume of 0.09 mole of CO_2 at 300 K

Pressure $p \times 10^3$ *Pa*	*Volume* $V \times 10^{-3}\ m^3$	$1/V$ (m^{-3})	$pV \times 10^2$ *Pa* m^3
2.0	112.0	8.90	2.24
2.5	89.2	11.2	2.23
3.5	64.2	15.6	2.247
4.0	56.25	17.7	2.25
6.0	37.40	26.7	2.244
8.0	28.1	35.6	2.248
10.0	22.4	44.6	2.240

Example 2.1. *In a J tube partially filled with mercury the volume of air column is 4.2 mL and the mercury level in the two limbs is same. Some mercury is, now added to the tube so that the volume of air enclosed in shorter limb is now 2.8 mL. What is the difference in the levels of mercury in this situation. Atmospheric pressure is reported to be 1.0 bar.*

Solution.

$$\text{Initial pressure } p_1 = 1 \text{ bar} = 0.987 \text{ atm}$$
$$= 0.987 \times 760 = 750.12 \text{ mm Hg}$$
$$\text{Final pressure } p_2 = (p_1 + h)$$
$$V_1 = 4.2 \text{ mL}; V_2 = 2.8 \text{ mL}$$
$$p_2V_2 = p_1V_1 \quad \text{or} \quad p_2 = \frac{p_1V_1}{V_2}$$
$$= \frac{750.12 \times 4.2}{2.8} = 1125.18 \text{ mm Hg}$$

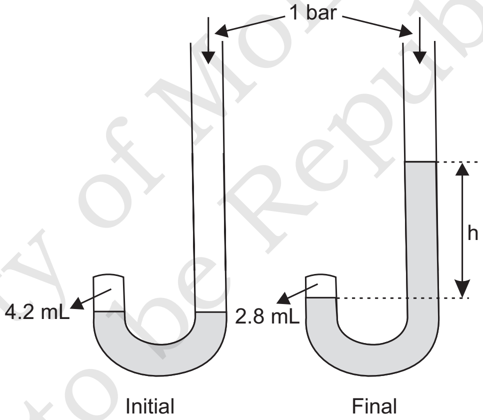


Fig. 2.4

$$\text{Now,} \quad 1125.18 = 750.12 + h$$
$$\text{or} \quad h = 1125.18 - 750.12$$
$$= 375.06 \text{ mm Hg} \quad \text{or} \quad \mathbf{37.50 \text{ cm Hg.}}$$

CHARLES' LAW—Volume Temperature Relationship

This law describes the ***volume-temperature*** relationship of gases at constant pressure. It was put forwarded by the French chemist *Jacques Charles* in 1787 and was further developed in 1802 by *Joseph Gay Lussac*. This law can be stated as:

The volume of a fixed mass of a gas increases or decreases by $\frac{1}{273.15}$ of its volume at 0°C for each degree rise or fall of temperature, provided pressure is kept constant.

If V_0 is the volume of given mass of the gas at 0°C

Then, V_1, the volume of the gas at 1°C

$$= V_0 + \frac{V_0}{273.15} = V_0\left(1 + \frac{1}{273.15}\right)$$

V_2, the volume of the gas at 2°C

$$= V_0\left(1 + \frac{1}{273.15}\right)$$

V_t, the volume of the gas at t°C

$$= V_0\left(1 + \frac{t}{273.15}\right) \qquad ...(2.1)$$

Absolute scale of temperature. By carrying out the similar calculations it can be shown that the volume of the gas below 0°C will be less than V_0. For example, the volume of the gas at – t°C

$$V_{(-t)} = V_0\left(1 - \frac{t}{273.15}\right)$$

Thus, decrease of temperature results in the decrease in the volume of the gas and ultimately, the volume should become *zero* at – 273.15°C. It means that any further lowering of temperature is impossible because it would correspond to negative volume which is meaningless. Hence, an important conclusion can be drawn from the above discussion that the *lowest possible temperature* is – 273.15°C. This lowest possible temperature at which all the gases are supposed to occupy zero volume is called **Absolute zero.** A scale of temperature based upon this choice of zero is called **absolute scale of temperature.** Since this scale was suggested by the British scientist *Lord Kelvin,* it is also known after his name as **Kelvin scale of temperature.**

Careful measurements have revealed that absolute zero of temperature is – 273.15°C. Temperatures on the Kelvin scale are indicated by writing the letter K. By convention, the degree sign (°) is not used while expressing temperatures on Kelvin scale. For example,

$$-273.15°\text{C} = 0\ \text{K}$$

The relationship between Kelvin scale and celsius scale is:

$$\mathbf{T(K) = t(°C) + 273.15}$$

where, '**T**' is the temperature on Kelvin scale while '**t**' is the temperature on Celsius scale.

Alternative Statement of Charles' Law

We have already derived the relationship between the volume of a given mass of the gas at t°C (V_t) and that at 0°C (V_0).

$$V_t = V_0\left(1 + \frac{t}{273.15}\right)$$

$$= V_0\left(\frac{273.15 + t}{273.15}\right) = V_0\,\frac{T_t}{T_0}$$

where T is corresponding temperature on Kelvin scale.

or $$\frac{V_t}{T_t} = \frac{V_0}{T_0}$$

$$\therefore \quad \frac{V}{T} = \text{constant} = k_2 \qquad \text{(at constant } p \text{ and } n\text{)}$$

Thus, $V = k_2T$ or $V \propto T$ (at constant p and n)

Here, k_2 is a constant whose value depends upon pressure of the gas, amount of the gas and the units of volume (V).

This leads to an alternative statement of Charles' law as:

> ***The volume of the fixed mass of a gas at constant pressure is directly proportional to the temperature on Kelvin scale.***

Let V_1 be the volume of a certain mass of a gas at temperature T_1 and at pressure p. If temperature is changed to T_2 keeping pressure constant, the volume changes to V_2. The relationship between four variables V_1, T_1, V_2 and T_2 is:

$$\frac{\mathbf{V_1}}{\mathbf{T_1}} = \frac{\mathbf{V_2}}{\mathbf{T_2}} \qquad (p \text{ and } n \text{ constant})$$

The **experimental verification** of the law can be done by measuring the volumes of the given mass of a gas at different temperatures keeping the pressure constant. In each case the ratio V/T comes out to be constant. The *volume-temperature* data for 1 mol of N_2 at 1 bar pressure is given in Table 2.2.

Table 2.2. Volume-Temperature Data for N2 Gas at 1 bar Pressure

Temperature		*Volume*	*(V/T)*
°C (t)	*K(T)*	*(dm^3)*	*(dm^3K^{-1})*
– 50	223.15	18.52	0.083
0	273.15	22.67	0.083
50	323.15	26.82	0.083
100	373.15	30.97	0.083
150	423.15	35.12	0.083

GAY LUSSAC'S LAW—Pressure Temperature Relationship

This law describes the ***pressure-temperature*** relationship of gases at constant volume. It is also called **Amonton's law.**

The law is similar to Charles' law and is given by **Joseph Gay Lussac.** It states that ***pressure of a fixed mass of a gas at constant volume is directly proportional to the temperature on Kelvin scale.***

Mathematically, $p \propto T$ (*At constant n, V*)

or $$\frac{p}{T} = k_3 \quad \text{(constant)}$$

The value of k_3 depends upon volume of gas, amount of the gas and the units of pressure (p).

Let p_1 be the pressure of a certain mass of a gas at temperature T_1 and having a volume V. Now, if temperature is changed to T_2 at the same volume so that the corresponding pressure becomes p_2. Then according to the law:

$$\frac{p_1}{T_1} = \frac{p_2}{T_2} \quad (\textit{At constant n and V})$$

The law can be illustrated by pressure-temperature graph. The plot of p *vs* T for a fixed mass of a gas at constant volume is a straight line as shown in Fig. 2.5. This plot of p *vs* T at constant T and n is called **isometric**. The slops of various isometrics at different volumes are different but all these lines meet the temperature axis on extrapolation at 0 (K) as shown in Fig. 2.5.

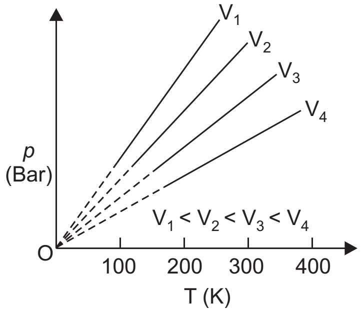


Fig. 2.5. Isometrics of ideal gas.

Example 2.2. *A sample of a gas is found to occupy a volume of 900 cm*^{3} *at 27°celsius. Calculate the temperature at which it will occupy a volume of 300 cm*^{3}*, provided the pressure is kept constant.*

Solution. Here, $V_1 = 900 \text{ cm}^3 \qquad V_2 = 300 \text{ cm}^3$

$$T_1 = (27 + 273) \text{ K} = 300 \text{ K}, \; T_2 = ?$$

Applying Charles' law, $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$

$$T_2 = \frac{V_2 \times T_1}{V_1} = \frac{300 \text{ cm}^3 \times 300 \text{ K}}{900 \text{ cm}^3}$$

$$= 100 \text{ K} = 100 - 273 = -\mathbf{173°C}.$$

AVOGADRO'S LAW—Volume Amount Relationship

This law describes the ***volume-amount*** relationship of gases at constant temperature and pressure. It was given by Amedeo Avogadro in 1811. It states that ***equal volumes of all the gases under similar conditions of temperature and pressure contain equal number of molecules.***

For example, 1 mol of all the gases contain 6.023×10^{23} molecules. At the same time 1 mol of all the gases at 273.15 K (0°C) and 1 bar pressure occupy a volume of 22.7 L (22.7×10^{-3} m^3). This means that as long as the temperature and pressure remain constant the volume of the gas is directly proportional to the number of molecules or in other words, the amount of the gas. Mathematically we can write

$$V \propto N \qquad (T \text{ and } p \text{ are constant})$$

The number of molecules N is directly proportional to number of moles (n)

$$\therefore \qquad V \propto n \qquad (T \text{ and } p \text{ are constant})$$

or $\qquad V = k_4 n \qquad$ k_4 is constant of proportionality

Now, if m is the mass of the gas having molar mass equal to M, then the number of moles (n) are given as

$$n = \frac{m}{M}$$

$$\therefore \qquad V = k_4 \frac{m}{M}$$

or $\qquad M = k_4 \dfrac{m}{V} \quad$ or $\quad k_4 . d$

where d is density of gas.

The above relationship implies that density of the gas at a given temperature and pressure is directly proportional to its molar mass.

2.3. IDEAL GAS EQUATION

A gas that follows Boyle's law, Charles' law and Avogadro's law strictly at all conditions, is called **Ideal gas.** It is assume that inter-molecular forces are not present between the molecules of ideal gas. Real gases follow these laws only under certain specific conditions when forces of interaction are practically negligible. In all other situations the real gases deviate from ideal behaviour.

The combination of various gas laws namely; *Boyle's law, Charles' law* and *Avogadro's law* leads to the development of the mathematical relation which relates four variables *pressure, volume, absolute temperature* and *number of moles of ideal gas*. The equation so formulated is called **ideal gas equation.**

The ideal gas equation can be derived by combining Boyle's law, Charles' law and Avogadro's law as follows:

According to Boyle's law

$$V \propto \frac{1}{P} \quad (\textit{at constant } T \textit{ and } n) \qquad \ldots(i)$$

According to Charle's law

$$V \propto T \text{ (at constant } P \text{ and } n) \qquad \ldots(ii)$$

According to Avogadro's law

$$V \propto n \; (\textit{at constant } T \textit{ and } P) \qquad \ldots(iii)$$

Combining (*i*), (*ii*) and (*iii*)

$$V \propto \frac{nT}{P}$$

or $$pV \propto nT$$

or $$\mathbf{pV = nRT} \qquad \ldots(2.2)$$

where, **R** is constant of proportionality and is known as **universal gas constant.**

Equation (2.2) is called **ideal gas equation.** This equation is applicable to any gas under those conditions when behaviour of gas approaches ideal behaviour. Since this equation relates four variables which are used to describe the state of any gas, it is also known as **equation of state for ideal gas.** It may be noted that out of the four variables, the two namely; *pressure* (p) and *temperature* (T) are **intensive** variables as they do not depend on the bulk or quantity of the gas. The other two variables, *i.e., volume* (V) and *mole* (n) are **extensive** variables as they depend upon the bulk or quantity of the gas.

2.4. DENSITY AND MOLAR MASS OF GASEOUS SUBSTANCE

We have studied in unit one that the number of moles (n) of the substance is related to the molar mass (M) as

$$n = \frac{w}{\mathrm{M}}$$

where, w = mass in gram.

Substituting this value in the ideal gas equation we can get the relationship between density and molar mass,

$$p\mathrm{V} = n\mathrm{RT} = \frac{w}{\mathrm{M}}\mathrm{RT}$$

$$p = \frac{w\mathrm{RT}}{\mathrm{MV}} \quad \text{or} \quad p = \frac{d\mathrm{RT}}{\mathrm{M}}$$

where d is the density of gas $\left[d = \frac{\text{Mass}}{\text{Volume}} = \frac{w}{\mathrm{V}}\right]$

or $$\boldsymbol{p} = \frac{\mathbf{dRT}}{\mathbf{M}} \qquad \ldots(2.3)$$

Nature of the Gas Constant (R)

In order to understand the significance of R, let us examine the nature of quantities in the ideal gas equation:

$$p\mathrm{V} = n\mathrm{RT} \quad \text{or} \quad \mathrm{R} = \frac{p\mathrm{V}}{n\mathrm{T}} = \frac{\text{Pressure} \times \text{Volume}}{\text{Moles} \times \text{Temperature}}$$

$$\mathrm{R} = \frac{\frac{\text{Force}}{\text{Area}} \times \text{Volume}}{\text{Moles} \times \text{Temperature}} = \frac{\frac{\text{Force}}{(\text{Length})^2} \times (\text{Length})^3}{\text{Moles} \times \text{Temperature}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Moles} \times \text{Temperature}}$$

Since force × length = work energy

$$\therefore \qquad \mathrm{R} = \frac{\text{Work}}{\text{Moles} \times \text{Temperature}}$$

Thus, **R** *represents* ***work done per degree per mole.***

Since work can be expressed in different systems of units, **R** will have different numerical values in different systems.

2.5. DALTON'S LAW OF PARTIAL PRESSURES

This law describes the relation between the pressure of the mixture of non-reacting gases enclosed in a vessel to their individual pressures. The law was given by John Dalton in 1807. It states:

At constant temperature, the pressure exerted by a mixture of two or more non-reacting gases enclosed in a definite volume, is equal to the sum of the individual pressures which each gas would exert if present alone in the same volume at the same temperature.

The individual pressures of gases are known as **partial pressures.**

If p_{Total} is the pressure of the mixture of non-reacting gases at temperature T and volume V, and $p_1, p_2, p_3, \ldots\ldots$ represent the partial pressures of the gases, then

$$p_{\text{Total}} = p_1 + p_2 + p_3 + \ldots\ldots \; (T, V \textit{ are constant})$$

The law can be **illustrated** by considering the following example. Suppose we have three containers of capacity 1 litre each; one containing *x moles* of nitrogen, the other *y moles* of oxygen and the third having a mixture of *x moles* of nitrogen and *y moles* oxygen. All the three containers, are kept at the same temperature.

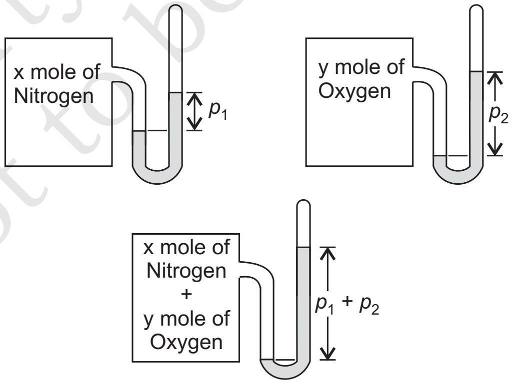


Fig. 2.6. Illustration of Dalton's law of partial pressures.

Now, if the manometer, attached to first container shows a pressure p_1 and that attached to second container shows a pressure p_2. Then the pressure in the third container is $p_1 + p_2$.

Utility of Dalton's law. This law is useful in calculating the pressure of the gas collected by the displacement of water. The gas being collected over water also contains water vapours. The observed pressure of the moist gas is equal to the sum of the pressure of the dry gas and the pressure of the water vapours. The pressure of the water vapours is constant at a given temperature and is known as **aqueous tension** at that temperature. Thus,

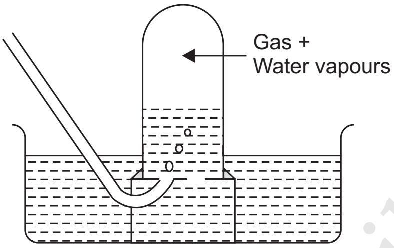


Fig. 2.7. Collection of gas over water.

$$p_{\text{observed}} = p_{\text{gas}} + \textit{aqueous tension}$$

$$\therefore \quad p_{\text{gas}} = p_{\text{observed}} - \textit{aqueous tension}$$

Aqueous tension of water at different temperatures is given in Table 2.3.

Table 2.3. Aqueous Tension (Vapour Pressure) of Water as a Function of Temperature

Temperature (K)	*Pressure (bar)*	*Temperature (K)*	*Pressure (bar)*
273.15	0.0060	295.15	0.0260
283.15	0.0121	297.15	0.0295
288.15	0.0168	299.15	0.0331
291.15	0.0204	301.15	0.0372
293.15	0.0230	303.15	0.0418

Example 2.3. *A certain quantity of a gas occupies a volume of 0.1 L when collected over water at 288 K and 0.92 bar pressure. The same gas occupied a volume of 0.085 L at S.T.P. in dry conditions. Calculate the aqueous tension at 288 K.*

Solution. Let the aqueous tension at 288 K be p bar

Thus, pressure of the dry gas at 288 K

$$= (0.92 - p) \text{ bar.}$$

Now, $p_1 = (0.92 - p)$ bar $\quad p_2 = 1$ bar.

$V_1 = 0.1$ L $\quad V_2 = 0.085$ L

$T_1 = 288$ K $\quad T_2 = 273.15$ K.

According to gas equation,

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \quad \text{or} \quad p_1 = \frac{p_2V_2T_1}{V_1T_2}$$

Substituting the values,

$$0.92 - p = \frac{1 \times 0.085 \times 288}{0.1 \times 273.15} = 0.896$$

$$p = \mathbf{0.024\ bar.}$$

2.6. KINETIC MOLECULAR THEORY OF GASES

The various gas laws which we have studied so far were based on the experimental facts. There was no theoretical background for their justification. In order to explain the behaviour of gases and answer the questions such as, why do they exert pressure or why a volume is inversely proportional to pressure, etc., it became necessary to develop a molecular theory, *i.e., a mental picture* which is able to provide explanation for our experimental observations. Maxwell, Boltzmann, Clausius, etc., suggested a theoretical model which is known as **kinetic molecular theory of gases** or **microscopic model of gases.**

The Microscopic Model of Gases

The various assumptions of kinetic theory are related to atoms and molecules which cannot be seen. Thus, kinetic theory is said to give us a *microscopic model* of gases. The **various postulates** of the theory are:

1. *All gases are made up of very large number of extremely small particles called* **molecules.**
2. *The molecules are separated from one another by large spaces so that the actual volume occupied by the molecules is negligible as compared to the total volume of the gas.*
3. *The molecules are not at rest but possess rapid random motion. During their motion, they collide with one another and also against the walls of the container.*
4. *The pressure of the gas is due to bombardment of the gas molecules against the walls of the container.*
5. *The collisions of the molecules with each other and with the walls of the container are perfectly elastic, i.e., there is no loss or gain of kinetic energy. However, there may be redistribution of energy during such collisions.*

6. *There are no attractive or repulsive forces between the molecules of the gas. They are completely independent of each other.*
7. *At any instant, different molecules possess different velocities and hence, different energies. However, the average kinetic energy of the molecules is directly proportional to the absolute temperature.*

Kinetic Gas Equation

Kinetic gas equation is the mathematical relation that has been derived on the basis of various postulates of kinetic molecular theory. It relates pressure (p), volume (V) of N molecules of the gas at a given temperature to the root mean square speed. If m is mass of gas molecule, c is the r.m.s. N is total number of molecules then *kinetic gas equation* is:

$$\boldsymbol{p\mathrm{V} = \frac{1}{3}\,\mathrm{mNc}^2.}$$

Average Kinetic Energy of Gas

The ***average kinetic energy*** of gas molecules can be calculated on the basis of kinetic gas equation.

According to kinetic gas equation

$$p = \frac{1}{3}\,(\mathrm{N/V})\;mc^2$$

For one mol of the gas, $\mathrm{N} = \mathrm{N_A}$

$$\therefore \qquad p\mathrm{V} = \frac{1}{3}\,\mathrm{N_A}\;mc^2$$

Also for 1 mol of ideal gas, $p\mathrm{V} = \mathrm{RT}$

$$\therefore \qquad \frac{1}{3}\,\mathrm{N_A}\;mc^2 = \mathrm{RT}$$

$$\text{or} \qquad \frac{1}{2}\times\frac{2}{3}\,\mathrm{N_A}\;mc^2 = \mathrm{RT} \quad \text{or} \quad \frac{1}{2}\,mc^2 = \frac{3}{2}\,\mathrm{RT}$$

Now $\frac{1}{2}\,mc^2$ represents average kinetic energy ($\overline{\mathrm{E}}_k$) of the molecule.

$$\therefore \qquad \overline{\mathbf{E}}_{\boldsymbol{k}} = \frac{3}{2}\,\mathbf{RT} \quad \text{or} \quad \overline{\mathbf{E}}_{\boldsymbol{k}} = \frac{3}{2}\,\mathbf{kT}$$

(where $k = \mathrm{R/N_A}$ and called Boltzmann constant)

Since R or k are constant, thus, it can be concluded that $\overline{\mathbf{E}}_{\boldsymbol{k}}$ ***of gas*** $\propto$ ***T.***

2.7. MOLECULAR VELOCITY

Molecular velocity is generally expressed in terms of: (*i*) *Most probable velocity*, (*ii*) *average velocity* and (*iii*) *root mean square velocity.*

(*i*) **Most probable velocity (c^* or u_{mp}).** *It is the velocity possessed by maximum number of gas molecules at a given temperature. c^* is related to temperature (T) and molar mass (M) as follows*

$$c^* \text{ (or } u_{mp}) = \sqrt{\frac{2RT}{M}}$$

(*ii*) **Average velocity ($\bar{c}$ or u_{av}).** *It is the arithmatic mean of the velocity of different molecules of the gas at a given temperature.* If n_1 molecules have velocity v_1, n_2 molecules have velocity v_2, n_3 molecules have velocity v_3 and so on. Then,

$$\bar{c} \text{ (or } u_{av}) = \frac{n_1v_1 + n_2v_2 + n_3v_3 + \ldots\ldots}{(n_1 + n_2 + n_3 + \ldots\ldots)}$$

Average *velocity* is related to the molar mass (M) of the gas and the temperature (T) as follows.

$$\bar{c} \text{ (or } u_{av}) = \sqrt{\frac{8RT}{\pi M}}$$

(*iii*) **Root mean square velocity (c or $u_{r.m.v.}$).** *It is the square root of the arithmatic mean of the squares of velocities of various molecules of the gas at a given temperature.* If v_1, v_2, v_3, …… are velocities of n_1, n_2, n_3, …… molecules respectively, then

$$c \text{ or } u_{\text{r.m.v.}} = \sqrt{\frac{n_1v_1^2 + n_2v_2^2 + n_3v_3^2 + \ldots\ldots}{(n_1 + n_2 + n_3 + \ldots\ldots)}}$$

Root mean square velocity is related to temperature (T), pressure (p), volume (V) and molar mass (M) of the gas by the following expressions

$$c \text{ or } u_{\text{r.m.v.}} = \sqrt{\frac{3RT}{M}} \quad \text{or} \quad \sqrt{\frac{3pV}{M}}$$

Relationship between different types of velocities.

The different types of velocities are related as :

$$\mathbf{c^* : \bar{c} : c} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$= 1.414 : 1.596 : 1.732$$

$$= \mathbf{1 : 1.128 : 1.224}$$

For any gas at a given temperature,

$$c > \bar{c} > c^*$$

It may also be noted that

$$\bar{\mathbf{c}} = \mathbf{0.921 \times c} \text{ and}$$

$$\mathbf{c^* = 0.817 \times c}$$

Example 2.4. *Calculate Average kinetic energy of 32 g of methane molecules at 27°C. R = 8.314 JK^{-1} mol^{-1}.*

Solution. Average kinetic energy is given as

$$E_K = \frac{3nRT}{2}$$

Here, $n = \frac{32}{16} = 2$; R = 8.314 JK^{-1} mol^{-1};

$$T = 300 \text{ K}$$

$$\therefore \quad E_K = \frac{3 \times 2 \times 8.314 \times 300}{2} = \mathbf{7482.6\ J}$$

Maxwell's Distribution of Speeds

Gases consist of tiny particles separated from the one another by large empty space and moving rapidly at random in all the directions. In the course of their motion, they collide with one another and also with the walls of the container. Due to frequent collisions, the speeds and direction of motion of molecules keep on changing. Thus, all the molecules in a sample of a gas do not have same speeds. Although it is not possible to find out the speeds of individual molecules, yet from the probability considerations it has become possible to work out the distribution of molecules between different speeds. This distribution is referred to as *Maxwell-Boltzmann* distribution in honour of the scientists who developed it. It may be noted that ***distribution of speeds remains constant at given temperature although individual speeds of molecules may change.*** Maxwell plotted the fraction of molecules having different speeds against the speeds at given temperature.

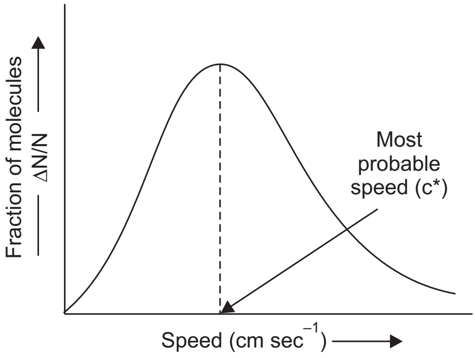


Fig. 2.8. Maxwell's distribution of speeds at a particular temperature.

The curve so obtained is shown in Fig. 2.8 and is called *Maxwell's distribution curve.*

The important **features of Maxwell's distribution curve** can be summed up as follows:

(*i*) *The fraction of molecules with very low or very high speeds is very small.*

(*ii*) *The fraction of molecules possessing higher and higher speeds goes on increasing till it reaches the peak and thereafter it starts decreasing.*

(*iii*) *The area under the curve gives the total number of gas molecules.*

(*iv*) *The maximum fraction of molecules possesses a speed corresponding to the peak in the curve. This speed corresponding to the peak in the curve is referred to as most probable speed.*

The **most probable speed** may be defined as the *speed possessed by the maximum fraction of molecules at a given temperature.*

As most probable speed is **inversely** proportional to molar mass ($c^* = \sqrt{2RT/M}$). This implies that at the same temperature; lighter gases move faster than heavier gases. It is evident from the distribution curves of Cl_2 and N_2 gases at 300 in Fig. 2.9.

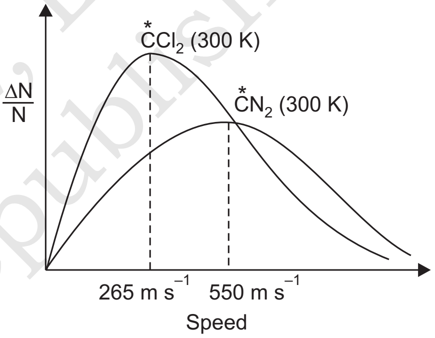


Fig. 2.9. Maxwell Boltzmann distribution curves for Cl_2 and N_2 at 300 K.

Effect of Temperature on Distribution of Speeds

It may be noted carefully that fraction of molecules having most probable speed remains the same so long as temperature remains same. However, on increasing the temperature of the gas, the molecular motion becomes rapid and consequently, the value of *most probable speed* also increases.

From the curves shown in Fig. 2.10. It is evident that as the temperature rises, following changes are observed.

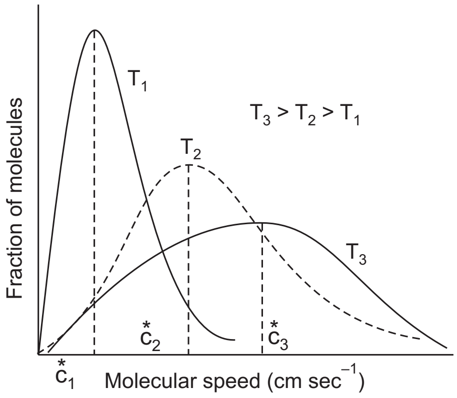


Fig. 2.10. Maxwell's distribution curves at different temperatures.

- The entire curve shifts towards right.
- The most probable speed increases.
- The fraction of molecules having most probable speed decreases.
- The curve becomes broader in the middle range, indicating that more number of molecules have speeds near most probable speed.
- The fraction of molecule having higher speed increases.
- The fraction of molecules having lower speed decreases.

2.8. BEHAVIOUR OF REAL GASES; DEVIATION FROM IDEAL GAS BEHAVIOUR

So far we have been discussing the *p*VT behaviour for an ideal gas, *i.e.,* a *gas which obeys the gas laws and the gas equation $pV = nRT$ strictly at all temperatures and pressures*. The molecules of ideal gas are assumed to be volumeless points with no attractive/repulsive forces between one another. In fact, no real gas strictly obeys the ideal gas law at all temperatures and pressures. Deviations from ideal behaviour are observed particularly at high pressures and low temperatures.

For example, if we plot a graph between the product *p*V versus *p* for different gases at constant temperature we should get a straight line parallel to the pressure axis because according to Boyle's law, *p*V is constant at all pressures. In fact, we do not get a straight line. There is a significant deviation from the ideal behaviour. Plots of *p*V versus *p* for different real gases at 273 K is given in Fig. 2.11. There are two type of curves in Fig. 2.11.

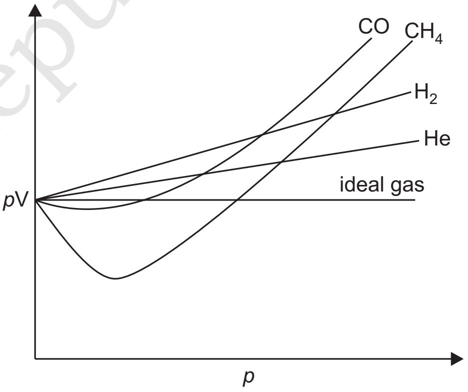


Fig. 2.11. Plots of *p*V *vs p* of some real gases at 273 K.

(*a*) Gases like H_2 and He follow the gas equation at extremely low pressures, but *p*V increases regularly as the pressure increases. Such gases are said to show *positive deviation.*

(*b*) For gases like CO and CH_4, *p*V shows a negative deviation in the beginning, reaches a minimum value (which is different for different gases) and there after it starts increasing with increase of pressure. It crosses the line for ideal gas and then shows a positive deviation continuously.

Cause of Deviation

The study of the curves given in Fig. 2.11 raises the following questions

- *Why do gases deviate from ideal behaviour? and*
- *What are the conditions under which real gases deviate from ideality?*

In order to find answer to these questions let us examine the postulates of Kinetic theory once again. We find that two of the assumptions of the kinetic theory do not hold good at all conditions. These are:

(*a*) *There is no force of attraction and repulsion between the molecules of a gas.*

(*b*) *Volume of the molecules of a gas is negligibly small in comparison to the empty space between them.*

If assumption ***'a'*** is correct, the gases will never undergo liquefaction. However, on the contrary, we know that gases do liquify at low temperatures and high pressures. This indicates the presence of attractive forces among the gas molecules. This view is also supported by the observation that cooling is caused when the compressed gas is allowed to expand. The decrease of temperature occurs because work has to be done to overcome the attractive forces. Further, the liquid obtained as a result of liquefaction of gas is difficult to compress. This shows the existence of repulsive forces which are powerful enough to prevent further squashing of molecules in tiny volume.

If assumption ***'b'*** is correct, then the plot of p *vs* V at constant T based on the experimental data and that based on theoretical calculations from Boyle's law (ideal gas) should coincide. However, deviations are observed in the behaviour at high pressures as shown in Fig. 2.12.

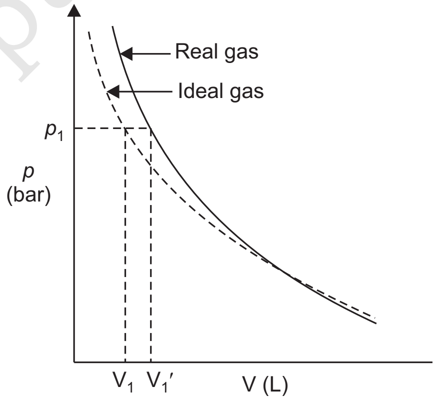


Fig. 2.12. Plot of p vs V for real and ideal gas.

It is apparent that at high pressures (p_1) the measured volume (V_1') is more than the ideal volume (V_1). At low pressures the measured volume and ideal volumes approach each other. The reason for this behaviour is that at high pressures molecules of gases are very close to each other and the volume occupied by the molecules cannot be neglected in comparison to the empty space between them. It is because the total volume of gas decreases considerably but volume of molecules remains same as they are not compressible. For examples, if we assume molecules to be hard spheres ($r = 2 \times 10^{-9}$ m), then volume of the molecules at room temperature (25°C) is about 0.1% of the volume of gas at 1 bar pressure and it is about 1% of the volume of gas at 10 bar pressure. Thus, at high pressures gas molecules get less space for free movement and *molecular interaction* start operating. This affects the actual pressure exerted by the molecules on the walls of the container. Molecules do not strike the walls with full impact because these are dragged back by other molecules due to molecular attractive forces. ***Hence, real gases show ideal behaviour when pressure approaches zero but deviations from ideal behaviour is observed at high pressures.*** Therefore, the two postulates **'*a*'** and **'*b*'** of kinetic-molecular theory need revision.

Van Der Waal's Equation of State for Real Gases

Van Der Waal in 1873 modified the ideal gas equation $p_i V_i = n\text{RT}$ by introducing two correction terms, *one for the volume* and *the other for the pressure*, to make the equation applicable to real gases as well.

(*a*) **Volume correction.** As pointed out earlier, that the volume of the molecules is not negligible as compared to the total volume of the gas. This implies that the molecules are not free to move about in the entire volume (V) which we observe. Thus, the free volume available to the gas molecules is smaller than the observed volume. In other words, *the ideal volume (V_i) is smaller than the observed volume (V).* Hence some correction term has to be subtracted from the observed volume to get the ideal volume.

Let the correction term by v

$\therefore$ ideal volume $V_i = (V - v)$

Now v the volume to be excluded is directly proportional to the number of molecules (N) which in turn depends upon the number of moles (n).

Thus, $v \propto n$ or $v = nb$

where, b is constant of proportionality and is called van der Waal constant. Substituting the value of v, we get

Ideal volume, $(V_i) = (V - nb)$

Here, n = Number of moles of real gas

b = Constant which depends on nature of real gas.

Significance of constant 'b'. The constant '**b**' is called *co-volume* or *excluded volume per mol of a gas*. Its units are **litre mol^{-1}.** It is a measure of effective size of gas molecules. The value of **b** is *four times* the actual volume of the molecules (*Refer solution of VSAQ. 17 of Study Questions).*

(*b*) **Pressure correction.** The pressure of the gas is due to the force with which molecules of the gas collide with the walls of the container. Since the intermolecular attractions cannot be neglected at low temperatures and high pressures. Therefore the molecules which are going to strike the walls experience some backward drag due to inward pull of adjacent molecules as shown in the diagram. As a result, the molecules strike the walls with a smaller force because of the *inward pull*. Consequently, the pressure that we observe (P) is relatively smaller than the pressure if there were no attractive forces. In other words, *the observed pressure (p) is smaller than the ideal pressure (p_i).* Thus, in order to get the ideal pressure (p_i) some correction term has to be added to the observed pressure (p).

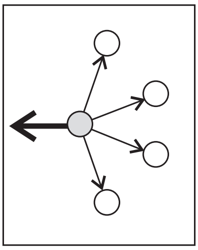


Fig. 2.13. Molecule striking the wall experiences inward pull.

Let the correction terms be p'

$\therefore$ Ideal pressure $p_i = (p + p')$

Now, p is directly proportional to the square of the density or square of (n/V)

Thus, $p' \propto (n/V)^2$

$= a\, n^2/V^2$

where, a is constant of proportionality called another van der Waal constant.

Hence, ideal pressure $(p_i) = \left(p + \dfrac{an^2}{V^2}\right)$

Here, n = Number of moles of real gas

V = Volume of the gas

a = A constant, whose value depends upon the nature of the gas.

Significance of 'a'. The value of constant '**a**' gives the idea of the magnitude of attractive forces between the molecules of the gas. Its units are **atm L^2 mol^{-2} or bar L^2 mol^{-2}.** Larger the value of **a,** larger will be the intermolecular attraction among the gas molecules.

Substituting the values of ideal volume and ideal pressure, the modified equation is obtained as

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \qquad \text{...(2.8)}$$

The constants *a* and *b* are also called **van der Waal constants.**

It may be noted that gases show *positive deviations* (Z > 1) when *effect of molecular volume dominates*. Similarly, *negative deviations* (Z < 1) are shown when the *effect of molecular attraction predominates*.

van der Waal constants for some gases are given in Table 2.4.

Table 2.4. van der Waal Constants for Some Gases

Gas	*a* *(atm* L^2 *mol^{-2})*	*b* *(L mol^{-1})*	*Gas*	*a* *atm* L^2 *mol^{-2})*	*b* *(L mol^{-1})*
He	0.034	0.0236	CO_2	3.6	0.043
H_2	0.0245	0.0267	HCl	3.8	0.041
O_2	1.36	0.0318	NH_3	4.0	0.036
N_2	1.37	0.0391	SO_2	6.7	0.056

Difference between Ideal Gas and Real Gas

The main differences between ideal gas and real gas are given below in tabular form.

Ideal Gas	*Real Gas*
1. Ideal gas obeys all the gas laws at all temperature and pressures.	1. It obeys gas law only at very low pressures and high temperatures.
2. Volume of molecules is negligible as compared to total volume of gas.	2. Volume of molecules is not negligible.
3. Attractive forces among the molecules do not exist.	3. Attractive forces among the molecules do exist particularly high pressures and low temperatures.
4. It obeys the equation of state $pV = nRT$.	4. It obeys van der Waal equation $(p + an^2/V^2)(V - nb) = nRT$.
5. It is hypothetical.	5. All existing gases are real.

Example 2.5. *Calculate the pressure exerted by 8.5 g of ammonia (NH_3) contained in 0.5 L vessel at 300 K. For ammonia a = 4.0 atm L^2 mol^{-2}, b = 0.036 L mol^{-1}. Compare the value with the calculated value if the gas were considered as ideal.*

Solution. Number of moles of ammonia

$$n = \frac{8.5}{17} = 0.5 \text{ mols}$$

According to van der Waal's equation,

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$p = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$$

$$= \frac{0.5 \times 0.082 \times 300}{(0.5 \times 0.5 \times 0.036)} = \frac{4(0.5)^2}{(0.5)^2}$$

$$= \mathbf{21.51 \text{ atm.}}$$

If the gas were considered ideal, then the value of pressure (p) can be obtained by using ideal gas equation as

$$p = \frac{nRT}{V} = \frac{0.5 \times 0.82 \times 300}{0.5} = \mathbf{24.6 \text{ atm.}}$$

2.9. EFFUSION AND DIFFUSION

Gas molecules move almost freely in the space available to them. When a gas contained in a container is allowed to come out of a hole, the process is called **effusion**. Rate of effusion depends upon the difference in pressure inside and outside of the container and mass of the gas molecules as a result of which lighter gases effuse with more speed and heavier gases effuse with less speed.

Gas molecules travel freely and collide with other molecules and hence travel in many different directions until they occupy the available space uniformly. This process is called **diffusion**. In diffusion molecules move from high concentration to low concentration of molecules. When a bottle of perfume is opened in one corner of a room, perfume molecules move and spread in the room evenly making perfume smell available throughout the room.

Effusion. Effusion is the process in which a gas escapes from a container through a whole of diameter considerably smaller than the mean free path of molecules. The gas effuses out of the balloon overtime.

Molecules move randomly and collide with other molecules consistently. The average distance travelled by a molecule between two collisions is known as **mean free path** of that particle. Nitrogen gas has a greater rate of effusion than oxygen because lighter gases travel faster than heavier and dense gases. Denser the gas, the shorter the mean free path. When density decreases the mean free path become longer as frequency of collision is less.

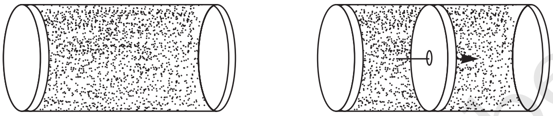

Diffusion Effusion

Fig. 2.14

Diffusion: Diffusion is the gradual mixing of gases due to persistent movement of particles without any mechanical effort like stirring. Molecules keep on moving till mixing is done uniformly. Diffusion takes place in liquids and solids also but to a lesser extent.

Graham's Law

Graham's law states that the ratio of the effusion and diffusion rates of two gases is the square root of the inverse ratio of their molar masses.

Rate of effusion or diffusion $\alpha \frac{1}{\sqrt{M}}$

$$\frac{\text{Rate of effusion A}}{\text{Rate of diffusion B}} = \sqrt{\frac{M_B}{M_a}}$$

Hydrogen will effuse or diffuse more rapidly than helium as hydrogen has less molecular mass hence less dense. According to Graham's law all gases at same temperature have same kinetic energy. The kinetic energy of two gases with different molar masses will be

$$kE = \frac{1}{2}\frac{M_A}{N_A}V^2_{rms\ A} = \frac{1}{2}\frac{M_B}{N_B}V^2_{rms\ B}$$

Multiply both sides by 2 and rearrange

$$\frac{V^2_{rmv}\ B}{V^2_{rmv}\ A} = \frac{M_A}{M_B}$$

Take square root of both sides.

$$\frac{V_{rmv}\ B}{V_{rmv}\ A} = \sqrt{\frac{M_A}{M_B}}$$

Hence, the rate of effusion or diffusion of molecules is directly related to the speed of molecules. Graham's law shows that gaseous molecules have same average kinetic energy at same temperature.

Use of Diffusion in Enrichment of Uranium

Uranium which is used in nuclear power plants, and weapons is enriched using the process of gaseous diffusion. The uranium occuring naturally contain about 0.72% of ^{235}U. This kind of uranium is capable of sustaining nuclear fission chain reaction hence is "fissile". In nuclear reactors 2–5% ^{235}U is used and even ^{235}U with even more concentration is used in nuclear bombs. In order to enrich uranium to the desired level advantage of Graham's law is taken. In uranium enrichment plant UF_6 (the passed uranium compound that is volatile enough to work) is slowly through large cylindrical vessels called diffusers, which contain porous barriers with microscopic holes. The process used here is gaseous diffusion. The ^{235}UF have little higher average speed and diffuse through the barrier a little faster than $^{238}UF_6$ molecules. The gas after passing through the diffuser is slightly enriched in ^{235}UF and the residual gas is slightly depleted. There is a small difference is molecular masses of $^{235}UF_6$ and $^{238}UF_6$, hence about 0.4% enrichment is done in one diffuser. But by connecting many diffusers in a series (called a cascade), the desired level of enriched ^{235}UF can be obtained. This process was first used in World War II during development of first atom bomb. In this process barrier (diffuser) have tiny and uniform holes of about 10^{-6} cm in diameter were used.

Difference between Effusion and Diffusion

Effusion	*Diffusion*
1. Effusion happens when the gaseous molecules tend to escape through a pin hole of a container to the vacuum.	1. Diffusion happens when one gas tries to mix with another by random motion which result in collision between gas molecules.
2. Effusion is the ability of a gas to pass through microscopic hole.	2. Diffusion is the ability of a gases to mix, with each other evenly and uniformly in the absence of a barrier.
3. During effusion the diameter of the hole is much smaller than mean free path of the molecules.	3. The rate of diffusion depends up on the size and the kinetic energy of molecules.

4. Effusion takes place when there is difference in pressure inside and outside the container.	4. Diffusion takes place when there is a difference in concentration between to points.

Is the Rate of Effusion and Diffusion Same

Rate of diffusion depends upon surface area, difference in concentration between two points, travelling distance, and the time which is inversely proportional.

Rate of effusion depends up on size of the hole, density of the gas, and size of the molecules. Hence rate of effusion and diffusion are not equal but their ratios are same.

2.10. CHEMISTRY IN ATMOSPHERE

Chemistry in atmosphere is about chemical process which go on within earth's atmosphere. Researches in this area are critical to the improved understanding of climate forcing, air quality and interaction between atmosphere and biosphere. This field is rapidly evolving due to advances in fundamental understanding of chemical processes in the atmosphere. This involves the chemical composition of natural atmosphere and the way gases, liquids and solids in the atmosphere interact with each other and with the earth's surface and associated biota and how human activities change the chemical and physical characteristics of atmosphere. Atmosphere, for convenience is considered as composed of four layers on the basis of temperature variation as the altitude increases. The four layers according to the variation of temperature are

1. Thermosphere or Ionosphere
2. Mesosphere
3. Stratosphere
4. Troposphere

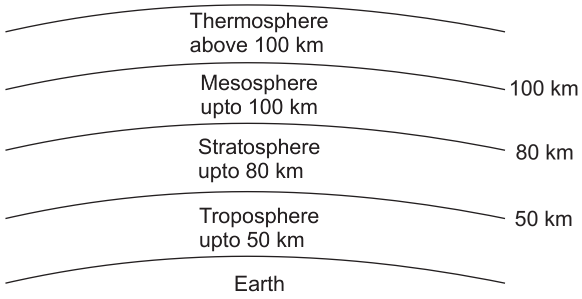


Fig. 2.15

As we go up temperature increases on increase of altitude. Temperature increases from 200 K to 500 K when we go up from 100 km to 300 km. At an altitude from 100–200 km gases are present in the form of biatomic molecules like O_2, N_2, NO etc. but at altitude higher than 200 km gases and present in atomic form H, He and O etc. The thermosphere or ionosphere is full of electrically charged ions. The ultra violet rays ionize these gases to form ions.

The reactions which take place in ionosphere are

$$O + h\nu \longrightarrow O^+ + e^-$$
$$N + h\nu \longrightarrow N^+ + e^-$$

The reactions which take place in neutral thermosphere

$$N + O_2 \longrightarrow NO + O$$
$$N + NO \longrightarrow N_2 + O$$
$$O + O \longrightarrow O_2$$

Thermosphere: Thermosphere is the outer layer of atmosphere which ranges from altitude above 100 km. Lower layer of thermosphere is neutral thermosphere or ionosphere. Above that is exosphere. These layers are favorites for space explorations, environmental studies and space sciences. Atmosphere in the outer space is more like a plasma than a gas.

Mesosphere: Mesosphere lies below thermosphere and ranges from 50 km-100 km altitude. In mesosphere temperature decreases as altitude increases. In mesosphere O_2, O_3, OH, H and NO are prominently available. The reactions which take place in mesosphere are

$$H_2O + h\nu \longrightarrow OH + H.$$
$$H_2O_2 + O \longrightarrow OH + OH$$

Stratosphere: Stratosphere is the layer below mesosphere. In stratosphere the altitude increases from 10 km-50 km. Reactions which take place in stratosphere are

$$NO_2 \longrightarrow NO + O$$
$$N_2O \longrightarrow N_2 + O$$
$$H_2 + O \longrightarrow OH + H$$
$$CH_4 + O \longrightarrow OH + CH_3$$

Upper stratosphere has a high concentration of ozone forming an ozone layer. In stratosphere air flows horizontally. Ozone layer absorbs ultraviolet rays coming from sun. Ozone is produced in stratosphere according to following reaction

$$O_2 + h\nu \rightarrow O + O$$
$$O_2 + O \rightarrow O_3$$

Weather takes place in troposphere. It is the region where air flows. The air pressure at sea level is 1 atmosphere while at the top of the troposphere it is only 0.1 atmosphere (10% of air pressure at sea level).

Tropopause is the thin buffer zone between the troposphere and the next layer (stratosphere).

Composition of Air in Stratosphere

N_2 – 78%
O_2 – 21%
Ar – 1%
CO_2 – 0.3% approx.
CH_4, H_2O, NO_2, N_2O, CO and O_3 – Variable amounts

Pollutants in the atmosphere

Atmosphere is polluted by different gases thrown in the atmosphere by industries.

Following gases pollute the atmosphere

- Nitrogen oxides such as NO, N_2O_4, NO_2 due to production of NO in engines during to internal combustion.
- Carbon dioxide produced by burning of fuel containing carbon.
- Carbon monoxide, a very toxic gas produced by automobiles.
- Ozone is produced by internal combustion engines and also formed in the ozone layer as explained earlier.
- SO_2 produced in mines and by combustion of sulphur containing fuel. SO_2 when reacts with water in the atmosphere producer H_2SO_4 and H_2SO_4 and cause **acid rains**.
- Chlorofluorocarbon (CFC) gases are used as refrigerant cause ozone layer to decrease.
- Water vapours are produced in atmosphere due to radiations from sun. Water vapours when condenses cause rains, storms, cyclones etc.

SUMMARY

- **Gas Laws.** The generalisations regarding the behaviour of gases.
- **Boyle's Law.** The volume of a fixed mass of a gas is inversely proportional to the pressure at constant temperature.
- **Charle's Law.** The volume of fixed mass of a gas is directly proportional to the temperature (in Kelvin scale) at constant pressure.
- **Gay Lussac's Law.** The pressure of fixed mass of a gas at constant volume is directly proportional to its temperature in Kelvin.
- **Avogadro's Law.** Under similar conditions equal volumes of various gases contain equal number of molecules.
- **Dalton's Law.** The pressure of the mixture of non-reacting gases is equal to the sum of their partial pressure when enclosed in the same volume under similar conditions.
- **Graham's Law of Diffusion.** The rate of diffusion of gases (V/t) is inversely proportional to square root of their densities under similar conditions.

EVALUATION

I. Multiple Choice Questions

1. The ratio of root mean square speed of hydrogen at 50 K and that of oxygen at 800 K is:

(a) 0.25 (b) 4

(c) 2 (d) 1

2. Which of the following sets consists of gases with same rate of diffusion?

(a) H_2, D_2, He (b) CO_2, NO_2, C_3H_8

(c) CO_2, N_2O, C_3H_8 (d) N_2, CO_2, C_2H_4.

3. The rate of diffusion of methane is twice that of X. The molecular mass of X is

(a) 64.0 (b) 32.0

(c) 40 (d) 80.

4. At what temperature, the rate of effusion of N_2 would be 1.625 times that of SO_2 at 50°C?

(a) 110 K (b) 173 K

(c) 373 K (d) 273 K.

5. The average K.E. of an ideal gas per molecule in S.I. units at 25°C will be

(a) 61.7×10^{-21} J (b) 6.17×10^{-21} J

(c) 6.17×10^{-20} J (d) 7.16×10^{-20} J

6. The density of chlorine relative to air is

(a) 2.46 (b) 3

(c) 4 (d) 5.1

7. Which of the following is not an assumption of the kinetic theory of gases?

(a) Gas particles have negligible volume

(b) Collisious of gas particles are perfectly elastic

(c) At high pressure, gas particles are difficult to compress

(d) A gas consists of many identical particles which are in continual motion.

8. When does a gas deviate the most from its ideal behaviour?

(a) At low pressure and low temperature

(b) At low pressure and high temperature

(c) At high pressure and high temperature

(d) At high pressure and low temperature

9. The root mean square velocity (rms) of N_2 molecules at certain temperature is u. If temperature is doubled and all the nitrogen molecules dissociate into nitrogen atoms, then the new rms will be:

(a) 14 u (b) 2 u

(c) $u/2$ (d) 4 u

10. Among the following, the incorrect statement is:

(a) At low pressures real gases show ideal behaviour.

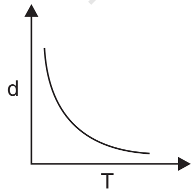
(b) At very low temperatures real gases show ideal behaviour

(c) At very large volume real gases show ideal behaviour

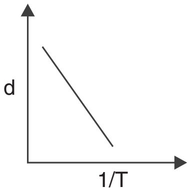
(d) At Boyle's temperature, real show should ideal behaviour.

11. Which of the following graph is correct for ideal gas?

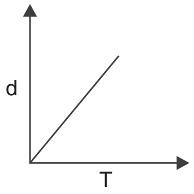
(a)



(b)



(c)



(d) None of these

II. Descriptive Questions

1. Explain the concept of root mean square velocity.
2. What is the difference between effusion and diffusion?
3. Which are the four layers of atmosphere?
4. What do you understand by tropopause?
5. What is the composition of air in stratosphere?
6. What is the difference between ideal gas and real gas?
7. Explain the important features of Maxwell's distribution curve.
8. Is the rate of effusion and diffusion same?

III. Numerical Questions

1. Reading of mercury level in closed end arm of a manometer is 100 mm and in the arm attached to the system is 70 mm. What is the pressure of system? (**Ans.** 30 mm Hg.)
2. 200 cm^3 of a gas at 800 mn pressure is allowed to expand till the pressure is 0.9 atm keeping the temperature constant. Calculate the volume of gas. (**Ans.** 233.92 cm^3)
3. A gas occupies 100.0 mL at 50°C and 1 atm pressure. The gas is cooled to reduce volume to 50.0 mL at constant pressure. What will be the final temperature? (**Ans.** –111.57°C)
4. Calculate the pressure exerted by 56 g of an ideal gas (with molar mass 80 g mol^{-1}) enclosed in a vessel of volume 0.1 m^3 at 300 k. (R = 8.314 Nm mol^{-1} k^{-1}) (**Ans.** 49884 Nm^{-2})
5. A gaseous mixture containing 8 g of O_2 and 227 mL of N_2 at STP is enclosed in a flask of 5 L capacity at 0°C. Find the partial pressure of each gas and also calculate the total pressure in the vessel. (**Ans.** Total P = 1.16 atm, PO_2 = 1.115 atm PN_2 = 0.044 atm)

SEMESTER–I (Period–III)

3
TOPIC

Electrolytes—Acid, Bases and Salts

C11CH3

Learning Objectives

Upon completion of this topic, learners will:

- Discuss electrolytes and non-electrolytes
- Elaborate on Acids and Bases involving the Arrhenius and Bronsted-Lowry theories
- Solve sample problems involving the concept of pH and pOH
- Demonstrate calculations that analyze amounts of acid and base dissociated
- Determine the effects of salt on pH and pOH concentrations
- Discuss the concept of Lewis acids and bases
- Interpret the behavior of buffer solutions
- Describe the behavior of certain salts towards hydrolysis and
- Analyze the concentrations of acids and bases using titration

3.1. ELECTROLYTES AND NON-ELECTROLYTES

We know that aqueous solutions of certain substances such as sodium chloride, sulphuric acid, etc., conduct electricity whereas aqueous solutions of certain substances such as sugar, urea, etc., do not conduct electricity. Michael Faraday, in 1824, classified substances into electrolytes and non-electrolytes on the basis of conductivity behaviour of their aqueous solutions. *The substances which conduct electricity in their aqueous solutions* were termed **electrolytes** while those which do not conduct electricity were termed **non-electrolytes.** Svante Arrhenius (1880) explained that electrolytes, when dissolved in water split into charged particles, called ions. This process is called ionisation or dissociation. Certain electrolytes, such as NaCl, KCl, HCl are almost completely ionized in solutions whereas electrolytes such as NH_4OH, CH_3COOH are weakly ionised. *The electrolytes which are almost completely ionized in solutions are called* **strong electrolytes.** On the other hand, *the electrolytes weakly ionized in their solutions are called* **weak electrolytes.** In case of solutions of weak electrolytes the ions produced by dissociation of electrolyte are in equilibrium with undissociated molecules of the electrolyte. The equations for the dissociation of strong electrolytes are written with only a single arrow directed to the right.

$$\mathrm{KCl}(aq) \longrightarrow \mathrm{K^+}(aq) + \mathrm{Cl^-}(aq)$$

$$\mathrm{NH_4Cl}(aq) \longrightarrow \mathrm{NH_4^+}(aq) + \mathrm{Cl^-}(aq)$$

On the other hand, equations for the dissociation of weak electrolytes are written with double arrows ($\rightleftharpoons$).

$$\mathrm{CH_3COOH}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CH_3COO^-}(aq)$$

$$\mathrm{NH_3}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{NH_4^+}(aq) + \mathrm{OH^-}(aq)$$

This type of equilibrium involving ions in aqueous solution is called **ionic equilibrium.**

Activities/Lab Work

List several acids and bases. Then write chemical equation to show how they behave as electrolytes.

As we know that electrolytes conduct electricity in their aquous solution. These conduct electricity because aquous solutions of electrolytes ionize into ions. More is the degree of ionization more strong the electrolyte is. Acids and bases ionize in their aquous solutions hence these are electrolytes. Here are some acids and bases which behave as electrolytes.

$$\mathrm{HCl\ (aq)} \longrightarrow \mathrm{H^+\ (aq) + Cl'\ (aq)}$$

$$\mathrm{H_2SO_4\ (aq)} \longrightarrow \mathrm{2H^+\ (aq) + SO_4''\ (aq)}$$

$$\mathrm{HNO_3\ (aq)} \longrightarrow \mathrm{H^+\ (aq) + NO_3'\ (aq)}$$

$$\mathrm{NaOH\ (aq)} \longrightarrow \mathrm{Na^+\ (aq) + OH'\ (aq)}$$

$$\mathrm{KOH\ (aq)} \longrightarrow \mathrm{K^+\ (aq) + OH'\ (aq)}$$

$$\mathrm{Ca(OH_2)\ (aq)} \longrightarrow \mathrm{Ca^{++}\ (aq) + 2OH'\ (aq)}$$

Acids, Bases and Salts

Electrolytes may be acids, bases or salts. Acids are sour in taste. Vinegar contains acetic acid whereas citrous fruits such as orange, lemon, etc., contain citric acid. Tamarind contains tartaric acid. All these substances you know, are sour in taste. Acids turn litmus paper red. **Bases** are bitter in taste. They turn litmus paper blue. Caustic soda (NaOH), washing soda ($Na_2CO_3.10H_2O$) and aqueous ammonia are commonly used bases. **Salts** are made up of oppositely charged ions. In solid state these ions are held by strong electrostatic forces of attraction. When a salt is dissolved in water the attractive forces between the ions are highly weakened. This is due to the reason that electrostatic forces are inversely proportional to the dielectric constant of the medium and water has a very high dielectric constant of 80. This means that when some electrolyte such as sodium chloride is dissolved in water, the electrostatic interactions between the ions are reduced by a factor of 80 and this facilitates the free movement of ions in the solution. The ions, in solution, are further stabilized by their solvation with water molecules. Water molecules being polar molecules can have ion-dipole interactions with ions of the salt. Thus, ionic compounds get dissociated when dissolved in water.

Now let us consider the case of substances containing polar molecules, such as HCl, CH_3COOH, HCN, etc. These substances when dissolved in water ionize due to dipole-dipole interaction between molecules of water and the polar molecules of the substance.

It may be mentioned here that the term **dissociation** refers to the process of separation of ions in water in case of ionic solids whereas the term **ionization** is used in cases where a molecule splits into ions when dissolved in water.

EXPERIMENT 1

Aim: Experiment to demonstrate the conductivity of electrolytic solutions.

Requirements: Beaker, 6 volts battery, a bulb, a switch, two graphite rods or metal rods, connecting wire, any electrolyte (we take H_2SO_4 (aq) sol.)

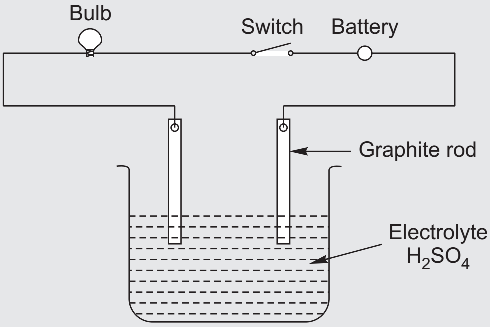


Fig. 3.1. Testing the conductivity of electrolyte

Procedure: Take aqueous solution of H_2SO_4 in a beaker. Place two graphite or metal rods in this solution. Connect graphite rods to the battery, a bulb, a switch with the help of connecting wires. Now switch the current on.

Precautions:

1. Wire connections should be tight.
2. There should be no earthing problem in the circuit.
3. Electrodes (graphite rods) should not touch with each other.

Observations: It is observed that the bulb starts glowing showing that solution of H_2SO_4 conducts electricity.

Result: Glowing of bulb shows that current is passing through the electrolyte hence electrolytes conduct electricity.

3.2. ARRHENIUS AND BRONSTED-LOWRY CONCEPT OF ACIDS AND BASES

Arrhenius Concept of Acids and Bases

According to Arrhenius concept,

An acid is a substance which can furnish hydrogen ions in its aqueous solution.

A base is a substance which can furnish hydroxyl ions in its aqueous solution.

For example, substances such as HNO_3, HCl, CH_3COOH are acids whereas substances such as NaOH, KOH, NH_4OH are bases, according to this concept

$$HNO_3(aq) \rightleftharpoons H^+(aq) + NO_3^-(aq)$$
$$HCl(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$$
$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$
$$NaOH(aq) \rightleftharpoons Na^+(aq) + OH^-(aq)$$
$$KOH(aq) \rightleftharpoons K^+(aq) + OH^-(aq)$$
$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Acids such as HCl and HNO_3, which are almost completely ionized in aqueous solutions are termed as **strong acids** whereas acids such as CH_3COOH which are weakly ionized are called **weak acids.**

Similarly, bases which are almost completely ionized in aqueous solution are called **strong bases,** for example, NaOH and KOH. The bases such as NH_4OH are only slightly ionized and are called **weak bases.**

According to Arrhenius theory, neutralisation of acids and bases is basically a reaction between H^+ and OH^- ions in solutions.

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$$

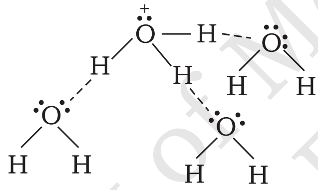
Nature of Hydrogen Ion and Hydroxyl Ion in Aqueous Solution

Hydrogen atom contains one proton and one electron. H^+ ion is formed by loss of this electron. Therefore, H^+ ion is simply a proton. Charge density of this unshielded proton is very high. Therefore, it is not likely to exist independently as H^+ ion. In an aqueous solution H^+ ion is considered to be present in hydrated form in combination with a water molecule as H_3O^+.

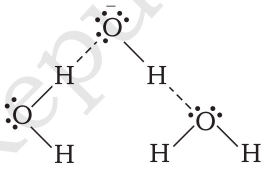
$$H^+ + H_2O \longrightarrow H_3O^+$$

H_3O^+ ion is called **hydronium ion.** It has **trigonal pyramidal** shape.

In aqueous solution hydronium ion is further hydrated to give species such as $H_5O_2{}^+$, $H_7O_3{}^+$ and $H_9O_4{}^+$. Similarly, hydroxyl ion is hydrated to give species such as $H_3O_2{}^-$, $H_5O_3{}^-$, etc.



$H_9O_4^+$ species



$H_5O_3^-$ species

Arrhenius concept of acids and bases has the following **limitations**:

1. Arrhenius concept is applicable only to aqueous solutions. Thus, this concept has a limited application.
2. It does not account for the acidity of substances such as sulphur dioxide, sulphur trioxide, etc., which do not contain any hydrogen ions.
3. It does not account for the basicity of substances such as ammonia, calcium oxide which do not possess hydroxyl group.

Bronsted-Lowry Concept of Acids and Bases

In 1923, a Danish Chemist J.H. Bronsted and an English Chemist T.M. Lowry independently proposed new definitions for acids and bases. They proposed that :

An acid is a substance that can donate a hydrogen ion or a proton.

A base is a substance that can accept a hydrogen ion or a proton.

These definitions are more general because according to these definitions even ions can behave as acids or bases. Moreover, these definitions are not restricted to reactions taking place in aqueous solution only. In order to understand this concept of acids and bases let us take some specific examples.

$$\underset{\text{Acid}}{HCl(aq)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

$$\underset{\text{Acid}}{NH_4^+(aq)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

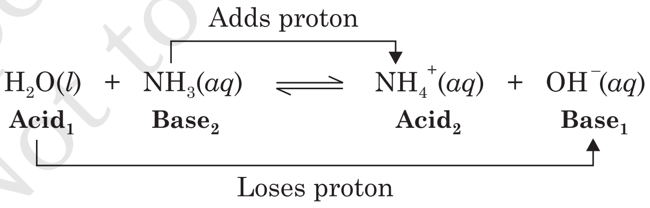
$$\underset{\text{Acid}}{H_2O(l)} + \underset{\text{Base}}{NH_3(aq)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$\underset{\text{Acid}}{H_2O(l)} + \underset{\text{Base}}{CO_3^{2-}(aq)} \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

From the above equations, it is obvious that acid base reactions according to Bronsted-Lowry concept involve transfer of a hydrogen ion or a proton from the acid to a base. A substance can act as an acid only if another substance capable of accepting a hydrogen ion or a proton, is present.

Conjugate Acid-Base Pairs

An acid after losing a hydrogen ion or a proton becomes a base whereas a base after accepting the hydrogen ion or a proton becomes an acid. For example, let us consider the reaction between water and ammonia as represented by the following equilibrium:



$$\underset{\text{Acid}_1}{H_2O(l)} + \underset{\text{Base}_2}{NH_3(aq)} \rightleftharpoons \underset{\text{Acid}_2}{NH_4^+(aq)} + \underset{\text{Base}_1}{OH^-(aq)}$$

In the *forward reaction*, water donates a proton to ammonia (base) and acts as acid. In the *reverse reaction*, NH_4^+ ions donate a proton to the OH^- ions (base) and act as acid. *A base formed by the loss of proton by an acid* is called **conjugate base** of the acid whereas *an acid formed by gain of a proton by the base* is called **conjugate acid** of the base. In the above example, $OH^-$is the conjugate base of H_2O and NH_4^+ is conjugate acid of NH_3. *Acid-base pairs such as H_2O/OH^- and NH_4^+/NH_3 which are formed by loss or gain of a proton are called conjugate acid-base pairs.*

A strong acid would have large tendency to donate a proton. Thus, *conjugate base of a strong acid would be a weak base.* Similarly, *conjugate base of a weak acid would be a strong base.*

Some more conjugated acid-base pairs have been given in the following equations:

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Acid}_2 + \text{Base}_1$$

(1) $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

(2) $H_2O(l) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

(3) $HCO_3^-(aq) + NH_3(aq) \rightleftharpoons NH_4^+(aq) + CO_3^{2-}(aq)$

(4) $HCl(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) + Cl^-(aq)$

It may be noticed that in equation (1) H_2O is behaving as a base whereas in equation (2) it is behaving as an acid. Similarly, HCO_3^- ion in equation (3) acts as an acid and in equation (4) it acts as a base. *Such substances which can act as acids as well as bases are called amphoteric substances.*

Activities/Lab Work

Write an acid base reaction explaining the concept of Arrhenius theories as well as write an acid base reaction analysing the concept of Bronsted-Lowery theories, identifying conjugate acid base pair.

$$\text{NaOH (aq)} + \text{HCl (aq)} \rightleftharpoons \text{NaCl (aq)} + \text{H}_2\text{O}$$

$$\text{OH}' \text{ (aq)} + \text{H+ (aq)} \rightleftharpoons \text{H}_2\text{O}$$

Sodium Hydroxide react with hydrochloric acid to form sodium chloride and water. Here HCl is an acid as it gives H^+. As per Arrhenius theory an acid is substance which furnishes Hydrogen ion in aquous solution hence HCl is an acid.

Same way according to Arrhenius theory base is a substance which furnishes OH′ in its aqueous solution. Hence NaOH is a base as it furnishes OH′.

Concept of Bronsted-Lowery Theory:

According to Bronsted Lowery Theory acid is a substance which can donate a proton or hydrogen ion. Now let us check with some acids whether these donate hydrogen ion or proton or not.

$$\begin{array}{ccccccc}
\textbf{Acid} & & \textbf{Base} & \rightleftharpoons & \textbf{Conjugate acid} & & \textbf{Conjugate base} \\
\text{HCl (aq)} & + & \text{H}_2\text{O (l)} & \rightleftharpoons & \text{H}_3\text{O}^+ \text{ (aq)} & + & \text{Cl (aq)} \\
\text{H}_2\text{SO}_4 \text{ (aq)} & + & \text{H}_2\text{O (l)} & \rightleftharpoons & \text{H}_3\text{O}^+ \text{ (aq)} & + & \text{SO}''_4 \\
\text{HNO}_3 \text{ (aq)} & + & \text{H}_2\text{O (l)} & \rightleftharpoons & \text{H}_3\text{O}^+ \text{ (aq)} & + & \text{NO}_3 \\
\text{NH}_4^+ \text{ (aq)} & + & \text{H}_2\text{O (l)} & \rightleftharpoons & \text{H}_3\text{O}^+ \text{ (aq)} & + & \text{NH}_3\text{(aq)}
\end{array}$$

Here HCl, H_2SO_4, HNO_3 and NH_4^+ are acids as they donate. Hydrogen ion or Proton and H_2O acts as base as H_2O received H^+ or proton.

HCl is an acid and Cl′ is its conjugate base H_2O here acts as base and H_3O^+ (aq) is its conjugate acid.

Example 3.1: *Write conjugate acid or base for following species.*

$$HNO_2 \xrightarrow{\text{Conjugate base}} NO_2^-$$
$$CN^- \xrightarrow{\text{Conjugate acid}} HCN$$
$$HClO_4 \xrightarrow{\text{Conjugate base}} ClO_4^-$$
$$F^- \xrightarrow{\text{Conjugate acid}} HF$$
$$OH \xrightarrow{\text{Conjugate acid}} H_2O$$
$$CO_3^{2-} \xrightarrow{\text{Conjugate acid}} HCO_3^-$$
$$S^{2-} \xrightarrow{\text{Conjugate acid}} HS$$

3.3. LEWIS ACIDS AND BASES

Although Bronsted-Lowry theory was more general than Arrhenius theory of acids and bases but it failed to explain the acid base reactions which do not involve transfer of proton. For example, it fails to explain how acidic oxides such as anhydrous CO_2, SO_2, SO_3, etc., can neutralise basic oxides such as CaO, BaO, etc., even in the absence of solvent.

G.N. Lewis (1923) proposed broader and more general definitions of acids and bases, which do not require the presence of protons to explain the acid base behaviour. According to Lewis concept,

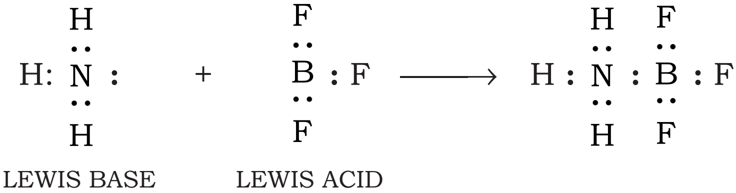
An acid is a substance which can accept a pair of electrons.

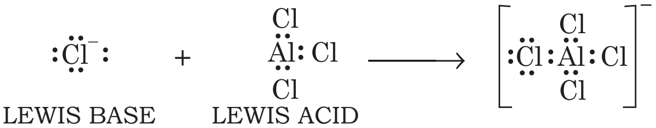
A base is a substance which can donate a pair of electrons.

Acid-base reactions according to this concept involve *donation of electron pair by a base to an acid to form a co-ordinate bond.* Lewis bases can be neutral molecules such as $\ddot{N}H_3$, $CH_3\text{—}\underset{\cdot\cdot}{\ddot{O}}H$, $H_2\underset{\cdot\cdot}{\ddot{O}}$, etc., having one or more unshared pairs of electrons, or anions such as CN^-, OH^-, Cl^-, etc.

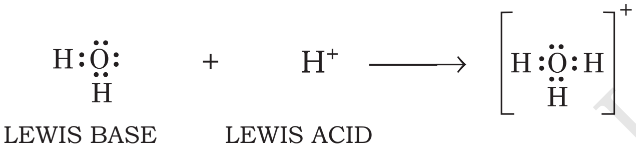
Lewis acids are the species having vacant orbitals in the valence shell of one of its atoms. The following species can act as Lewis acids.

(*a*) *Molecules having an atom with incomplete octet.* For example, BF_3 and $AlCl_3$



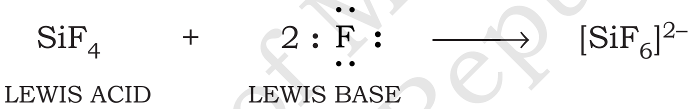


(*b*) *Simple cations.* For example, H^+, Ag^+, etc.



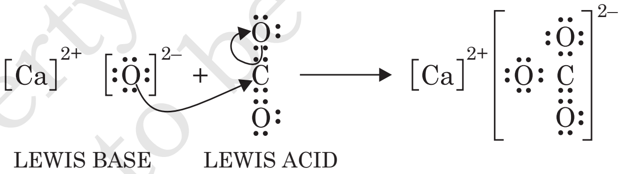
$$2\ddot{N}H_3 + Ag^+ \longrightarrow [H_3N : Ag : NH_3]^+$$

(*c*) *Molecules in which central atom has vacant orbitals and may acquire more than an octet of valance electrons***.** For example, SiF_4.



$$SiF_4 + 2 : \ddot{\underset{\cdot\cdot}{F}} : \longrightarrow [SiF_6]^{2-}$$

(*d*) *Molecules containing multiple bonds***.** For example, CO_2, SO_2, etc.



Limitations of Lewis Concept

Though Lewis concept of acids and bases is more general than the Arrhenius as well as Bronsted concepts, yet it has several drawbacks as discussed below:

1. It is too general and includes all the co-ordination compounds and co-ordination reactions.
2. It does not help to assign the relative strengths of acids and bases.
3. It does not explain the behaviour of protonic acids such as HCl, H_2SO_4, etc., which do not form co-ordinate bond with bases which is the primary requirement of Lewis theory.

4. Normally, formation of co-ordination compounds is slow. Therefore, acid-base reactions should also be slow, but in actual practice, acid-base reactions are extremely fast.
5. The catalytic activity of many acids is due to $H^+(aq)$ ion. Since a Lewis acid need not contain hydrogen, many Lewis acids will not possess catalytic property.

Example 3.2: *Classify following into acids and bases according to Lewis concept.*

SO_2, CaO, OH^-, BF_3, RNH_2, S^{2-}, Ag^+, H^+

Solution.

Lewis acid: SO_3, BF_3, Ag^+, H^+

Lewis base: OH^-, CaO, RNH_2, S^{2-}

3.4. DISSOCIATION OR IONIZATION OF ACIDS AND BASES

Acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) are termed *strong* because they are almost completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton (H^+) donors. Similarly, strong bases like sodium hydroxide ($NaOH$), potassium hydroxide (KOH), caesium hydroxide ($CsOH$) and barium hydroxide $Ba(OH)_2$ almost completely dissociate into ions in an aqueous medium giving hydroxyl ions, OH^-. According to Arrhenius concept they are strong bases as they are able to completely dissociate and produce OH^- ions in the medium.

According to Bronsted-Lowry concept of acids and bases, the strength of an acid is measured in terms of its tendency to lose proton whereas strength of a base is measured in terms of its tendency to accept proton. An acid is considered to be strong if it has great tendency to lose proton. ***The conjugate base of a strong acid is a weak base.***

$$\underset{\text{Strong acid}}{HCl(aq)} + H_2O(l) \rightleftharpoons H_3O^+(aq) + \underset{\text{Weak base}}{Cl^-(aq)}$$

On the other hand, ***conjugate base of a weak acid is a strong base.***

$$\underset{\text{Weak acid}}{CH_3COOH(aq)} + H_2O(l) \rightleftharpoons H_3O^+(aq) + \underset{\text{Strong base}}{CH_3COO^-(aq)}$$

A base is considered to be strong if it has great tendency to accept a proton. Therefore, conjugate acid of strong base has little tendency to lose proton and hence is a weak acid.

$$\underset{\text{Strong base}}{CH_3COOH(aq) + OH^-(aq)} \rightleftharpoons \underset{\text{Weak acid}}{H_2O(l) + CH_3COO^-(aq)}$$

On the other hand, conjugate acid of a weak base is a strong acid.

$$\underset{\text{Weak base}}{HCl(aq) + H_2O(l)} \rightleftharpoons \underset{\text{Strong acid}}{H_3O^+(aq) + Cl^-(aq)}$$

The strength of acids or bases is experimentally measured by determining its ionization constants or dissociation constants.

Calculation of $[H_3O^+]$ and Degree of Dissociation

From the knowledge of K_a it is possible to calculate hydronium ion concentration and degree of ionization of a weak acid. As an example, let us take the case of acetic acid. The following equation represents the ionisation of acetic acid in aqueous solution:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Suppose C moles of CH_3COOH are dissolved per litre of solution and let α be the degree of ionization of CH_3COOH, then at equilibrium the concentration of various species would be as follows:

$$[CH_3COOH] = C(1-\alpha)$$

$$[H_3O^+] = C\alpha$$

$$[CH_3COO^-] = C\alpha$$

Therefore, $K_a = \dfrac{(C\alpha)(C\alpha)}{C(1-\alpha)} = \dfrac{C\alpha^2}{(1-\alpha)}$

Since for weak acid α is very small as compared to 1, α in the denominator can be neglected. The expression of K_a then becomes

$$K_a = C\alpha^2$$

Knowing the value of K_a it is possible to calculate the degree of ionization of the acid at any particular concentration C.

$$\alpha = \sqrt{\frac{K_a}{C}}$$

From the degree of ionization, hydronium ion concentration can be calculated as:

$$[H_3O^+] = C\alpha$$

Dissociation Constants of Bases in Water

The **relative strengths of bases** are also compared in terms of their dissociation or ionization constants. The ionization constant $\mathbf{K}_b$ for a weak base B can be represented as follows:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

Smaller the value of ionization constant for a base, weaker is the base.

If C is the molar concentration of base and α is its degree of dissociation, then by similar calculation (as in case of acids) we can derive the relations,

$$\alpha = \sqrt{\frac{K_b}{C}}$$

and $[OH^-] = C\alpha$.

The values of ionization constants for some weak bases are given in Table 3.1.

Table 3.1. The Ionization Constants of Some Bases at 298 K

Base	*Ionization Constant, K_b*
Ammonia, NH_3	1.8×10^{-5}
Methylamine, CH_3NH_2	4.6×10^{-4}
Dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}
Trimethylamine, $(CH_3)_3N$	6.5×10^{-5}
Aniline, $C_6H_5NH_2$	4.3×10^{-10}
Pyridine, C_5H_5N	1.8×10^{-9}

Polyprotic Acids and Polyhydroxy Bases

The acids, such as HCl, CH_3COOH, HCN, etc., which have only one ionizable hydrogen are known as **monoprotic acids.**

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

On the other hand, there are many acids, such as phosphoric acid (H_3PO_4), sulphuric acid (H_2SO_4), oxalic acid ($H_2C_2O_4$), which have more than one ionizable hydrogen atoms. Such acids are known as **polyprotic acids.** Thus:

The acids which have more than one ionizable hydrogen atoms are known as polyprotic acids.

Polyprotic acids are also known as **polybasic acids.** A polybasic acid ionizes stepwise. The stepwise ionization of phosphoric acid, H_3PO_4 is as follows:

$$H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$$

$$K_{a_1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$$

$$K_{a_2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.2 \times 10^{-8}$$

$$HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$$

$$K_{a_3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.2 \times 10^{-13}$$

Here, K_{a_1}, K_{a_2} and K_{a_3} are the first, second and third ionization constants of phosphoric acid respectively. It may be noted that K_{a_1} is greater than K_{a_2} which in turn is greater than K_{a_3}. The reason for this is that it is more difficult to remove a proton (H^+) from a negative ion due to electrostatic forces. For example, it is more difficult to remove a proton from HPO_4^{2-} than from $H_2PO_4^-$ or H_3PO_4. The ionization constants for some common polyprotic acids are listed in Table 3.2.

Table 3.2. Ionization Constants of Some Common Polyprotic Acids at 298 K

Acid	K_{a_1}	K_{a_2}	K_{a_3}
Carbonic acid	4.3×10^{-7}	5.6×10^{-11}	
Oxalic acid	5.9×10^{-2}	6.4×10^{-5}	
Hydrogen sulphide	1.0×10^{-7}	1×10^{-19}	
Adipic acid	3.7×10^{-5}	3.9×10^{-6}	
Sulphurous acid	1.7×10^{-2}	6.4×10^{-8}	
Sulphuric acid	Strong acid (very large)	1.2×10^{-2}	
Ascorbic acid	7.0×10^{-5}	3.0×10^{-12}	
Phosphoric acid	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}
Citric acid	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}

Similarly, polyhydroxy or polyacidic bases ionize in steps and have the corresponding dissociation constants such as K_{b_1}, K_{b_2}, etc. For example, $Ba(OH)_2$ is a diacid base, $Fe(OH)_3$ is a triacid base. However, these polyhydroxy bases have very less solubility.

Example 3.3: *Ionization constant of HF is 3.2×10^{-4}. Calculate the degree of ionization of HF and hydronium ion concentration is 0.02 M solution of HF.*

Solutions.

$$\underset{(0.02-x)\ \text{M}}{\text{HF (aq)}} + \text{H}_2\text{O} \rightleftharpoons \underset{x\ \text{M}}{\text{H}_3\text{O}^+\ \text{(aq)}} + \underset{x\ \text{M}}{\text{F}^-\ \text{(aq)}}$$

$$K_\alpha = \frac{[H_3O^+][F]}{[HF]} = \frac{(x)(x)}{(0.02-x)}$$

$$3.2 \times 10^{-4} = \frac{x^2}{0.02-x} = \frac{x^2}{0.02} \qquad \because 0.027x$$

$$x^2 = 3.2 \times 10^{-4} \times 0.02$$

$$x^2 = 6.4 \times 10^{-6}$$

$$x = 6.4 \times 10^{-6}$$

$$x = 2.5 \times 10^{-3}\ \text{m}$$

$$\alpha = \frac{2.5 \times 10^{-3}}{0.02} = 0.125$$

3.5. EXPRESSING HYDRONIUM ION CONCENTRATION—pH SCALE

We have seen that concept of ionic product of water enables us to classify solutions as acidic, basic, or neutral by specifying the H_3O^+ ion concentration. For expressing the H_3O^+ ion concentration a logarithmic scale was devised by P.L. Sorensen (1909). This scale is called **pH scale.** *The pH of a solution may be defined as negative logarithm of the activity of hydrogen ion (a_{H^+}).*

Do You Know?

The symbol pH is derived from *Potenz*, the Danish word for power, pH refers to potency of hydronium ion in solution. The potency of hydroxyl ions of solution is expressed in terms of pOH.

In dilute solutions activity of hydrogen ions is equal in magnitude to the concentration of hydrogen ions in moles per litre *i.e.,* molarity. Activity is a dimensionless quantity and is defined as

$$a_{H^+} = \frac{[H^+]}{\text{mol L}^{-1}}$$

From the definition of pH, we can write pH

$$= -\log [H^+] \quad \text{or} \quad -\log [H_3O^+]$$

In the present text we shall be using concentration of hydrogen ions or hydronium in place of activity for calculating the pH of solutions. Thus, mathematically, pH may be expressed as

$$pH = -\log [H^+] \text{ or } -\log [H_3O^+]$$

From the above relation, the concentration of $[H^+]$ can be written as

$$[H^+] = 1 \times 10^{-pH}$$

This enables us to give alternative definition of pH as the *negative power to which 10 must be raised in order to express the hydrogen ion or hydronium ion concentration of the solution.*

For pure water or neutral solutions, at 298 K, $[H_3O^+] = 1 \times 10^{-7}$ mol L^{-1}. Therefore, pH of such solutions is given as:

$$pH = -\log [H_3O^+] = -\log [1 \times 10^{-7}] = 7.$$

For acidic solutions, $[H_3O^+]$ concentration is more than 1×10^{-7} mol L^{-1}. Therefore, pH of acidic solution is **less than 7.** For basic solutions, the pH value is **greater than 7.** Correspondingly, range of pH is from 0 to 14.

The solutions having pH between 0 and 2 are strongly acidic, those with pH between 2 to 4 are moderately acidic while others having pH between 4 to 7 are weakly acidic. Similarly, the solutions having pH value between 7 to 10 are weakly basic, those having pH 10 to 12 are moderately basic whereas others which have pH range between 12 to 14 are strongly basic.

The complete range of $[H_3O^+]$ and pH has been illustrated in Fig. 3.4.

The approximate pH of a solution can be determined with the help of **pH papers.** pH papers have different colours in solutions of different pH. A pH paper can determine pH of a solution with an accuracy of about 0.5. However, for accurate measurement of pH (upto accuracy of 0.001 units) **pH metres** are used.

The approximate pH of some common substances are given in Table 3.3.

Table 3.3. The pH of Some Common Substances

Name of the Fluid	*pH*
Saturated solution of NaOH	~ 15
0.1 M NaOH solution	13
Lime water	10.5
Milk of magnesia	10
Egg white, sea water	7.8
Human blood	7.4
Tears	7.4
Milk	6.8
Human saliva	6.4
Black coffee	5.0
Tomato juice	~ 4.2
Soft drinks and vinegar	~ 3.0
Lemon juice	~ 2.2
Gastric juice	~ 1.2
1 M HCl solution	~ 0
Concentrated HCl	~ –1.0

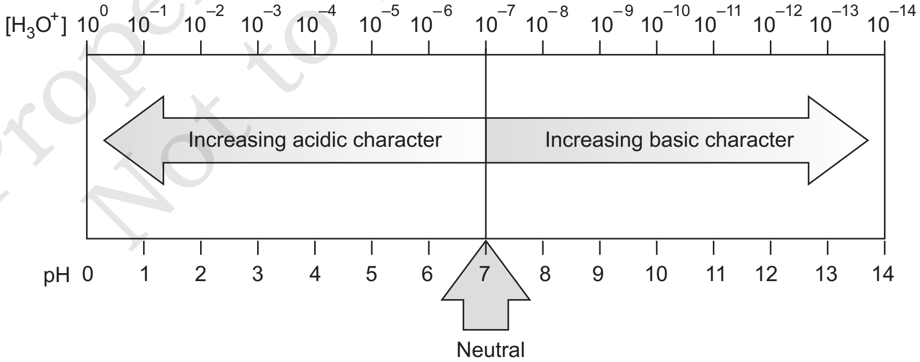


Fig. 3.2. Range of pH and [H_3O^+].

Add to Your Knowledge

- **pOH of the solution**

  Like pH, pOH may be defined as the negative logarithm of hydroxyl ion concentration of the solution in moles per litre

  $$\text{pOH} = -\log[\text{OH}^-].$$

- **Relationship between pH and pOH of solution**

  $$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}, \text{ at } 25°\text{C}$$

  $$\log K_w = \log[\text{H}_3\text{O}^+] + \log[\text{OH}^-] = -14$$

  or $$-\log K_w = -\log[\text{H}_3\text{O}^+] + (-\log[\text{OH}^-]) = 14$$

  or $$\mathbf{pK_w = pH + pOH = 14} \quad \text{at } 25°\text{C}$$

- As the temperature increases K_w increases and pK_w decreases. Consequently, pH and pOH of solution also decrease.
- pH of neutral water is < 7 at high temperatures. For example, the pH of neutral water at 37°C, the body temperature, is 6.98.
- It is more appropriate to express the strengths of acids and bases in terms of their pK_a or pK_b values

  $$pK_a = -\log K_a;\ pK_b = -\log K_b$$

- Lower the value of pK_a, stronger will be the acid.

EXPERIMENT NO. 2

Aim: To measure the pH of a solution using pH paper and universal indicator.

Requirements: Test tubes, measuring cylinders, glass rod, pH paper, universal indicator solution, 0.1 M HCl, 0.01 M HCl, 0.001 M HCl and 0.0001 M HCl.

Procedure: 1. Using pH paper. Put 2–3 drops of sample solution on pH paper by means of a glass rod and observe the colour on pH paper. Now compare the shades of colour formed with various colours given on "pH indicator chart". Note down the approximate pH of sample colour and record in the table.

2. **Using universal indicator solution.** Take clean and dry test tube. Take 5 ml of each of given solution in different test tubes with the help of measuring cylinder. Put 2–3 drops of universal indicator in each test tube by means of a dropper. Note the colour of solution in each test tube and compare its colour with different colour shades as given in "pH indicator chart" after comparing the colour in each tube, note the pH of solution and record in the table.

3. **Using pH meter.** Take a pH meter, turn it on. Put meter on pH mode. Now place the electrode in the appropriate solution and begin reading. Press the measure button to begin reading pH once your electrode is placed in the solution. Take four readings and record in the table.

Observations:

Sample No.	*Molarity of acid sol.*	*For pH paper*		*For universal indicator*		*For pH meter*	*Calculated pH*
		colour	*pH value*	*colour*	*pH*	*pH*	*– log (H_3O^+)*
1.							
2.							
3.							
4.							
5.							

Example 3.4: *How many grams of NaOH must be dissolved in one litre of the solution to have a solution of pH = 12?*

Solution.

$$\text{pH} = -\log[H_3O^+] = 12$$

$$\log[H_3O^+] = -12$$

$$\therefore \quad [H_3O^+] = 1 \times 10^{-12} \text{ mol L}^{-1}$$

We know that

$$K_w = [H_3O^+][OH^-]$$

$$\therefore \quad [OH^-] = \frac{K_w}{[H_3O^+]}$$

3.6. ACID-BASE PROPERTIES OF SALTS

A ***salt*** *is a compound formed by replacement of either all or a part of the ionisable hydrogen atoms of an acid by some other cation.*

A salt is formed by neutralization of an acid by a base.

$$\text{Acid + Base} \longrightarrow \text{Salt + Water}$$

For example, sodium chloride (NaCl) is formed by neutralization of hydrochloric acid with sodium hydroxide.

$$\underset{\text{Hydrochloric acid}}{HCl\,(aq)} + \underset{\text{Sodium hydroxide}}{NaOH\,(aq)} \longrightarrow \underset{\text{Sodium chloride}}{NaCl\,(aq)} + \underset{\text{Water}}{H_2O\,(l)}$$

Similarly, potassium nitrate (KNO_3) is formed by neutralization of nitric acid with potassium hydroxide.

$$\underset{\text{Nitric acid}}{HNO_3\,(aq)} + \underset{\text{Potassium hydroxide}}{KOH\,(aq)} \longrightarrow \underset{\text{Potassium nitrate}}{KNO_3\,(aq)} + \underset{\text{Water}}{H_2O\,(l)}$$

Types of Salts

1. ***Normal salts*** *are the salts formed by complete replacement of all the ionisable hydrogen atoms of an acid by metallic or ammonium ions.*

Some **examples** of normal salts are:

$NaCl$, KNO_3, Na_2CO_3, Na_2SO_4, $(NH_4)_3PO_4$

$$\mathbf{H}Cl + NaOH \longrightarrow \mathbf{Na}Cl + H_2O$$

$$H_2SO_4 + 2NaOH \longrightarrow \mathbf{Na}_2SO_4 + 2H_2O$$

2. ***Acid salts*** *are the salts formed by partial replacement of ionizable hydrogen atoms by metal or ammonium ions.*

For example,

$NaHSO_4$, $NaHCO_3$, KH_2PO_4, K_2HPO_4

Because there is still some replaceable hydrogen present in this type of salts, these salts behave as an acid as well as a salt and hence are known as **acid salts**.

Acid salts ionize in water to yield hydrogen ions.

$$NaHSO_4 \longrightarrow Na^+ + H^+ + SO_4^{2-}$$

3. ***Basic salts*** *are the salt formed by partial replacement of hydroxyl groups of a base by some other anion.*

For example,

Basic lead chloride, $Pb(OH)Cl$, basic magnesium bromide, $Mg(OH)Br$.

Chemicals from Common Salt

Sodium chloride ($NaCl$) is known as common salt. It is present in sea water along with many other salts. Sodium chloride is separated from these salts. Sodium chloride also exists as solid salt, in the form of rocks, in several parts of the world. The large crystals of sodium chloride obtained from rocks are generally brown in colour due to impurities present in them. This is known as **Rock salt**. Rock salt is mined just like any other mineral. Common salt is an important component of our food. It is also used for the extraction of sodium metal.

The common salt is an important raw material for many materials of daily use. Some of these compounds are : Caustic soda ($NaOH$), Washing soda ($Na_2CO_3 . 10H_2O$), baking soda ($NaHCO_3$) and bleaching powder ($CaOCl_2$).

Now let us study preparation and uses of some of these compounds.

Sodium Hydroxide, Caustic Soda (NaOH)

Preparation

Sodium hydroxide is prepared by passing electricity through an aqueous solution of sodium chloride (also known as brine) in a specially designed cell. As a result of electrolysis chlorine gas is given off at anode and hydrogen gas at the cathode. Sodium hydroxide solution is formed near the cathode.

$$\underset{\text{Brine}}{2NaCl\,(aq)} + 2H_2O\,(l) \xrightarrow{\text{Electricity}} \underset{\substack{\text{Caustic soda} \\ \textbf{(Near cathode)}}}{2NaOH\,(aq)} + \underset{\substack{\text{Chlorine} \\ \textbf{(At anode)}}}{Cl_2(g)} + \underset{\substack{\text{Hydrogen} \\ \textbf{(At cathode)}}}{H_2(g)}$$

This process is known as **chlor-alkali process** due to the formation of chlorine and sodium hydroxide (an alkali) as the products.

All the three products formed in chlor-alkali process are used for variety of purposes.

For example,

- **Sodium hydroxide** is used in the manufacture of soaps, detergents, paper and artificial silk. It is used for degreasing metals and for purification of bauxite. It is also used in the preparation of many other compounds such as sodium chlorate, sodium hypochlorite, etc.
- **Hydrogen** is used in the manufacture of important compounds such as ammonia, hydrochloric acid, methyl alcohol, etc. It is also used for hydrogenation of oils. Hydrogen is also used as a fuel.
- **Chlorine** is used for disinfection of drinking water and swimming pools. It is used in the preparation of insecticides and pesticides. It is also used in the preparation of many chloro compounds such as CCl_4, $CHCl_3$, sodium chlorate, hydrochloric acid, sodium hypochlorite, etc.

Bleaching Powder, $CaOCl_2$

Bleaching powder is prepared on industrial scale by passing chlorine gas through dry slaked lime. Chemically it is **calcium oxychloride** and is represented by the formula, **$CaOCl_2$**.

It is also known as chloride of lime.

$$\underset{\text{Slaked lime}}{Ca(OH)_2} + Cl_2 \longrightarrow \underset{\substack{\text{Bleaching} \\ \text{powder}}}{CaOCl_2} + H_2O$$

Uses of Bleaching Powder

1. Bleaching powder is chiefly used for bleaching cotton and linen textiles, wood and paper pulp. Delicate articles like silk, wool, straw, etc., are not bleached by it, *as these are likely to be damaged*.
2. It is a strong disinfectant and is therefore, used for sterilization of water.
3. It is employed for making wool unshrinkable.
4. It is also used as an oxidizing agent in the manufacture of many chemicals.

Washing Soda ($Na_2CO_3 . 10H_2O$)

Preparation

Washing soda is prepared from sodium chloride by **Ammonia-soda process** or **solvay process**. In this process carbon dioxide gas is bubbled through a brine solution saturated with ammonia. It results in the formation of sodium hydrogencarbonate.

$$NaCl + H_2O + CO_2 + NH_3 \longrightarrow \underset{\text{Ammonium chloride}}{NH_4Cl} + \underset{\text{Sodium hydrogencarbonate}}{NaHCO_3}$$

Sodium hydrogencarbonate so formed precipitates out in the presence of excess of sodium chloride. The precipitated sodium hydrogencarbonate is filtered off and then ignited to get sodium carbonate Na_2CO_3).

$$\underset{\text{Sodium hydrogencarbonate}}{2NaHCO_3} \longrightarrow \underset{\text{Sodium carbonate}}{Na_2CO_3} + CO_2 + H_2O$$

Anhydrous sodium carbonate thus formed is called **soda ash**. When soda ash is dissolved in water and subjected to crystallisation, the crystals at separate out are of sodium carbonate decahydrate ($Na_2CO_3.10H_2O$) which is also known as **washing soda**.

$$\underset{\text{Soda ash}}{Na_2CO_3} + 10H_2O \longrightarrow \underset{\text{Washing soda}}{Na_2CO_3.10H_2O}$$

Uses of Sodium Carbonate

1. Large quantities of sodium carbonate are used in the manufacture of glass, borax, soap and caustic soda.
2. It is used in paper, paints and textile industries.
3. It is used for softening hard water. It remove temporary as well permanent hardness.

4. It is used for washing purposes in laundry.
5. As an important laboratory reagent both in qualitative and quantitative analysis.

Preparation of Salts in Laboratory

Salts are generally the outcome of neutralization reaction between acids and bases. When an acid react with a base, results in the formation of salts and water. **For example,** hydrochloric acid reacts with sodium hydroxide to form sodium chloride and water.

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

Salts can be prepared in laboratory by following processes:

1. **Reaction of active metal with acid:** The metals which are more active than hydrogen as per activity series react with dilute acid solutions to form salt and hydrogen.

$$\text{Metal} + \text{Acid} \longrightarrow \text{Salt} + \text{Hydrogen gas}$$
$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$
$$2Fe + H_2SO_4 \longrightarrow Fe_2SO_4 + H_2$$
$$Mg + HCl \longrightarrow MgCl_2 + H_2$$

2. **Reaction of strong acid and strong base:** Strong acids like HCl, H_2SO_4, or HNO_3 react with strong base like NaOH, KOH; for corresponding salt and water.

$$\text{Acid} + \text{Base} \longrightarrow \text{Salt} + \text{water}$$
$$HCl + NaOH \longrightarrow NaCl + H_2O$$
$$H_2SO_4 + NaOH \longrightarrow Na_2SO_4 + H_2O$$

3. **Reaction between a metal and a non-metal:** Metal and a non-metal combine to form a salt. For example: sodium reacts with chlorine gas to form sodium chloride.

$$\text{Metal} + \text{Non-metal} \longrightarrow \text{Salt}$$
$$2Na + Cl_2 \longrightarrow 2NaCl$$
$$Fe + S \longrightarrow \underset{\text{Ferrous Sulphide}}{FeS}$$

4. **Reaction between acidic oxide and basic oxide:** Basic oxide like CaO and Na_2O undergo a combination reaction with acidic oxides like CO_2 and SO_3 to form their corresponding salts.

$$CaO + CO_2 \longrightarrow CaCO_3$$
$$Na_2O + SO_3 \longrightarrow Na_2SO_4$$

5. **Reaction between metal and a base:** A strong base react with less active metal and form salt and water. When zink is heated with aqous

solution of NaOH, sodium zincate is formed, sodium zincate (Na_2ZnO_2) is a complex salt.

Manufacturing of Salts in Industries

The common salt NaCl which is used in our kitchens is prepared in industries by various methods.

1. **Manufacture from rock salts:** Beds of rocks are mined and rock salt so obtained if of high degree of purity, is grounded, screened and marketed without much processing. The salt is mined in large lumps that are first crushed, then move finely ground and screened by size into various grades. The salt is then bulk loaded into bags and sent to market.

2. **Manufacture of salt from sea water:** Sea water contains common salt NaCl and so many other salts. Sea water is stored in series of shallow ponds. In these ponds solution is concentrated to a specific gravity of about 1.22 which means that it is 1.22 times more dense as a given volume of pure water. Here suspended impurities like sand, clay and less soluble salt such as calcium carbonate or chalk and calcium sulphate are removed. Solar evaporation of dead sea water is increased by adding dye to the water. Dye permits more heat to be absorbed from sunlight in thinner layers of brine so that shallow ponds may be used and penetration of the brine to the ground is reduced.

When concentrated the brine is passed through a series of crystallizing pan when salt is deposited as evaporation proceeds. The specific gravity of salt increases from 1.22 to 1.26 finally. The crystallizing pans are racked in two rows where those are allowed to drain for several days. After that salt is collected into heaps, drained again lifted from pans and finally dried. In many countries, the industries the salt is harvested mechanically and washed with saturated brine. It is then dewatered, washed with fresh water and stored for further processing or direct sale.

Hydrolysis of Salts

Hydrolysis may be defined as the process in which water reacts with salt to form an acid and a base.

$$\text{Salt} + \text{Water} \rightleftharpoons \text{Acid} + \text{Base}$$

$$K = \frac{[\text{Acid}]\,[\text{Base}]}{[\text{Salt}]\,[\text{Water}]}$$

$$K\,[\text{Water}] = \frac{[\text{Acid}]\,[\text{Base}]}{[\text{Salt}]}$$

Since [Water] remains practically constant during hydrolysis we can write

$$K_h = \frac{[\text{Acid}]\,[\text{Base}]}{[\text{Salt}]}$$

where K_h is the hydrolysis constant of the salt.

The fraction of the total salt that is hydrolysed at equilibrium is called degree or extent of hydrolysis. It is denoted by '*h*'.

1. Hydrolysis of Salt of a Weak Acid and a Strong Base. This type of salts includes salts of sodium and potassium except halides, nitrates and sulphates. For example, sodium carbonate, potassium cyanide, sodium acetate, etc. This type of salts produce ***alkaline solutions*** on hydrolysis. Let us discuss the hydrolysis of a salt MX of this type.

$$\text{MX} + \text{H}_2\text{O} \rightleftharpoons \underset{\text{Strong base}}{\text{MOH}} + \underset{\text{Weak acid}}{\text{HX}}$$

In solution MX and the strong base MOH undergo complete dissociation whereas acid HX being weak acid remains almost undissociated. Therefore, we can write,

$$\text{M}^+ + \text{X}^- + \text{H}_2\text{O} \rightleftharpoons \text{M}^+ + \text{OH}^- + \text{HX}$$

or $$\text{X}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HX}$$

Applying law of mass action,

$$K_h = \frac{[\text{OH}^-]\,[\text{HX}]}{[\text{X}^-]}$$

For the dissociation of weak acid, we can write

$$\text{HX} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{X}^-$$

$$K_a = \frac{[\text{H}_3\text{O}^+]\,[\text{X}^-]}{[\text{HX}]}$$

Multiplying with K_h

$$K_a \times K_h = \frac{[\text{H}_3\text{O}^+]\,[\text{X}^-]}{[\text{HX}]} \cdot \frac{[\text{OH}^-]\,[\text{HX}]}{[\text{X}^-]}$$

$$= [\text{H}_3\text{O}^+][\text{OH}^-]$$

$$= K_w$$

$$\therefore \qquad K_h = \frac{K_w}{K_a} \qquad \ldots(3.1)$$

Degree of Hydrolysis

$$X^- + H_2O \rightleftharpoons OH^- + HX$$

Suppose initial conc. of salt is C and h is the degree of hydrolysis, then

$$[X^-] = C(1 - h),\ [OH^-] = Ch,\ [HX] = Ch$$

$$K_h = \frac{[OH^-][HX]}{[X^-]} = \frac{(Ch)(Ch)}{C(1-h)}$$

$$= Ch^2 \qquad (\because\ 1 - h \approx 1)$$

$$h = \sqrt{\frac{K_h}{C}} \qquad ...(3.2)$$

Thus, degree of hydrolysis of salt of this type is inversely proportional to the square root of conc. of the salt. Substituting the value of K_h from equation (3.1) in equation (3.2)

$$h = \sqrt{\frac{K_w}{K_a \times C}}$$

Hydronium ion conc. and pH

$$[OH^-] = Ch = C\sqrt{\frac{K_w}{K_a \times C}} = \sqrt{\frac{K_w \times C}{K_a}}$$

$$[H_3O^+] = \frac{K_w}{OH^-} = \frac{K_w}{\sqrt{\frac{K_w \times C}{K_a}}} = K_w\sqrt{\frac{K_a}{K_w \times C}}$$

$$= \sqrt{\frac{K_w \times K_a}{C}}$$

$$pH = \frac{1}{2}(-\log K_w - \log K_a + \log C)$$

$$pH = \frac{1}{2}(pK_w + pK_a + \log C)$$

2. Hydrolysis of Salt of a Strong Acid and a Weak Base. This type of salts includes halides, nitrates and sulphates of all metals except that of sodium and potassium. For example, zinc nitrate, copper sulphate, aluminium sulphate, ferric chloride etc. This type of salts produce ***acidic solutions*** on hydrolysis. Let us discuss the hydrolysis of a salt MX of this type

$$MX + H_2O \rightleftharpoons \underset{\text{Weak base}}{MOH} + \underset{\text{Strong acid}}{HX}$$

In solution MX and the strong acid HX undergo complete dissociation whereas the weak base MOH remains almost undissociated. Therefore, we can write,

$$M^+ + X^- + 2H_2O \rightleftharpoons MOH + H_3O^+ + X^-$$

or

$$M^+ + 2H_2O \rightleftharpoons MOH + H_3O^+$$

Applying law of mass action

$$K_h = \frac{[MOH][H_3O^+]}{[M^+]}$$

For the dissociation of weak base we can write

$$MOH \rightleftharpoons M^+ + OH^-$$

$$K_b = \frac{[M^+][OH^-]}{[MOH]}$$

Multiplying with K_h

$$K_b \times K_h = \frac{[M^+][OH^-]}{[MOH]} \cdot \frac{[MOH][H_3O^+]}{[M^+]}$$

$$= [H_3O^+][OH^-] = K_w$$

or

$$K_h = \frac{K_w}{K_b} \qquad \text{...(3.3)}$$

Degree of Hydrolysis

$$M^+ + 2H_2O \rightleftharpoons MOH + H_3O^+$$

Suppose initial conc. of salt is C and h is the degree of hydrolysis. Then at equilibrium

$$[M^+] = C(1 - h), [H_3O^+] = Ch, [MOH] = Ch$$

$$K_h = \frac{[MOH][H_3O^+]}{[M^+]} = \frac{(Ch)(Ch)}{C(1-h)} = Ch^2$$

$$(\because \quad 1 - h \approx 1)$$

$$h = \sqrt{\frac{K_h}{C}} \qquad \text{...(3.4)}$$

Thus, degree of hydrolysis of salts of this type increases with dilution (or decrease in conc.). Substituting the value of K_h from equation (3.3) in equation (3.4)

$$h = \sqrt{\frac{K_w}{K_b \times C}}$$

Hydronium ion conc. and pH

$$[H_3O^+] = Ch = C\sqrt{\frac{K_w}{K_b \times C}}$$

$$= \sqrt{\frac{K_w \times C}{K_b}}$$

$$-\log [H_3O^+] = \frac{1}{2}\,[-\log K_w - \log C + \log K_b]$$

$$pH = \frac{1}{2}\,[pK_w - \log C - pK_b]$$

3.7. BUFFER SOLUTIONS

Generally, pH of the solution changes on addition of small amounts of acids or bases to it. But if the solution contains a weak acid and its conjugate base, or a weak base and its conjugate acids, such a solution can resist change in pH and is called a buffer solution.

A buffer solution is the solution which can resist the change in pH on addition of small amount of acid or base. The ability of buffer solution to resist change in pH on addition of acid or base is called buffer action.

Depending upon pH values, buffer solutions are divided into two classes. If the pH of the buffer solution is *less than 7*, it is called **acidic buffer** and if it is *more than 7*, it is called **basic buffer.**

1. **Strong Acid Buffers:** A strong acid such as nitric acid or hydrochloric acid can act as a buffer with a low pH. Strong acids are completely ionized in aqueous solution and there the concentration of hydrogen ions is high. The addition of a small amount of acid or base to the acid will have negligible effect on the pH of the solution.

2. **Strong Base Buffers:** A strong base such as NaOH, KOH etc., can act as a buffer with a high pH. The addition of small amount of acid or base has negligible effect on pH of solution of such bases. For example, when 1 cm^3 of 0.1 M HCl is added to 100 cm^3 of 0.01 M NaOH solution, the pH changes from 12.00 to 11.96, which is negligible change.

3. **Weak Acid Buffers:** Buffer solutions with pH range 4 to 7 can be prepared from weak acids and their salts with strong bases. For example, acetic acid and sodium acetate are commonly used for this purpose.

4. **Weak Base Buffers:** Buffer solutions with pH values between 7 and 10 can be prepared from weak bases and their salts with strong acids. For example, a solution containing NH_4OH and NH_4Cl acts as a buffer.

Importance of Buffer Solutions

Buffer solutions play an important role in many industrial processes such as electroplating, manufacture of medicines, dyes, photographic materials, etc. Many biological fluids such as blood, urine, etc., have a definite pH which is maintained by buffer action of many substances. The pH of human blood is maintained between 7.35 and 7.45 by buffer action of carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-) and carbon dioxide (CO_2). The pH values of some biological fluids and other systems are given in Table 3.3.

pH of a Buffer Solution

pH of a buffer solution is calculated by applying **Henderson-Hasselbalch equation.** In order to derive this equation let us consider an acidic buffer consisting of weak acid HA and its salt NaA

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \quad \text{...}\textit{Weakly dissociated}$$

$$NaA \longrightarrow Na^+ + A^- \quad \text{...}\textit{Completely dissociated}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Since HA is weakly dissociated, the concentration of HA in solution can be taken equal to the initial concentration of the acid. Since NaA is completely dissociated, concentration of A^- can be taken equal to the concentration of NaA (salt)

$$K_a = \frac{[H_3O^+][\text{Salt}]}{[\text{Acid}]}$$

$$[H_3O^+] = \frac{K_a\,[\text{Acid}]}{[\text{Salt}]}$$

Taking the logarithm on both the sides, we get

$$-\log\,[H_3O^+] = -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

$$pH = pK_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

From the above equation, it is clear that the pH of an acidic buffer solution consisting of a weak acid and its salt depends on the pK_a of the acid, and the concentrations of the salt and acid in the buffer solution.

A buffer solution containing equimolar concentrations of the salt and acid has $pH = pK_a$.

Similarly, for basic buffers,

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

Further, the pH of the basic buffer solution can be calculated from pOH using the relation:

$$pH + pOH = 14$$

or

$$pH = 14 - pOH$$

3.8. ACID-BASE TITRATIONS

An acid-base titration is a method of quantitative analysis for determining the concentration of an acid or base by exactly neutralizing it with a standard solution of acid or base having known concentration. The progress of titration (process of neutralization) is monitored by using pH indicator.

The acid-base titration is useful in case of strong or weak acid or base. Objective of acid-base titration is to know

1. The concentration of acid or base
2. Whether the unknown acid or base is strong or weak.
3. pK_a of unknown acid or pK_b of the unknown base

In titration acid is treated with base and a base is treated with acid. End point of titration is decided by an indicator. Acid-base titration are in use to calculate the amount of known acidic or basic substance through acid base reactions. Hence implies the determination of concentration of solution with respect to water whose pH is 7. A standard solution is added from an apparatus known as burette. The process of adding a standard solution until the reaction is complete is known as titration. All reactions are not titrations. A reaction is a titration if it satisfies following conditions.

(*a*) The reaction has to be fast.

(*b*) The change in free energy during the reaction must be large enough for spontaneity of reaction.

(*c*) It should be possible to decide the completion of reaction very clearly.

End point of titration: End point of titration is a stage that shows the completion of reaction. The end point is detected by a physical change that is either produced by solution itself or by addition of a reagent known as **indicator**.

The **end point** or the **equivalence point** reaches when the stoichiometric amount of acid has been added to the alkali solution. At this point all the alkali has been neutralised and the solution contains salt and water only.

From the end point we can find the volume of the base (V_b) having molarity M_b required to neutralize a certain volume of the acid (V_a) of molarity M_a. Now, number of moles in V mL of a solution of molarity M is given by M × V/1000. For the titrations involving monobasic acid and monoacid base, one mole of base is required to completely neutralize one mole of the acid.

Therefore,

$$\frac{M_a V_a}{1000} = \frac{M_b V_b}{1000} \text{ or } M_a V_a = M_b V_b$$

For titration involving polyacid bases and polybasic acids the above equation takes the form

$$n_a M_a V_a = n_b M_b V_b$$

where n_a is the basicity of the acid while n_b is the acidity of the base.

Thus, for the titration of sulphuric acid with sodium hydroxide, the equation applicable is

$$2M_a V_a = M_b V_b$$

Similarly, for the titration of barium hydroxide (a diacid base) against hydrochloric acid (a monobasic acid) the equation becomes

$$M_a V_a = 2M_b V_b$$

The end point is indicated by colour change of the indicator or a sudden rise or fall in pH. The pH of the reaction mixture changes during the course of titration.

The equivalent point: The equivalent point is a stage of titration, where the amount of reagent added is exactly equal to the amount of the reacting substance in the titrated solution.

End point and equivalent point are supposed to be same. But most often they are not identical as the end point is detected only after addition of a slightly excess amount of titrant. If there is a difference between end point and the equivalent point, then it amounts to an error in the experiment.

Indicator: Acid-base indicators are substances change colour or develop turbidity at a certain pH. This indicates the equivalence point as well as the pH. They are soluble in acid and base and are organic in nature. Phenolphthalein is used to titrate strong acid with strong alkali or weak acid with strong alkali. Phenolphthalein is pink in alkaline medium and colourless in acidic medium. Methyle orange is used to treat strong acid with weak alkali. Methyle orange has yellow colour in alkaline medium and pink or red colour in acidic medium. Phenolphthalein changes colour between 8.3–10 in a pH range hence suitable indicator. Methyle orange changes colour between pH range 2.5–6.5.

Table 3.4. Indicators and their pH ranges

Indicator	*Colours*		pK_{In}	*pH Range*
	Acid	*Base*		
Thymol blue (first change)	Red	Yellow	1.5	1.2 – 2.8
Methyl orange	Red	Yellow	3.7	3.2 – 4.4
Bromocresol green	Yellow	Blue	4.7	3.8 – 5.4
Methyl red	Yellow	Red	5.1	4.8 – 6.0
Bromothymol blue	Yellow	Blue	7.0	6.0 – 7.6
Phenol red	Yellow	Red	7.9	6.3 – 8.4
Thymol blue (second change)	Yellow	Blue	8.9	8.0 – 9.6
Phenolphthalein	Colourless	Pink	9.4	8.2 – 10.0

Titrant or Titrator: Titrant is a standard solution of known strength. During titration it is taken in the burette.

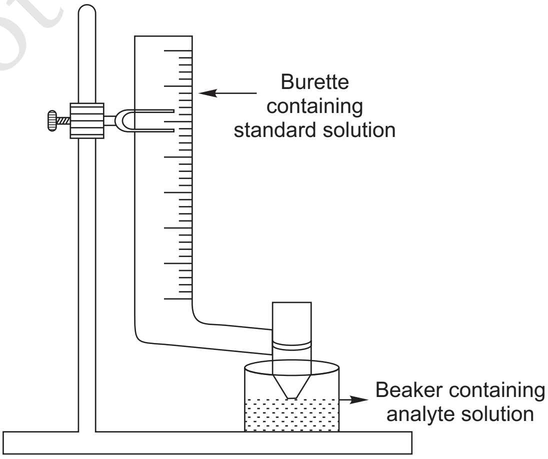


Fig. 3.3

Titrand: Titrand is the sample or the **analyte** whose concentration and volume are unknown. It is the solution to which a titrant reacts.

Titration Volume: Titration volume is the volume of titrant reacted with the titrand.

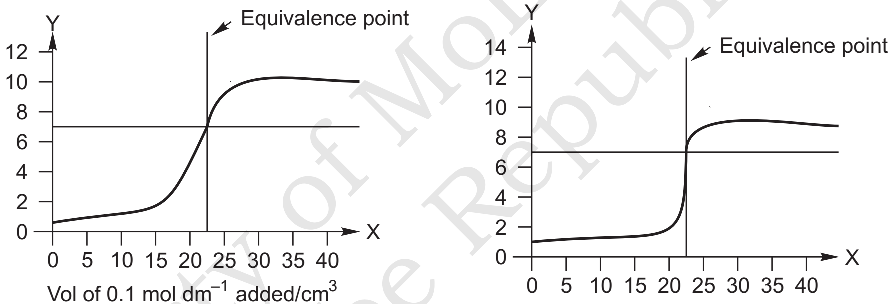
Acid-base titration are of four types:

1. Strong acid – strong alkali
2. Weak acid – strong alkali
3. Strong acid – weak alkali
4. Weak acid – weak alkali

Titration curves: Titration curve is the plot between volume of titrant dripped into the analyte or titrand versus the pH of analyte solution.

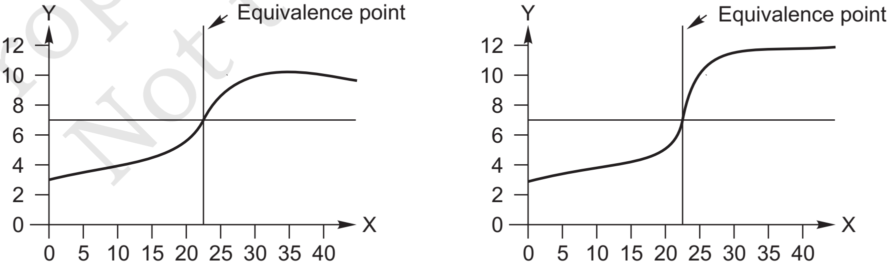
X-cordinate: Volume of titrant added or used during the course of titration is taken on X-cordinate.

Y-cordinate: pH of the analyte solution is taken on Y-cordinate.



Titration curve of strong acid and strong base

Titration curve of weak acid and weak base



Titration curve of weak acid and strong base

Titration curve between weak acid and strong base

Fig. 3.4

During titration pH of the analyte solution does not change in a regular manner as alkali is added. Horizontal section of curve shows that there is a very small change in pH even if large amount of alkali is added. The steep portion of each curve shows that even a single drop of alkali can change the pH considerably except in case of weak acid and week base. At equivalence point there is a large change of pH even though it is not centred on pH7.

SUMMARY

- **Acid.** A substance which furnishes H^+ ions in aqueous solution (*Arrhenius concept*) proton donor (*Bronsted concept*) and acceptor of electron pair (*Lewis concept*).
- **Base.** A substance which gives OH^- ions in aqueous solution, (*Arrhenius concept*); acceptor of proton (*Bronsted concept*) and donor of electron pair (*Lewis concept*).
- **pH of Solution.** Potency of H^+ in solution. It is negative logarithm of H_3O^+ ion concentration in solution.
- **pOH of Solution.** It is negative logarithm of OH^- ion concentration of the solution.
- **Hydrolysis.** It is reverse of neutralisation. It involves the interaction of the ions of electrolyte with H_2O molecules in solution to give acidic or basic solution.

  Salts of strong acids and strong bases do not undergo hydrolysis and their aqueous solutions are neutral.

  Salts of strong acids with weak bases undergo cationic hydrolysis and give acidic solutions.

  Salts of strong bases with weak acids undergo anionic hydrolysis and yield basic aqueous solutions.

  Salts of weak acids with weak bases undergo complete hydrolysis and yield almost neutral solutions.
- **Buffer Solution.** A solution which resists the change in its pH value on addition of small amount of acid or a base.

  A buffer solution is generally a mixture of weak acid and its conjugate base or weak base and its conjugate acid.
- pH of Buffer solution is given by Henderson-Hasselbalch equation.

$$pH = pK_a + \log \frac{[Salt]}{[Acid]} \qquad \text{...for acidic buffers}$$

$$pOH = pK_b + \log \frac{[Salt]}{[Base]} \qquad \text{...for basic buffers}$$

$$pH = pK_a \text{ when } [Salt] = [Acid]$$

$$pOH = pK_b \text{ when } [Salt] = [Base]$$

EVALUATION

I. Multiple Choice Questions

1. Which of the following is the strongest base?
(a) Cl^-
(b) SO_4^{2-}
(c) CH_3COO^-
(d) NO_3^-.

2. Which of the following is the weakest base?
(a) OH^-
(b) $HCOO^-$
(c) CH_3O^-
(d) Br^-.

3. H_2O acts as a base according to
(a) Arrhenius concept only
(b) Lewis concept only
(c) Bronsted concept only
(d) Lewis as well as Bronsted concept.

4. The pH of 0.1 M solution of the following compounds increases in the order:
(a) $NaCl < NH_4Cl < NaCN < HCl$
(b) $HCl < NH_4Cl < NaCl < NaCN$
(c) $NaCN < NH_4Cl < NaCl < HCl$
(d) $HCl < NaCl < NaCN < NH_4Cl$.

5. The pH at the equivalence point of a titration may differ from 7.0 because of:
(a) the self ionization of water
(b) hydrolysis of the salt formed
(c) the indicator used
(d) the concentration of the standard solution.

6. Which of the following aqueous solutions will have highest pH?
(a) Sodium acetate
(b) Sodium chloride
(c) Ammonium phosphate
(d) Calcium chloride.

7. Among the following, the weakest Bronsted base is
(a) F^-
(b) Cl^-
(c) Br^-
(d) I^-.

8. Which of the following is least likely to behave as a Lewis base?
(a) OH^-
(b) H_2O
(c) NH_3
(d) BF_3.

9. For a buffer solution, which of the following is true?
(a) pH does not change at all on addition of acid or base
(b) pH change is very little on addition of acid or base
(c) It is a mixture of strong acid and its salt
(d) It is a mixture of strong base and its salt.

10. Buffer solutions have constant acidity and alkalinity because:

(a) acids and alkalies in these solutions are shielded from attack by other ions

(b) they have large excess of H^+ or OH^- ions

(c) they have fixed value of pH

(d) these give unionised acid or base on reaction with added acid or alkali.

II. Descriptive Questions

1. Which is more acidic, a solution having a pH of 4 or one having pH of 3?

2. State the formula and the name of the conjugate base of each of the following acids:

(*i*) H_3O^+ (*ii*) HSO_4^-
(*iii*) NH_4^+ (*iv*) HF
(*v*) CH_3COOH (*vi*) $CH_3NH_3^+$
(*vii*) H_3PO_4 (*viii*) $H_2PO_4^-$.

3. State the formula and name of the conjugate acid of each of the following bases:

(*i*) OH^- (*ii*) HPO_4^{2-}
(*iii*) $H_2PO_4^-$ (*iv*) CH_3NH_2
(*v*) CO_3^{2-} (*vi*) NH_3
(*vii*) CH_3COO^- (*viii*) HS^-.

4. pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained by diluting the given solution a 100 times?

5. Decide whether solutions of the following salts are acidic, basic or neutral

(*i*) Sodium acetate (*ii*) Ammonium acetate
(*iii*) Ferric nitrate (*iv*) Sodium carbonate
(*v*) Potassium sulphate.

6. Write the conjugate acids for the following Brönsted bases: NH_2^-, NH_3 and $HCOO^-$.

7. Classify the following species into Lewis acids and Lewis bases and show how these act as such:

(*i*) HO^- (*ii*) F^-
(*iii*) H^+ (*iv*) BCl_3

SEMESTER–II (Period–IV)

4
TOPIC

Electrochemistry

C11CH4

Learning Objectives

Upon completion of this topic, learners will:

- Explain the concept of balancing redox reaction
- Discuss the electrochemical cell
- Make use of the cell diagram
- Apply the principle of electrolysis to distinguish electrochemical cell
- Discuss the factors that influence the discharge of species
- Simplify cell reactions for the electrolysis of various species
- State Faraday's first and second laws, solving sample problems
- Discuss the various batteries, together with their applications and
- Explain how electroplating materials can prevent rusting and corrosion.

It is a well known fact that energy manifests itself in different forms which are interconvertible into one another. Among different forms of energy, the electrical energy plays a very significant role in our daily life. Many chemical transformations and industrial processes are based on electrical energy and its relationship with chemical energy. There are large number of spontaneous redox reactions which form the basis of *production of electrical energy*. The device in which such chemical processes are carried out is called ***electrochemical cell*** or ***galvanic cell.*** For example, Daniell cell is based on the following redox reaction

$$Cu^{2+}(aq) + Zn(s) \longrightarrow Cu(s) + Zn^{2+} + \text{Electrical Energy}$$

At the same time many of the non-spontaneous redox reactions can be made to occur *by the use of electrical energy*. Some examples are:

$$2H_2O(l) \xrightarrow{\text{Electricity}} 2H_2(g) + O_2(g)$$

$$2Al_2O_3(l) \xrightarrow{\text{Electricity}} 4Al + 3O_2$$

The process associated with such transformation is called ***Electrolysis*** and the device used for electrolysis is called ***electrolytic cell.***

The branch of chemistry which deals with the study of relationship between electrical energy and chemical energy and interconversion of one form of energy into another is called **electrochemistry.** Electrochemistry is very vast and interdisciplinary branch of chemistry which finds tremendous applications. Its study is very important as it helps in development of new technologies which are economical and environment-friendly. In this unit we shall focus on the study of some aspects of electrochemical cells, batteries, fuel cells, electrolytic cells, conductance and its measurement.

4.1. REDOX REACTIONS

Chemical reactions involving oxidation and reduction processes are called *redox reactions.* **Oxidation** may be defined as the *process in which a species* (*atom, molecule or ion*) *increases oxidation number by losing one or more of electrons.* The substance undergoing oxidation is called **reducing agent. Reduction,** on the other hand, is *a process in which a species* (*atom, molecule or ion*) *decreases oxidation number by gaining one or more electrons.* The species undergoing reduction is called **oxidising agent.** Neither oxidation nor reduction can take place alone. These are complementary processes and occur side by side. **Redox reaction** can, thus, be termed *as the chemical reaction involving transferrence of electrons from reducing agent to oxidising agent.*

Some examples of redox reactions are as follows:

$$\underset{\text{Reducing agent}}{\overset{0}{\mathrm{Zn}(s)}} + \underset{\text{Oxidising agent}}{\mathrm{Cu}^{2+}(aq)} \longrightarrow \mathrm{Zn}^{2+}(aq) + \overset{0}{\mathrm{Cu}(s)}$$

$$\underset{\text{Reducing agent}}{\overset{0}{\mathrm{I}_2(s)}} + \underset{\text{Oxidising agent}}{10\mathrm{H}\overset{(+5)}{\mathrm{N}}\mathrm{O}_3(l)} \longrightarrow 2\mathrm{H}\overset{(+5)}{\mathrm{I}}\mathrm{O}_3 + 10\overset{(+4)}{\mathrm{N}}\mathrm{O}_2 + 4\mathrm{H}_2\mathrm{O}$$

Redox reactions form the basis electrochemical cells and electrolytic cells which are discussed later in this chapter.

Classical Idea of Redox Reactions—Oxidation and Reduction Reactions

Oxygen present in our atmosphere combines with many elements to form their respective oxides. Thus, the term ***oxidation*** was originally used to describe the ***addition of oxygen*** to an element or a compound. For example,

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(s)$$
$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

In the second reaction, methane is oxidised because of addition of oxygen to it. At the same time the hydrogen of methane molecule has been replaced by oxygen. In view of the above interpretation, the scope of term oxidation was broadened as process of ***addition of oxygen*** or ***removal of hydrogen*** from the substance. With the progress in chemistry the term oxidation was further extended to reactions which do not involve oxygen or hydrogen, and the process of ***addition of electronegative*** element or ***removal of electropositive*** element was also considered as ***oxidation.*** For example, addition of electronegative elements such as fluorine, chlorine, sulphur, etc. cause oxidation of magnesium.

$$Mg(s) + F_2(g) \longrightarrow MgF_2(s)$$
$$Mg(s) + S(s) \longrightarrow MgS(s)$$

Similarly, removal of electropositive element, potassium causes oxidation of $K_4Fe(CN)_6$.

$$2K_4[Fe(CN)_6](aq) + H_2O_2(aq) \longrightarrow 2K_3[Fe(CN)_6](aq) + 2KOH(aq)$$

On similar grounds the *term reduction was considered as removal of oxygen or addition of hydrogen*. The terminology was further broadened as the knowledge of chemists grew. The *addition of electropositive element* or *removal* of *electronegative element* was also considered as *reduction process*. Some examples are:

$$2HgO(s) \xrightarrow{\Delta} 2Hg(l) + O_2(g)$$

(Removal of oxygen from mercuric oxide)

$$2FeCl_3(aq) + H_2(g) \longrightarrow 2FeCl_2(aq) + 2HCl(aq)$$

(Removal of electronegative element chlorine from ferric chloride)

$$CH_2 = CH_2(g) + H_2(g) \longrightarrow H_3C - CH_3(g)$$

(Addition of hydrogen)

$$2HgCl_2(aq) + SnCl_2(aq) \longrightarrow Hg_2Cl_2(s) + SnCl_4(aq)$$

(Removal of electronegative element chlorine from mercuric chloride)

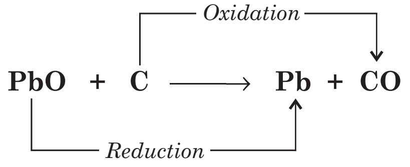
Let us now sum up the definitions of oxidation and reduction process.

Oxidation. It is a process of *addition of oxygen or any electronegative radical or removal of hydrogen or any electropositive radical from a substance.*

Reduction. It is a process of *addition of hydrogen or any electropositive radical or removal of oxygen or any electronegative radical to a substance.*

Some **examples** of oxidation and reduction reactions are:

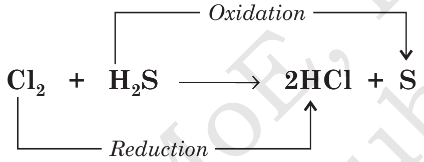
(*i*) *Reaction of PbO and carbon*



$$PbO + C \longrightarrow Pb + CO$$

Here, oxygen is being removed from lead oxide (PbO) and is being added to carbon (C). Thus, PbO is *reduced* while C is *oxidised.*

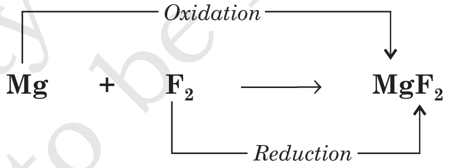
(*ii*) *Reaction of H_2S and Cl_2*



$$Cl_2 + H_2S \longrightarrow 2HCl + S$$

Here, hydrogen is being removed from hydrogen sulphide (H_2S) and is being added to chlorine (Cl_2). Thus, H_2S is *oxidised* and Cl_2 is *reduced.*

(*iii*) *Reaction between Mg and F_2*



$$Mg + F_2 \longrightarrow MgF_2$$

Here, electronegative radicals fluoride ion is added to magnesium while electropositive radical Mg^{2+} is added to fluorine. Hence, Mg is *oxidised* and F_2 is *reduced.*

Looking at all the reactions given above we observe that oxidation and reduction always occurs simultaneously, hence the word **"redox"** was coined for this class of chemical reactions.

Oxidation Half and Reduction Half Reactions

Every redox reaction can be split up into two **half reactions,** one representing loss of electrons *i.e.*, **oxidation half reaction** while the other representing gain of electrons, *i.e.*, **reduction half reaction.** Some examples are given below:

(*i*) The reaction: **$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$,** can be split up into two half reactions as

$Zn \longrightarrow Zn^{2+} + 2\bar{e}$ (*Oxidation half reaction*)

$Cu^{2+} + 2\bar{e} \longrightarrow Cu$ (*Reduction half reaction*)

(*ii*) The reaction:

$Sn^{2+} + 2Hg^{2+} \longrightarrow Sn^{4+} + Hg_2^{2+}$, can be split up into half reaction as

$Sn^{2+} \longrightarrow Sn^{4+} + 2\bar{e}$ (*Oxidation half reaction*)

$2Hg^{2+} + 2\bar{e} \longrightarrow Hg_2^{2+}$ (*Reduction half reaction*)

Example. *Split the following redox reactions in the oxidation and reduction half reactions:*

(*a*) $2K(s) + Cl_2(g) \longrightarrow 2KCl(s)$

(*b*) $2Al(s) + 3Cu^{+2}(aq) \longrightarrow 2Al^{+3}(aq) + 3Cu(s)$

Solution. The oxidation half reaction is the one which represents oxidation and the reduction half reaction shows reduction

(*a*) $\overset{0}{K} \longrightarrow \overset{+1}{K}Cl + e^-$ (*Oxidation half reaction*)

$\overset{0}{Cl_2}(g) + e^- \longrightarrow K\overset{-1}{Cl}$ (*Reduction half reaction*)

(*b*) $2Al \longrightarrow 2Al^{3+} + 6e^-$ (*Oxidation half reaction*)

$3Cu^{+2}(aq) + 6e^- \longrightarrow Cu(s)$ (*Reduction half reaction*)

Balancing of Redox Reactions

For balancing of redox reactions we can either use oxidation number method or the half reaction method.

(*i*) **Oxidation number method:** To balance redox reactions by oxidation number method following steps are to be followed

- Correct formula for each reactant should be written.
- Assign the change in oxidation number.
- Calculate the oxidation number per atom with respect to reactants. If more than one atom is present then multiply by number of atom.
- Balance the equation with respect to all atoms, Balance hydrogen and oxygen also.
- For acidic medium use H^+ ions while for basic medium use OH^- ions.

- To balance hydrogen atom in the expression can be balanced by adding (H_2O) molecules to the reactants and products.
- Now same number of oxygen atoms on both sides of equation represent the balanced redox reaction.

Example: Balance the following equation by oxidation number method.

$$P_4(s) + OH^- (aq) \longrightarrow PH_3 (g) + H_2PO_2^- (aq)$$

Oxidation number decreased by 3 per atom

$$P_4(s) + OH^- (aq) \longrightarrow PH_3(g) + H_2PO^-_2(aq)$$

Oxidation number increased by 1 per atom

P_4 is acting both as an oxidizing agent as well as reducing agent.

Total number of increase in O.N. of P_4 in $H_2PO_2^- = 1 \times 4 = 4$

Total number of decrease in O.N. of P_4 in $PH_3 = 3 \times 4 = 12$

Hence, multiply PH_3 by one and $H_2PO_2^-$ by 3 to balance the increase and decrease in oxidation number.

$$P_4(s) + OH^- (aq) \longrightarrow PH_3(g) + 3H_2PO^-_2(aq)$$

To balance O atoms, multiply OH^- by 6

$$P_4(s) + 6OH^- (aq) \longrightarrow PH_3(g) + 3H_2PO^-_2(aq)$$

To balance H atoms add $3H_2O$ to LHS and $3OH^-$ to the RHS we have

$$P_4(s) + 6OH^- (aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO_2^- + 3OH^- (aq)$$

$$P_4(s) + 3OH^- (aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO^-_2 (aq)$$

Hence balanced.

(*ii*) **Half reaction method:** In half reaction method, Oxidation half equation and reduction half equation is balanced separately then added together to give balanced equation.

Example: Balance following redox reaction by using half reaction method.

$$Mn^{2+} (aq) \longrightarrow Mn^{2+} (aq) + MnO_2(s) + H^+ (aq)$$

Oxidation half reaction:

$$Mn^{3+} (aq) \longrightarrow MNO_2^{+4}(s)$$

Balance oxidation number on both sides by adding one electron to product side.

$$Mn^{3+} (aq) \longrightarrow MnO_2(s) + e^-$$

Balance charge by adding 4H ions

$$Mn^{3+} (aq) \longrightarrow MnO_2(s) + .2H^+ (aq) + e^- \qquad ...(i)$$

Balance O atom by adding H_2O

$$Mn^{3+} (aq) + 2H_2O (l) \longrightarrow MnO_2 (s) + 4H^+ (aq) + e^-$$

This is balanced oxidation half reaction.

Reduction half equation

$$Mn^{+3}\ 3+ (aq) \longrightarrow Mn^{+2}\ 2+ (aq)$$

Balance oxidation number by adding electron.

$$Mn^{3+} (aq) + e^- \longrightarrow Mn^{2+} (aq) \qquad \ldots(ii)$$

Adding equation (*i*) and (*ii*), we get balance redox equation

$$2Mn^{3+}(aq) + 2H_2O (l) \longrightarrow MnO_2 (s) + Mn^{2+} (aq) + .4H^+(aq)$$

4.2. ELECTROCHEMICAL CELL

Daniel Cell

Daniel cell is a type of electrochemical cell invented in 1836 by John Frederic Daniel in 1836 a british chemist and meterologist. To make a Daniel Cell take two beakers, one containing copper sulphate solution and another containing, zinc sulphate solution, zinc rod is taken as anode and dipped in zinc sulphate solution while copper rod is taken as cathode and dipped in copper sulphate solutions. These two electrolytes are connected by a salt bridge (a U tube containing KCl or NH_4NO_3 solidified by boiling with agar-agar). Salt bridge is a link between two electrolytes without these actual mixing. Zinc and copper electrodes are connected in a circuit with connecting wire, a switch and an ammeter. When we put the switch on, a flow of current is observed in the circuit. There is a movement of electrons from anode to cathode through metallic wire. Movement of ions takes place through the salt bridge. At anode oxidation takes place and solid zinc converts into zinc ions while at cathode copper ions get reduced to copper metal and get deposited. The flow of free electrons produces electricity in the direction opposite to the direction of flow of electrons.

Representation of Daniel cell.

$$Zn \mid Zn^{+2} (aq) \mid\mid Cu^{+2} (aq) \mid Cu$$

EMF of Daniel cell is 1.4 V.

Uses of Daniel Cell

Daniel cells are used to generate electricity and to store electricity. Daniel cells are used in development of battery and electrical telegraphy.

Unique thing about Daniel Cell

Unique design of Daniel cell separates the copper and zinc ions from each other which prevents the polarisation of from interrupting the electricity flow, while at the same time allow ions in the electrolytes to pass between two electrodes in order to complete the electric circuit.

Daniel cell is a Galvanic cell but all Galvanic cells are not Daniel cells

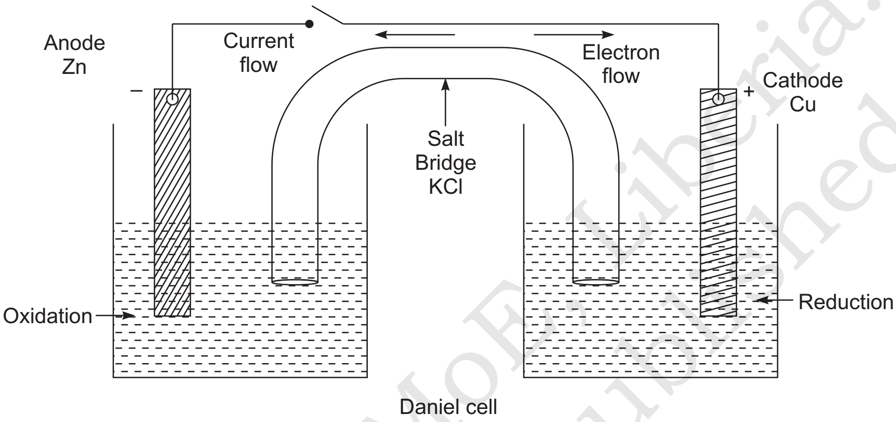


Fig. 4.1. Daniel cell

EXPERIMENT 1

Aim: To set up simple Daniell cell and determine its EMF.

Theory: When a copper electrode dipped in copper sulphate solution is connected to a zinc electrode dipped in the zinc sulphate solution, then electrons flow from zinc electrode to copper electrode and the chemical reactions take place as:

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$

Overall reaction: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

Apparatus and Chemicals: One beaker, a porous pot, connecting wires, milli voltmeter, sand paper, zinc strip, copper strip, 1 M $ZnSO_4$ solution and 1 M $CuSO_4$ solution.

Procedure:

1. Take copper sulphate solution in a clean beaker.
2. Clean the copper strip with the help of sand paper and dip it into copper sulphate solution.
3. Take zinc sulphate solution in a porous pot.

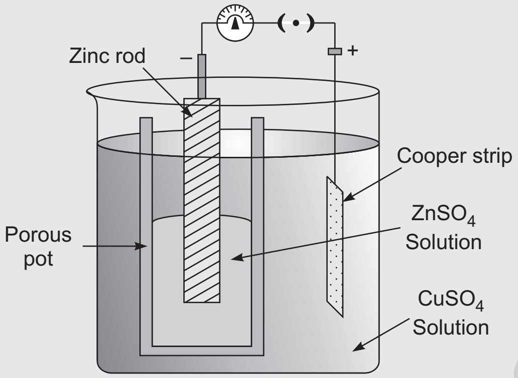


Fig. 4.2. A Daniell cell

4. Clean the zinc strip with the help of sand paper and dip it into zinc sulphate solution.
5. Keep the porous pot in the beaker.
6. Connect the copper strip with the positive terminal and zinc strip with the negative terminal a voltmeter as shown in Fig.
7. Note the position of the pointer in the voltmeter and record the reading in your note-book.

Observation:

The EMF of the Daniell cell is ...... volts.

Precautions:

1. The concentration of copper sulphate and zinc sulphate should neither be too low nor too high.
2. The porous pot should not be completely dipped into the copper sulphate solution, *i.e.*, the copy sulphate solution should not be allowed to enter the porous pot.
3. Clean zinc and copper strips with sand paper before use.
4. Carry out dilution of the solution carefully.
5. Note the reading only when the pointer becomes stable.
6. Connect copper strip with the positive terminal of voltmeter and zinc strip with negative terminal.

Galvanic Cells

The device in which chemical energy is converted into electrical energy is called **galvanic cell** (after the name of Luigi Galvani) or **electrochemical cell** or **voltaic cell** (after the name of Alessandro Volta)**.** In a galvanic cell, a redox reaction is carried out in an *indirect manner* and the decrease in free energy during the chemical process is made to appear as electrical energy. An indirect redox reaction involves the occurrence of reduction and oxidation processes in separate vessels. In order to understand this phenomenon, let us consider the Zn—$CuSO_4$ reaction as the basis of the cell reaction.

In its simple form, a *zinc strip* is dipped in the $ZnSO_4$ solution and a *copper strip* is dipped in the $CuSO_4$ solution taken in separate beakers. The two metallic strips which act as electrodes are connected by the conducting wires through a voltmeter. The two solutions are joined by an inverted U-tube known as **salt bridge.** The U-tube is filled with the solution of some electrolyte such as KCl, KNO_3 or NH_4Cl to which *gelatin* or *agar-agar* has been added to convert it into semi-solid paste. A schematic diagram of this cell has been shown in Fig. 4.3.

The deflection in voltmeter indicates that there is a potential difference between the two electrodes. It has been found that the conventional current flows through the outer circuit from copper to zinc strip. It implies that the electrons flow occurs from zinc to copper strip.

Let us now understand the working of the cell.

(*i*) Zinc undergoes oxidation to form zinc ions

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \ (\textit{Oxidation})$$

(*ii*) The electrons liberated during oxidation are pushed through the connecting wires to copper strip.

(*iii*) Copper ions move towards copper strip, pick up the electrons, and get reduced to copper atoms which are deposited at the copper strip.

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \ (\textit{Reduction})$$

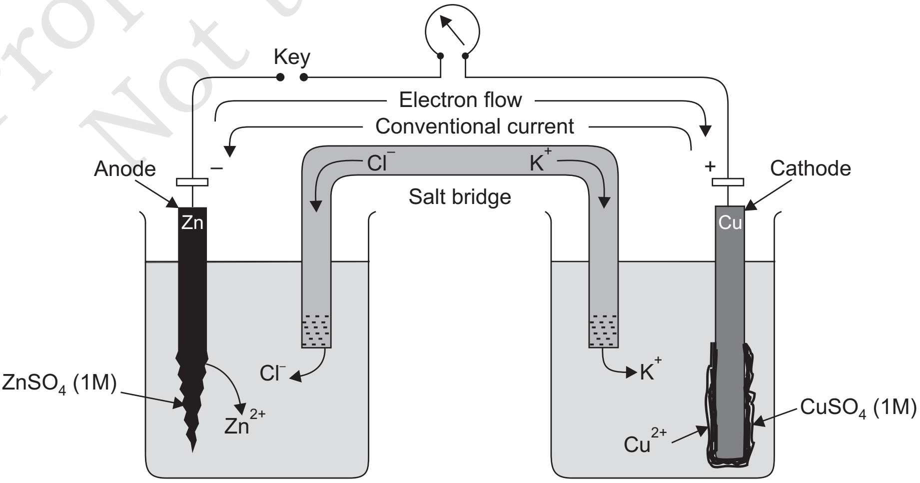


Fig. 4.3. Electrochemical cell.

The electrode at which *oxidation occurs* is **anode** and that at which *reduction occurs* is **cathode.** In the above cell, zinc strip is anode and the copper strip is cathode. Due to the oxidation process occurring at the anode it becomes a source of electrons and acquires a negative charge in the cell. Similarly, due to reduction process occurring at the cathode it acquires positive charge and becomes a receiver of the electrons. Thus, in the electrochemical cell, **anode electrode** acts as **negative terminal** and **cathode electrode** acts as **positive terminal.**

Salt Bridge and its Functions. Salt Bridge is a U-shaped tube containing a semi-solid paste of some inert electrolyte like KCl, KNO_3, NH_4Cl, etc., in *agar-agar* and *gelatine*. An inert electrolyte is one which:

(*a*) does not react chemically with the solution in either of the compartment.

(*b*) does not interfere with the net cell reaction.

Function of Salt Bridge. In the electrochemical cell a salt bridge serves two very important functions:

(*i*) *It allows the flow of current by completing the circuit.*

(*ii*) *It maintains electrical neutrality.*

Electrode Potential

When a strip of metal (M) is brought in contact with the solution containing its own ions (M^{n+}), then either of the following three possible processes can take place:

(*i*) The metal ion M^{n+} may collide with the metallic strip and bounce back without any change.

(*ii*) The metal ion M^{n+} may collide with the strip, gain *n* electrons and get converted into metal atom, *i.e.*, the ion is *reduced.*

$$M^{n+} + ne^- \longrightarrow M$$

(*iii*) The metal atom on the strip may lose *n* electrons and enter the solution as M^{n+} ion, *i.e.*, metal is *oxidised.*

$$M \longrightarrow M^{n+} + ne^-$$

The above changes have been shown in Fig. 4.4.

Now, if the metal has a relatively *high tendency to get oxidised*, its atoms would start losing electrons, change into positive ions and pass into the solution. The electrons lost, accumulate in the metal strip and cause it to develop *negative charge*. The negative charge developed on the strip does not allow metal atoms to continue losing electrons but it would reattract the metal ions from the solution in an attempt to neutralise its charge. Ultimately, a state of equilibrium will be established between the metal and its ions at the interface.

$$\underset{\text{(Metal strip)}}{\mathrm{M}} \rightleftharpoons \underset{\text{(Solution)}}{\mathrm{M}^{n+}} + \underset{\text{(In metal strip)}}{ne^-}$$

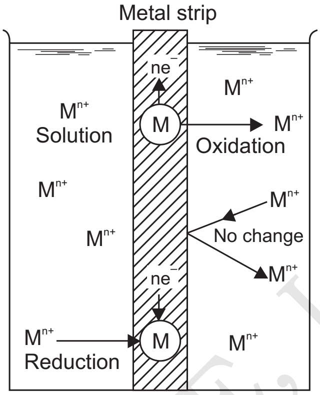
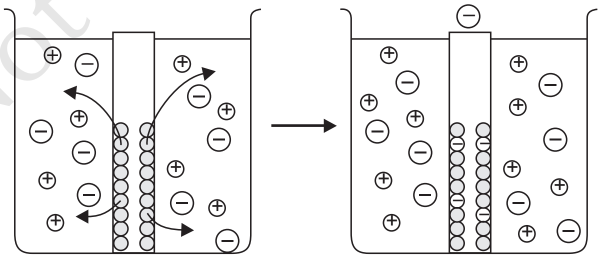


Fig. 4.4. Electrode equilibrium.

Similarly, if the metal ions have relatively *greater tendency to get reduced,* they will accept electrons at the strip from the metal atoms and consequently, a *net positive* charge is developed on the metal strip. Ultimately, a similar equilibrium is established between the metal ions and the metal atoms at the interface.

$$\underset{\text{(Solution)}}{\mathrm{M}^{n+}} + \underset{\text{(From metal strip)}}{ne^-} \rightleftharpoons \underset{\text{(Metal)}}{\mathrm{M}}$$

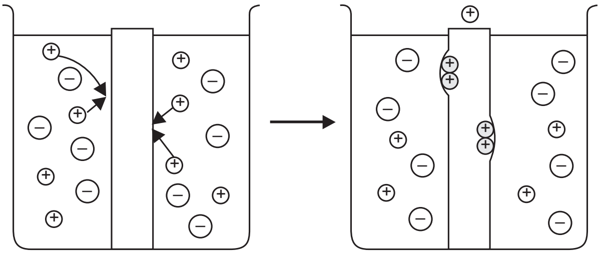
The development of negative and positive charges on the metal strip has been shown in Fig. 4.5 (*a*) and (*b*) respectively.



Metal atoms change to cations by giving electrons to the strip

Negative charge on strip

Fig. 4.5. (*a*) Development of –ve charge on metal strip.



Metal ions gain electrons from the strip and get deposited as metal atoms

Positive charge on strip

Fig. 4.5. (*b*) Development of +ve charge on the metal strip.

In either case, the separation of charges at the equilibrium state results in the electrical potential difference between the metal and the solution of its ions and is known as **electrode potential.**

The exact potential difference at the equilibrium depends on the **nature of metal, its ions, the concentration of ions** and the **temperature.**

Cell Potential or EMF of the Cell

The electrochemical cell consists of two half cells. The electrodes in these half cells have different electrode potentials. When the circuit is completed the loss of electrons occurs at the electrode having lower reduction potential whereas the gain of electrons occurs at the electrode with higher reduction potential. The difference in the electrode potentials of the two electrodes of the cell is termed as **electromotive force** (abbreviated as **EMF** or **emf**) or **cell voltage** ($\mathbf{E_{cell}}$). Mathematically, it can be expressed as

$$\mathbf{EMF} = \mathbf{E_{red}}\ (\textit{Cathode}) - \mathbf{E_{red}}\ (\textit{Anode}) \text{ or simply}$$

as $$\mathbf{E_{cell}} = \mathbf{E_{cathode}} - \mathbf{E_{anode}}$$

Since in the representation of a cell, the cathode is written on right hand side and the anode on left hand side, therefore, EMF of a cell is also sometimes written as:

$$\mathbf{EMF} = \mathbf{E_{Right}} - \mathbf{E_{Left}} = \mathbf{E_R} - \mathbf{E_L}$$

EMF of the cell may be defined as the ***potential difference between the two terminals of the cell when either no current is drawn from it.*** It is measured with the help of *potentiometer* or *vacuum tube voltmeter.*

The EMF of the cell depends on *nature of the reactants, concentration of the solutions in the two half cells,* and the *temperature*. The EMF of the cell at the standard state conditions is called standard EMF and can be calculated from the standard electrode potentials of the two half cells.

$$E^{\ominus}_{cell} = E^{\ominus}{}_{cathode} - E^{\ominus}{}_{anode}$$

Standard Hydrogen Electrode (SHE)

Standard hydrogen electrode (Fig. 4.6) consists of a platinum wire sealed into a glass tube and carrying a platinum foil at one end. The platinum foil is coated with finely divided platinum. The electrode is placed in beaker containing an aqueous solution of some acid having **one molar concentration of H^+ ions.** Hydrogen gas at 1 bar pressure is continuously bubbled through the solution at a temperature of 298 K. The oxidation or reduction in the SHE takes place at platinum foil. Hence, it can act as **anode** as well as **cathode** and may be represented as:

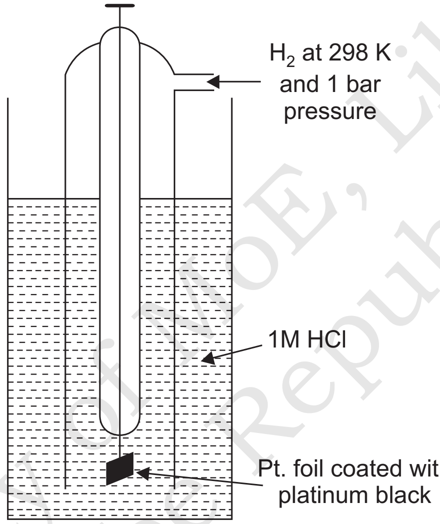


Fig. 4.6. Standard hydrogen electrode (SHE).

Pt, $\frac{1}{2}H_2$ (1 bar)/H^+(1 M) or

H^+(1 M)/$\frac{1}{2}H_2$ (1 bar), Pt respectively.

*If SHE acts as **anode** then oxidation will take place at it as*

$$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$$

*If SHE acts as **cathode** then reduction will take place at it as*

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

Electrochemical Series

We have seen that different *metal/metal ion* combinations have different values of electrode potentials. The various elements can be arranged in order of increasing or decreasing values of their reduction potentials. *The arrangement of various elements in the order of increasing values* *of standard reduction potentials* is called **electrochemical series.** The electrochemical series, also called activity series consisting of some electrodes along with their respective reduction reactions.

Applications of Electrochemical Series

Some of the important applications of electrochemical series are discussed as follows:

1. Comparing the Relative Oxidising and Reducing Powers of Various Substances. Substance with higher reduction potential have greater tendency to undergo reduction. For example, F_2 has highest reduction potential which means it is most easily reduced to F^- ions. In other words, F_2 the is best oxidising agent. Li^+ ion, on the other hand, had lowest reduction potential. Hence Li^+ is the weakest reducing agent or conversely Li metal is the best reducing agent. Thus, it can be concluded that *substances with **higher reduction potentials** are **strong oxidising agents** while substances with **lower** reduction potentials are **strong reducing agents**.*

2. Calculation of Standard EMF of the Cell ($E^\ominus_{cell}$). Standard EMF of the cell can be calculated by applying the formula

$$E^\ominus_{cell} = E^\ominus\text{ (cathode)} - E^\ominus\text{ (anode)}$$

The electrode with higher electrode potential ($E^\ominus$) act as cathode while that with lower electrode potential will act as anode.

3. Predicting the Feasibility of Redox Reaction. Electrochemical series help to predict the feasibility of the redox reaction in a given direction. In the given redox reaction, the species undergoing reduction should have relatively higher $E^\ominus$ value than the species which undergo oxidation. If this condition is fulfilled the redox reaction is feasible otherwise it is non-feasible.

For example, let us predict whether the reaction

$Zn^{2+} + Cu \longrightarrow Zn + Cu^{2+}$ is feasible or not.

In the given reaction Zn^{2+} ions are getting reduced while Cu atoms are oxidised. This process will be feasible if $E^\ominus_{Zn^{2+}/Zn}$ is greater than $E^\ominus_{Cu^{2+}/Cu}$ but in fact, $E^\ominus_{Zn^{2+}/Zn}$ (– 0.76 V) is less than $E^\ominus_{Cu^{2+}/Cu}$ (0.34 V). Hence Zn^{2+} ions cannot oxidise Cu atoms. Thus, the given reaction is not feasible.

4. Predicting the Capability of Metal to Displace H_2 Gas from Acid. The chemical reaction between metal M and acid to liberate H_2 gas is represented by the reaction

$$\mathrm{M} + n\mathrm{H}^{+}(aq) \longrightarrow \mathrm{M}^{n+}\,(aq) + \frac{n}{2}\,\mathrm{H}_2$$

For the above reaction to occur, the $E^{\ominus}_{M^{n+}/M}$ should be smaller than $E^{\ominus}_{H^{+}/H_2}$. Thus, all metals lying above hydrogen in electrochemical series can liberate H_2 gas by reaction with acids. On the other hand, the metal lying below hydrogen in the electrochemical series cannot undergo such a reaction.

4.3. ELECTROLYTIC CELLS AND ELECTROLYSIS

So far we have been discussing the process of conversion of chemical energy into electrical energy by means of electrochemical cell. In the reverse process, the passage of electricity through the electrolytes in their molten or dissolved state can cause chemical changes under suitable conditions. **For example,** the passage of electricity through the acidified water results in the formation of hydrogen and oxygen gases. *The process of chemical decomposition of the electrolyte by the passage of electricity through its molten or dissolved state is called* ***electrolysis****.*

Electrolytic cell. The device in which the process of electrolysis is carried out is called electrolytic cell. It consists of:

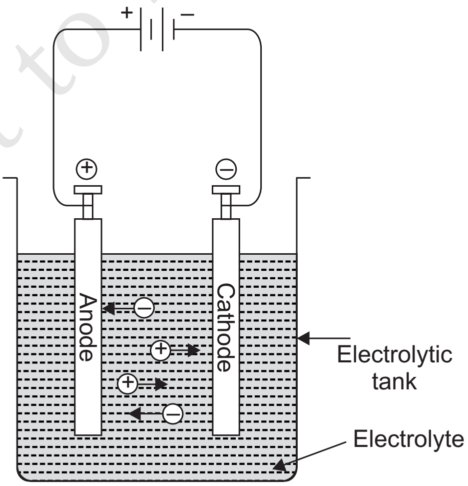


Fig. 4.7. Electrolytic cell.

(*i*) *Electrolytic tank,* which is made of some non-conducting material like glass, wood or bakelite.

(*ii*) *Electrolyte* in its dissolved state or molten state.

(*iii*) *Source of electricity;* an electrochemical cell or battery.

(*iv*) Two *metallic rods*, suspended in the electrolyte and connected to the battery through conducting wires. These rods are called *electrodes*. The electrode connected to the negative terminal of battery is called *cathode* while the other one which is connected to the positive terminal is called *anode*. The apparatus used to constitute electrolytic cell has been shown in Fig. 4.7.

Mechanism of Electrolysis

The process of electrolysis can be explained on the basis of the *theory of ionisation*. When an electrolyte is dissolved in water, it splits up into charged particles called *ions*. The positively charged ions are called cations while the negatively charged ions are called anions. The ions are free to move about in aqueous solution. When electric current is passed through the solution, the ions respond to the applied potential difference and their movement is directed towards the oppositely charged electrodes. The cations move towards the *negatively charged electrode* while *anions* move towards the *positively charged electrode*. The formation of products at the respective electrodes is due to **oxidation** (*loss of electrons*) at the anode and **reduction** (*gain of electrons*) at the **cathode**.

EXPERIMENT 2

Aim: To perform experiment on indicator of electrolysis.

Theory: During electrolysis when an indicator like phenolphthalein, is added to the electrolyte salt, it shows the change of pH of electrolyte solution during process of electrolysis. The colour of phenolphthalein changes to purple if the solution is basic in nature *i.e.*, if the pH of solution is more than 7. The phenolphthalein remains colourless if the solution is acidic or if it is neutral like water. During electrolysis if the concentration of positive ions (metal ions) increases in the solution the electrolytes will show purple colour.

Apparatus and chemicals: Beaker, drycell, connecting wires. Two graphite electrocles, electrolyte solution, phenolphthalein etc.

Procedure:

1. Take a beaker. Fill it more than half with electrolyte solution.
2. Add few drops of phenolphthalein solution to the electrolyte.

3. Arrange two electrodes and connect them with dry cell, a key as shown in the diagram.
4. Put the circuit on so that current passes through the electrolyte. As electrolyte dissociates into cations and anions.
5. Cations move towards cathode and anions move towards anode.
6. Phenolphthalein added in the electrolyte acts as an indicator. If the solution is acidic it remains colourless while if the solution is alkaline phenolphthalein gives purple colour to the electrolyte.

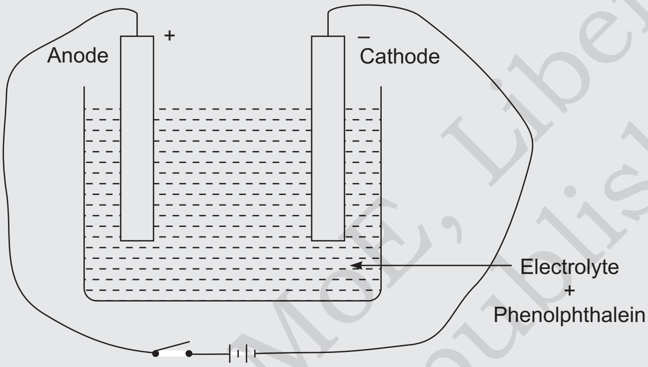


Fig. 4.8

Precautions:

1. Concentration of electrolyte should not be too high or too low.
2. Electrodes should be cleaned by sand paper before use.
3. Chemicals should be handled carefully.
4. Electrolyte should not be too heated.

Conclusion: The positive ions accumulate non-cathode (negative electrode). More purple colour is seen near a cathode. While less purple colour is seen towards the anode. If we stir the electrolyte, the uniform colour is seen throughout the electrolyte.

4.4. FACTORS INFLUENCING DISCHARGE OF SPECIES (IONS)

Ions are formed as a result of dissociation of electrolyte. When electric current is passed through the electrolyte, these ions move freely. The positively charged (particles) cations move towards negatively charged electrode (cathode) while negatively charge particles (anions) move towards positively charged electrode (anode). Discharge of species (ions) depends upon following factors:

1. **Position of metallic ions in electrochemical series:** During electrolysis those metallic ions which are placed lower in the electro chemical series are usually discharged in preference to those at the top of series. In case of non-metals, those which are placed higher up in the series are discharged in preference to those which are placed lower in the series.

2. **Concentration of Ions:** More is the concentration of an ion more are the chances of being discharged in preference to others. The distance of competing ions has to be close in the electro chemical series. If the distance of those two ions is not close in the electrochemical series this rule will not work.

Example: The Na^+ ion can not be discharged in preference to H^+ aqueous NaCl solution irrespective of the concentration of NaCl (aq) solution.

3. **Nature of Electrode:** Innert electrodes, made of less reactive material such as graphite, platinum etc have practically no role in deciding the preferential discharge of an ion on it. Active electrons which are made up of active material such as Cu, Ag, Ni, etc., actively take part in electrode reaction and have an active role in deciding the preferential discharge of ions. In such case anions migrate to the anode but do not get discharged, instead the active anode itself looses electron and forms ions.

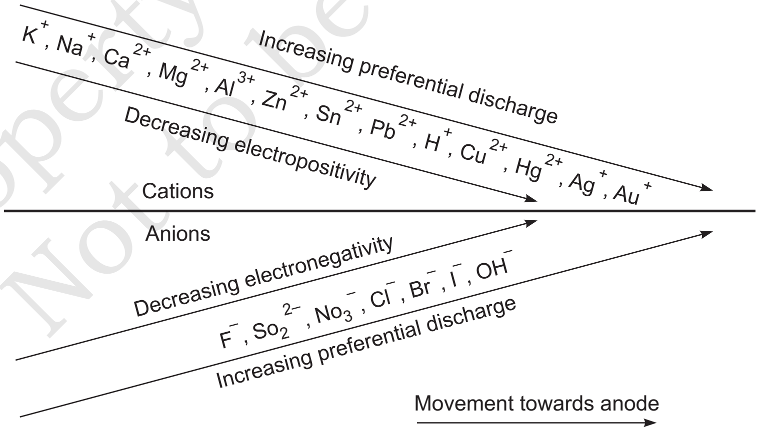


Fig. 4.9

Product of Electrolysis

The products of electrolysis, in general, depend on the following factors:

1. **Nature of the materials being electrolysed.** It is because of the fact that reactions occurring at the electrodes are controlled by their respective electrode potentials.

2. **Types of electrodes being used.** ***Inert electrodes*** such as Pt or Au do not participate in the electrode reactions. They simply act as source and sink for the electrons. ***Active electrodes***, on the other hand, participate in the electrode reactions. Therefore, the electrolysis products of same electrolyte may differ in case of inert and active electrodes.

3. **Kinetic barrier and over voltage.** Sometimes thermodynamically feasible electrochemical reactions do not seem to occur because at lower voltage they are kinetically slow. Their slowness creates electrical resistance at the electrodes and they require extra voltage (or potential) than the theoretical value of their standard electrode potential. This extra voltage required is referred to as **over voltage.** Let us now discuss some examples of electrode reactions.

(*a*) Cathodic reactions. *Cathode electrode involves reduction process at its surface.* Therefore, for the different competing reduction processes, the one with ***higher reduction potential, will preferably take place.*** For example, during the electrolysis of aqueous solution of sodium chloride there is possibility of following reactions at the cathode:

Reduction of Na^+ ions

$$Na^+(aq) + e^- \longrightarrow Na(s); \qquad E^{\ominus}_{red} = -2.71 \text{ V}$$

Or

Reduction of H_2O molecules

$$H_2O(l) + 2e^- \longrightarrow \tfrac{1}{2} H_2(g) + OH^-(aq); \qquad E^{\ominus}_{red} = -0.41 \text{ V}$$

The reduction of water will preferably take place at the cathode because $E^{\ominus}_{red}$ of water is higher. Hence, the product of electrolysis of aqueous solution of NaCl at the cathode will be H_2 gas instead of Na(*s*).

Similarly, during electrolysis of aqueous solution of copper sulphate reduction of Cu^{2+} ions will take place at the cathode in preference to the reduction of H_2O molecules because $E^{\ominus}_{Cu^{2+}/Cu}$ is greater than $E^{\ominus}_{H_2O/H_2}$.

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s); \qquad E^{\ominus} = 0.34 \text{ V}$$

$$H_2O(l) + 2e^- \longrightarrow \tfrac{1}{2} H_2(g) + OH^-(aq); \qquad E^{\ominus} = -0.41 \text{ V}$$

(*b*) Anodic reactions. *Anode electrode involves oxidation process at its surface.* Therefore, for different competing oxidation processes, the one with ***higher oxidation potential*** (or *lower reduction potential) will* *preferably occur*. For example, if we carry out electrolysis of aqueous solution of copper sulphate using Pt electrodes, the competing oxidation processes at the anode are as follows:

Oxidation of SO_4^{2-} *ions*

$$2SO_4^{2-}\,(aq) \longrightarrow S_2O_8^{2-} + 2e^-; \qquad E^{\ominus}_{oxi} = -\,2.01\text{ V}$$

Or

Oxidation of water molecules

$$H_2O(l) \longrightarrow \tfrac{1}{2}\,O_2(g) + 2H^+(aq) + 2e^-; \qquad E^{\ominus}_{oxi} = -\,1.23\text{ V}$$

As oxidation potential of water is higher, the product formed at the anode will be O_2 gas instead of $S_2O_8^{2-}$ ion.

Similarly, if the electrolysis of copper sulphate solution is carried out using *copper electrodes*, then the process occurring at the anode will be *oxidation of copper atoms to copper* ions instead of oxidation of water because oxidation potential of Cu is higher.

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-; \qquad E^{\ominus}_{oxi} = -\,0.34\text{ V}$$

$$2H_2O(l) \longrightarrow \tfrac{1}{2}\,O_2(g) + 2H^+(aq) + 2e^-; \qquad E^{\ominus}_{oxi} = -\,1.23\text{ V}$$

Thus, in such a case copper from anode will go on dissolving into solution as Cu^{2+} ions while Cu^{2+} ions from solution will go on depositing at the cathode as copper atoms.

The above discussion leads us to a general conclusion that for different competing reactions at the electrodes:

Cathodic reaction will be the one with higher $E^{\ominus}_{red}$ value.

Anodic reaction will be the one with higher $E^{\ominus}_{oxi}$ value or lower $E^{\ominus}_{red}$ value.

(*c*) Unexpected products due to overvoltage. In some cases the **unexpected results** are obtained due to *overvoltage*. For example, let us compare the oxidation potentials of Cl^- ion and water

$$H_2O(l) \longrightarrow \tfrac{1}{2}\,O_2(g) + 2H^+(aq) + 2e^-; \qquad E^{\ominus}_{oxi} = -\,1.23\text{ V}$$

$$Cl^-(aq) \longrightarrow \tfrac{1}{2}\,Cl_2(g) + e^-; \qquad E^{\ominus}_{oxi} = -\,1.36\text{ V}$$

Although oxidation potential of H_2O is more than that of Cl^- ions, yet during the electrolysis of *concentrated solution of sodium chloride*, the chloride ions oxidise in preference to H_2O molecules at the anode giving Cl_2 gas as the product.

In the light of the above discussion let us discuss the product formed during the electrolysis of some of the electrolytes.

1. Electrolysis of Aqueous Solution of NaCl. NaCl in aqueous solutions ionises as

$$\mathrm{NaCl}(aq) \longrightarrow \mathrm{Na}^+(aq) + \mathrm{Cl}^-(aq)$$

Reaction at anode :

$$\mathrm{Cl}^-(aq) \longrightarrow \frac{1}{2}\,\mathrm{Cl}_2(g) + \mathrm{e}^-$$

Reaction at cathode :

$$\mathrm{H_2O}(l) + \mathrm{e}^- \longrightarrow \frac{1}{2}\,\mathrm{H}_2(g) + \mathrm{OH}^-(aq)$$

Thus, Cl_2 gas is liberated at the anode whereas H_2 gas is liberated at the cathode.

2. Electrolysis of Copper Sulphate Solution Using Platinum inert Electrodes. Copper sulphate ionises in aqueous solution

$$\mathrm{CuSO_4}(aq) \longrightarrow \mathrm{Cu}^{2+}(aq) + \mathrm{SO_4}^{2-}(aq)$$

Reaction at anode :

$$\mathrm{H_2O}(l) \longrightarrow \frac{1}{2}\,\mathrm{O}_2(g) + 2\mathrm{H}^+(g) + 2\mathrm{e}^-$$

Reaction at cathode :

$$\mathrm{Cu}^{2+}(aq) + 2\mathrm{e}^- \longrightarrow \mathrm{Cu}(s)$$

Thus, copper is deposited at the cathode, and O_2 gas is liberated at the anode.

3. Electrolysis of Copper Sulphate Solution Using Copper Electrodes. Copper sulphate ionises as:

$$\mathrm{CuSO_4}(aq) \longrightarrow \mathrm{Cu}^{2+}(aq) + \mathrm{SO_4}^{2-}(aq)$$

Reaction at anode :

$$\mathrm{Cu}(s) \longrightarrow \mathrm{Cu}^{2+}(aq) + 2\mathrm{e}^-$$

Reaction at cathode :

$$\mathrm{Cu}^{2+}(aq) + 2\mathrm{e}^- \longrightarrow \mathrm{Cu}(s)$$

Thus, copper dissolves at the anode and is deposited at the cathode.

EXPERIMENT 3

Aim: Determine electrolysis food (lemon juice).

Theory: Food items like lemon juice, salt, sugar etc have either acid or alkali in the those may be strong or weak acid or base. Hence while undergoing electrolysis those conduct electricity as those dissociated into ions.

Lemon juice contains citric acid which dissociates into Hydrogen ion (cation) and citrate ion (anion). Fee movement of those ions facilitate electrolysis.

Chemicals and apparatus: Electrodes (carbon rod as zinc plate as electrodes, connecting wire, galvanometer light bulb, lemon juice, galvanometer, light bulb. etc. Big bottle or beaker.

Procedure:

1. Take a beaker or bottle.
2. Take lemon juice in the beaker.
3. Make electric connections taking carbon rod and zinc road as electrodes, light bulb, galvanometer, a key and a dry cell.
4. When electrolysis is done on passage of current through the lemon juice, we see that galvanometer shows deflection and the bulb lights. It show that lemon juice is dissociated into ions and electric current flows through lemon juice.

Precautions:

1. Concentration of electrolyte should not be too high or too low.
2. Electrodes should be cleaned by sand paper before use.
3. Chemicals should be handled carefully.
4. Electrolyte should not be too heated.

Result/Conclusion: Lemon juice is a conductor of electricity.

Faraday's Laws of Electrolysis

The relationship between the quantity of electricity passed and the quantity of a substance liberated at the electrode is given in the form of Faraday's laws of electrolysis.

1. Faraday's First Law of Electrolysis. This law states that *the mass of a substance liberated at the electrode is directly proportional to the quantity of electricity passed through the electrolyte.*

$$\begin{aligned} m &\propto Q \\ &\propto I \times t \\ &= Z \times I \times t \end{aligned}$$

Here, Q = quantity of electricity

I = current in amperes

t = time in seconds

Z = constant of proportionality called *electrochemical equivalent* (ECE)

If $I = 1$ ampere and $t = 1$ second, then $m = Z$

Thus, **electrochemical equivalent** *of a substance is the amount of substance liberated at the electrode when current of one ampere is passed through the electrolyte for one second.*

2. Faraday's Second Law of Electrolysis. This law states that *the amounts of different substances liberated by the same quantity of electricity passing through their electrolytic solution are directly proportional to their chemical equivalent masses (chemical equivalent mass of metal can be obtained by dividing its atomic mass with number of electrons required to reduce its cation). The law can also be stated as follows; when same quantity of electricity is passed through different electrolytes connected in series then the masses of the substances liberated at the electrodes are in the ratio of their chemical equivalent masses (atomic mass ÷ Number of electrons required to form the product) or the ratio of their electrochemical equivalents.*

For example, if the two electrolytic cells A (Containing $AgNO_3$ solution) and B (Containing $CuSO_4$ solution) are connected in series and same quantity of electricity is passed through the cells. Then the ratio of the mass of copper deposited at cathode in electrolytic cell B (x g) to that of silver deposited in cell A (y g) is equal to the ratio of their chemical equivalent masses.

$$\frac{\text{Mass of Cu}(x)}{\text{Mass of Ag}(y)} = \frac{\text{Chemical Equivalent Mass of Cu}}{\text{Chemical Equivalent Mass of Ag}} = \frac{Z_{Cu}}{Z_{Ag}}$$

Now, each copper (Cu^{2+}) ion requires 2 electrons to form Cu and each Ag^+ needs 1 electron to form Ag. Thus, chemical equivalent mass of Cu is 63.5/2 and that of Ag is 108/1.

Thus, the ratio $\frac{x}{y} = \frac{63.5}{2 \times 108}$.

4.5. DIFFERENCE BETWEEN ELECTROCHEMICAL CELL AND ELECTROLYTIC CELL

We have learnt that there are two types of cells namely: *electrochemical cells* and *electrolytic cells.* The former is a device which converts chemical energy into electrical energy. On the other hand, electrolytic cell is a device which converts electrical energy into chemical energy. The two cells also differ significantly with respect to the charges on the electrodes. For example, in electrochemical cell anode is negative whereas in electrolytic cell, the anode is positive. Similarly, cathode is positive in electrochemical cell whereas it is negative in the electrolytic cell. The main points of difference have been summed up as follows in Table 4.1.

Table 4.1. Differences between Galvanic Cell and Electrolytic Cell

Galvanic Cell	*Electrolytic Cell*
1. In galvanic cell, electrical energy is produced.	1. In electrolytic cell, electrical energy is consumed.
2. In galvanic cell, reaction taking place is spontaneous.	2. In electrolytic cell, reaction taking place is non-spontaneous.
3. The two half cells are set up in different containers and are connected through salt bridge or porous partition.	3. Both the electrodes are placed in the solution or molten electrolyte in the same container.
4. In galvanic cell, anode is negative and cathode is positive.	4. In electrolytic cell, the anode is positive and cathode is negative.
5. The electrons move from anode to cathode in external circuit.	5. The electrons are supplied by the external source. They enter through cathode and come out through anode.

4.6. BATTERIES

Any cell or battery that we employ as a source of electrical energy is basically an electrochemical cell. The term **battery** is used to represent the *arrangement of two or more galvanic cells connected in series.* Theoretically, indirect redox reaction is, primarily, the basis of all electrochemical cells. However, in practice the redox reaction used should give the arrangement which fulfills the following requirements:

(*i*) It should be *light* and *compact*;
(*ii*) Its voltage should not vary appreciably during its use;
(*iii*) It should provide power for a longer period; and
(*iv*) It should be rechargeable.

The galvanic cells can be broadly classified into two categories, namely; *primary cells* and *secondary cells.*

Primary Batteries

This type of batteries become dead over a period of time and the chemical reaction stops. They cannot be recharged or used again. Some common examples are *dry cell, mercury cell,* etc.

(*a*) **Dry Cell.** It is a compact form of ***Leclanche cell*** known after its discoverer. In this cell, *anode* consists of *zinc container* while *cathode* is a *graphite rod* surrounded by powdered MnO_2 and carbon. The space between the electrodes is filled with the paste of NH_4Cl and $ZnCl_2$. The arrangement is shown in Fig. 4.10.

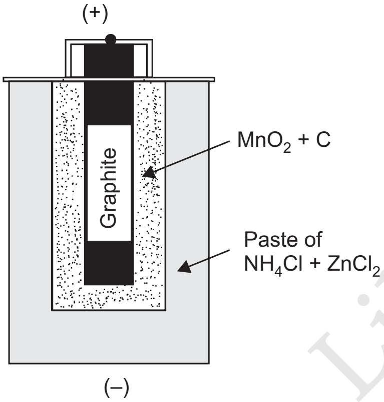


Fig. 4.10. A dry cell.

The reactions taking place at the electrodes are given in their simplified form as follows:

Cathode:

$$MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$$

(*Oxidation state of Mn changes from + 4 to + 3*)

Anode:

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

The zinc ions (Zn^{2+}) so produced combine with ammonia liberated in cathodic reaction to form diammine zinc (II) cation.

$$Zn^{2+} + 2NH_3 \longrightarrow [Zn(NH_3)_2]^{2+}$$

Dry cells do not have long life as NH_4Cl which is acidic, corrodes the zinc container even if the cell is not in use. The cell potential of dry cells lies in the range *1.25 V* to *1.5 V.*

(*b*) **Mercury Cell.** It is miniature cell which finds a frequent use these days to supply energy for watches, video cameras, hearing aids and other compact devices. In mercury cell the *anode* is *zinc-mercury amalgam* and the *cathode* is a paste of *mercury(II) oxide* and *carbon.* Electrolyte is a moist paste of KOH-ZnO. The arrangement in its simple form is shown in Fig. 4.11.

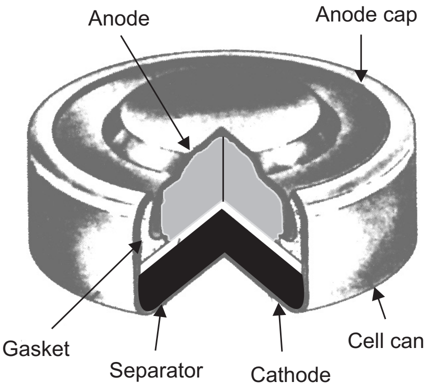


Fig. 4.11. Commonly used mercury cell. The reducing agent is zinc and the oxidising agent is mercury (II) oxide.

The operating voltage for mercury cell is $\simeq 1.35$ V and the cell reactions are as follows:

Anode:

$$\underset{\text{(Amalgam)}}{\text{Zn (Hg)}} + 2OH^- \longrightarrow ZnO(s) + H_2O(l) + 2e^-$$

Cathode:

$$HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH^-$$

Net reaction:

$$\underset{\text{(Amalgam)}}{\text{Zn(Hg)}} + HgO(s) \longrightarrow ZnO(s) + Hg(l)$$

Such a cell shows constancy in its potential throughout its life.

Secondary Batteries

This type of cells can be recharged by passing *direct current* through them and can be used again and again. Some examples are lead-storage battery, nickel-cadmium storage cell, etc. Let us study the working of *lead storage cell.*

(*a*) **Lead-storage Battery.** It is the most frequently used battery in automobiles. It consists of six voltaic cells connected in series. In each cell *anode* is made of *spongy lead* and *cathode* is a grid of lead *packed with lead dioxide* (PbO_2). The electrolyte is the aqueous solution of H_2SO_4 which is 38% by mass. The reactions taking place in this type of cell can be represented as:

Anode:

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-; \qquad E^\ominus_{oxi} = 0.36\ V$$

Cathode:

$$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O; \qquad E^\ominus_{red} = 1.69\ V$$

Net reaction:

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O; \qquad E^\ominus_{cell} = 2.05\ V$$

During the working of the cell, the concentration of H_2SO_4 decreases as sulphate ions are consumed to form $PbSO_4$. The $PbSO_4$ precipitates and partially gets coated on both the electrodes. The water formed dilutes the sulphuric acid. With the decrease in the concentration of H_2SO_4 the density of the solution also decreases. The condition of the battery can be easily checked by measuring the density of the solution.

To enhance the output of the cell, the anode and cathode plates are arranged in alternating manner and they are separated by sheets of insulating material. The anode and cathode plates are separately connected to each other so as to increase the electrode area in contact with electrolyte solution. This increases current delivering capacity of the cell. The *groups of electrodes* constitute *one cell* are shown in Fig. 4.12. The cells are further connected in series so as to increase the voltage of the battery. In 6 volts battery there are 3 cells and in 12 volts battery there are 6 cells.

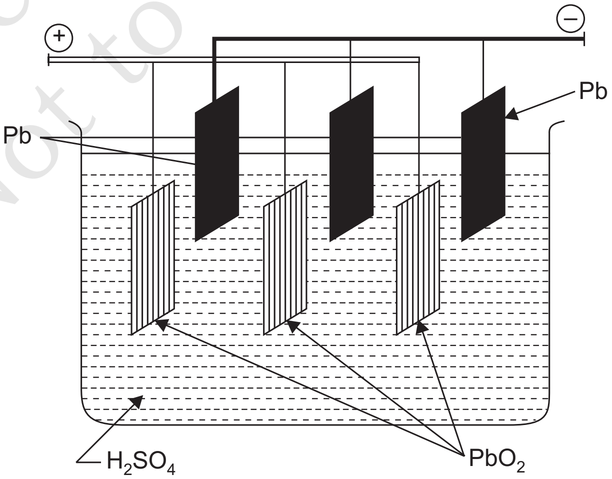


Fig. 4.12. Lead storage cell.

Recharging the battery. The battery can be recharged by connecting it to an external source of *direct current* with voltage greater than 12 V. It forces the electrons to flow in opposite directions resulting in the deposition of Pb on the anode and PbO_2 on the cathode.

During *recharging* operation, the cell behaves as *electrolytic cell.* The recharging reactions are:

Cathode (–ve):

$$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$$

Anode (+ve):

$$PbSO_4(s) + 2H_2O(l) \longrightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$$

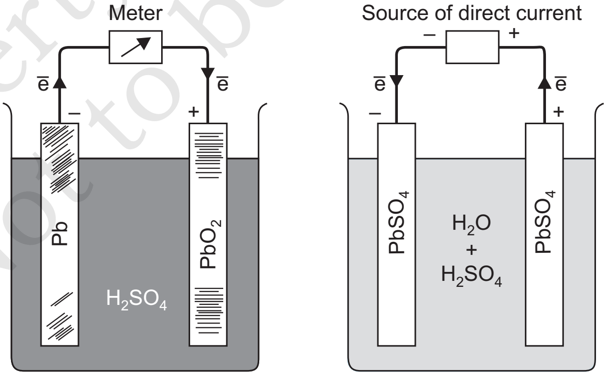
Net:

$$2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq)$$

Such an operation becomes possible because $PbSO_4$ formed during discharge operation is solid and sticks to the electrodes. Therefore, it is in a position to lose or gain electrons during electrolysis.

The discharging and recharging of lead storage battery has been shown in Figs. 4.13 (*a*) and 4.13 (*b*) respectively.

In an automobile, the battery is discharged when the engine is started. While running, the engine powers the alternator which produces electrical energy sufficient enough to recharge the battery. Thus, battery is constantly recharged as long as the automobile is being driven.



Discharging
(a)

Recharging
(b)

Fig. 4.13. Charging and recharging of lead storage cell.

(*b*) **Nickel-cadmium Storage Cell.** It is another rechargeable cell. It consists of *cadmium anode* and the cathode made of a metal grid containing *nickel (IV) oxide*. These are immersed in KOH solution. The reactions occurring are:

Anode:

$$Cd(s) + 2OH^{-}(aq) \longrightarrow Cd(OH)_2(s) + 2e^{-}$$

Cathode:

$$NiO_2(s) + 2H_2O(l) + 2e^{-} \longrightarrow Ni(OH)_2(s) + 2OH^{-}(aq)$$

Net reaction:

$$Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

The cell is also called ***nicad cell*** and has *voltage* ≈ **1.4 V.**

As is evident, there are no gaseous products, the products formed adhere to the electrodes and can be reconverted by *recharging process*. This cell is becoming more popular these days and finds use in electronic watches and calculators.

Fuel Cells

In recent years, the scientists have designed the cells which convert **chemical energy of a fuel directly into electrical energy.** Such cells are called **fuel cells.** These are the voltaic cells in which, the fuels such as H_2, CO, CH_4, C_3H_8, etc., are used to generate electrical energy without the intervention of thermal devices like boiler, turbines, etc.

The conventional method of conversion of chemical energy of a fuel into electrical energy involves combustion of a fuel to liberate heat. The heat energy so produced is used to generate steam for spinning the turbines which are coupled to electrical generators. This process is approximately 40% efficient.

Fuel cells are designed in such a way that the materials to be oxidised and reduced at the electrodes are stored outside the cell and are constantly supplied to the electrodes. In fact, fuel cell is a *flow battery* that continues to operate as long as the reactants from out side are fed into it. One of the most successful fuel cells uses the reaction of *hydrogen* and *oxygen* to form water and is known as H_2—O_2 fuel cell. The H_2—O_2 fuel cell is also called **Bacon cell** after the name of its inventor and it had been used to power the *Apollo space Missions*. The water vapours produced during the reaction were condensed and added to drinking water supply for the astronauts. The experimental arrangement is shown in Fig. 4.14.

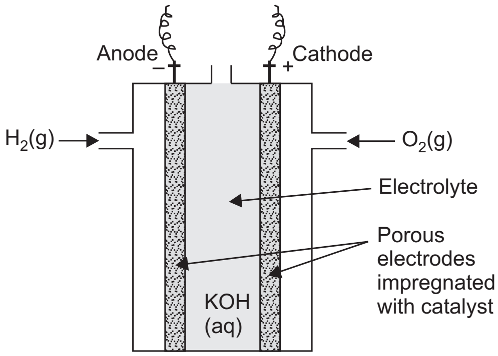


Fig. 4.14. A single bacon cell.

The cell consists of porous carbon electrodes which are impregnated with catalyst (Pt, Ag or CoO). Hydrogen and oxygen are bubbled through the electrodes into electrolyte which is an aqueous solution of NaOH or KOH.

The electrode reactions are:

Anode:

$$[H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-] \times 2$$

Cathode:

$$O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$$

Net reaction:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

The cell runs continuously as long as the gases hydrogen and oxygen are supplied at the temperature 525 K and 50 atm. pressure.

Advantages of Fuel Cells

Some prominent advantages of fuel cells are being described as follows:

1. **Pollution Free Working.** There is no harmful or objectionable product formed in fuel cells. Hence they do not cause pollution problems.
2. **High Efficiency.** The efficiency of fuel cells is approximately 70—75%, which is much higher than the conventional cells.

4.7. CORROSION

It is commonly observed that surface of certain metallic objects slowly gets coated with oxide or some other salt of the metal on long exposure to the atmosphere. **For example**:

- silver gets tarnished,

- copper develops green coating on its surface,
- iron rusts, and
- lead loses its lustre.

In fact, such metals react with the gases or moisture present in the environment to develop the coating of undesirable compounds and the metal is slowly eaten up. This process in general is referred to as *corrosion.* **Corrosion** may, thus, be defined as *the process of slow conversion of metals into their undesirable compounds (usually oxides) by reaction with moisture and other gases present in the atmosphere.*

Factors Which Affect Corrosion

The factors which affect the rate of corrosion are:

(*i*) **Reactivity of the metal.** The more active metals are more prone to corrosion.

(*ii*) **Presence of impurities.** Presence of impurities helps in setting up a corrosion cell and makes the corrosion to occur rapidly. For example, pure iron does not rust.

(*iii*) **Air and moisture.** Air and moisture are quite helpful in corrosion. The presence of gases like CO_2 and SO_2 in air makes it still rapid. For example, no rusting is caused if iron is kept in vacuum.

(*iv*) **Strains in metal.** Strains in metal also help in corrosion. For example, in iron articles, rusting is more pronounced on the areas having bends, dents, scratches, nicks and cuts.

(*v*) **Presence of electrolytes.** The presence of electrolytes also makes the corrosion process faster. For example, iron rusts more rapidly in saline water in comparison to pure water.

Let us understand the **mechanism of corrosion** by studying the most familiar example of **rusting of iron.** Chemically rust is hydrated iron (III) oxide, $Fe_2O_3 . xH_2O$. It is generally caused by moisture, CO_2, O_2 of air. Rust is a non-sticking brown-coloured material which can be easily removed by scratching. There are a number of theories about the mechanism of rusting. The most widely accepted theory is *electrochemical theory* which is being discussed here.

Electrochemical Theory of Rusting

According to this theory, the *impure iron* surface behaves like a small electrochemical cell in presence of water containing dissolved oxygen or carbon dioxide. Such a cell is also called *corrosion cell* or *corrosion couple.* In these miniature corrosion cells, pure iron acts as anode and impurity site acts as cathode. Moisture having dissolved oxygen and carbon dioxide in it constitutes electrolytic solution.

Developments in Fuel Cells

One of the problem with H_2—O_2 fuel cells is that their power per unit mass is too low. This makes their practical use difficult in automobiles. Intensive developments are being done to use different catalysts and different electrolytes in these cells. Some examples of H_2—O_2 fuel cells which use different electrolytes are as follows:

(*i*) *Alkaline fuel cells (AFCs).* Here, the electrolyte is aqueous KOH

The reaction involved are

$$2H_2\,(g) + 4OH^-\,(aq) \longrightarrow 4H_2O\,(l) + 4e^-$$

$$O_2\,(g) + 2H_2O\,(l) + 4e^- \longrightarrow 4OH^-$$

(*ii*) *Phosphoric acid fuel cells (PFCs).* Here, the electrolyte is aqueous H_3PO_4

(*iii*) *Molten carbonate fuel cells.* The electrolyte is $K_2CO_3\,(l)/Si_2CO_3\,(l)$

In addition to this, the fuel cells based on the combustion of **hydrocarbons** like CH_4, C_2H_6, C_3H_8, etc, and **alcohols** such as CH_3OH, C_2H_5OH, etc., in the presence of catalysts, have been designed. Some examples are

(*i*) *Direct methanol fuel cell (DMFC).* Here, the electrolyte is polymer membrane and the electrode reactions are

$$\textit{Anode: } CH_3OH + H_2O \longrightarrow 6H^+ + CO_2 + 6e^-$$

$$\textit{Cathode: } 3/2\ O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$$

$$\textit{Net reaction: } CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 3H_2O$$

(*ii*) *Propane oxygen fuel cell.* The electrode reactions are

$$\textit{Anode: } C_3H_8 + 6H_2O \longrightarrow 3CO_2 + 20H^+ + 20e^-$$

$$\textit{Cathode: } 5O_2 + 20H^+ + 20e^- \longrightarrow 10H_2O$$

$$\textit{Net reaction: } C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 10H_2O$$

In recent years **zinc-air fuel cell (ZAFC)** has been developed in U.S. as a source of power in automobiles. Here, electrolyte is aqueous alkali (KOH) and the electrode reactions are

$$\textit{Anode: } \quad Zn + 2OH^- \longrightarrow Zn\,(OH) + 2e^-$$

$$\textit{Cathode: } \quad O_2 + 2H_2O + 4e^- \longrightarrow 4OH^{-2}$$

$$\textit{Net reaction: } \quad 2Zn + 2O_2 + 2H_2O \longrightarrow 2\ Zn\,(OH)_2$$

Anodic reaction involves oxidation of Fe atoms to Fe^{2+} ions

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^- \; ; \; E^{\ominus}_{oki} = -0.44 \text{ V} \qquad \ldots (i)$$

The Fe^{2+} ions so produced go into solution and the electrons lost are pushed through in the metal to cathodic site.

The *cathodic reaction* involves the reduction of dissolved O_2 to H_2O in the presence of H^+ ions present in the electrolyte solution. The H^+ ions are believed to be formed by dissolution of CO_2 and other acidic gaseous oxides from the atmosphere in water

$$(CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-).$$

$$2H^+ + \tfrac{1}{2} O_2 + 2e^- \longrightarrow H_2O \; ; \; E^{\ominus}_{red} = 1.23 \text{ V} \qquad \ldots (ii)$$

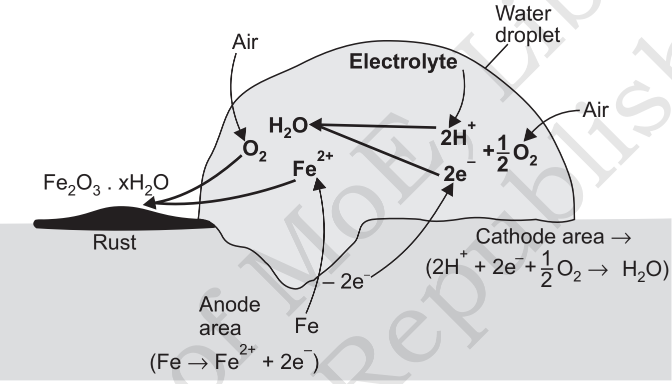


Fig. 4.15. Rusting of iron.

The net reaction of the corrosion cell can be obtained by adding equations (*i*) and (*ii*).

$$Fe + 2H^+ + \tfrac{1}{2} O_2 \longrightarrow Fe^{2+} + H_2O \; ; \; E^{\ominus}_{cell} = 1.67 \text{ V}$$

The ferrous ions so formed move through electrolyte and come at the surface of iron object where these are further oxidised to *ferric state* by atmospheric oxygen and constitute rust which is hydrated iron (III) oxide.

$$2Fe^{2+} + \tfrac{1}{2} O_2 + 2H_2O \longrightarrow Fe_2O_3 + 4H^+$$

$$Fe_2O_3 + xH_2O \longrightarrow \underset{\text{(Rust)}}{Fe_2O_3.xH_2O}$$

It is worth mentioning here, that H^+ ions play significant role in redox reaction leading to rusting. Decrease in the concentration of H^+ ions (*i.e.*, increasing the pH) makes rusting less favourable. It has been observed that at a pH > 9–10 rusting does not occur.

Prevention of Corrosion

Corrosion causes severe damage to briges, buildings, ships and all other structures made of metals espacially iron. Lot of money has to be spent every year to repair or replace the rusted structures. However, these are several methods for protecting metals from corrosion (iron from rusting). Some of these methods are being discussed as follows:

1. Barrier Protection. In this method, a barrier film is introduced between iron and atmospheric oxygen and moisture. Barrier protection can be achieved by any of the following methods:

(*i*) *by painting the surface.*

(*ii*) *by coating the surface with a thin film of oil or grease.*

(*iii*) *by electroplating iron with some non-corrosive metal such as nickel, chromium, copper, etc.*

In this type of protection, if scratches or cracks appear in the protective layer then surface of iron may get exposed. In this region, moisture and oxygen may come in contact with iron and rusting starts. This rusting extends beneath the protective layer and eventually peels off the protective layer.

2. Sacrificial Protection. In this method, surface of iron is covered with a layer of *more active metal* like zinc. This active metal loses electrons in preference to iron and hence, prevents the rusting of iron. However, the covering metal gets consumed in due course of time, but so long as it is present, even the nearly uncovered surfaces of iron do not get rusted. In this way, scratches in the protective layer of this type are not harmful. This type of protection is called **sacrificial protection.**

Zinc metal is generally used for protecting iron and the process is called **galvanization.** Galvanized iron sheets maintain their shine due to the formation of a thin protective layer of basic zinc carbonate, $ZnCO_3 . Zn(OH)_2$ due to the reaction between zinc, oxygen, CO_2 and moisture in air.

Zinc, magnesium and aluminium powders dissolved in paints can also be applied as protective layers. The well known aluminium paint contains aluminium powder suspended in varnish.

3. Electrical Protection. This is also a case of sacrificial protection. In this method, the exposed surface of iron is protected by connecting it to some more active metal such as magnesium. The other metals which can be used for this purpose are aluminium, zinc, etc. The more active metal acts as anode and loses electrons in preference to iron. The iron surface, acts as cathode. This method, therefore, is also called **cathodic**

protection of iron. Underground water pipes or tanks made of iron are protected by connecting them to more easily oxidisable metal as shown in Fig. 4.16.

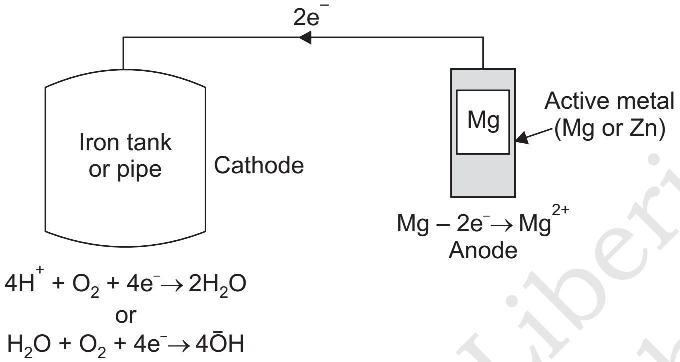


Fig. 4.16. Protection of underground pipe or tank.

4. Use of Anti-rust Solutions. The alkaline solutions of some phosphate and chromate salts act as anti-rust solutions. For example, when iron articles are dipped into the boiling and strongly alkaline solution of sodium phosphate, a protective insoluble film of iron phosphate is formed on them. This film protects the articles from rusting. The alkaline nature of solutions decreases the availability of H^+ ions which facilitate the oxidation of iron to Fe^{2+}.

EXPERIMENT 4

Aim: Electroplating of copper.

Theory: Electroplating is done to prevent objects from corrosion and for decoration purpose when any object is to be electroplated by copper that object is made cathode. Anode taken is of pure copper and aqueous solution of copper sulphate is used as electrolyte. When current is passed through the circuit copper ions are released from anode and a thin, fine, file of copper is deposited on cathode. An equivalent amount of copper is lost, by the pure copper anode and is dissolved in copper sulphate solution.

$$CuSO_4\ (aq) \rightleftharpoons Cu^+ + SO_4$$

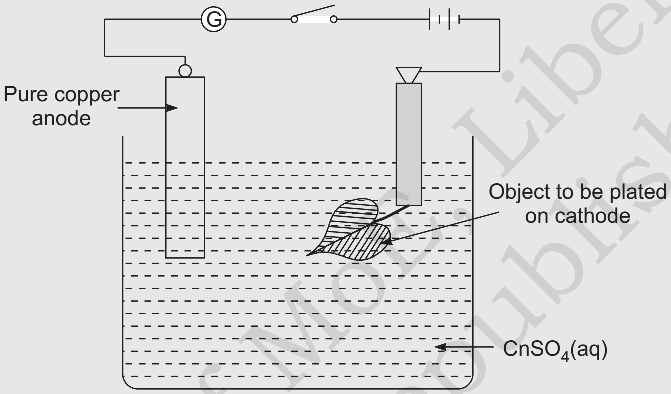
Apparatus and chemicals: One beaker or a tub, pure copper rod for anode, the object to be plated, aqueous copper sulphate solution, connecting wires, a battery galvanometer, etc.

Procedure:

1. Take beaker or the tub.

2. Fill it more than half with aqueous copper sulphate solution.
3. Immerse copper rod and the object to be plated in aqueous solution and connect with the battery with the help of connecting wires, as shown in the picture.
4. Allow the current to flow in the circuit.

Observation: When current is passed through $CuSO_4$(aq) solution, we observe that a thin, fine film of copper is deposited on the surface of the object.



Copper electroplating

Fig. 4.17

Precautions:

1. Follow all electric safety precautions.
2. Ventilation should be good so that copper sulphate fumes do not accumulate in the lab or room as copper sulphate is poisonous.
3. Do not overheat the electrolyte ($CaSO_4$(aq))
4. Do not use rings and other jewelleries while doing electroplating.

EXPERIMENT 5

Aim: To extract and purify metal (copper) by using the process of electroplating.

Theory: For extraction and purification of copper electroplating can be used. Electrolyte of copper can be used. When electrolysis is done the copper ions get depleted from anode (Impure copper rod) and dissolve in copper sulphate (electrolyte). Copper sulphate dissociates into Cu^{++} ions and SO_4 ions. Copper ions depleted from anode get deposited on cathode after passing through the copper sulphate solution leaving impurities in the base of vessel in which electrolyte is filled. Copper deposit on cathode is pure.

Procedure:

1. Take a beaker, bottle or any other vessel as per requirement and pour $CuSO_4$ (aq) solution in it.
2. Take impure copper rod as anode and pure rod as cathode.
3. Now pass too current through the electrolyte.

Observation: We see that thickness of anode decreases due to depletion of copper ions while thickness of cathode increases due to deposition of pure copper on it.

Precautions:

1. Concentration of electrolyte should not be too high or too low.
2. Electrodes should be cleaned by sand paper before use.
3. Chemicals should be handled carefully.
4. Electrolyte should not be too heated.

Hydrogen Economy

One of measure of progress and development of any country is the per capita consumption of energy. The energy requirement increases as more and more people aspire to improve their living standard. At present the main source of energy that drives our economy is carbonaceous fossil fuels such as coal, oil, gas, etc. The major drawbacks with fossil fuels are as under:

(*i*) Their reservoirs are getting exhaused very fast.

(*ii*) CO_2, the major product of their combustion is responsible for *Greenhouse Effect* which leads to serious globle problems.

Thus, the use of carbonaceous fuels has to be made limited so as to avoid these problems. Hydrogen economy is the future vision of energy. In fact, **hydrogen economy** *is a proposal of energy distribution system based on hydrogen gas as energy carrier.* The hydrogen could be used either for burning to generate heat or in fuel cells to generate electricity. Thus, hydrogen provides an alternative source of energy which is renewable as well as non-polluting. The vision of hydrogen economy lies in its production by electrolysis of water using solar energy and its use as fuel and making fuel cells. All these technologies are based on electrochemical principles.

4.8. PRACTICAL APPLICATIONS OF ELECTROLYSIS

Electrolysis is the process of chemical dissociation, when current is passed through an electrolyte. The electrolyte contains positive and negative ion which are the cause of passage of electric current through it. Electrolysis is used in industries for several purposes. Practical applications of electrolysis are:

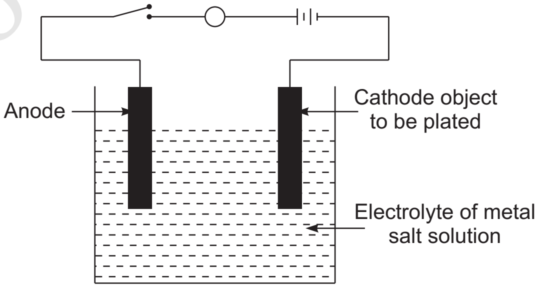
1. **Electroplating:** Electroplating uses the process of electrolysis for coating an object with thin film of metal during electrolysis by an electrolytic solution. During electroplating the article to be plated is used as cathode in the electroplating process and the metal plated on the object is used as anode. The electrolytic solution on bath contains an electrolytic solution of the metal to be plated. When a low voltage electric current is passed through the electrolyte, the metal ions from the electrolyte gain electrons from the cathode (object) as metal coating. Some way metal atoms on the anode loose electrons on the anode and go as ions into the electrolyte. Metal ions from the anode keep on depleting from anode and keep on depositing on cathode via electrolyte keeping the concentration of metal ion in the electrolyte.

Quality of electroplating depends upon following factors:

(*a*) Concentration of metal ions to be deposited on the object has to be carefully controlled in the plating solution so that a fine uniform layer of the plating material is deposited on the object to be electroplated.

(*b*) The type of electrolyte and its concentration should be carefully selected.

(*c*) Such compound which control the acidity and increase the conductivity must be included in the solution.



Electroplating

Fig. 4.18

(*d*) Metal to be deposited on the object has to be selected wisely as per requirement so as to make it brighter or smoother.

(*e*) It is better if anode is shaped like cathode where object is place, so as to achieve even metal coating.

(*f*) To get even deposit all over the object either cathode should be surrounded by several anodes or the cathodes must be rotated at uniform speed.

It is to be noted that for gold and silver plating, the electrolyte used should be alkaline white for nickel or copper plating the electrolyte should be acidic.

2. **Extraction and refining of metals:** In the process of extraction and refining of metal by using electrolysis, the impure metal rode is used as anode and the aqueous solution of salt of metal to be refined is taken as electrolyte. When process of electrolysis is done, the metal from anode gets dissolved in the electrolyte and pure metal gets deposited on the cathode, maintaining the metal ion concentration in the electrolyte.

3. **Production of Chemicals:** Electrolysis is used in many industries for bulk production of chemicals like caustic soda, potassium permanganate, ammonium per sulphate hydrogen, oxygen etc.

4. **Production of non-metal:** Electrolysis is used to obtain non-metals such as hydrogen, fluorine, chlorine. Hydrogen is obtained in the presence of electrolytes such as H_2SO_4, and KNO_2, through the electrolysis of water.

5. **Electrotyping:** Electroplating is an electrolytic process for making metal parts that exactly reproduce the given design. It is a special application of electroforming and mainly used to reproduce printing.

6. **Anodizing:** The process of deposition of a thin film of protective oxide on a surface of metal by using electrolytic process is known as anodizing. It is mainly used to protect the metal from corrosion.

6. **Electropolishing:** Electropolishing is an electrolytic process used to remove flaws from the surface of any metal part. In electrolytic polishing a layer of material, is removed from metallic surface to give it a polished surface.

7. **Electrocleaning:** It is the process of soil, scale, greese or corrosion from the surface of a metal. Here article to be cleaned is made cathode. When heavy current is passed through electrolyte caustic soda and hydrogen are produced which remove the greese from article surface. This type of cathodic cleaning zinc and aluminium articles are cleaned. In anodic cleaning article to be cleaned are made anode.

SUMMARY

- **Electrochemical Cell:** A device that converts chemical energy into electrical energy.
- **Anode:** In electrochemical cells, the anode is the electrode at which oxidation takes place. It is the negative terminal.
- **Cathode:** In electrochemical cells, the cathode is the electrode at which reduction takes place. It is the positive terminal.
- **Electrochemical Series:** Arrangement of various elements and electrode reactions in the increasing order of their reduction potentials.
- **Fuel Cell:** A device which converts chemical energy of a fuel directly into electrical energy.
- **Electrolyte:** A substance that dissociates in solution to produce ions and hence conducts electricity in dissolved state or molten state.
- **Degree of Dissociation (α):** Fraction of total number of molecules that dissociates in solution.

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^c}$$

- **Electrolysis:** The process of decomposition of electrolyte as a result of passage of electricity through its aqueous solution or through its molten state.

EVALUATION

1. Which of the following is the strongest oxidising agent?

(*a*) Cl^-	(*b*) Mn^{2+}
(*c*) MnO_4^-	(*d*) Cr^{3+}

2. Which among the following is the most stable oxidised species?

(*a*) Cr^{3+}	(*b*) MnO_4^-
(*c*) $Cr_2O_7^{2-}$	(*d*) Mn^{2+}

3. Which of the following is the strongest reducing agent?

(*a*) Cr^{3+}	(*b*) Cl^-
(*c*) Cr	(*d*) Mn

4. What is true about the cell constant of a conductivity cell?
   (*a*) It changes with change of electrolyte.

(*b*) It changes with change of concentration of electrolyte.
(*c*) It changes with temperature of electrolyte.
(*d*) It remains constant for given cell.

5. Which of the following statement is correct?
(*a*) E_{cell} and $\Delta_r G$ of cell reaction both are extensive properties.
(*b*) E_{cell} and $\Delta_r G$ of cell reaction both are intensive properties.
(*c*) E_{cell} is an intensive property while $\Delta_r G$ of cell reaction is an extensive properties.
(*d*) E_{cell} is an extensive property while $\Delta_r G$ of cell reaction is an intensive property.

6. An electrochemical cell can behave like an electrolytic cell when
(*a*) $E_{cell} = 0$
(*b*) $E_{cell} > E_{ext}$
(*c*) $E_{ext} > E_{cell}$
(*d*) $E_{cell} = E_{ext}$

7. During charging of lead storage battery,
(*a*) $PbSO_4$ cathode is reduced to Pb.
(*b*) $PbSO_4$ anode is reduced to Pb.
(*c*) $PbSO_4$ cathode is oxidised to Pb.
(*d*) $PbSO_4$ anode is oxidised to PbO_2.

8. An increase in equivalent conductance of a strong electrolyte with dilution is mainly due to
(*a*) increase in number of ions
(*b*) increase in ionic mobility
(*c*) 100% ionisation of electrolyte at normal dilution
(*d*) increase in both, *i.e.*, number of ions and ionic mobility of ions.

9. Identify the correct statement
(*a*) Corrosion of iron can be minimized by forming an impermeable barrier at its surface
(*b*) Iron corrodes in oxygen free water
(*c*) Iron corrodes more rapidly in salt water because its electrochemical potential is higher.
(*d*) Corrosion of iron can be minimized by forming a contact with another metal with higher reduction potential.

10. Consider the statement S_1 and S_2

S_1: Conductivity always increases with decrease in concentration of electrolyte.

S_2: Molar conductivity always increases with decrease in concentration of electrolyte.

Mark the correct answer:
(*a*) Both S_1 and S_2 are wrong
(*b*) S_1 is wrong S_2 is correct

(*c*) S_1 is correct S_2 is wrong
(*d*) Both S_1 and S_2 are correct

II. Descriptive Questions

1. State and explain Faraday's first law of electrolysis.
2. What is battery ?
3. What are the fuel cells ? Explain the working of $H_2 - O_2$ fuel cell.
4. Differentiate between electrochemical cell and electrolytic cell.
5. What is uses of Daniel cell?
6. What is meant by electrochemical cell?
7. What are differences between galvanic cell and electrolytic cell?
8. Define the fuel cells.
9. Write the some advantages of fuel cell.
10. Explain the factors which affect the rate of corrosion.

III. Numerical Questions

1. Identify oxidants and reductants in the following reactions.
   (*a*) $CH_4(g) + 4Cl_2(g) \longrightarrow CCl_2(g) + 4HCl(g)$
   (*b*) $H_2S(aq) + Cl_2(aq) \longrightarrow S(s) + Cl^-(aq)$
   (*c*) $MnO_4^- + C_2H_5OH(aq) \longrightarrow Mn^{+2}(aq) + CH_2COOH(aq)$
   (*d*) $AS_2S_2(s) + NO_3^-(aq) \longrightarrow AsO_4^{-2}(aq) + NO_2(g) + S(s)$
2. How many coulombs of electricity are required for
   (*i*) Oxidation of 90 g of water
   (*ii*) Reduction of 0.2 moles of CrO_7^{2-} and Cr^{3+}.
   (*iii*) Complete reduction of MnO_4^- ions in 500 ml of 0.5 m solution to Mn^{2+} ions. (**Ans.** (*i*) 9.65×10^5 C (*ii*) 115800 C (*iii*) 120625 C)
3. In the reactions given below, identify the species undergoing oxidation and reduction
   (*i*) $H_2S(g) + Cl_2(g) \longrightarrow 2HCl(g) + S(s)$
   (*ii*) $3Fe_3O_4(s) + 8Al(s) \longrightarrow 9Fe(s) + 4Al_2O_3(s)$
   (*iii*) $2Na(s) + H_2(g) \longrightarrow 2NaH(s)$
4. How many grams of chlorine can be produced by the electrolysis of molten NaCl by a current of 1.00 amp for 15 minutes? (**Ans.** 0.33 g)
5. The electrolysis of an acetate of an acetate solution produces ethane according to the reaction.
   $2CH_3COO^- \longrightarrow C_2H_6 + 2CO_2 + 2e-$ (**Ans.** 1.35 L, 2.70 L)
6. Potassium chlorate is prepared by electrolysis of KCl in basic solution as
   $$6OH^- + Cl^- \longrightarrow ClO_3^- + 3H_2O + 6e^-$$
   What is the time required to produce 10 g of $KClO_3$ using current of 3 amp? (**Ans.** 4.37 ms)

SEMESTER–II (Period–V)

5

TOPIC

Chemical Energetics

C11CH5

Learning Objectives

Upon completion of this topic, learners will:

- Identify the systems and the surroundings in the chemical process
- Identify the ways in which energy is transferred in the chemical process
- Investigate the relationship between internal energy and enthalpy
- Calculate change in enthalpy of a reaction using Hess' Law of heat
- Calculate change in standard enthalpy of a reaction using tables of change in enthalpy of formation
- Appreciate the origin of heat release in net bond breakage and
- Discuss the concept of ionic systems.

5.1. THERMODYNAMICS

Thermodynamics, literally, means conversion of heat into work and *vice versa* because **therm** refers to *heat* and **dynamics** refers to *movement.* Now-a-days the term thermodynamics is used in much wider sense as it deals with almost all forms of energies. **Thermodynamics** may, therefore, be defined as *the branch of science which deals with the quantitative relationship between heat and other forms of energies.* When we confine our study to thermodynamics of chemical processes, it is referred to as **chemical thermodynamics.**

Thermodynamics is primarily based upon three fundamental generalisations which have been arrived at, purely on the basis of human experience. These generalisations are called first, second and third laws of thermodynamics. In addition to these laws another generalisation was put forth at a later stage which came to be known as zeroth law of thermodynamics. These laws of thermodynamics apply only when the system is in equilibrium or move from one equilibrium state to another equilibrium state. The predictions based upon these laws have been verified in most of the cases and so far no case has been reported where these laws break down. In general,

- ***Zeroth Law*** provides the basis for the measurement of temperature.
- ***First Law*** deals with the equivalence of different forms of energies.
- ***Second Law*** deals with the direction of chemical change.
- ***Third Law*** helps to evaluate the thermodynamic parameters like entropy.

Scope and Limitations of Thermodynamics

The **importance** of thermodynamics lies in its ability to

(*i*) provides explanation of the macroscope (*i.e.*, bulk) properties of matter in terms of the concepts which are supported by the microscopic views of our material world.

(*ii*) predict the feasibility of the chemical reaction under the given set of conditions.

(*iii*) predict the extent to which the chemical reaction can occur before the equilibrium is attained.

The significant **limitations** of thermodynamics include the following:

(*a*) its failure to tell about the speed or rate of the reaction,

(*b*) its inability to tell the mechanism or path of the reaction because it deals with initial and final states of the system and

(*c*) its non-applicability to microscopic systems such as individual atoms and molecules.

Thermodynamic Terms

In this section, we shall study some basic terms and concepts of thermodynamics which are needed in the study of laws of thermodynamics and other parameters.

System and Surroundings

For the study of thermodynamics, the Universe in divided into two parts, system and surroundings.

A system is defined as that part of the Universe which is under investigation. **For example,** if we are interested in investigating the neutralization of NaOH with HCl, the solutions of sodium hydroxide and hydrochloric acid constitute the system. Similarly, if we are studying the effect of temperature on the properties of water, then water will be taken as the system.

The part of the Universe other than the system is known as surroundings.

Thus, *Universe = System + Surroundings*

The entire universe, other than the system is not affected by the changes taking place in the system. Therefore for all practical purposes, the surroundings represent that portion of the remaining universe which can interact with the system. Generally, the region of space in the neighbourhood of the system constitutes its surroundings.

In order to keep track of exchange of matter and energy between system and surroundings, it is necessary to think of the system as separated from the surroundings by some sort of wall which may be real or imaginary. The wall which separates the system from the surroundings is called **boundary.** For example, if a reaction mixture is taken in a beaker, the reaction mixture constitutes the system, the walls of the beaker constitute the boundary and everything else is the surroundings.

Types of System

Systems may be classified into three types on the basis of movement of matter and energy in and out of the system:

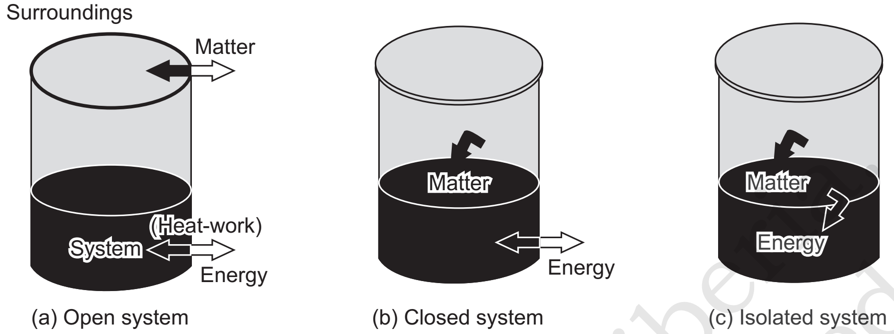
(*a*) *Open system*
(*b*) *Closed system*
(*c*) *Isolated system.*

(*a*) **Open System.** *A system which can exchange mass as well as energy with the surroundings,* is called an **open system.** For example, heating of calcium carbonate in an open vessel. In this case heat is supplied to the system by the burner, while CO_2 escapes into the surroundings.

$$CaCO_3(s) \xrightarrow{\text{Heat}} CaO(s) + CO_2(g)$$

(*b*) **Closed System.** *A system which can exchange energy with the surroundings but not mass* is called a **closed system.** For example, calcination of $CaCO_3$ taken in sealed bulb. On heating, $CaCO_3$ decomposes into CaO and CO_2, however, CO_2 cannot escape and remains trapped in the bulb.

(*c*) **Isolated System.** *A system which can neither exchange mass nor energy with the surroundings* is called an isolated system. For example, a reaction carried out in a closed, well insulated container (such as thermos flask). The open, closed and isolated systems have been shown in Fig. 5.1.



(a) Open system (b) Closed system (c) Isolated system

Fig. 5.1. Open, closed and isolated systems.

Homogeneous System: A system is said to be homogeneous when all its constituents are in the same phase are uniform throughout the system.

Example: column of atmospheric gas

Heterogeneous System: A system is said to be heterogeneous which its constituents are in two or more phase and are not uniform throughout the system.

Example: Ice, water and steam. This system has three homogeneous bodies *e.g.*, steam, water and ice. The chemical composition of three phases is same but their physical properties differ significantly.

Change of State of the System

We know that thermodynamics is a process of transformation of thermodynamic system from an initial thermodynamic state to a second thermodynamical state. The change of state can be studied from the change of thermodynamic state variables like temperature, pressure, volume, internal energy, enthalpy, heat capacity, and entropy.

In order to make useful calculations, it is necessary to describe the system completely before and after it undergoes any change. The state of the system can be described by specifying certain minimum number of macroscopic properties such as *pressure* **(p)**, *volume* **(V)**, *temperature* **(T)** and *amount* **(n)** or *composition*. Once these minimum number of properties are fixed, the other macroscopic properties automatically acquire definite values. Some notable features about the thermodynamic state are as follows:

- Variation in one or more macroscopic properties brings a **change in the state** of the system, when other macroscopic properties attain new values. The macroscopic properties are thus, called **state variables** or **state functions.**
- **Initial state** refers to the starting state of system in equilibrium. After interaction with surroundings (involving exchange of matter or energy or both) the system attains another equilibrium state which is referred to as a **final state** of the system.
- Thermodynamic state of the system must not be confused with *physical state* or *phase*.
- A system is said to be in thermodynamic equilibrium state if its macroscopic properties do not change with time.

State Functions

The thermodynamic properties whose values depend only on the initial and final states of the system are called **state functions.** *These are independent of the manner as to how the change is brought about.* The concept of state function can be easily understood from the following analogy. If we consider '*h*' as the height between the top and bottom of the mountain, then '*h*' is independent of the path followed in reaching the top of the mountain. Here, the parameter *h* is analogous to state function. In thermodynamics, some common state functions are *internal energy* **(U)**, *enthalpy* **(H)**, *entropy* **(S)**, *Gibb's free energy* **(G)**, *pressure* **(p)**, *temperature* **(T)**, *volume* **(V)**, etc. It may be noted that two very important thermodynamic parameters namely; *heat* **(q)** and *work* **(w)** are not the state functions because they are *path dependent*.

The Thermodynamic Process

The operation which brings about the changes in the state of the system is termed as **thermodynamic process.** A thermodynamic process may be further classified into different types depending upon the conditions under which the changes are brought about. These are:

(*i*) **Isothermal Process.** It is a process which is carried out at *constant temperature* ($\Delta T = 0$).

(*ii*) **Adiabatic Process.** It is a process in which *no heat exchange* occurs between the system and the surroundings ($\delta q = 0$).

(*iii*) **Isobaric Process.** It is a process which is carried out at *constant pressure* ($\Delta p = 0$).

(*iv*) **Isochoric Process.** It is a process which is carried out at constant volume ($\Delta V = 0$).

The graphical representation of various chemical processes w.r.t. pressure volume behaviour of given amount of ideal gas has been shown in Fig. 5.2.

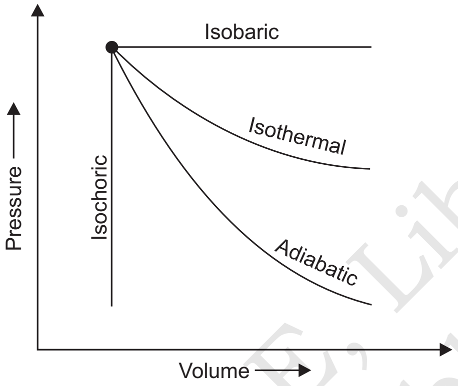
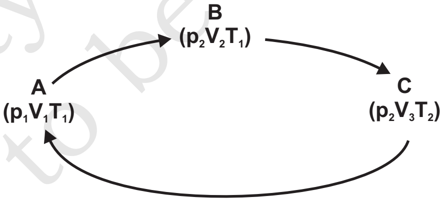


Fig. 5.2. Graphic representation of various thermodynamic processes.

(*v*) **Cyclic Process.** It is a process in which the system returns to the original state after undergoing series of changes. **For example,** in a process shown below the system returns to the original state **A** after successive changes.



Cyclic process, $\Delta H = 0$; $\Delta U = 0$

Fig. 5.3

Table 5.1. Difference between Reversible and Irreversible Process

Reversible Process	*Irreversible Process*
1. It is process which follows reversible path.	1. It is process which follows irreversible path.
2. It is an ideal process and takes infinite time.	2. It is a spontaneous process and takes finite time.

3. It occurs through infinite number of steps under equilibrium conditions at each step.	3. Equilibrium exists only in the beginning and at the completion stage.
4. In this process, the opposing force and driving force differ only by infinitesimally small magnitude.	4. In this process, there is large difference between driving and opposing force.
5. Work obtained is maximum.	5. Work obtained is not maximum.
6. It is only an imaginary process and cannot be realised in actual practice.	6. It is a natural process and occurs in a particular direction under given set of conditions.

Chemical Energy

Chemical energy is the energy stored in bonds of a chemical compound. This chemical energy may be released during a chemical reaction as in **exothermic** reactions. Some times energy input is required in chemical energy as in **endothermic** reactions.

Examples of stored chemical energies are, batteries, biomass, natural gas, petroleum and coal.

Heat and Work

The exchange of energy between the system and surroundings can occur in several ways. *Heat and Work* are two important modes of transference of energy between system and surroundings.

1. Heat (q)

The transference of energy takes place as **heat** if the system (reaction mixture) and surroundings are at different temperatures. The exchange of heat occurs through the thermally conducting walls which constitute boundary between system and surrounding. If the system is at higher temperature, the energy is lost to the surrounding as heat, causing a fall in the temperature of the system. The energy transfer continues till the system and the surroundings attain the same temperature. If the system is at lower temperature than the surroundings, the energy is gained by the system from the surroundings causing a rise in the temperature of the system. The amount of heat gained or lost by the system is represented by **q.** According to the international conventions,

Heat absorbed by the system is positive, i.e., q > 0.
Heat given out by the system is negative, i.e., q < 0.

2. Work (w)

Exchange of energy between system and surrounding can occur in the form of work. Which may be *mechanical work, pressure volume work* or *electrical work*. For example let us take a system containing some quantity of water in a thermos flask which does not allow any exchange of heat between system and surrounding. Let temperature of water be T_A. We now insert a set of small paddles in water and rotate them causing churning of water for sometimes. This will result in the increase in the temperature of water. This indicates increase in the internal energy of water by adding ***mechanical work*** to the system. The same increase in the temperature of water can be produced by adding equal amount of ***electrical work*** with the help of an immersion rod. Let us now become familiar with ***pressure volume work.*** The exchange of energy as pressure-volume work can occur if system consists of gaseous substance and there is a difference of pressure between system and surrounding. The amount of work done by the system or on the system is denoted by *w*. According to international conventions,

Work done on the system is positive, i.e., $w > 0$
Work done by the system is negative, i.e., $w < 0$

The sign conventions of heat and work have been diagramatically represented in Fig. 5.4.

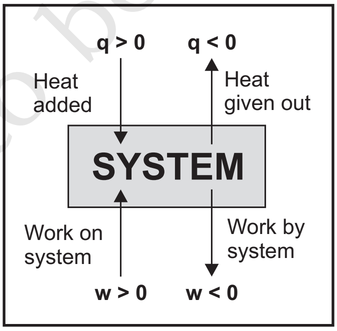


Fig. 5.4. Sign conventions of heat (*q*) and work (*w*).

Units of work. In *CGS* units, the work is expressed in *ergs* but in *SI* units, work is expressed in *joules.* The equivalence between joules and other units of work is

$$1\ J = 10^7\ ergs = 1\ Nm = 1\ kg\ m^2\ s^{-2}.$$

The common forms of work that we come across in the study of the thermodynamics are:

(*a*) *Pressure volume work* and

(*b*) *Electrical work.*

(*a*) **Pressure volume work.** This type of work is also called ***expansion work*** and it is significant in systems which consist of gases and involve changes in volume against the external pressure.

Expression for pV-work. In order to derive the expression for the pressure-volume (pV) work let us consider a 1 mol of ideal gas enclosed in a cylinder fitted with a frictionless piston having area of cross-section equal to 'a'. The total volume of the gas is V_i and the pressure inside the cylinder is p_{in}. Let the pressure on the piston is p_{ex} which is less than the internal pressure of the gas. This pressure difference causes the gas to expand against the external pressure p_{ex} forcing the piston to move out through a small distance l. Now, work of expansion is given by

$$w = \text{Force} \times \text{displacement}$$
$$= F \times l$$

F, the force responsible for moving the piston is given by the product of *pressure* and *area i.e.*,

$$F = p_{ex} \times a$$
$$\therefore \quad w = p_{ex} \times al$$

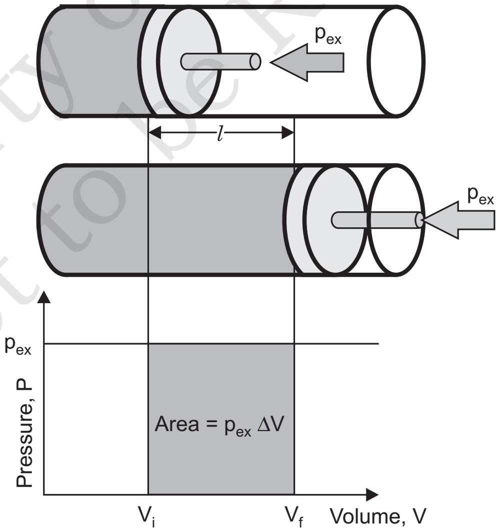


Fig. 5.5. Irreversible expansion against the constant pressure p_{ex}.

Since al refers to the change in volume (ΔV), *i.e.*, ($V_f - V_i$), therefore, work done is given by

$$w = p_{ex}\,\Delta V$$

During expansion, the work is done by the system and ΔV, *i.e.,* $(V_f - V_i)$, is *positive*. Therefore, in order to satisfy the sign conventions, a negative sign is put in the expression for work

$$w = -p_{ex}\,\Delta V$$

It may be noted that above expression of work also holds good even for compression process in which the work is done on the system. ΔV, for compression is *negative*. Therefore, work as obtained from the above expression comes out to be *positive* and satisfies the conventions.

Following the above discussion, *the general expression for all type* of **pV-work** *can be written as*:

$$\mathbf{w = -p_{ex}\,\Delta V} \qquad \text{...(5.1)}$$

The above expression of work represents the work done during **irreversible expansion.** The work done during expansion of ideal gas in a reversible manner and in isothermal conditions can be calculated as follow.

Difference between Heat and Work

In order to understand the difference between heat and work, let us compare the effect of adding heat and work to a gaseous system.

(*i*) When heat is added to a gas, its molecules start moving faster in different directions causing increase in disorder or randomness. Thus heat can be regarded as a mode which stimulates the random motion.

(*ii*) When work is done on a system by forcing the piston down, the initial effect is to force the molecules to move in the direction of movement of piston. Thus, work can be regarded as a mode that stimulates the organised motion.

To conclude, *HEAT refers to random form of energy whereas WORK refers to organised form of energy.*

Internal Energy (U) and Internal Energy Change (ΔU) of the System

Since chemical changes are always accompanied by energy changes, it indicates that reactants and products must be having certain amounts of energy. A fixed quantity of any substance is associated with a definite amount of energy which depends upon chemical nature of the substance and its state of existence. This energy is called **internal energy or intrinsic energy** of the substance and is represented by **U**. Internal energy of the system, is the energy possessed by all its constituent molecules. The various forms of energies which contribute towards the energy of the molecule are *translational energy* (E_t), *rotational energy* (E_r), *vibrational energy* (E_v), *electronic energy* (E_e), *nuclear energies of constituent atoms* (E_n) and *potential energy due to interaction with neighbouring molecules* (E_{PE}). Internal energy is an *extensive property* and is also a *state function.* Its value depends upon state of the substance but does not depend upon how that state is achieved. For example, CO_2 can be obtained by various methods such as by heating calcium carbonate or by burning coal. However, one mole of CO_2 at S.T.P. is associated with a definite amount of internal energy which does not depend upon the source from which it is obtained.

It may be noted that the absolute value of internal energy cannot be determined because it is not possible to determine the exact values for the constituent energies such as translational, vibrational, rotational energies, etc. However, we can determine the change in internal energy ($\Delta \mathbf{U}$) of the system when it undergoes a change from initial sate ($\mathbf{U_i}$) to final state ($\mathbf{U_f}$). For example, the change in internal energy ($\Delta \mathbf{U}$) of a reaction is the difference between the internal energies of the products ($\Sigma \mathbf{U_P}$) and the reactants ($\Sigma \mathbf{U_R}$).

$$\Delta \mathbf{U} = \Sigma \mathbf{U_P} - \Sigma \mathbf{U_R}$$

Significant Features of U

- Internal energy depends upon the quantity of substance in the system and hence, it is an *extensive property.*
- Change in internal energy ($\Delta \mathbf{U}$) represents the ***heat evolved or absorbed in a reaction at constant temperature and constant volume.***
- For processes involving evolution of energy, $U_P < U_R$. Thus, $\Delta \mathbf{U} < \mathbf{0}$ or *sign of* $\Delta \mathbf{U}$ *is* **negative.**
- For processes involving absorption of energy, $U_P > U_R$. Thus, $\Delta \mathbf{U} > \mathbf{0}$ or *sign of* $\Delta \mathbf{U}$ *is* **positive.**
- For isothermal processes involving ideal gas, T is constant. Hence, $\Delta \mathbf{U} = \mathbf{0}$.

Thermodynamic Scale of Temperature

In our daily routine we come across different objects having different degree of hotness according to our physical senses. In order to differentiate different degree of hotness or coldness, we need to develop some parameter or scale with reference to which measurement of hotness can be made. **Temperature** is one such parameter and one of the familiar scale of temperature is *celcius scale.* In celcius scale, the reference points are ice point (0°C) and steam point (100°C) for water and the interval between them has been divided into 100 equal parts called **degrees.** The zero point of this scale is arbitrary creation of its inventor. In 1954, **international committee on weights and measures** adopted **Kelvin Scale** of temperature which is based on *absolute zero* of temperature (– 273.16°C) and **triple point** of water. The triple point of water is a fixed temperature and pressure (0.01°C and 4.58 torr) at which all the three physical states of water, *ice, water* and *water vapour* exist in equilibrium. *Kelvin* **(K)** has been adopted as the basic SI unit of temperature which is $\frac{1}{273.16}$ of the triple point temperature (273.16 K) of water. This kelvin scale of temperature is called **thermodynamic temperature scale** and its zero point refers to the lowest possible temperature.

Law of conservation of energy (First Law of Thermodynamics)

It is a common experience that energy cannot be generated without consuming energy of some other kind. If a certain amount of one kind of energy is produced, an equal amount of some other kind of energy disappears so that the total energy of the Universe remains constant. This observation forms the basis of **first law of thermodynamics** which is also known as **law of conservation of energy.** The law states that:

Energy can neither be created nor destroyed although it may be changed from one form to another.

From this statement it follows that *total energy of the universe, i.e., system and surroundings taken together is always constant during any physical or chemical process.*

Mathematical Expression of First Law

In order to derive mathematical expression for first law of thermodynamics let us assume that a system having internal energy $\mathbf{U_1}$ absorbs a certain amount of heat energy (**q**).

∴ Its internal energy becomes = $q + U_1$.

Let a **w** amount of work be done on it, so that its internal energy changes to $\mathbf{U_2}$.

Now, final internal energy U_2 is given by

$$U_2 = U_1 + q + w$$

$$\text{or} \quad U_2 - U_1 = q + w \quad \text{or} \quad \Delta U = q + w \qquad \ldots(5.2)$$

i.e., (*Change in internal energy*) = (*Heat absorbed*)
+ (*Work done on the system*)

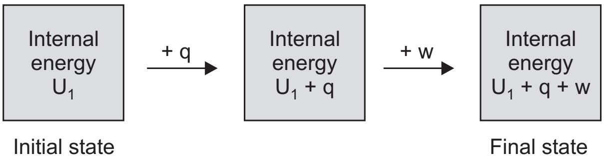


Fig. 5.6

Let the change in volume during the process be $\mathbf{\Delta V}$ at constant pressure $\mathbf{p}$, then the work is referred to as pressure-volume work and its expression is given as $-\mathbf{p \, \Delta V}$.

Thus, $$\mathbf{w = -p \, \Delta V} \quad \text{...(5.3)}$$

Now if there is only pressure-volume work, expression (5.2) can be written as

$$\mathbf{\Delta U = q - p \, \Delta V} \quad \text{...(5.4)}$$

Some Important Results From the First Law Equation, $\mathbf{\Delta U = q + w}$

1. For *isothermal reversible* as well *irreversible expansion* of ideal gas $\Delta U = 0$

$$\therefore \quad 0 = q + w \quad \text{or} \quad q = -w$$

(*a*) For *irreversible expansion*, $w = -p_{ext}\Delta V$

$$\mathbf{q = -w = p_{ex}\Delta V} \quad \text{...(5.5)}$$

(*b*) For *reversible expansion*,

$$w = -2.303\, nRT \log \frac{V_2}{V_1}$$

$$\therefore \mathbf{q = -w = 2.303\, nRT \log \frac{V_2}{V_1}} \quad \text{...(5.6)}$$

2. For *expansion of ideal gas into vacuum*

$$\Delta U = 0;\ w = 0 \quad \therefore \quad q = 0$$

3. *For adiabatic process*, $q = 0$

$$\therefore \quad \mathbf{\Delta U = -w_{ad}} \quad \text{...(5.7)}$$

4. For *isochoric process*, $\Delta V = 0$

$$\therefore \quad \mathbf{\Delta U = q_{(v)}} \quad \text{...(5.8)}$$

Equation (5.8) implies that ΔU represents heat change taking place during the process occurring at constant temperature and constant volume.

Example 5.1. *A gas expands isothermally against constant external pressure of 1 atm from a volume of 10 dm^3 to a volume of 20 dm^3. In the process, it absorbs 800 J of thermal energy from surroundings. Calculate the value of internal energy change.*

Solution. Here, $p_{ex} = 1$ atm

$$\Delta V = (V_2 - V_1) = (20 - 10) = 10 \text{ dm}^3$$

$$w = -p_{ex}\Delta V = -1 \times 10 = -10 \text{ dm}^3\text{-atm}$$

$$= -10 \times 101.3 \text{ J} = -1013 \text{ J}$$

$$q = +800 \text{ J}$$

$$\therefore \quad \Delta U = q + w = 800 + (-1013) = \mathbf{-213\ J.}$$

Enthalpy (H)-Another Useful State Function

We have studied that energy change occurring during the reaction at *constant temperature* and *constant volume* is given by internal energy change. However, most of the reactions in the laboratory are carried out in open beakers or test tubes, etc. In such cases, the reacting system is open to atmosphere. Since atmospheric pressure is almost constant, therefore, such reactions may involve the changes in volume. The energy change occurring during such reactions may not be equal to the internal energy change. In order to understand this, let us assume a chemical reaction involving gaseous substances which proceeds with the evolution of heat. When the reaction is carried out at constant pressure, two possibilities arise.

(*a*) If the reaction proceeds with the increase in volume the system has to expand against the atmospheric pressure and energy is required for this purpose. The heat **evolved** in this case would be little less than the heat **evolved** at constant volume because a part of the energy has to be utilised for expansion.

(*b*) If the reaction proceeds with decrease in volume at constant pressure, the work is done on the system and heat **evolved** will be greater than the heat **evolved** at constant volume.

Thus, it can be concluded from the above discussion that heat changes occurring at constant pressure and constant temperature are not simply due to the changes in internal energy alone but also include energy changes due to expansion or contraction against the atmospheric pressure. In order to study the heat changes of chemical reactions at constant temperature and pressure a new function, *enthalpy* is introduced. **Enthalpy** *is the total energy associated with any system which includes its internal energy and also energy due to environmental* *factors such as pressure-volume conditions.* This can be understood as follows:

A substance has to occupy some space in its surroundings depending upon its volume (V). It does so against the compressing influence of the atmospheric pressure (p). Due to this, the substance possesses an additional energy called pV energy which is given by the product of pressure (p) and volume (V) of the system.

The sum of internal energy and pV energy of any system, under given set of conditions, is called **enthalpy.** It is denoted by H and is also called ***heat content*** of the system.

Mathematically, it may be put as

$$\mathbf{H = U + pV} \quad \ldots(5.9)$$

Some *important features* of enthalpy are:

- It is a state function and is an extensive property,
- It is also called ***heat content*** of the system,
- Its value depends upon amount of the substance, chemical nature of the substance and conditions of temperature and pressure.

Enthalpy Change (ΔH)

It is not possible to determine the absolute value of enthalpy of a system because absolute value of internal energy (U) is not known. However, change in enthalpy (ΔH) taking place during the process can be experimentally determined. Change in enthalpy is equal to difference between the enthalpies of products ($\Sigma \boldsymbol{H_P}$) and reactants ($\Sigma \boldsymbol{H_R}$).

The change in enthalpy may be expressed as

$$\mathbf{\Delta H = \Sigma H_P - \Sigma H_R}$$

Significance of ΔH

Significance of ΔH also follows from the first law of thermodynamics

$$\Delta U = q - p\Delta V$$

or

$$\begin{aligned} q &= \Delta U + p\Delta V = (U_2 - U_1) + p(V_2 - V_1) \\ &= (U_2 + pV_2) - (U_1 + pV_1) \\ &= H_2 - H_1 = \Delta H \end{aligned}$$

or

$$\mathbf{\Delta H} = \boldsymbol{q_p} \quad \ldots(5.10)$$

In short:

ΔU: Heat Changes at Constant T and V.

ΔH: Heat Changes at Constant T and P.

Exothermic and Endothermic Reactions

We know that the chemical reactions are always accompanied by the energy changes. There are many reactions in which energy is evolved while in others energy is absorbed. Depending upon the evolution or absorption of energy, the chemical reactions can be classified into two types : *exothermic* and *endothermic.*

Exothermic Reactions

The chemical reactions which proceed with the evolution of heat energy are called **exothermic reactions.** The heat energy produced during the reaction is indicated by writing + *q* or more precisely by giving the actual numerical value along with products. In general, exothermic reactions may be represented as :

$$A + B \longrightarrow C + D + \mathbf{q} \text{ (heat energy)}$$

The heat evolved is expressed in the units of *joules (J)* or *kilo joules (kJ).*

Now, if the reaction is carried out *at constant temperature and constant volume,* heat evolved is equal to internal energy change (ΔU). For exothermic reactions there is an evolution of heat energy and consequently, the energy of the products (ΣU_P) becomes less than internal energy of the reactants (ΣU_R). Thus, ΔU will be **negative.**

$$\Delta U = \Sigma U_P - \Sigma U_R$$

$$\text{As} \qquad \Sigma U_P < \Sigma U_R$$

$$\therefore \qquad \mathbf{\Delta U = -ve}$$

For example, when one mole of carbon (coal) is burnt in oxygen, there is an evolution of 393.5 kJ of energy. It can be expressed as:

$$C(s) + O_2(g) \longrightarrow CO_2(g) + 393.5 \text{ kJ}$$

$$\text{or} \qquad C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta U = -\ 393.5 \text{ kJ}$$

For a reaction carried out at *constant temperature* and *constant pressure,* the heat evolved is equal to enthalpy change (ΔH). In exothermic reactions the enthalpy of products (ΣH_P) becomes less than the enthalpy of reactants (ΣH_R). Therefore, the enthalpy change for exothermic reaction is **negative.**

$$\Delta H = \Sigma H_P - \Sigma H_R$$

$$\text{As} \qquad \Sigma H_P < \Sigma H_R$$

$$\mathbf{\Delta H = -ve.}$$

For example, formation of one mole of water from hydrogen and oxygen gases is accompanied by the evolution of 286.0 kJ of heat. It can be expressed as:

$$2H_2(g) + O_2(g) \xrightarrow{\quad} 2H_2O(l) + 286.0\ \text{kJ}$$

or

$$2H_2(g) + O_2(g) \xrightarrow{\quad} 2H_2O(l);\ \Delta H = -\,286.0\ \text{kJ}$$

Endothermic Reactions

The chemical reactions which proceed with the absorption of heat energy are called endothermic reactions. The heat energy absorbed during the reaction can be indicated by writing +**q** (or the actual numerical value) with the reactants. It can be indicated by writing –**q** (or the actual numerical value) with the products. In general, an endothermic reaction can be represented as:

$$A + B + \mathbf{q}\ (\text{heat}) \xrightarrow{\quad} C + D$$

or

$$A + B \xrightarrow{\quad} C + D - \mathbf{q}\ (\text{heat})$$

where **q** is the heat absorbed.

When the reaction is carried out at *constant temperature* and *constant volume* the internal energy of the products (ΣU_P) will become more than the internal energy of the reactants (ΣU_R) due to absorption of heat. Consequently, the value of ΔU will be **positive.**

$$\Delta U = \Sigma U_P - \Sigma U_R,\ \text{As } \Sigma U_P > \Sigma U_R$$

$$\mathbf{\Delta U = +ve}$$

For example, formation of nitric oxide from nitrogen and oxygen proceeds with the absorption of 180.5 kJ of heat. It can be represented as:

$$N_2(g) + O_2(g) \xrightarrow{\quad} 2NO(g) - 180.5\ \text{kJ}$$

or

$$N_2(g) + O_2(g) \xrightarrow{\quad} 2NO(g)\ ;\ \Delta U = +\ 180.5\ \text{kJ}$$

When, endothermic reaction is carried out at *constant temperature* and *constant pressure*, the heat absorbed increases the enthalpy of the products. In such a case the **enthalpy change** of the reaction is **positive.**

$$\Delta H = \Sigma H_P - \Sigma H_R,\ \text{As } \Sigma H_P > \Sigma H_R$$

$$\therefore \quad \mathbf{\Delta H = +ve}$$

For example, decomposition of 2 moles of mercuric oxide a constant temperature and pressure proceeds with the absorption of 180.4 kJ of heat. It can be represented as:

$$2HgO(l) \xrightarrow{\quad} 2Hg(l) + O_2(g) + 180.4\ \text{kJ}$$

or

$$2HgO(s) \xrightarrow{\quad} 2Hg(l) + O_2(g)\ ;\ \Delta H = -\ 180.4\ \text{kJ}$$

The enthalpy changes for exothermic and endothermic reactions have been shown in Figs. 5.7 (*a*) and (*b*) respectively.

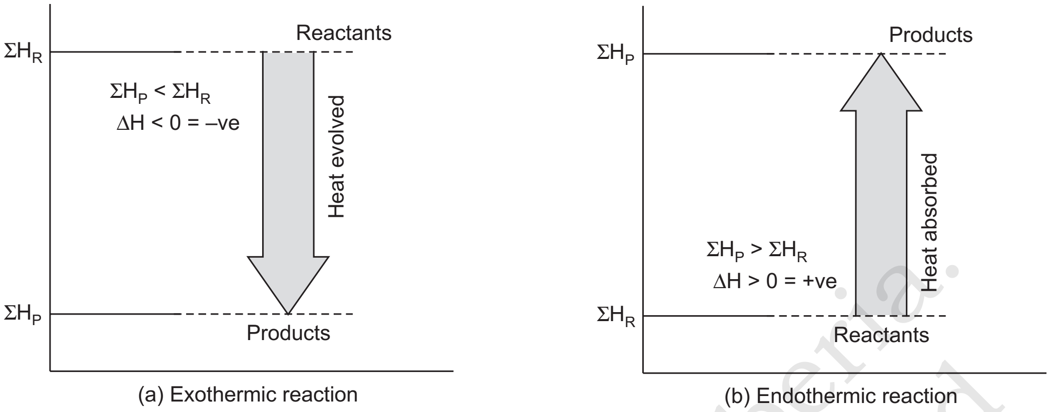


Fig. 5.7

EXPERIMENT 1

Aim: Demonstrate experiment to explain exothermic and endothermic reactions.

Theory: Exothermic reactions are those reactions during which energy or heat is liberated while endothermic reactions are those reactions in which energy or heat is required or absorbed.

Chemicals and Apparatus: Beaker, water, white vinegar, steelwool, detergent, sodium bicarbonate, thermometer etc.

Procedure:

1. Take 4 beakers.

S. No.	*Solvent*	*Solid*	*Initial temp.*	*Final temp.*	*Type of reaction*
1.	Water	Detergent			Exothermic
2.	H_2SO_4	Sugar			Exothermic
3.	Vinegar	Sodium bicarbonate			Endothermic
4.	Water	NaCl			Endothermic

2. Half fill four beakers with solvent as given in the table.
3. Note down temperature of solvent in all four beakers and record in the table.
4. Now add solid solute as mentioned in the table.

5. Note down temperature of solution after 2 minutes of adding the solid solute.
6. If final temperature is more than reaction is exothermic and if final temperature that is less reaction is endothermic.

Thermochemical Equations

Chemical equation is a brief representation of a chemical change in terms of symbols or formulae of reactants and products. When the heat change accompanying the chemical reaction is also included in the chemical equation it is known as *thermochemical equation.* Thus, a **thermochemical equation** may be defined as *a chemical equation which indicates the amount of heat evolved or absorbed during the chemical reaction in addition to the quantities of reactants or products.* It may be noted that in thermochemical equations the fractional coefficients are also commonly used contrary to our usual practice for balancing the chemical equations. A thermochemical equation can be written in two ways:

(*a*) Heat effect can be written as one of the term along with the products.

For example,

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) + 694.6 \text{ kJ}$$

(*b*) Heat evolved or absorbed can be expressed in terms of ΔH.

For example,

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g) \text{ ; } \Delta H = -\,694.6 \text{ kJ.}$$

It is very important to mention the **physical states** *of various reactants and products while writing thermochemical equations because change of physical state is also accompanied by the enthalpy changes.* For example:

When 1 mol of hydrogen gas reacts with $\frac{1}{2}$ mol of oxygen gas to produce 1 mol of liquid water, 286 kJ of heat is produced.

$$H_2(g) + \tfrac{1}{2}\ O_2(g) \longrightarrow H_2O(l); \quad \Delta H = -\,286 \text{ kJ}$$

On the other hand, if 1 mol of water vapours is produced instead of 1 mol of liquid water, the value of ΔH will be different.

$$H_2(g) + \tfrac{1}{2}\ O_2(g) \longrightarrow H_2O(g); \quad \Delta H = -\,249 \text{ kJ}$$

Some Important Conventions about Thermochemical Equations

1. *The coefficients of various substances of chemical equation represent the number of their respective moles. In thermodynamic interpretation of* *an equation, we never interpret the coefficients as number of molecules. Hence, it is acceptable to write coefficients in fractions wherever necessary.*

2. *The value of ΔH in a thermochemical equation corresponds to the enthalpy change taking place when a specified number of moles of various reactants and products* (as indicated by the coefficients of the various substances in the chemical equation), *are involved in the reaction.*

3. *In case, the coefficients in the chemical equation are multiplied or divided by some integer, the ΔH value must also be multiplied or divided by the same integer.* **For example**:

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)\ ; \quad \Delta H = -\ 286 \text{ kJ}$$

If the whole equation is multiplied by 2, the ΔH for the new thermochemical equation is given as:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l);$$

$$\Delta H = 2 \times (-\ 286) \text{ kJ} = -\ 572 \text{ kJ}$$

4. *When a chemical equation is reversed, the magnitude of the ΔH remains same, however, its sign is reversed.* For example, if ΔH is + ve for the forward reaction, it would be negative for the reverse reaction.

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l); \quad \Delta H = -\ 286 \text{ kJ}$$

$$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2} O_2(g);\ \Delta H = +\ 286 \text{ kJ}$$

The thermochemical equations for some exothermic and endothermic reactions are given as follows:

Exothermic reactions (ΔH = –ve):

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l); \quad \Delta H = -\ 286.0 \text{ kJ}$$

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);\ \Delta H = -\ 890.4 \text{ kJ}$$

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g); \quad \Delta H = -\ 92.3 \text{ kJ}$$

Endothermic reactions (ΔH = +ve):

$$C(s) + 2S(l) \longrightarrow CS_2(l); \quad \Delta H = +\ 92.00 \text{ kJ}$$

$$H_2(g) + I_2(g) \longrightarrow 2HI(g); \quad \Delta H = +\ 53.6 \text{ kJ}$$

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g);\ \Delta H = +\ 131.2 \text{ kJ}$$

Heat Capacity

In the previous sections, we have been studying about the heat changes. In this section, we shall focus on the measurement of heat change. The heat transferred to the system appears as a rise of its temperature. The increase in temperature (ΔT) is directly proportional to the quantity of heat (**q**) absorbed by the system. It can be put as

$$\mathbf{q} \alpha \Delta \mathbf{T} \quad \text{or} \quad \mathbf{q} = \mathbf{C}\Delta\mathbf{T} \qquad \text{...(5.11)}$$

where **C** is called **heat capacity** of the system the value of which depends upon the size, composition and nature of the system.

Now, if the temperature difference (ΔT) is unity, *i.e.,* 1° celsius or 1 kelvin then, **q** = **C**. Thus, ***heat capacity of the system is defined as the quantity of heat required to raise its temperature through 1°.***

Equation 5.15 reveals that a given amount of heat will raise the temperature of the system to a smaller extent if its heat capacity is large and *vice versa.*

The units of heat capacity are JK^{-1} or $J(°C^{-1})$

Specific Heat Capacity (c)

This term is used more frequently for *solids* and *liquids*. Heat capacity of the system is extensive property and therefore, depends upon the quantity of matter in the system. For example, large block of aluminium has a higher heat capacity than does a small piece of the same metal. ***Specific heat capacity*** or ***specific heat*** *(c)* is a heat capacity of 1 g of the sample of the substance. It is *the quantity of heat required to raise the temperature of 1 gram of substance through 1 K (or 1°C).*

$$\text{Specific heat capacity } (c) = \frac{\text{Heat capacity}}{\text{Mass}} = \frac{C}{m}$$

Now,

$$C = \frac{q}{\Delta T}$$

$$\therefore \quad \textbf{Specific heat capacity (c)} = \frac{\mathbf{q}}{\mathbf{m}\,\Delta\mathbf{T}} \qquad \text{...(5.12)}$$

Units of specific heat capacity are:

$$\mathbf{Jg^{-1}\,K^{-1}} \quad \text{or} \quad \mathbf{Jg^{-1}\,(°C^{-1})}$$

Combining equation 5.15 and 5.16 we get

$$\mathbf{q} = \mathbf{c} \times \mathbf{m} \times \Delta\mathbf{T} = \mathbf{C}\Delta\mathbf{T}$$

Molar Heat Capacity

This term is generally used for gaseous systems.

The molar heat capacity (C_m) of the substance is the ***heat required to raise the temperature of 1 mol of the gaseous system through 1°***. If C is the heat capacity of n mol of the system then its molar heat capacity, C_m is given by $C_m = \frac{C}{n}$ or $\mathbf{C_m = \frac{q}{n\,\Delta T}}$.

The units of molar heat capacity (C_m) are:

$$\mathbf{J\ mol^{-1}K^{-1}\ or\ J\ mol^{-1}\ (^{\circ}C^{-1})}$$

The specific heat capacity (c) and molar heat capacity (C_m) of the substance are related as

$$\mathbf{C_m = c \times molar\ mass} \qquad \text{...(5.13)}$$

Molar Heat Capacities at Constant Volume and Constant Pressure

We know that heat is not a state function but depends on the path. Likewise *heat capacity is also a path function*. Thus, conditions such as *constant volume* or *constant pressure* have to be specified to define the path for calculating the heat capacity of a system particularly if it is a gas. The heat capacities of 1 mole of a gas at constant volume and that at constant pressure are represented by C_v and C_p respectively.

Relationship between C_p and C_v

Consider 1 mol of ideal gas whose temperature is to be raised through one degree (1 K). When the gas is heated at constant volume, no external work is done by the gas. Heat supplied increases the internal energy of gas. However, when the gas is heated at constant pressure, there will be increase in its volume. The gas will expand and do some external work. Some extra heat must be supplied to the gas to enable it to perform this external work. Thus, heat capacity at constant pressure (C_p) is larger than that at constant volume (C_v). The difference between the two *i.e.*, ($C_p - C_v$), evidently gives the work done by 1 mol of the gas in expansion when it is heated through one degree. In other words, it represents *work done per mol per degree rise in temperature* which is nothing but universal gas constant (R). Thus,

$$\mathbf{C_p - C_v = R}$$

Experimental Data Analysis

The heat changes associated with chemical reactions can be measured by experimental technique called **calorimetry.** In calorimetry, the process is carried out in a vessel called calorimeter, which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved or absorbed in the process by measuring temperature changes. Measurements are made under two different conditions:

(*a*) at constant volume, q_V or ΔU

(*b*) at constant pressure, q_p or ΔH

(*a*) Δ***U measurements:***

There are different types of calorimeters depending upon the requirements of a particular experiment. In general, reactions taking place at constant volume and involving gases are carried out in a closed container with rigid walls which could withstand high pressures developed. One such vessel is a **bomb calorimeter.** It is made of heavy steel. The steel vessel is coated inside with gold or platinum to avoid oxidation of steel during the chemical reactions. The vessel is fitted with a tight screw cap. There are two electrodes R_1 and R_2 which are connected to each other through a platinum wire S as shown in Fig. 5.8. The wire S remains dipping in a platinum cup just below it.

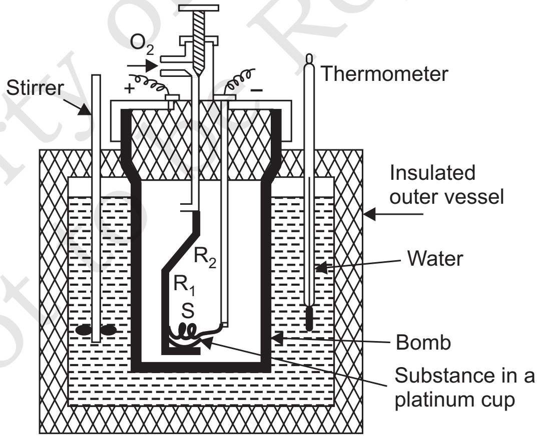


Fig. 5.8. Bomb calorimeter.

A small amount of the substance under investigation is taken in platinum cup. The vessel is then filled with excess of oxygen at a pressure of about 20 to 25 atmospheres and is subsequently sealed. It is now dipped in a insulated water bath which is also provided with a mechanical stirrer and a thermometer, sensitive enough to read upto 0.01°C (Beckmann's thermometer).

The initial temperature of water is noted and combustion is initiated by passing electric current through the platinum wire. The heat evolved during the chemical reactions raises the temperature of water which is recorded from the thermometer. By knowing the heat capacity of calorimeter and also the rise in temperature, the heat of combustion at constant volume can be calculated by using the following expression.

$$\Delta U = C \times \Delta T \times \frac{M}{w}$$

where, C = Heat capacity of calorimeter system
ΔT = Rise in temperature
M = Molar mass of the substance
w = Mass of substance taken in grams.

(*b*) ***Measurement of ΔH***

The change in enthalpy of a reaction can also be measured by calorimetry. The reaction is carried out in a calorimeter which is polythene bottle or foamed polystyrene cup fitted with thermometer and stirre as shown in Fig. 5.9. The calorimeter is, however kept open to atmosphere so as to carry out the process at constant pressure.

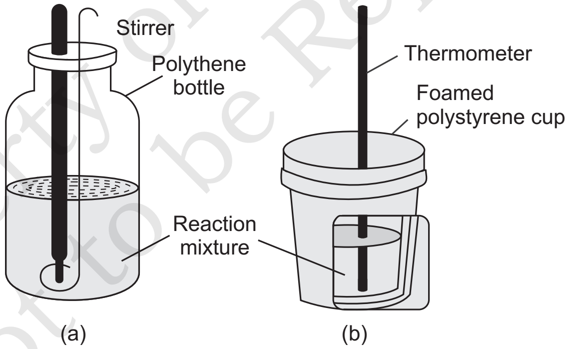


Fig. 5.9. (*a*) Polythene bottle as calorimeter. (*b*) Foamed polystyrene cup with cover

In case the calorimeter is made of conducting walls, it may be immersed in an insulated water bath fitted with stirrer and thermometer. The temperature of the bath is noted in the beginning and after the reaction and the rise (or fall) in temperature ΔT is recorded. Knowing the heat capacity (C) of water bath and calorimeter system, the heat evolved or absorbed in the reaction can be calculated. From the data so obtained enthalpy change (ΔH) of the reaction can be determined.

EXPERIMENT 2

Aim: Use calorimeter to determine the heat of reaction. (Heat of combustion of graphite)

Theory: Graphite burns in excess of oxygen to form carbon dioxide with release of heat.

$$C\ (\text{graphite}) + O_2(g) \rightarrow CO_2(g) + \text{Heat}$$

Chemicals and Apparatus: A calorimeter, thermometer, graphite

Procedure:

1. Take a calorimeter, fit it with a thermometer.
2. Take 18 g of graphite in solid form in the calorimeter cup.
3. The vessel surrounding the calorimeter cup is filled with water.
4. Now burn the graphite is burnt in the calorimeter in excess of oxygen.
5. Note down temperature before burning graphite and temperature when burning is over.
6. Do necessary calculations as per the formula.

Observations

t_1 = ...

t_2 = ...

ΔT = ...

If heat capacity of the calorimeter is 20.7 kJ K^{-1}

Heat absorbed by the calorimeter = $C\Delta T$.

$$q = C\Delta t$$

$$\text{Heat of reaction} = C \times \Delta T \times \frac{M}{w}$$

where C is heat capacity of calorimeter

ΔT = Rise in temperature

M = Molar mass of graphite

m_w = Mass of graphite taken

5.2. ENTHALPY CHANGE OF A REACTION, Δ_rH REACTION ENTHALPY

The **enthalpy of a reaction** is defined as the *enthalpy change accompanying the chemical reaction when the molar quantities of reactants and products are the same as indicated in the chemical equation.* It is also known as *heat of reaction or reaction enthalpy*. It is represented by $\Delta_r H$.

It can be mathematically expressed as follows

$$\Delta_r H = [\text{Sum of enthalpies of products}] - [\text{Sum of enthalies of reactants}]$$

$$= \Sigma a_i H_{\text{Products}} - \Sigma b_i H_{\text{Reactants}}$$

here, the symbol sigma Σ represents summation, whereas a_i and b_i represent stoichiometric coefficients of products and reactants respectively.

Standard Enthalpy of Reaction ($\Delta_r H$)

The reaction enthalpy $\Delta_r H$ depends on the conditions at which the reaction is carried out. Therefore, for the sake of comparison. It is more appropriate to express the values of $\Delta_r H$ for different reactions at their standard state conditions. *The standard state of a substance at a specified temperature is its pure form at one bar pressure*. For example, standard state of ethanol at 298 K is pure liquid ethanol at 1 bar, standard state of iron at 500 K is solid pure iron at 1 bar. The thermodynamic data is generally taken at 298 K. According to IUPAC recomendations, *the enthalpy change of a reaction when all the participating substances (reactants and products) are in their standard state* is called **standard enthalpy of the reaction** and is denoted by $\Delta_r H^\ominus$. The superscript ($^\ominus$) represents standard state. It is worthwhile to mention here, *that unless otherwise mentioned, the ΔH values are the standard enthalpy changes of the reactions.*

Enthalpy Changes During Phase Transformations

It is a matter of common observation that energy is required to convert a *solid* into *liquid* or a liquid into gas. The conversion of solid into liquid is called *melting* or *fusion* and the process of conversion of liquid into gas is termed as ***vaporisation***. These processes are collectively known as **phase transformations** or **phase changes.** The magnitude of enthalpy change accompanying the phase transition depends largely on the strength of intermolecular forces in the substance undergoing phase transformation. Let us study the enthalpy changes accompanying the phase changes.

Standard or Molar Enthalpy of Fusion ($\Delta_{fus} H^\ominus$)

It is the enthalpy change accompanying the melting of 1 mole of a solid substance in standard state at its melting point. For example, when one mole of ice changes into water at its melting point 273 K, 6.0 kJ of heat is absorbed. It is represented as:

$$H_2O(s) \longrightarrow H_2O(l);\ \Delta_{\text{fus}} H^\ominus = +\,6.0 \text{ kJ mol}^{-1}$$

The values of enthalpy of fusion give an idea about the magnitude of interparticle forces in solids. For example, ionic solids have very strong interparticle forces. Consequently, they have high values of enthalpy of fusion. On the other hand, molecular solids have weak interparticle forces which reflect that their values of enthalpy of fusion are low. The enthalpies of fusion of some substances are given in Table 5.2.

Standard or Molar Enthalpy of Vaporisation ($\Delta_{vap}H^\ominus$) or Evaporation

It is the enthalpy change accompanying the conversion of one mole of a liquid in standard state into its vapours at the boiling point and standard pressure (1 bar). For example, when one mole of water is converted into steam at 273 K, the enthalpy change accompanying the process is 40.6 kJ. It can be expressed as:

$$H_2O(l) \longrightarrow H_2O(g);\ \Delta_{vap}H^\ominus = +\ 40.6\ \text{kJ mol}^{-1}$$

The values of enthalpy of vaporisation give some idea about the magnitude of interparticle forces in liquids. The values of enthalpy of vaporisation of some substances are given in Table 5.2.

Table 5.2. Standard Enthalpy Changes of Fusion and Vaporisation

Substance	T_f*(K)*	$\Delta_{fus}H^\ominus$ *(kJ mol^{-1})*	T_b*(K)*	$\Delta_{vap}H^\ominus$ *(kJ mol^{-1})*
O_2	55	0.45	90	0.67
He	03	0.021	04	0.092
N_2	63.15	0.72	77.35	5.59
NH_3	195.40	5.65	239.73	23.35
HCl	159.0	1.992	188.0	16.15
CO	68.0	6.836	82.0	6.04
CH_3COCH_3	177.8	5.72	329.4	29.1
CCl_4	250.16	2.5	349.69	30.0
H_2O	273.15	6.01	373.15	40.79
NaCl	1081.0	28.8	1665.0	170.0
C_6H_6	278.65	9.83	353.25	30.8

Enthalpy of Sublimation ($\Delta_{sub}H^\ominus$)

It is the enthalpy change accompanying the sublimation of one mole of a solid substance into its gaseous state at a constant temperature below its melting point at the standard pressure.

Sublimation is direct conversion of a solid into vapour. **For example** solid CO_2 (*dry ice*) sublimes at 195 K with $\Delta_{sub}H^{\ominus} = 25.2$ kJ mol^{-1}. Similarly $\Delta_{sub}H^{\ominus}$ of naphthalene and iodine are 73.0 kJ mol^{-1} and 62.4 kJ mol^{-1} respectively. The thermochemical equations are as under

$$CO_2(s) \longrightarrow CO_2(g);\ \Delta_{sub}H^{\ominus} = 25.2 \text{ kJ mol}^{-1}$$

$$C_{10}H_8(s) \longrightarrow C_{10}H_8(g);\ \Delta_{sub}H^{\ominus} = +\,73 \text{ kJ mol}^{-1}$$

$$I_2(s) \longrightarrow I_2(g);\ \Delta_{sub}H^{\ominus} = +\,62.4 \text{ kJ}$$

The enthalpy of sublimation can be calculated with the help of Hess's law. The process of sublimation consists of change of solid state into vapour state in one step. The same change may be brought about in two steps:

(*i*) the melting of solid into its liquid and the enthalpy change is $\Delta_{fus}H^{\ominus}$.

(*ii*) the vaporisation of the liquid into its gaseous state and the enthalpy change is $\Delta_{vap}H^{\ominus}$

$$\boldsymbol{\Delta_{sub}H^{\ominus} = \Delta_{fus}H^{\ominus} + \Delta_{vap}H^{\ominus}}.$$

Standard Enthalpy of Formation ($\Delta_fH^{\ominus}$)

The **standard molar enthalpy of formation** of a compound is defined as the *enthalpy change accompanying the formation of one mole of a compound from its constituent elements in their most stable state of aggregation (also called reference state)*. It is generally denoted by $\Delta_fH^{\ominus}$ where, the subscript '*f*' represents the word *formation*.

For example, standard enthalpy of formation of carbon dioxide (CO_2) and that of ethyl alcohol (C_2H_5OH) are – 393.5 and – 277.0 kJ mol^{-1} respectively. These are expressed as follows:

$$C(graphite) + O_2(g) \longrightarrow CO_2(g);\quad \Delta H^{\ominus} = -\,393.5 \text{ kJ mol}^{-1}$$

$$2C(graphite) + 3H_2(g) + \tfrac{1}{2}\ O_2(g) \longrightarrow C_2H_5OH(l);\quad \Delta H^{\ominus} = -\,277.0 \text{ kJ mol}^{-1}$$

It may be noted that:

(*i*) *The reference state of elements is the pure element in its most stable state of aggregation at 298 K and one* **bar** *pressure.* For example, the reference state of *carbon, oxygen, sulphur, mercury, bromine, and iodine* are: **C (graphite), $O_2(g)$, S_8 (rhombic), $Br_2(l)$ and $I_2(s)$** respectively.

(*ii*) *By conventions, the standard molar enthalpies of formation of free elements in their reference state are taken to be zero.*

(*iii*) *Standard molar enthalpy of formation of the substance is also called its standard enthalpy and can also be denoted as* $\mathbf{H^{\ominus}}$**.**

The values of standard molar enthalpies of formation of some substances at 298 K are given in Table 5.2.

Importance of standard molar enthalpies of formation. The knowledge of standard molar enthalpies of formation of various substances can help us to calculate standard enthalpy change of any reaction. Standard enthalpy change of a reaction is equal to the difference of the standard molar enthalpies of formation of all the products and standard molar enthalpies of formation of all the reactants.

$$\begin{bmatrix}\text{Standard}\\ \text{enthalpy}\\ \text{of}\\ \text{reaction}\end{bmatrix} = \begin{bmatrix}\text{Sum of standard}\\ \text{molar enthalpies}\\ \text{of formation}\\ \text{of products}\end{bmatrix} - \begin{bmatrix}\text{Sum of standard}\\ \text{molar enthalpies}\\ \text{of formation}\\ \text{of reactants}\end{bmatrix}$$

or $$\Delta_r H^{\ominus} = \Sigma\Delta_f H^{\ominus}\ (\text{Products}) - \Sigma\Delta_f H^{\ominus}\ (\text{Reactants})$$

For example, consider a hypothetical reaction

$$aA + bB \longrightarrow lL + mM$$

$$\begin{aligned}\Delta_r H^{\ominus} &= \Sigma\ \Delta_f H^{\ominus}\ (\textit{Products}) - \Sigma\ \Delta_f H^{\ominus}\ (\textit{Reactants})\\ &= [l\Delta_f H^{\ominus}\ (\text{L}) + m\Delta_f H^{\ominus}\ (\text{M})] - \\ &\qquad [a\Delta_f H^{\ominus}\ (\text{A}) + b\Delta_f H^{\ominus}\ (\text{B})].\end{aligned}$$

Standard Enthalpy of Combustion ($\Delta cH^{\ominus}$)

It is the enthalpy change accompanying the complete combustion of one mole of a substance in excess of oxygen or air all the reactants and products being in their standard state at the specified temperature. It is denoted by $\Delta_c H^{\ominus}$ where subscript ***c*** represents the word combustion.

It may be noted that combustion reactions are always exothermic, thus, the values of $\Delta_c H^{\ominus}$ is always negative. The combustion reactions find tremendous applications in industry, rocketry and other walks of life. Some examples of combustion reactions are as follows.

(*i*) Combustion of *carbon*

$$\text{C(graphite)} + \text{O}_2(g) \longrightarrow \text{CO}_2(g);$$

$$\Delta_c H^{\ominus} = -\ 393.5\ \text{kJ mol}^{-1}$$

(*ii*) Combustion of *methane* (*CH_4*)

$$\text{CH}_4(g) + 2\text{O}_2(g) \longrightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l);$$

$$\Delta_c H^{\ominus} = -\ 891\ \text{kJ mol}^{-1}$$

(*iii*) Combustion of *butane* (C_4H_{10})

$$C_4H_{10}(g) + \frac{13}{2} O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l);$$

$$\Delta_c H^{\ominus} = -2658 \text{ kJ mol}^{-1}$$

Combustion of Food in our Bodies

Our body requires energy for performing various functions. This energy mainly comes from carbohydrates and fats that we take as food. Carbohydrates are decomposed into glucose or its derivatives in the stomach. Glucose is soluble in blood. It is transported by blood cells to various parts of the body where it reacts with oxygen in a series of steps producing CO_2, H_2O and energy.

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g);$$

$$\Delta H = -2900 \text{ kJ}$$

This combustion of glucose, in the human body, takes place at the body temperature because of the catalytic action of enzymes.

Efficiency of Foods and Fuels

Just as the major source of energy in our bodies is the combustion of foods in the similar way, the major source of energy for industries is the combustion of fuels. The efficiency of foods and fuels is compared in terms of their *calorific values.* The **Calorific Value** of food or fuel is defined as the *amount of heat produced when one gram of the substance (food and fuel) is completely burnt.* The calorific values of some common foods and fuels are given below:

Food	*Calorific Value ($kJ\ g^{-1}$)*	*Fuel*	*Calorific Value ($kJ\ g^{-1}$)*
Curd	2.5	*Wood*	17
Milk	3.2	*Charcoal*	33
Egg	7.3	*Kerosene*	48
Meat	12.0	*Fuel oil*	45
Honey	13.3	*Butane (LPG)*	55
Ghee	37.6	*Hydrogen*	150

The normal human needs 3000 kcal (≈ 14450 kJ) of energy per day. The food consisting of carbohydrates, fats, oils, vitamins proteins, mineral salts which provide required calories is termed as **balanced diet.**

5.3. HESS'S LAW OF CONSTANT HEAT SUMMATION

On the basis of numerous thermochemical observations, the Russian Chemist, *Germain Henry Hess* gave one of the most important generalisation of thermochemistry in 1840 which is known after his name as **Hess's Law.** This generalisation is primarily based on the fact that enthalpy is a path independent thermodynamic function. In other words, the enthalpy change in a chemical reaction is same whether it occurs in one step or in more than one steps. This may be stated in the form of Hess's law as follows. *The standard enthalpy of reaction is the algebraic sum of the standard enthalpies of intermediate reactions into which the overall reaction may be splitted or divided at the same temperature.*

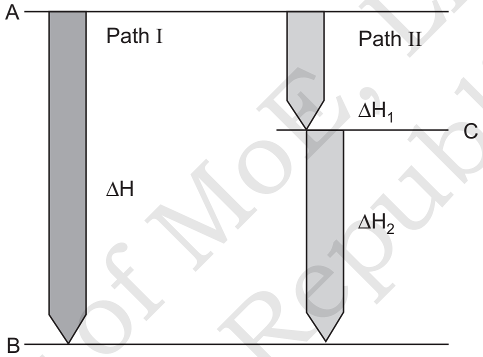


Fig. 5.10. Illustration of Hess's law.

Consider a process involving the conversion of reactant A into B in one step (path I). The enthalpy change of a process is represented by ΔH. Now suppose the process is split up into two steps involving a change from A to C and C to B according to path II, (Fig. 5.10). Let ΔH_1 and ΔH_2 be enthalpy changes from A to C and C to B respectively. Then, according to Hess's law :

$$\Delta H = \Delta H_1 + \Delta H_2$$

Hess's law is simply a corollary of the law of conservation of energy. It implies that the enthalpy change of reaction depends only on the states of reactants and products and not on the manner by which the change is brought about. If ΔH were not independent of the manner in which the corresponding change was brought about, it would have been possible to create or destroy energy, by taking a system from A to B by one path and then returning it to state A by second path.

Illustration of Hess's Law

Let us consider the formation of carbon dioxide from carbon and oxygen. There are two ways by which the change can be brought about.

(*a*) *Conversion of carbon to carbon dioxide*

$$C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H = -\,393.5\ kJ$$

(*b*) *Conversion of carbon to carbon monoxide and subsequent oxidation of carbon monoxide to carbon dioxide.*

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g);\quad \Delta H_1 = -\,110.5\ kJ$$

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g);\ \Delta H_2 = -\,283.0\ kJ$$

The two paths by which carbon can be converted into carbon dioxide have been shown in Fig. 5.11.

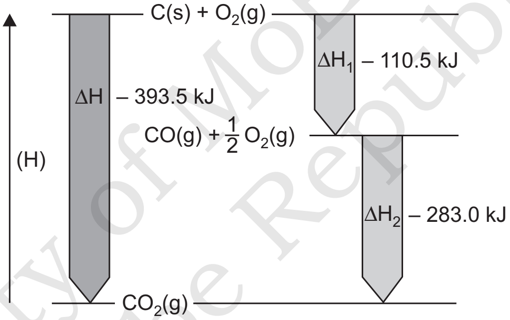


Fig. 5.11. Hess's law cycle for CO_2.

As is clear,

$$\Delta H = \Delta H_1 + \Delta H_2$$

$$-\,393.5\ kJ = -\,110.5 + (-\,283.0)\ kJ$$

$$= -\,393.5\ kJ.$$

Applications of Hess's Law

The practical utility of Hess's law lies in the fact that it allows us to carry out thermochemical calculations to predict the enthalpies of different reactions whose direct measurement is not possible. The thermochemical equations, like the algebraic equations can be added or substracted, multiplied or divided by any numerical factor. Some of the important applications of Hess's law are discussed below:

1. ***Determination of Standard Enthalpy of Formation:*** There are large number of compounds such as methane, benzene, carbon monoxide,

ethane, etc., which cannot be directly synthesised from their elements. Hence, their standard enthalpies of formation cannot be determined by the calorimetric method. In case of such substances the standard enthalpies of formation can be determined by an indirect method based upon Hess's law. The unknown reaction is made one segment of the closed cycle of reactions. The enthalpy changes of the reactions which represent other segments of the cycle can be determined experimentally. Then by applying Hess's law the desired value of ΔH can be calculated.

For example, let us study the calculation of enthalpy of formation of SO_3.

The enthalpy of formation of SO_2 (ΔH_1) and enthalpy of combustion of SO_2 (ΔH_2) have been found to be $-$ 297.4 kJ mol^{-1} and $-$ 97.9 kJ mol^{-1} respectively. These changes have been shown in Fig. 5.12.

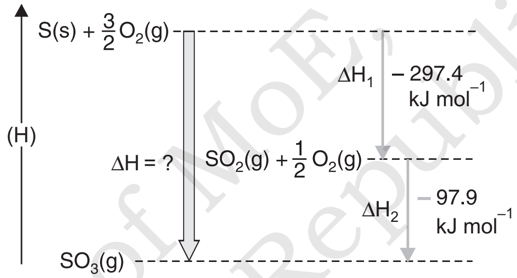


Fig. 5.12. Hess's law cycle for SO_3.

Now according to Hess's law,

$$\Delta H = \Delta H_1 + \Delta H_2 = -\,297.4 + (-\,97.9) = -\,\mathbf{395.3\ kJ.}$$

The same result can be arrived at by means of thermochemical calculations

(*i*) *Conversion of sulphur to sulphur dioxide*

$$S + O_2 \longrightarrow SO_2; \quad \Delta H_1 = -\,297.4 \text{ kJ}$$

(*ii*) *Combustion of sulphur dioxide to SO_3*

$$SO_2 + \frac{1}{2} O_2 \longrightarrow SO_3; \quad \Delta H_2 = -\,97.9 \text{ kJ}$$

Add equations (*i*) and (*ii*),

$$S + \frac{3}{2} O_2 \longrightarrow SO_3;$$

$$\Delta H = \Delta H_1 + \Delta H_2 = -\,297.4 - 97.9 = \mathbf{-\,395.3\ kJ.}$$

2. ***Determination of Enthalpy of Transition:*** Transition implies the conversion of one allotropic form of a substance to another. For example, change of graphite to diamond, red phosphorus to yellow phosphorus and rhombic sulphur to monoclinic sulphur, etc. Such reactions are very slow and enthalpy change accompanying them cannot be measured directly. However, Hess's law is quite helpful in determining the enthalpy of transition.

For example, let us calculate the enthalpy of the process $S_R \longrightarrow S_M$ from the enthalpies of combustion of monoclinic sulphur (S_M) and rhombic sulphur (S_R) which have been found to be – 296.4 and – 295.1 kJ mol^{-1} respectively. Now Hess's law cycle is constituted as $S_{(R)} \longrightarrow SO_2$ (path I) and $S_{(R)} \longrightarrow S_{(M)} \longrightarrow SO_2$ (path II). These changes have been shown in Fig. 5.13.

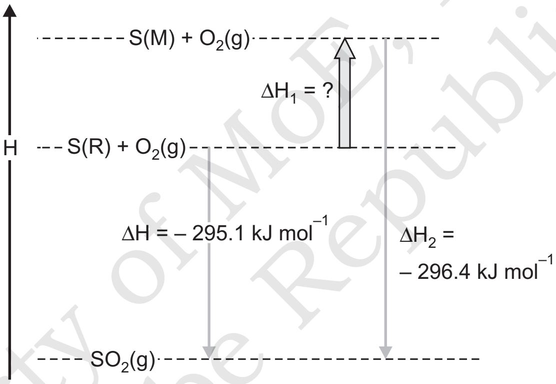


Fig. 5.13. Hess's law cycle for $S_{(R)}$ to SO_2.

Now according to Hess's law:

$$\Delta H = \Delta H_1 + \Delta H_2$$

or

$$\Delta H_1 = \Delta H - \Delta H_2 = -295.1 - (-296.4)$$

$$= \mathbf{1.3\ kJ\ mol^{-1}}.$$

The enthalpy of allotropic transformation of rhombic sulphur to monoclinic sulphur can also be calculated as follows by thermochemical calculations:

1. *Combustion of rhombic sulphur*

$$S_{(R)} + O_2(g) \longrightarrow SO_2(g); \quad \Delta H_1 = -295.1 \text{ kJ}$$

2. *Combustion of monoclinic sulphur*

$$S_{(M)} + O_2(g) \longrightarrow SO_2(g); \quad \Delta H_2 = -296.4 \text{ kJ}$$

Subtracting equation (2) from equation (1)

$$S_{(R)} \longrightarrow S_{(M)}; \quad \Delta H = \Delta H_1 - \Delta H_2$$
$$= -295.1 - (-296.4) = +\mathbf{1.3\ kJ\ mol^{-1}}.$$

3. ***Determination of Standard Enthalpy of Reaction:*** Hess's law cycle can also be used for the determination of standard enthalpy of the reaction from the knowledge of standard enthalpies of formation of various reactants and the products. The Hess's law cycle for elements in their standard states, reactants and products can be written as shown in Fig. 5.14.

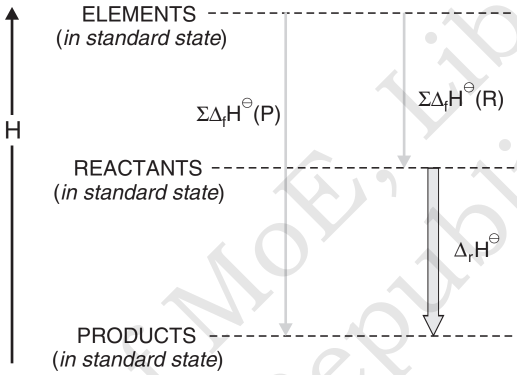


Fig. 5.14. Hess's law cycle for enthalpy of reaction.

$\Sigma\Delta_f H^\ominus(R)$ = Sum of the standard enthalpy of formation of reactants

$\Sigma\Delta_f H^\ominus(P)$ = Sum of the standard enthalpy of formation of the products

$\Delta_r H^\ominus$ = Standard enthalpy change of the reaction

Now according to Hess's law,

$$\Sigma\Delta_f H^\ominus\ (P) = \Sigma\Delta_f H^\ominus\ (R) + \Delta_r H^\ominus$$

or

$$\boldsymbol{\Delta_r H^\ominus = \Sigma\Delta_f H^\ominus\ (P) - \Sigma\Delta_f H^\ominus\ (R)}$$

Let us now proceed to solve some numerical problems based upon *thermochemical calculations.*

5.4. ENTHALPY CHANGE FOR DIFFERENT TYPES OF REACTIONS

In this section, we shall focus on the enthalpy change associated with different chemical processes.

Standard Enthalpy of Solution ($\Delta_{SOL}H^{\ominus}$)

It is the enthalpy change accompanying the dissolution of one mole of a substance in specified amount of a solvent under standard conditions. The enthalpy change observed by dissolving one mole of substance in infinite amount of solvent so that interaction between solute molecules are negligible, is called ***enthalpy of solution at infinite dilution.***

If water is the solvent, then the notation (*aq*) is used to represent aqueous solution at infinite dilution. Some examples are as follows.

$$\underset{\text{Glucose}}{C_6H_{12}O_6(s)} + aq \longrightarrow C_6H_{12}O_6(aq); \qquad \Delta_{Sol}H^{\ominus} = +11.0 \text{ kJ mol}^{-1}$$

$$SO_2(g) + aq \longrightarrow SO_2(aq) \qquad \Delta_{Sol}H^{\ominus} = -39.5 \text{ kJ mol}^{-1}$$

$$KCl(s) + aq \longrightarrow K^+(aq) + Cl^-(aq) \qquad \Delta_{Sol}H^{\ominus} = +18.6 \text{ kJ mol}^{-1}.$$

Dissolution of Ionic Salts

Dissolution of ionic compounds can be viewed in terms of following steps.

(*i*) *Breaking of solute-solute interactions:* This step involves dismentalling of ionic crystal by breaking off the interionic attractions to form ions in gaseous state. This is endothermic process. The energy required for this purpose is expressed in the form of *lattice enthalpy.*

***Lattice Enthalpy* ($\Delta_L H^{\ominus}$).** It is the enthalpy change taking place when 1 mole of ionic compound dissociates into gaseous ions of opposite charge at the standard conditions. For example, lattice enthalpy of NaCl(*s*) is +788 kJ mol^{-1}.

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g) \qquad \Delta_L H^{\ominus} = +788 \text{ kJ mol}^{-1}$$

(*ii*) *Setting up of solute-solvent interactions.* Once the ions leave their ordered position in the crystal lattice, they get surrounded by the solvent molecules and start moving freely in the solution.

The interactions between the solvent molecules and the particles of solute is termed as ***solvation***, in general, or ***hydration*** *if the solvent is water*. The hydration of ions releases energy which is expressed in terms of **enthalpy of hydration of ions** and is represented by $\Delta_{Hyd}H^{\ominus}$. It is defined as *the energy released by hydration of the ions furnished by one mole of the ionic compound.* These energy changes are related to standard enthalpy of solution. $\Delta_{sol}H$ according to Hess's law cycle as shown in Fig. 5.15.

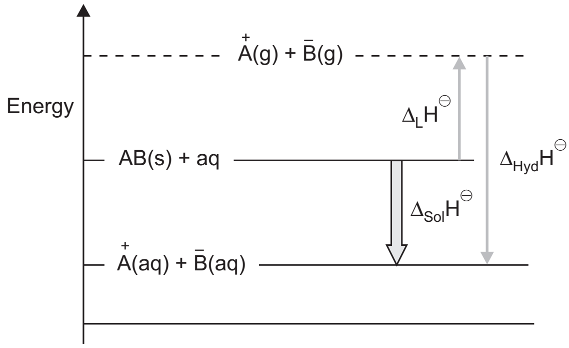


Fig. 5.15. Hess's law cycle for dissolution of ionic salt in water.

It is quite clear that

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

The value of $\Delta_{Sol}H^\ominus$ can be + ve or – ve depending upon the relative magnitudes of $\Delta_L H^\ominus$ and $\Delta_{Hyd}H^\ominus$. Dissolution of salt may not occur if the value of $\Delta_L H^\ominus$ is very high and that $\Delta_{Hyd}H^\ominus$ is very low.

Lattice Enthalpy and Born Haber Cycle

The **Lattice enthalpy** of ionic compound is the enthalpy change which occurs when one mole of ionic compound in solid state dissociates into its gaseous ions and vice versa at the standard conditions. It is represented by $\Delta_L H^\ominus$.

$$Na^+Cl^-(s) \longrightarrow Na^+(g) + Cl^-(g); \qquad \Delta_L H^\ominus = +\ 788 \text{ kJ mol}^{-1}$$

or

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s); \qquad \Delta_L H^\ominus = -\ 788 \text{ kJ mol}^{-1}.$$

The magnitude of lattice enthalpy gives the idea of the stability of the ionic crystal. It is not possible to determine lattice enthalpies of ionic compounds directly by experimental techniques. However, we can use indirect method by constructing an enthalpy diagram called ***Born Haber Cycle.*** Born Haber cycle is a simplified method which was developed in 1919 by *Max Born* and *Fritz Haber* to correlate lattice energies of ionic crystals to other thermodynamic data. The development of Born Haber cycle was primarily based on Hess's law. Let us consider the energy changes during the formation of sodium chloride crystal from the *metallic sodium* and *chlorine gas* to calculate lattice enthalpy of NaCl(*s*). The net enthalpy of formation of sodium chloride is given as $\Delta_f H^\ominus$ (NaCl) = –411.2 kJ mol⁻¹.

$$Na(s) + \frac{1}{2}\ Cl_2(g) \longrightarrow NaCl(s); \qquad \Delta_f H^\ominus = -\ 411.2 \text{ kJ mol}^{-1}$$

The overall process can be imagined to occur in following steps.

(*i*) *Sublimation of metallic sodium*

$$Na(s) \longrightarrow Na(g);\ \Delta_{sub}H^{\ominus} = 108.4\ kJ\ mol^{-1}$$

(*ii*) *Ionization of sodium atoms*

$$Na(g) \longrightarrow Na^{+}(g) + e^{-};\ \Delta_{i}H^{\ominus} = 495.6\ kJ\ mol^{-1}$$

$\Delta_{i}H^{\ominus}$ is ionization enthalpy of sodium.

(*iii*) *Atomisation of Cl_2.* This step involves dissociation of $Cl_2(g)$ into $Cl(g)$ atoms. The reaction enthalpy is half of the *bond dissociation enthalpy* of chlorine.

$$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g);\ \Delta_{a}H^{\ominus} = \frac{1}{2}\Delta H^{\ominus}_{Cl-Cl}$$

$$= 121\ kJ\ mol^{-1}.$$

(*iv*) *Conversion of $Cl(g)$ to $Cl^{-}(g)$.*

$$Cl(g) + e^{-} \longrightarrow Cl^{-}(g);\qquad \Delta_{e}H^{\ominus} = -348.6\ kJ\ mol^{-1}$$

$\Delta_{e}H^{\ominus}$ is electron gain enthalpy of chlorine.

(*v*) Combination of $Na^{+}(g)$ and $Cl^{-}(g)$ ions to form 1 mole of $NaCl(s)$. The energy released here is called lattice enthalpy ($\Delta_{L}H^{\ominus}$). The sequence of steps I–V is shown in Fig. 5.16 and is known as Born Haber cycle. The sum of the enthalpy changes round a cycle is zero.

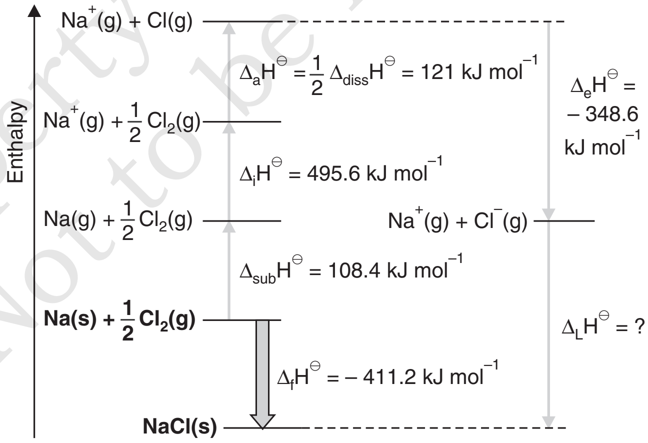


Fig. 5.16. Bron Haber cycle for lattice enthalpy of NaCl.

Applying Hess's law we get

$$\Delta_{f}H^{\ominus} = \Delta_{sub}H^{\ominus} + \Delta_{i}H^{\ominus} + \frac{1}{2}\Delta_{diss}H^{\ominus} + \Delta_{e}H^{\ominus} + \Delta_{L}H^{\ominus}$$

or $\quad \Delta_L H^\ominus = -411.2 - 108.4 - 121 - 495.6 + 348.6$

$\quad = -787.6$ kJ.

Enthalpy of Hydration Anhydrous Salt ($\Delta_{HYD}H^\ominus$)

It is the enthalpy change accompanying the hydration of one mole of an anhydrous salt by combining with specific number of moles of water. For example, enthalpy of hydration of anhydrous copper sulphate can be represented as:

$$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4.5H_2O(s); \quad \Delta_{Hyd}H^\ominus = -78.2 \text{ kJ mol}^{-1}.$$

Standard Enthalpy of Neutralisation ($\Delta_n H^\ominus$)

Neutralisation process refers to the combination of H^+ ions furnished by acid and OH^- ions furnished by the base in aqueous solutions to form H_2O molecules. The formation of 1 mol of water by combination of 1 mol of H^+ ions and 1 mol of OH^- ions in aqueous solution proceeds with liberation of 57.1 kJ of heat. Thus, enthalpy of neutralisation can be represented as

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l); \ \Delta_n H^\ominus = -57.1 \text{ kJ}$$

The enthalpy of neutralisation may, therefore, be defined as the *enthalpy change accompanying the formation of one mole of H_2O by combination of one mol H^+ ions furnished by acid and one mole of OH^- ions furnished by base in dilute solutions* at *the standard conditions.*

- *$\Delta_n H^\ominus$ of strong acid-strong base is constant. i.e., -57.1 kJ mol^{-1}.* According to arrhenius theory of ionisation the strong acids and strong bases are almost completely ionised in dilute aqueous solutions. The neutralisation of strong acid and strong bases simply involve the combination of H^+ ions (from acid) and OH^- ions (form base) to form water molecules.

  $$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l); \qquad \Delta H = -57.1 \text{ kJ}.$$

  For example, the net process in the neutralisation of HCl(aq) and NaOH(aq) can be represented as:

  $$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow H_2O(l) + Na^+(aq) + Cl^-(aq)$$

  or cancelling out the common ions on both sides of arrow, we get

  $$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l); \qquad \Delta H = -57.1 \text{ kJ}$$

During neutralisation of all strong acids and strong bases same reaction takes place. Hence *the value of enthalpy of neutralisation of strong acid or strong base is constant.*

- $\Delta_n H^\ominus$ *of weak acid-strong base or vice-versa is less negative than –57.1 kJ.*

If either acid or base is weak, then its ionization is not complete in aqueous solutions. Therefore, a part of the energy liberated during combination of H^+ ions and OH^- ions is utilised for the ionisation of weak acid (or base). Consequently, *the value of enthalpy of neutralisation of weak acid/strong base or strong acid/weak base is numerically less than 57.1 kJ.*

For example, enthalpy of neutralisation of weak acid, CH_3COOH and NaOH is – 56.1 kJ. The difference between the values – 56.1 – (– 57.1), *i.e.*, 1.0 kJ mol^{-1} represents the **enthalpy of ionisation** of CH_3COOH. Similarly, enthalpy of neutralisation of ammonium hydroxide (weak base) and hydrochloric acid (strong acid) is – 51.5 kJ. Therefore, enthalpy of ionisation of NH_4OH is – 51.5 – (– 57.1), *i.e.,* 5.6 kJ mol^{-1}.

Enthalpy of Atomisation ($\Delta_a H^\ominus$)

The **enthalpy of atomisation ($\Delta_a H^\ominus$)** *may be defined as the enthalpy change accompanying the dissociation of one mole of the substance completely into its atoms in the gaseous state.*

In case of elements, however, the enthalpy of atomisation is enthalpy change accompanying the formation of **one mole** of **gaseous atoms**.

Let us study few examples

(*i*) Enthalpy of atomisation of hydrogen is represented as

$$\frac{1}{2}H_2(g) \longrightarrow H(g); \qquad \Delta_a H^\ominus = 217.7 \text{ kJ mol}^{-1}$$

(*ii*) Enthalpy of atomisation of sodium is represented as

$$Na(s) \longrightarrow Na(g); \qquad \Delta_a H^\ominus = 108.4 \text{ kJ mol}^{-1}$$

In this case enthalpy of atomisation also represents *enthalpy of sublimation* of sodium.

(*iii*) Enthalpy of atomisation of methane is represented as

$$CH_4(g) \longrightarrow C(g) + 4H(g); \qquad \Delta_a H^\ominus = 1664 \text{ kJ mol}^{-1}.$$

5.5. BOND ENTHALPY ($\Delta_{BOND}H^{\ominus}$)

We have learnt in unit 4 that the process of formation of a chemical bond is accompanied by the release of energy. Conversely, the energy has to be supplied for the breaking of a bond. *The energy required to break a particular bond in a gaseous molecule* is referred to as **bond dissociation enthalpy.** It is a definite quantity and is expressed in *kJ mol*$^{-1}$.

In a **diatomic molecule**, the *bond dissociation* enthalpy is same as *bond enthalpy*. For example, the energy required to break one mol of H—H bonds in gaseous state is 435.4 kJ. Therefore, bond enthalpy of H—H bond is 435.4 kJ mol^{-1}. This may be expressed as:

$$\Delta_{H—H}H^{\ominus} = 435.4 \text{ kJ mol}^{-1}$$

However, in a **polyatomic molecule** having more than one similar bonds the bond dissociation enthalpy is not the same for successive bonds. Therefore, in such a case the bond enthalpy is not equal to the bond dissociation enthalpy. For example, in H_2O molecule, the bond dissociation enthalpies of the two O—H bonds differ from one another as described below:

$$HO—H(g) \longrightarrow H(g) + OH(g); \qquad \Delta H = 498 \text{ kJ}$$

$$O—H(g) \longrightarrow H(g) + O(g); \qquad \Delta H = 430 \text{ kJ.}$$

In such a case, therefore, the *bond enthalpy* is expressed as the average of the *bond dissociation* enthalpies of various similar bonds. For example, the ***average*** **bond enthalpy** of O—H bond is expressed as

$$\Delta_{O—H}H^{\ominus} = \frac{498 + 430}{2} = 464 \text{ kJ mol}^{-1}.$$

Thus, **mean bond enthalpy,** in general, may be defined as the *average amount of energy required to break one mole bonds of that type in gaseous molecules.*

Calculation of Bond Enthalpies

The thermochemical data makes it possible to calculate the bond enthalpies of different bonds. As an illustration the bond enthalpy of C—H bond in methane can be obtained if enthalpy of atomisation of methane is known.

$$CH_4(g) \longrightarrow C(g) + 4H(g); \qquad \Delta H = ?$$

The bond enthalpy of C—H bond is one fourth of the ΔH value for the above reaction. The value of ΔH can be calculated from the type of data available to us.

(a) Direct use of Hess's law if $\Delta_f H^\ominus$ values of H(g), C(g) and $CH_4(g)$ are given.

$\Delta_f H^\ominus$ values of H(*g*); C(*g*) and $CH_4(g)$ are 218.0, 717.0 and 750 kJ mol^{-1} respectively.

$$\text{Now,} \qquad \Delta_r H^\ominus = \Sigma\Delta_f H^\ominus\ (\textit{Products}) - \Sigma\Delta_f H^\ominus\ (\textit{Reactants})$$

$$= 4\Delta_f H^\ominus\ H(g) + \Delta_f H^\ominus\ C(g) - \Delta H^\ominus_f\ CH_4(g)$$

$$= 4(218) + 717 - (-75.0) = 1664\ \text{kJ}$$

$$\therefore \qquad \Delta_{C—H}H^\ominus = \frac{1664}{4} = 416\ \mathbf{kJ\ mol^{-1}}.$$

(b) Use of thermochemical calculations if the data has values other than $\Delta_f H^\ominus$.

Let the given data be:

$$\Delta_d H^\ominus \text{ of } H_2(g) = +436\ \text{kJ mol}^{-1}$$

$$\Delta_{Sub}H^\ominus \text{ of carbon} = +717\ \text{kJ mol}^{-1}$$

$\Delta_c H^\ominus$ of Carbon, Hydrogen and Methane are – 394 kJ, – 286 kJ and – 891 kJ respectively.

Let us write thermochemical equation of each of the above.

(*i*) *Enthalpy of combustion of methane*

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l);\ \Delta H_1 = -891\ \text{kJ}$$

(*ii*) *Enthalpy of combustion of carbon*

$$C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H_2 = -394\ \text{kJ}$$

(*iii*) *Enthalpy of combustion of hydrogen*

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\ \Delta H_3 = -286\ \text{kJ}$$

(*iv*) *Enthalpy of sublimation of carbon*

$$C(s) \longrightarrow C(g); \qquad \Delta H_4 = +717\ \text{kJ}$$

(*v*) *Enthalpy of dissociation of hydrogen molecule*

$$H_2(g) \longrightarrow 2H(g); \qquad \Delta H_5 = +436\ \text{kJ}$$

From the above equations enthalpy change for the atomisation of methane

$$CH_4(g) \longrightarrow C(g) + 4H(g)$$

can be calculated as follows:

Multiply equation (*v*) and also equation (*iii*) by 2. Now add *equation (i), equation (iv)* and *twice of equation (v)*. From the resulting expression subtract *equation (ii)* and *twice of equation (iii)*. The resulting value of enthalpy change comes out to be

$$\begin{aligned}\Delta H &= \Delta H_1 - \Delta H_2 - (2 \times \Delta H_3) + \Delta H_4 + (2 \times \Delta H_5)\\ &= -\,891 - (-\,394) - (-\,2 \times 286) + (717) + (2 \times 436)\\ &= +\,1664 \text{ kJ}\end{aligned}$$

This represents the energy required for the cleavage of **four** C—H bonds.

Therefore, $\Delta_{C—H}H^{\ominus} = \frac{1664}{4} = \mathbf{416\ kJ\ mol^{-1}}$.

The bond enthalpies of various bonds are given Table 5.3.

Table 5.3. Bond Enthalpies of Some Bonds

Bond	*Bond Enthalpy* (kJ mol^{-1})*	*Bond*	*Average Bond Enthalpy** (kJ mol^{-1})*
H—H	435.4	C = C	619
H—F	565	C ≡ C	812
H—Cl	431	O—H	463
H—Br	364	N—H	389
H—I	297	C—H	413
F—F	155	C—Cl	328
Cl—Cl	242	C—O	335
Br—Br	190	C = O	707
I—I	149	C—N	293
O = O	494	C = N	616
N ≡ N	941	C ≡ N	879
		C—Br	275.6
		O—O	138
		N—N	159
		N = N	418
		C—C	347

*These bond enthalpies are the dissociation energies of diatomic molecules that have only one bond, they are, therefore, exact values.

**These bond enthalpies are obtained from molecules that contain more than one bond, therefore, they are average values.

Use of Bond Enthalpy Data

The bond enthalpy data given in Table 6.4 is quite useful in determining the standard enthalpies of the reactions. The chemical reaction involves the cleavage of old bonds in reacting species and formation of new bonds to give product molecules. In general,

$$\begin{bmatrix}\text{Standard enthalpy}\\ \text{of reaction}\end{bmatrix}=\begin{bmatrix}\text{Sum of bond enthalpies}\\ \text{of reactants}\end{bmatrix}-\begin{bmatrix}\text{Sum of bond enthalpies}\\ \text{of products}\end{bmatrix}$$

or $$\Delta_r H^\ominus = \Sigma\ \textbf{Bond Enthalpies}_{(\textit{Reactants})} - \Sigma\ \textbf{Bond Enthalpies}_{(\textit{Products})}$$

Thus, the values given in bond enthalpy data can help us in:

(*i*) *Calculating standard enthalpy of reactions.*

(*ii*) *Calculation of bond enthalpies of some specific bond in the molecule.*

Some examples are being discussed as follows.

Limitations of Bond Enthalpy

Values of bond enthalpy calculated using the enthalpy terms are approximate and are far from the actual values of enthalpy found experimentally. These values are average values and do not consider the situations in which bond strength is different from the average.

Bond enthalphy is measured over a range of different gaseous molecules and do not take into account any inter or intra molecular forces which may influence the actual bond energy value of the molecule under consideration.

Reasons of these variations in the value of bond enthalpy are

(*i*) **The inductive effect:** Other electronegative atoms in the vicinity of a bond may weaken the bond by pulling the electrons toward themselves.

(*ii*) **Steric factors:** Sometimes weakening of bonds is caused by strain in the molecule caused by orientation of bonds in un-natural configuration, hence changing the bond enthalpy. example: propane bond enthalpy 348 kJ while cyclopropane bond enthalpy 210 kJ.

(*iii*) **Delocalization:** In cyclo compounds bonding is delocalised, causing reducing of bond length hence affecting the bond enthalpy

e.g., the C – C single bond length is = 0.159 nm

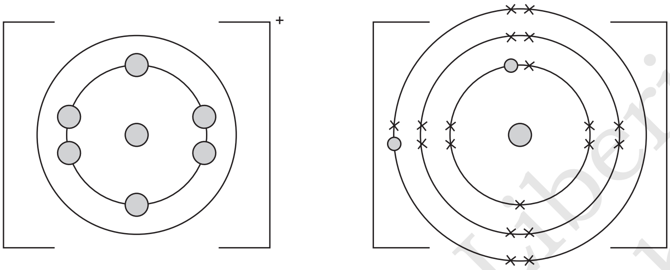
C = C bond length is = 0.134 nm, while

C – C bond length in bengeze is 0.139 nm.

Hence calculation of bond enthalpies using average bond energy can not be applied accurately to molecules containing benzene rings.

Limitations of Ionic Models

Dot and cross model of ions and ionic compound show the way ionic bonds are formed and the ratio atoms react but it does not show what way ions are arranged in space. A dot and cross model of NaCl shows that it is made up of a pair of sodium and chloride ions but it is not true.



Sodium ion Na^+

Chloride ion Cl^-

Fig. 5.17

In sodium chloride, Na^+ and Cl^- ions are arranged in a giantic ionic lattice structure with equal number of sodium and chloride ions. Ionic lattice structure of NaCl needs a 3D model or 2D representation of 3D model.

3D Models of Ionic Compounds

3D model shows arrangement of ions in a lattice structure. Different coloured balls are used to represent the ions and sticks to show the ionic bonds.

Limitations of 3D models:

(*i*) This model is not to scale hence does not give accuracy.

(*ii*) It gives no information about the forces of attraction between the ions, or the movement of electrons to form the ions. (Fig. 5.18)

2D representation of ionic compounds.

This 2D model shows the arrangement of one layer of ions but it does not show where the ions are located on the other layers. There may be different **possible arrangements** of the ions. (Fig. 5.19)

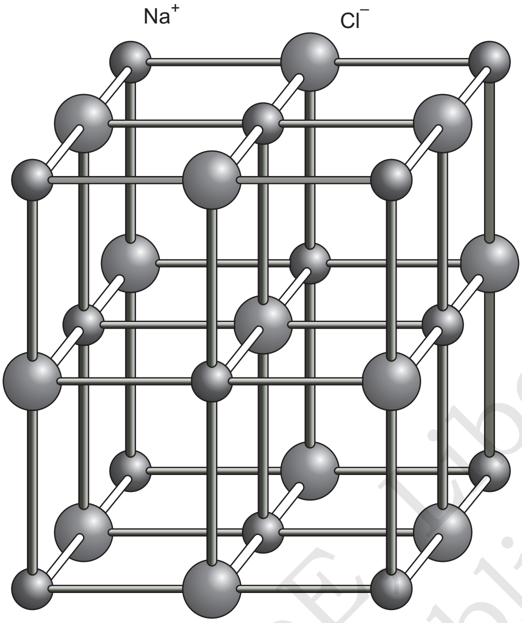
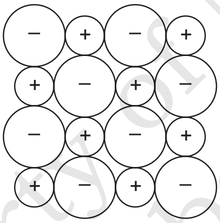


Fig. 5.18. 3D model of ionic lattice in sodium chloride.



2D representation of ionic lattice in NaCl

Fig. 5.19. 2D representation of ionic lattice in NaCl

5.6. FUELS

Fuels are dense repositories of energy that are consumed to provide energy services such as heating transportation and electrical generation. Sun is the ultimate source of energy. All fuels ultimately get energy from sun but even than they are considered as **Primary Energy Source**. **Primary fuels** provide about 95% of **human primary energy**. 85 of primary energy to generate electricity comes from primary fuels most of the fuels are non renewable, but as they are found extensively enough as to be considered sustainable.

Primary fuels: Primary fuels include

(*i*) Nuclear fuels
(*ii*) Bio fuels
(*iii*) Fossil fuels

Primary fuels are obtained from natural resources.

Secondary fuels: The fuels which are not directly obtained from natural resources but are derived from primary fuels are called secondary fuels. *e.g.*, gasoline, kerosene, diesel such fuels are also called **energy currencies**.

Fuels vary considerably energy density, cost and environmental impact *e.g.*, uranium has a significantly higher energy density than fossil fuels but is very expensive.

Classification of Fuels: Fuels can also be classified on the basis of their state or on the basis of their occurrence.

Classification on the basis of state

1. Solid Fuels
2. Liquid Fuels
3. Gaseous Fuels

Classification on the basis of their occurrence

1. Natural Fuels
2. Artificial Fuels

1. **Solid Fuels:** Solid fuels are various forms of solid material that can be burnt to release energy providing heat and light through the process of combustion. Commonly used solid fuels are wood, charcoal, peat, coal, hexamine fuel tablets, dry dung, wood pallets. Solid fuels are commonly used since ages to produce fire.

(*a*) **Wood:** Wood fuel can refer to fuels such as fire wood, charcoal, wood chips sheets, pallets and saw dust. Wood fuel can be used for cooking, heating and occasionally for fueling steam engines, and steam turbines that generate electricity, wood may be used indoors in furnace or fire place.

(*b*) **Biomass:** Of course wood is a biomass but actually biomass refers to other natural plant material that can be burnt for fuel. Common biomass fuel includes waste wheat, straw, nut shells and other fibrous material.

(*c*) **Peat:** Accumulation of decayed vegetation or organic matter that can be burnt when sufficiently dried. It has low calorific value.

(*d*) **Coal:** Coal is extracted from coal mines (opencast and underground mines). It is a combustible black or brownish black sedimentary rock. It is used as energy resource primarily burnt for the production of heat and electricity. It is also used for industrial purposes such as refining metals. It is the largest source of energy for generation of electricity world wide. By products of coal burning have environmental and health effects. Smokeless coal can be formed naturally in the form of **anthracite**.

(*e*) **Coke:** Coke is made from coal and has few impurities. It is derived from destructive distillation of low ash, low sulphur, bituminous coal. Petroleum coke or pet coke is derived from oil refinary cokes units.

(*f*) **Smokeless fuel:** Smokeless fuel is a solid fuel which produces little smoke and volatile and is made from powdered anthracite coal and supplied in the form of briquettes for domestic use. It burns at highest temperature.

(*g*) **Rocket propellant:** Solid rocket propellant consists of a solid oxidizer (NH_4NO_3) bond with flakes or powder of energy compounds (such as RDX) plus binders, plasticisers stabilizers and other additives. It has higher energy density and is much easier to store.

Advantage and disadvantage of solid fuels: Solid fuels are easy to store and easy to transport. Their production cost is less and ignition temperature is moderate.

Disadvantages: Wastage of energy is more. Ash content is high. Cost of handling is high in comparison to other type of fuels.

2. Liquid Fuels: Most of the fuels are obtained from dead remains of dead plants and animals by the exposure to heat and pressure in earth's crust. Fumes of liquid fuels are flamable. Liquid fuels are combustible or energy generating. Most of liquid fuels are fossil fuels, hydrogen fuel, ethanol and biodiesel are some examples of liquid fuels.

(*a*) **Petroleum fuels:** Most of the liquid fuels are derived from petroleum. **Gasoline** or **petrol** is derived by distillation of crude oil. **Diesel** is a mixture of alliphatic hydrocarbons extracted from petroleum **kerosene** is used in stoves, kerosene lamps and small engines. Highgrades kerosene is used as jet fuels. Kerosene is used as an additive in diesel fuel to prevent waxing in cold temperatures. **Liquefied Petroleum Gas (LPG)** is a mixture of propane and Butane. It is denser than air and is compressed easily. It is used for cooking and space heating.

(*b*) **Non-petroleum fossil fuels:** Liquid fuels can be derived from coal or natural gas by using Fischer-Tropsch process.

(*c*) **Natural gas:** Natural gas composed mainly of methane can be compressed to a liquid and can be used as a fuel in automobiles as GNG. Its boiling point is less hence need to be stored a high pressure to keep it in the liquid state. It ignites at high temperature and has low density.

(*d*) **Biodiesel:** Biodiesel is derived from plant. It has higher octane rate 45–60 compared to 45–50 for crude oil derived diesel. It gives 10% less energy than ordinary diesel.

(*e*) **Alcohols:** All alcohols are flamable but **ethanol** and **methanol** are used as fuels being sufficiently inexpensive. Methanol and ethanol are mixed with petrol to increase octane number.

(*d*) **Liquefied Hydrogen:** Liquefied hydrogen is used as rocket fuel, and fuel in internal combustion engines or fuel cells.

(*e*) **Ammonia:** Liquid amonia was once used in place of petrol when petrol was unavailable.

3. Gaseous Fuels: Fuel gases are produced by chemical transformations of solids, liquids, or gases. Some of the fuel gases are

- **Coal gas:** Produced by pyrolysis of coal
- **Water gas:** Produced from coke
- **Producer gas:** Produced from coke
- **Syn gas:** Produced from natural gas
- **Wood gas:** Produced from wood
- **Bio gas:** Obtained from landfills
- Oil gas and blast furnace gas.

Characteristics of Ideal Fuel

1. An ideal fuel should be easily available.
2. An ideal fuel should be cheap.
3. An ideal fuel should be readily flamable.
4. It should release high amount of energy (High calorific value)
5. It should not leave any harmful byproduct.
6. It should not be harmful to the environment
7. It should be easy to store, transport and handle
8. It should have low content of non-volatile substance.

SUMMARY

- **Chemical Thermodynamics.** Branch of science which deals with the energy changes associated with chemical reactions.
- **System.** Part of the universe selected for investigations.
- **Surroundings.** Part of the universe other than the system.
- **State of System.** The conditions of existence of a system when its macroscopic properties have definite values.
- **State Function.** The thermodynamic quantity which depends only on initial and final state of the system.
- **Heat (q).** It is a random form of energy. It is one of the mode of transference of energy between system and surroundings across the boundary.
- **Work (w).** It is organised form of energy. It is another mode of transference of energy between system and surroundings across the boundary.
- **Enthalpy (H).** It is sum total of internal energy and pV-energy of the system at particular conditions of temperature and pressure. It is also called heat content of the system

  $$(\mathbf{H = U + pV}).$$
- **Law of Conservation of Energy.** It is also called **first law of thermodynamics** and states that energy of universe always remain constant during chemical or physical changes. Mathematically,

  $$\mathbf{\Delta U = q + w.}$$
- **Relation between C_p and C_v:** $C_p - C_v = R$ for 1 mole of ideal gas $C_p - C_v = nR$ for n mole of ideal gas.
- **Enthalpy of Reaction.** The enthalpy change accompanying the chemical reaction in which number of moles of reactants consumed and those of products formed are the same as the stoichiometric coefficients.
- **Standard Enthalpy of Formation ($\Delta_f H^\ominus$).** It is the enthalpy change accompanying the formation of 1 mole of the substance from its constituent elements in their standard state. $\Delta_f H^\ominus$ can be >0 or <0.
- **Standard Enthalpy of Combustion ($\Delta_c H^\ominus$).** It is the enthalpy change occurring during the combustion of one mole of the substance in excess of oxygen. $\Delta_c H^\ominus$ is always less than zero.

- **Standard Enthalpy of Vaporisation ($\Delta_{vap.}H^{\ominus}$).** It is the enthalpy change taking place during the vaporisation of one mole of liquid at its boiling point.
- **Enthalpy of Neutralisation ($\Delta_n H$).** It is the enthalpy change taking place during formation of 1 mole of water by combination of 1 mole of H^+ ions and 1 mol of OH^- ions in dilute solutions.
- **Hess's Law.** The enthalpy change in a chemical or physical process is same whether the process is carried out in one step or in several steps.
- **Bond Enthalpy ($\Delta_{bond}H^{\ominus}$).** The average amount of energy required to break one mole of the bonds of a particular type in gaseous molecules.

EVALUATION

I. Multiple Choice Questions

1. Which of the following statements is correct?

(*a*) The presence of reacting species in a covered beaker is an example of open system.

(*b*) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.

(*c*) The presence of reactants in a closed vessel made up of copper is an example of a closed system.

(*d*) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

2. The volume of gas is decreased to half. The specific heat of the gas will

(*a*) remain same (*b*) be reduce to half

(*c*) increase four times (*d*) be doubled.

3. The enthalpies of elements in their standard states are arbitrarily taken as zero. The enthalpy of formation of compound

(*a*) is never negative (*b*) can be positive or negative

(*c*) is always negative (*d*) is never positive.

4. Which of the following is not a state function?

(*a*) T (*b*) H

(*c*) q (*d*) S.

5. The bond energy (in kCal mol^{-1}) of C—C bond is approximately

(*a*) 1 (*b*) 10

(*c*) 100 (*d*) 1000.

6. The species which by definition has ZERO standard molar enthalpy of formation is

(*a*) $Br_2(g)$ (*b*) $Cl_2(g)$

(*c*) $H_2O(g)$ (*d*) $CH_4(g)$.

7. For a reversible reaction,

$A(s) + B(g) \rightleftharpoons C(g) + D(g)$; $\Delta G = -350$ kJ

Which one of the following statement is true?

(*a*) The entropy change is negative

(*b*) The equilibrium constant is greater than zero

(*c*) The reaction should be instantaneous

(*d*) The reaction is thermodynamically not feasible.

8. Based on First law of thermodynamics which one of the following is correct?

(*a*) For an isochoric process, $\Delta U = -q$

(*b*) For an adiabatic process, $\Delta U = -w$

(*c*) For an isothermal process, $q = +w$

(*d*) For a cyclic process, $q = -w$.

9. $\Delta_f U^\ominus$ of formation of $CH_4(g)$ at certain temperature is -393 kJ mol^{-1}. The value of $\Delta_f H^\ominus$ is:

(*a*) $> \Delta_f U^\ominus$ (*b*) equal to $\Delta_f U^\ominus$

(*c*) zero (*d*) $< \Delta_f U^\ominus$.

10. The standard enthalpy of formation of H_2 from its atoms is -436 kJ mol^{-1} and that of N_2 from its atoms is -712 kJ mol^{-1}. The average bond enthalpy of N—H bond in NH_3 is

(*a*) -964 kJ mol^{-1} (*b*) 1056 kJ mol^{-1}

(*c*) $+352$ kJ mol^{-1} (*d*) -1102 kJ mol^{-1}.

II. Fill in the Blanks

1. The standard enthalpy of formation of elementary substances is taken to be _________ .

2. The amount of heat produced in the combustion of a 1 gram of a fuel is called _________.

3. A fuel having larger value of enthalpy of combustion _________ have larger calorific value.

4. $\Delta G = \Delta H -$ _________ .

5. The sign of ΔH and ΔU for combustion process is _________ .

III. Descriptive Questions

1. What type of system is constituted by coffee placed in thermos flask?
2. Heat capacity (C) is an extensive property but specific heat (*c*) is an intensive property. What is the relationship between them for 1 mole of water?
3. Which thermodynamic parameters are taken to be zero at reference state of elements?
4. The enthalpy of atomisation for the reaction

$$CH_4(g) \longrightarrow C(g) + 4H(g)$$

is 1665 kJ mol^{-1}. What is the bond enthalpy of C—H bond?

5. What is the basic difference between enthalpy of formation and enthalpy of reaction? Illustrate with example.
6. Write the thermochemical equations from each of the following data:
   (*i*) $\Delta_f H^\ominus$ for freon ($CHCl\,F_3$) is – 480.0 kJ mol^{-1}
   (*ii*) $\Delta_i H^\ominus$ of Rb is 403 kJ mol^{-1}
   (*iii*) $\Delta_e H_2^\ominus$ of sulphur is 590 kJ mol^{-1}
   (*iv*) $\Delta_L H^\ominus$ of $CaCl_2(s)$ is 2870.8 kJ mol^{-1}
   (*v*) $\Delta_f H^\ominus$ of $CaCl_2$ is – 795 kJ mol^{-1}.
7. First law of thermodynamics refers to conservation of energy. Yet the world is facing severe energy crisis. Does it goes against the first law? Comment.
8. Calculate the values of ΔU and ΔH when 1 mol of a diatomic ideal gas is heated at constant pressure of 1.0 atm. from 27°C to 57°C.

IV. Numerical Questions

1. (*i*) 2.5 mol of ideal gas at 2 atm and 27°C expands isothermally to 2.5 times of its original volume against the external pressure of 1 atm. Calculate the work done.

   (*ii*) If same gas expands isothermally in a reversible manner, then what will be the volume of work done?
2. A system gives out 20 J of heat and also does 40 Jouls of work. What is the internal energy change? (**Ans.** –60 J)
3. Heat produced by combustion of 1.0 g of benzene (C_2H_6) at constant volume is 41.80 kJ at 298 K. Calculate the value of enthalpy of combustion of benzene at 29 K. (**Ans.** – 3264.1 kJ mol^{-1})
4. The standard enthalpies of formation of four substances O_3, CaO, NH_3, HI are + 142.2, –634.9, –46 and +25.95 kJ mol^{-1} respectively. Arrange them in order of increasing stability with respect to decomposition into their elements. (**Ans.** O_3 < HI < NH_3 < CuO)

SEMESTER–II (Period–V)

6

TOPIC

Nuclear Chemistry

C11CH6

Learning Objectives

Upon completion of this topic, learners will:

- Describe radioactivity, including its historical development
- Explain how nuclear reactions differ from chemical reactions
- Describe the types and nature of radiations
- Explain the role of half-life in the stability of the nucleus
- Distinguish between fusion and fission and
- Explain the effects and applications of radioactivity.

6.1. HISTORY OF RADIOACTIVITY

Discovery of radioactivity in uranium by French physicist **Henri Becquerel** in 1896 forced scientist to radically changed their ideas about atomic structure. Discovery of cathode rays and anode rays showed that is neither indivisible nor immutable. Instead of serving merely as an inner matrix for electrons the atoms could change form and emit an enormous amount of energy. Radioactivity became an instrument for revealing the interior of atom. It was almost an accidental discovery when French physicist Henri Bequerel opened a drawer and discovered spontaneous radioactivity in March 1986. After the discovery of X ray which have ability to penetrate through black paper. X rays also penetrated the soft body tissues. This usefulness of X rays was seen as a good scope in the field of imaging. After learning about Rontgen finding of X rays, Baccqured thought that the phosphorescent uranium salts he had been studying might absorb sunlight and unit is as X rays. He in order to test wrapped photographic plates in black paper so that sunlight could not reach them. He then placed crystals of uranium salts on the top of wrapped plates and put the whose setup outside the sun. When plates were developed he saw an outline of the crystals. He also put coins and cut out metal shapes between the crystals and photographic plates and he found that outlines of those shapes appeared on photographic plates. He then concluded that uranium salts absorbed sunlight and emitted a penetrating radiation similar to X rays. He planned for further experiments but whether in Paris was not sunny. In order to wait in Feb. 1896 for sunny days he kept the uranium crystals and photographic plates away in the drawer. On March 1 1896 he opened the drawer and developed the plates. He was astonished to see very clear images of crystals on the photographic plates. He first thought that the effect was due to long lasting phosphorescence but soon he discovered that uranium salts emitted some new radiations of their own. He again did experiments on non phosphorescent uranium compounds and found that they also show the same effect.

He was firstly of the opinion that his rays were similar to X rays which were neutral but his rays, as he found, could be deflected by electric or magnetic field. It means those rays have some charged particles.

In 1898 Marie and Pierre curie in Paris began to study the storage uranium rays. During the course of they soon found other radioactive elements polonium, thorium and radium. Marie curie conived the term “radioactivity” to describe the new phenomenon. Soon Earnst Rutherford and Fredrick Soddy explained radioactivity as spontaneous transmutations of elements. For their discoveries Becquerel and the Curie shared the 1903 Nobel Prize for their work on radioactivity.

Definition: The spontaneous emission of active radiations by certain elements like uranium is called radioactivity and the elements are called radioactive elements.

The radioactive rays emitted when passed through strong electric on magnetic fields, are resolved into

(*a*) α **rays:** The rays which deflected slightly towards negative plate were named as α rays.

(*b*) β **rays:** The rays which deflected towards a positive plate were named as β rays.

(*c*) γ **rays:** The rays which remained undeflected were named as γ rays.

α rays consist of positively charged He^{2+} particles. The charge on α ray particles is 3.20×10^{-19} coulombs and its mass is 6.6×10^{-24} g. β rays are made up of electrons while γ rays are high energy electromagnetic radiations having no charge and negligible mass.

Table 6.1. Characteristics of α, β and γ-rays

Property	*α-rays*	*β-rays*	*γ-rays*
1. Mass	6.67×10^{-27} kg or 4 amu	9.11×10^{-31} kg	Negligible
2. Charge	+ 2 units	–1 unit	0
3. Identity	Helium nuclei (He^{++})	Electrons	High energy radiations
4. Velocity	Nearly 1/10th that of light	Nearly same as that of light (3.0×10^8 m/s)	Same as that of light
5. Effect of electric fields	Deflected towards negative plate	Deflected towards positive plate	Not deflected
6. Penetrating power	Small	Large, 100 times that of α-rays	Very large, 10000 times that of α-rays

Why atoms become radioactive?

There may be two possibilities with the atoms. Atoms may either be stable or unstable. If forces among constituent particles in the nucleus are balanced then atom is balanced. If forces among constituent particles are unbalanced then atoms are unstable. This unstability of atoms is the cause of radioactive decay of atoms. Unstability of nucleus of an atom because of excess of either neutrons or protons is the cause of radioactivity. A radioactive atom tries to attain stability by ejecting nucleons (protons or neutrons), as well as other particles or by releasing energy in other forms.

The nuclear stability bond shows various combinations of neutrons/ protons combinations that give rise to different types of observable nuclei with measurable half lives. Bond of nuclear stability shows that various types of radioactive processes undergone by various nuclides in the region from $z = 66$ (dysprosium) through $z = 79$ (Gold). Nuclides with lower neutron) proton ratio shows positron emission, electron capture, or alpha emission, while nuclei with higher neutron/proton ratio show beta emission.

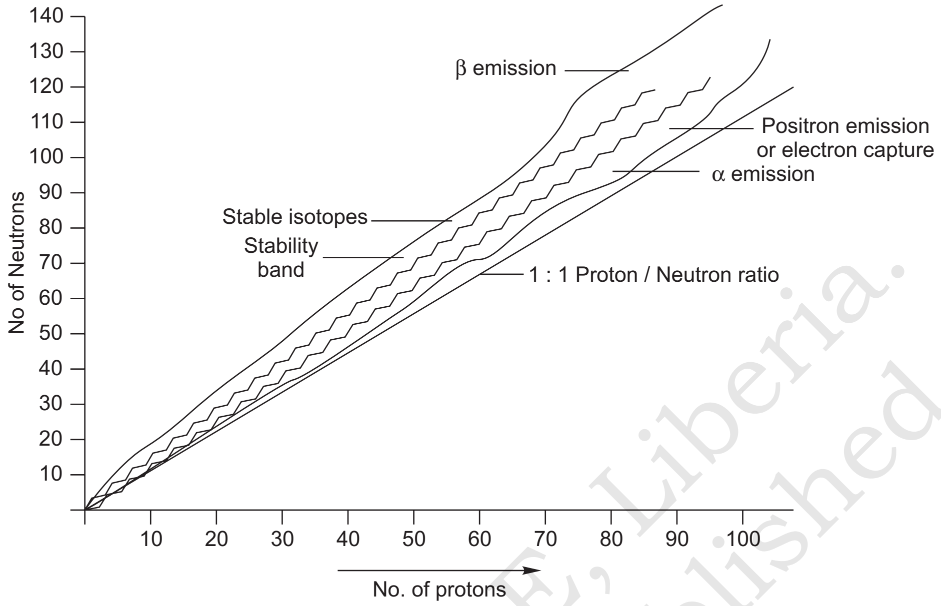


Fig. 6.1. Bond of nuclear stability

Second measure of stability is binding energy, which is the amount of energy required to overcome the strong nuclear force and pull apart a nucleon. When binding energy is more stability is also more.

Result of Emission of Radiations on Atoms

When a nucleus emits radiation or disintegrates, the radioactive atom (radionuclide) transforms to a different nuclide. This process of radioactive decay continues till the forces in the nucleus are balanced. When a radio nuclide decays, it will become a different isotope of the same element if it gives of neutrons. If it gives off protons, then a different element is formed.

Radiations in Everyday Life

Radioactivity is existed all along the globle. Natural radioactive materials are present in earth's crust in our homes, school offices and in the food we eat and drink. There are some radioactive gases in the air which we breath. In our body also, muscles, bones and tissues contain naturally occurring radio active elements. We are exposed to natural radiations emitted on the earth as well as coming from outside the earth. Such radiations which we receive from outer space is called cosmic radiations or cosmic rays. We also receive exposure from man made radiations such as X rays radiations used to diagnose diseases and for cancer therapy. Fall outs from nuclear explosive testing and small quantities of radioactive materials released to the environment from coal and nuclear power plants are also the source of radiation exposure to man.

Nuclear Reactions

As we know that nuclear chemistry is the study of reaction that involve changes in nuclear structure. Nuclear reactions are the reactions with are related with the nucleus and its constituents. Nuclear reaction is a process that occurs as a result of interaction between atomic nuclei when the interacting particles approach each other to within in distances of order of nuclear dimensions (-10^{-12} cm). While nuclear reactions occur in nature understanding of them and use of them as tools have taken place primarily in the controlled laboratory environment. In the usual experimental situation nuclear reaction are initiated by bombarding one of the interacting particles, the stationary target nucleus, with nuclear projectiles of some type, and the reaction product and their behaviour are studied.

How Nuclear Reactions Differ from Chemical Reactions

(*i*) Chemical reaction take place outside the nucleus while nuclear reactions occur only inside the nucleus. During chemical reactions atoms do not change their identity and nuclei of the atoms also remain unchanged. Nuclear reactions take place inside the nucleus as a result of which nuclei of atoms change completely and new elements are formed. In a chemical reaction reactants reacts chemical to form products by the way of chemical change. During a chemical reaction identity of elements remain same, and it does not change their identity. Elements and atoms on reactant side and product side in a chemical reaction remain same. No new atom or element is formed. But during nuclear reaction atoms and elements do not remain same and loose their identity to form new elements for example. In the following chemical reaction.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

The number of carbon, hydrogen and oxygen atoms remain same on reactant side as well as product side of a chemical reaction identity (atomic mass or atomic number) are not changed and no new atom or element is formed.

Now take an example of a nuclear reaction.

$$^{14}C \xrightarrow{\text{Radio active decay}} {}^{14}N + \beta^- \text{ (beta particles)}$$

Here identity of carbon is changed and a new element ^{14}N is formed. There is a change in the nuclear composition of 14c.

(*ii*) Rate of chemical reactions are influenced by external effects like temperature, pressure and catalyst while. Rates of nuclear reaction are spontaneous and are unaffected by such factors.

(*iii*) Nuclear reactions do not depend upon the chemical form of the element. Same amount of radioactive element shows similar radio-activity whether it is in elemental or in compound state.

(*iv*) Chemical reaction follow law of conservation of mass. Nuclear reaction to don't follow law of conservation of mass. In nuclear reactions a huge amount of energy is released due to destruction of mass as in atom bomb or in nuclear reactors. As per $E = mc^2$

(*v*) In a chemical reaction the reactivity of elements depend upon their oxidation states; but nuclear reaction the reactivity of an element in a nuclear reaction is independent of its oxidations state.

(*vi*) Chemical reactivity of different isotopes is almost same in chemical reactions while nuclear reactivity of an isotope of an element differ drastically. e.g. ^{238}U is less reactive than ^{235}U.

(*vii*) Chemical reaction are almost reversible, while nuclear reactions are almost irreversible.

(*viii*) In a chemical reaction generally in electrons present in outer orbits participate while neutrons and protons do not participate in chemical reaction. Neutrons and Protons participate in nuclear reactions.

(*ix*) During chemical reactions new bonds form and old bonds break between the reacting atoms. During nuclear reactions nuclear fission and nuclear fusion take place.

Soddy's Displacement Law of Radioactive Transformations

1. When a nucleus ejects an α-particle, the mass becomes less by 4 units and charge decreases by 2 units. Thus, the nucleus $^{A}_{Z}Y$ on emission of α-particle gets transformed into a new nucleus $^{A-4}_{Z-2}Y$.

$$\therefore \qquad ^{A}_{Z}Y \xrightarrow{\alpha} {}^{A-4}_{Z-2}Y$$

Thus, the substance shifts or is displaced from its original position in the periodic table, two steps backwards.

2. When a nucleus ejects a β-particle, the mass remains unchanged and the charge increases by 1 unit. So a material ${}^{A}_{Z}Y$ on emission of β-particle gets transformed into a new nucleus as ${}^{A}_{Z+1}Y$.

Thus, the original substance shifts or is displaced one step higher in the periodic table.

Thus, $${}^{A}_{Z}Y \xrightarrow{\beta} {}^{A}_{Z+1}Y$$

3. When a nucleus emits γ-rays, the mass or the charge or the position of the nucleus in the periodic table are not affected. Only some energy is radiated and the original nucleus shifts from higher energy level to lower energy level.

Rutherford and Soddy's Laws of Radioactive Decay

1. The disintegration of radioactive material is purely a random process and it is merely a matter of chance, which nucleus will suffer disintegration, or decay first.

2. The rate of decay is completely independent of the physical composition and chemical condition of the material.

3. The rate of decay is directly proportional to the quantity of material actually present at that instant. Thus, as the decay goes on, the original material goes on decreasing in quantity and the rate of decay consequently goes on decreasing.

Thus from the third law, if N is the number of radioactive atoms present at any instant, then the rate of decay,

$$-\frac{dN}{dt} \propto N \quad \text{or} \quad -\frac{dN}{dt} = \lambda N,$$

where λ is the decay constant or the disintegration constant.

$$\therefore \qquad \frac{dN}{dt} = -\lambda N$$

On rearranging, $$\frac{dN}{N} = -\lambda\, dt$$

On integration $$\log_e N = -\lambda t + C$$

where C is the integration constant.

If at $t = 0$, we had N_0 atoms, $\log_e N_0 = 0 + C$

Thus, we get, $\log_e N - \log_e N_0 = -\lambda t$

or $$\log_e \frac{N}{N_0} = -\lambda t$$

or $$\frac{N}{N_0} = e^{-\lambda t} \quad \text{or} \quad N = N_0\, e^{-\lambda t}.$$

This equation represents the radioactive decay law. It gives the number of active nuclei left after time *t*.

Radioactive Disintegration Constant λ

According to the laws of radioactive decay, we have

$$\frac{dN}{N} = -\lambda\, dt$$

If $dt = 1$ second, then $$\frac{dN}{N} = -\lambda$$

Thus, λ may be defined as the *relative number of atoms decaying per second.*

Again, since $N = N_0\, e^{-\lambda t}$

and if $t = \frac{1}{\lambda}$, we get $N = N_0\, e^{-1} = \frac{N_0}{e}$

Thus, λ is also defined as *the reciprocal of the time when* $\frac{N}{N_0}$ *falls to* $\frac{1}{e}$.

6.2. HALF LIFE OF RADIO ACTIVE ELEMENTS

Some isotopes of radioactive elements is an indefinitely stable while others are radioactive. Such radioactive and unstable isotopes are emit radiation during the process of decay using their mass into energy as a result of which with the passage of time the mass and number of atoms starts decreasing and a time comes whom its mass becomes just half in comparison of initial mass. Such time required to reduce the mass of a radioactive element to half is half life of that element. The decaying process continues, mass goes on decreasing but half life time is always same for that element.

Half life of a radioactive isotope is the amount of time it takes for one half of the radioactive isotope to decay. Half life of a specific radio active isotope is constant, and it is independent of the initial amount of that isotope.

The radio active isotope cobalt 60, which is used for radiotherapy, has a half life of 5.26 years. After passage of 5.26 years of time a sample of 12 g of Cobalt 60 will become 4 g and would emit only half amount of radiations. After another 5.26 years the sample would contain only 3 gms of Cobalt 60.

Visibly mass and volume of cobalt-60 seems to remain same inspite of radioactive decay. This is because the unstable cobalt-60 nuclei decay into stable nickel-60 nuclei remains with still undecayed cobalt.

Half lives are significant properties of unstable atomic nuclei of radioactive element. Alpha, beta, decay are slower process than gama decay. Half life of beta decay upwards from $\frac{1}{100}$th of a second, for alpha decay this period upwards from one millionth of a second. Half life for gamma rays may be around 10^{-14} second.

Half-Life Period

Consider the situation when the decaying material is reduced to exactly $\frac{1}{2}$ of its original quantity. The time taken for this decay $\left(\frac{N}{N_0} = \frac{1}{2}\right)$ is called the half-life period of the material. *It is defined as the time required for the disappearance of half of the amount of the radioactive substance originally present.*

If T represents the half-life period, then

$$\frac{N}{N_0} = \frac{1}{2} = e^{-\lambda T} \text{ or } e^{\lambda T} = 2$$

$$\therefore \quad \lambda T = \log_e 2 = 0.6931$$

$$\therefore \quad T = \frac{0.6931}{\lambda} \qquad \text{or} \qquad \lambda = \frac{0.6931}{T}$$

Combining these relations, we obtain

$$\frac{N}{N_0} = e^{-\lambda t} \qquad \text{or} \qquad \frac{N_0}{N} = e^{\lambda t}$$

$$\therefore \quad \log_e \frac{N_0}{N} = \lambda t \qquad \text{or} \quad 2.303 \log_{10} \frac{N_0}{N} = \frac{0.6931}{T} t$$

$$\text{or} \qquad t = \frac{2.303}{0.6931} T \log_{10} \frac{N_0}{N}$$

$$\text{or} \qquad t = 3.323 T \log_{10} \frac{N_0}{N}$$

This relation shows that a material with a half-life period T changes in quantity from N_0 to N in time *t*.

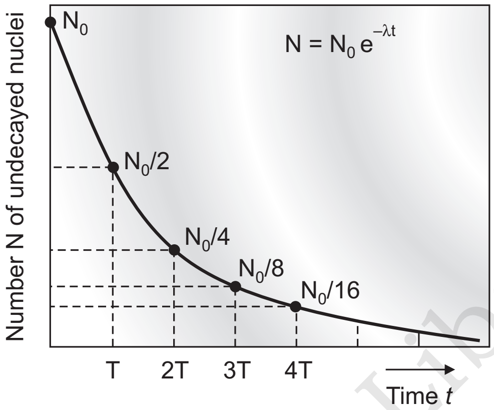


Fig. 6.2. Exponential decay of a radioactive species. After a lapse of T, population of the given species drops by a factor of 2.

Plutonium and tritium are not found in observable quantities in nature because their half life is very less.

Formula for Number of Atoms Left Behind after *n* Half-Lives

Let N_0 be the number of atoms of a radioactive substance in the beginning. After time T, the number of atoms left will be $\frac{N_0}{2}$. After a time 2T, the number of atoms left will be $\frac{1}{2} \times \frac{N_0}{2}$ *i.e.*, $N_0 \left(\frac{1}{2}\right)^2$. After a time 3T, the number of atoms left will be $\frac{1}{2} \times N_0 \left(\frac{1}{2}\right)^2$ *i.e.*, $N_0 \left(\frac{1}{2}\right)^3$. Proceeding in the same way, the number of atoms left behind after *n* half-lives will be $N_0 \left(\frac{1}{2}\right)^n$.

$$\therefore \qquad N = N_0 \left(\frac{1}{2}\right)^n$$

If *t* is the time corresponding to *n* half-lives, then $t = n\mathrm{T}$

$$\text{or} \qquad n = \frac{t}{\mathrm{T}} \qquad \therefore \qquad N = N_0 \left(\frac{1}{2}\right)^{t/\mathrm{T}}$$

Activity of a Radioactive Substance

The activity or rate of decay of a sample is defined as the number of radioactive disintegrations taking place per second in the sample.

If a radioactive sample contains N radioactive nuclei at any time t, then its activity or decay rate R at time t will be

$$R = \frac{dN}{dt}.$$

The negative sign indicates that the activity of the sample decreases with the passage of time.

According to the radioactive decay law,

$$-\frac{dN}{dt} = \lambda N$$

$$\therefore \qquad R = \lambda N$$

$$\text{But} \qquad N = N_0 e^{-\lambda t}$$

$$\therefore \qquad R = \lambda N_0 e^{-\lambda t}$$

$$\text{or} \qquad R = R_0 e^{-\lambda t}$$

This is another form of radioactive decay law. Here $R_0 = \lambda N_0$, is the decay rate at time $t = 0$. R is the decay rate at time t. Clearly, R decreases exponentially with time.

Units of Radioactivity

The activity of a radioactive sample is generally expressed in terms of its rate of decay. In other words, the activity of a radioactive sample is expressed in terms of the number of disintegrations per unit time. The radioactivity is measured in the following three units.

The definition of curie says nothing about the nature of decays. **This unit is not appropriate to describe the ionising effects of** X-rays from, say, a medical X-ray machine. The radiation must be emitted only from a radionuclide.

(*i*) The curie (Ci). This was originally defined as the activity of 1 g of radium in equilibrium with its by-products. But it is now defined as under :

The activity of a radioactive substance is said to be one curie if it undergoes 3.7×10^{10} disintegrations per second.

$$1 \text{ curie} = 3.7 \times 10^{10} \text{ disintegrations/s}$$

Smaller units are millicurie and microcurie.

$$1 \text{ millicurie} = 3.7 \times 10^7 \text{ disintegrations/s}$$

$$1 \text{ microcurie} = 3.7 \times 10^4 \text{ disintegrations/s}$$

(*ii*) The rutherford (Rd). *The activity of a radioactive substance is said to be one rutherford if it undergoes 10^6 disintegrations per second.*

$$1 \text{ rutherford} = 10^6 \text{ disintegrations s}^{-1}$$

Smaller units are millirutherford and microrutherford.

$$1 \text{ millirutherford} = 10^3 \text{ disintegrations s}^{-1}$$

$$1 \text{ microrutherford} = 1 \text{ disintegration s}^{-1}$$

(*iii*) The becquerel (Bq). *It is the SI unit for activity. The activity of a radioactive substance is said to be one becquerel if it undergoes 1 disintegration per second.*

$$1 \text{ becquerel} = 1 \text{ disintegration s}^{-1}$$

Relation between different units

$$\begin{aligned} 1 \text{ curie} &= 3.7 \times 10^4 \text{ rutherford} \\ &= 3.7 \times 10^{10} \text{ becquerel.} \end{aligned}$$

6.3. TYPES AND NATURE OF RADIATIONS

Alpha Decay

The phenomenon of emission of an α-particle from a radioactive nucleus is called **alpha decay**. When a nucleus undergoes alpha decay, it transforms to a different nucleus by emitting an alpha particle (a helium nucleus, ${}^{4}_{2}\text{He}$). Since an alpha particle consists of two protons and two neutrons, an alpha decay reduces the Z, N and A of the original nucleus by two, two and four respectively.

Transformation of ${}^{A}_{Z}\text{X}$ nucleus into ${}^{A-4}_{Z-2}\text{Y}$ nucleus by an alpha decay is expressed by the following equation :

$${}^{A}_{Z}\text{X} \longrightarrow {}^{A-4}_{Z-2}\text{Y} + {}^{4}_{2}\text{He}$$

The energy Q released in the process can be obtained from Einstein's mass-energy relation. It is given by

$$Q = (m_X - m_Y - m_{He})\, c^2$$

This energy is shared both by the daughter nucleus ${}^{A-4}_{Z-2}\text{Y}$ and the alpha particle ${}^{4}_{2}\text{He}$.

Some **examples** of emission of α-particle are :

$$^{210}_{84}\text{Po} \longrightarrow {}^{206}_{82}\text{Pb} + {}^{4}_{2}\text{He}$$

$$^{226}_{88}\text{Ra} \longrightarrow {}^{222}_{86}\text{Rn} + {}^{4}_{2}\text{He}$$

$$^{232}_{90}\text{Th} \longrightarrow {}^{228}_{88}\text{Ra} + {}^{4}_{2}\text{He}$$

$$^{238}_{92}\text{U} \longrightarrow {}^{234}_{90}\text{Th} + {}^{4}_{2}\text{He}$$

Speed of α-particles

Transformation of the $^{A}_{Z}X$ nucleus into the $^{A-4}_{Z-2}Y$ nucleus by an alpha-decay can be expressed by the equation

$$^{A}_{Z}X \longrightarrow {}^{A-4}_{Z-2}Y + {}^{4}_{2}\text{He} + Q$$

$$Q = (m_X - m_Y - m_{He})\, c^2$$

As the parent nucleus $^{A}_{Z}X$ is at rest before it undergoes alpha decay, alpha particles are emitted with fixed energy, which can be calculated by applying the principles of conservation of energy and momentum. Let v_{He} and v_Y be the velocities of the alpha particle and the daughter nucleus, $^{A-4}_{Z-2}Y$. The principle of conservation of momentum gives

$$m_Y\, v_Y = m_{He}\, v_{He} \qquad ...(1)$$

By equating the sum of kinetic energies of the nucleus Y and the alpha particle to the energy released in the alpha decay, we have another equation

$$\frac{1}{2}\, m_{He}\, v_{He}^2 + \frac{1}{2}\, m_Y\, v_Y{}^2 = Q$$

Substituting the value of v_y from eq. (1), we get

$$\frac{1}{2}\, m_{He}\, v_{He}^2 + \frac{1}{2}\, m_Y\, \frac{m_{He}^2\, v_{He}^2}{m_Y^2} = Q$$

or $$\frac{1}{2}\, m_{He}\, m_Y v_{He}^2 + \frac{1}{2}\, m_{He}^2\, v_{He}^2 = m_Y Q$$

or $$\frac{1}{2}(m_Y + m_{He}) = m_{He}\, v_{He}^2 = \mathrm{m}_Y Q$$

or $$\frac{1}{2}\, m_{He}\, v_{He}^2 = \frac{m_Y}{m_Y + m_{He}}\, Q \qquad ...(2)$$

If we substitute $m_Y \simeq A - 4$ amu and $m_{He} \simeq 4$ amu in eq. (2), the kinetic energy carried by the alpha particle can be approximated by the relation

$$KE_{He} = \frac{1}{2} m_{He} v_{He}^2 \simeq \frac{(A-4)}{A} Q$$

In the decay of $^{222}_{86}Rn$, Q = 5.587 MeV and KE_{He} = 5.486 MeV. The velocity of the alpha particle emitted by $^{222}_{86}Rn$ can be easily estimated from its kinetic energy.

$$v_{He} = \sqrt{\frac{2 \times 5.486 \times 1.6 \times 10^{-13}}{4.00 \times 1.66 \times 10^{-27}}} \text{ m s}^{-1} = 1.63 \times 10^7 \text{ m s}^{-1}.$$

Beta Decay

(*i*) Definition. Beta decay is a process in which a nucleus decays spontaneously by emitting an electron or a positron.

Like alpha decay, it is a spontaneous process with a definite disintegration energy and half-life.

In beta-minus (β^-) decay, an electron is emitted by the nucleus. In beta- plus (β^+) decay, a positron is emitted by the nucleus.

(*ii*) Difficulties in explanation of beta decay.

(*a*) *Presence of electron in the nucleus.* It is difficult to understand this process because there are strong arguments against the presence of electron in the nucleus. However, this difficulty is solved if we assume that (*i*) a neutron inside the nucleus breaks up into a proton and an electron (*ii*) the electron is ejected from the nucleus immediately after its creation. In other words, we have assumed that the neutron within the beta-emitting nucleus is radioactive just like a free neutron.

(*b*) *Apparent violation of law of conservation of energy.* If we study the energy distribution of electrons emitted in the β-decay of $^{210}_{83}Bi$, it is observed that the energy varies between zero and 1.17 MeV (Fig. 6.3). It is of course very rare that the emitted electron has an energy of 1.17 MeV. Most of the electrons have an energy of 0.15 MeV. This presents another serious difficulty in the proper understanding of the process of beta decay. For every $^{210}_{83}Bi$-decay, the same mass vanishes but very few emitted electrons possess an energy of 1.17 MeV. This creates doubts about the validity of the law of conservation of energy itself. We cannot even say that the 'energy difference' is taken away by γ-rays because there is no emission of γ-radiation in the example under consideration.

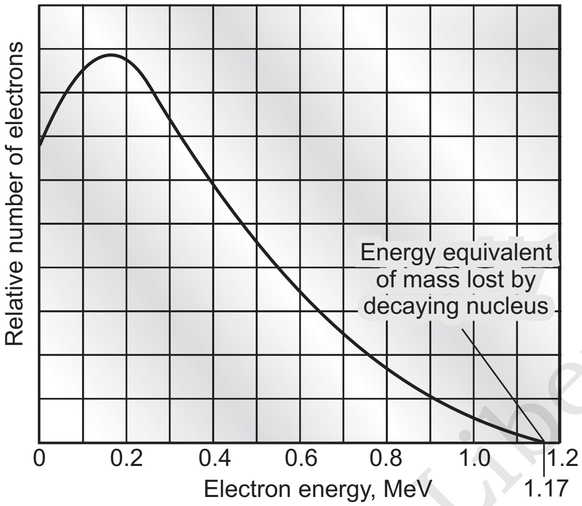


Fig. 6.3. Energy spectrum of electrons from the beta decay of $^{210}_{83}Bi$.

(*c*) *Apparent violation of law of conservation of momentum.* When the directions of the emitted electrons and of the recoiling nuclei are observed, they are almost never exactly opposite as required for linear momentum to be conserved.

(*d*) *Apparent violation of law of conservation of angular momentum.* The spins of the neutron, proton and electron are all $\frac{1}{2}$. If beta decay involves just a neutron becoming a proton and an electron, spin (and hence angular momentum) is not conserved.

(*iii*) Emission of neutrino/antineutrino. All the difficulties were overcome in 1933 by Wolfgang Pauli who proposed that a second particle is also emitted and assigned theoretically the following properties to this particle:

(*i*) zero rest mass (*ii*) zero charge (*iii*) a spin equal to $\frac{1}{2}$.

Enrico Fermi developed the theory of this new particle and called it neutrino. It was later on found that two kinds of neutrinos are involved in beta decay, the neutrino and the antineutrino. In the beta-minus decay, a neutron (inside the nucleus) transforms into a proton. An electron and anti-neutrino are emitted.

$$n \rightarrow p + e^- + \bar{\nu} \qquad \text{...(1)}$$

In the beta-plus decay, a proton (inside the nucleus) transforms into a neutron. A positron and neutrino are emitted.

$$p \rightarrow n + e^{+} + \nu \qquad \ldots(2)$$

These processes show why the mass number A of a nuclide undergoing beta decay does not change.

(*iv*) Sharing of disintegration energy. The disintegration energy is shared by the daughter nucleus, electron or positron and neutrino or antineutrino. So, kinetic energy of electron or positron in β-decay is not unique. The energy of electron or positron may range from zero to some maximum value. The maximum energy is called end-point energy.

(*v*) A free neutron can decay. In beta-minus decay, $n \rightarrow p + e^{-} + \bar{\nu}$

Since the mass of the neutron is greater than the combined mass of a proton and electron therefore the Q value is positive. The process is energetically allowed. So, a neutron outside the nucleus can decay as suggested by the above equation.

(*vi*) A free proton cannot decay. In beta-plus decay, $p \rightarrow n + e^{+} + \nu$

The Q value of this reaction is negative. So, a proton outside the nucleus cannot decay unless it gets additional energy in some collision. *Note that the behaviour of a free proton is different from the behaviour of a bound proton.* In-fact, a free proton is stable. The life time of a free proton is greater than the life of our universe.

(*vii*) Electron-capture (third type of beta decay). The third type of beta decay is electron capture. In electron capture, an orbital electron (usually in the K shell) combines with a proton in the nucleus to form a neutron and a neutrino. The neutron remains in the nucleus and the neutrino is emitted.

$$p + e^{-} \rightarrow n + \nu$$

A remains constant, N increases by one and Z decreases by one.

When one of the atom's outer electrons falls into the resulting vacant state, an X-ray photon is emitted.

Electron capture is competitive with positron emission. Both the processes lead to the same nuclear transformation. Electron capture occurs more often than positron emission in heavy nuclides. This is because the electrons in such nuclides are relatively close to the nucleus.

Gamma Decay

Just like an excited atom, an excited nucleus can make a transition to a state of lower energy by emitting a photon. The energies of the atomic states of hydrogen are of the order of electron volts. So, the wavelength of light emitted in atomic transitions correspond to photons having energy of the order of electron volts. On the other hand, the energies of the nuclear states are of the order of million electron volts. So, the photons emitted by nuclei can have energy of the order of several million electron volts. The wavelength of photons of such energy is a fraction of an angstrom. The short wavelength electromagnetic waves emitted by nuclei are called the gamma rays. Most radioisotopes, after an alpha decay or a beta decay, leave the daughter nucleus in an excited state. An excited nucleus is denoted by an asterisk after its usual symbol. Thus, ${}^{87}_{38}\mathrm{Sr}^*$ refers to ${}^{87}_{38}\mathrm{Sr}$ in an excited state.

Excited nuclei return to their ground states by emitting photons whose energies correspond to the energy differences between the various initial and final states in the transitions involved. The photons emitted by nuclei range in energy upto several MeV. These are traditionally called gamma rays.

Fig. 6.4 shows the beta decay of ${}^{27}_{12}\mathrm{Mg}$ to ${}^{27}_{13}\mathrm{Al}$. The half-life of the decay is 9.5 min and it may take place to either of the two excited states of ${}^{27}_{13}\mathrm{Al}$. The resulting ${}^{27}_{13}\mathrm{Al}^*$ nucleus then undergoes one or two gamma decays to reach the ground state.

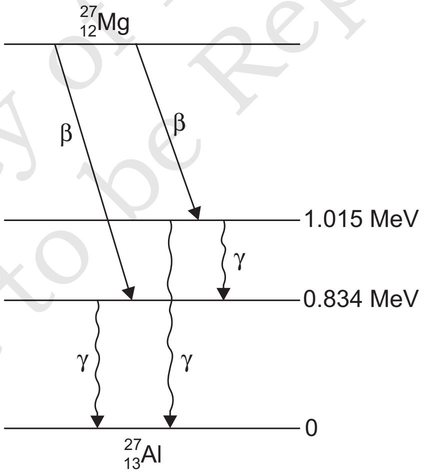


Fig. 6.4

Let us now consider another example. It is the decay of ${}^{60}_{27}\mathrm{Co}$. By beta emission, the ${}^{60}_{27}\mathrm{Co}$ nucleus is first transformed into an excited ${}^{60}_{28}\mathrm{Ni}$ nucleus which in turn reaches the ground state by emitting photons of energies 1.17 MeV and 1.33 MeV. Fig. 6.5 shows the process through an energy level diagram.

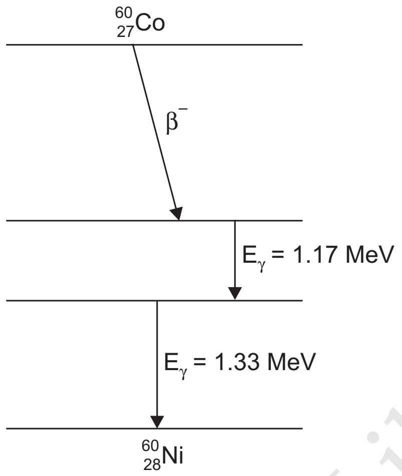


Fig. 6.5

As an alternative to gamma decay, an excited nucleus in some cases may return to its ground state by giving up its excitation energy to one of the orbital electrons around it. This process is known as internal conversion. It can be regarded as a kind of photoelectric effect in which a nuclear photon is absorbed by an atomic electron. The internal conversion in-fact represents a direct transfer of excitation energy from a nucleus to an electron. The emitted electron has a kinetic energy equal to the lost nuclear excitation energy minus the binding energy of the electron in the atom.

Most excited nuclei have very short half-lives against gamma decay. But a few remain excited for as long as several hours. A long-lived excited nucleus is called an isomer of the same nucleus in its ground state. The excited nucleus $^{87}_{38}\mathrm{Sr}^*$ has a half-life of 2.8 hour and is accordingly an isomer of $^{87}_{38}\mathrm{Sr}$.

6.4. NUCLEAR REACTIONS

When a nucleus is bombarded with nucleons or other sub-atomic particles, it undergoes a change in composition. A nuclear reaction indicates that change. *A nuclear reaction may be defined as the transformation in nuclei brought about by their interaction with elementary particles or with different nuclei themselves.*

Most nuclear reactions involve a nucleus A and a particle '*a*', This pair is known as *parent pair*. After a collision between these two, a new nucleus B is formed and another particle '*b*' is ejected. This pair is called the *final pair*. The nuclear reaction may be expressed as under :

$$A + a \longrightarrow B + b$$

In some reactions, energy Q is evolved. Such a reaction is known as **exothermic or exoergic reaction**. In a reaction in which energy is absorbed, the reaction is known as **endothermic or endoergic reaction**. So, in the final analysis, a nuclear reaction may be written as under :

$$A + a \longrightarrow B + b + Q$$

Here, in the usual expression, a is the bullet fired on a target A. This results in the recoil nucleus B and giving the product particle b with a release or absorption of reaction energy Q. Q is known as the reaction energy or Q-value of nuclear reaction. *The absorption or evolution of energy in a nuclear reaction takes place in accordance with Einstein's mass-energy equivalence relation.*

Important Nuclear Reactions

1. γ-ray photon as projectile. A nuclear reaction in which γ-ray photon is the projectile is known as *photo-nuclear reaction* or *photo disintegration reaction.*

(*i*) (γ-*n*) reaction. $^{2}_{1}H + \gamma \rightarrow {}^{1}_{1}H + {}^{1}_{0}n$

$$^{9}_{4}Be + \gamma \rightarrow {}^{9}_{4}Be \rightarrow {}^{8}_{4}Be + {}^{1}_{0}n$$

(*ii*) (γ-*p*) reaction. $^{9}_{4}Be + \gamma \rightarrow {}^{8}_{3}Li + {}^{1}_{1}H$

2. Neutron as projectile:

(*i*) (*n*-γ) reactions

$$^{1}_{1}H + {}^{1}_{0}n \longrightarrow {}^{2}_{1}H + \gamma$$

$$^{238}_{92}U + {}^{1}_{0}n \longrightarrow {}^{239}_{92}U \longrightarrow {}^{239}_{92}U + \gamma$$

(*ii*) (*n*-*p*) reactions

$$^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{15}_{7}N \longrightarrow {}^{14}_{6}C + {}^{1}_{1}H$$

$$^{27}_{13}Al + {}^{1}_{0}n \longrightarrow {}^{28}_{13}Al \longrightarrow {}^{27}_{12}Mg + {}^{1}_{1}H$$

(*iii*)

$$^{27}_{13}Al + {}^{1}_{0}n \longrightarrow {}^{28}_{13}Al \longrightarrow {}^{26}_{13}Al + 2\,{}^{1}_{0}n$$

(*iv*) (*n*-α) reactions

$$^{6}_{3}Li + {}^{1}_{0}n \longrightarrow {}^{7}_{3}Li \longrightarrow {}^{3}_{1}H + {}^{4}_{2}He$$

$$^{10}_{5}B + {}^{1}_{0}n \longrightarrow {}^{11}_{5}Li \longrightarrow {}^{7}_{3}Li + {}^{4}_{2}He$$

3. Proton as projectile:

(i) (p-α) reactions

$$^{7}_{3}\mathrm{Li} + ^{1}_{1}\mathrm{H} \longrightarrow ^{8}_{4}\mathrm{Be} \longrightarrow ^{4}_{2}\mathrm{He} + ^{4}_{2}\mathrm{He}$$

$$^{9}_{4}\mathrm{Be} + ^{1}_{1}\mathrm{H} \longrightarrow ^{10}_{5}\mathrm{B} \longrightarrow ^{6}_{3}\mathrm{Li} + ^{4}_{2}\mathrm{He}$$

(ii) (p-n) reactions

$$^{7}_{3}\mathrm{Li} + ^{1}_{1}\mathrm{H} \longrightarrow ^{7}_{4}\mathrm{Be} + ^{1}_{0}n$$

$$^{18}_{8}\mathrm{O} + ^{1}_{1}\mathrm{H} \longrightarrow ^{18}_{9}\mathrm{F} + ^{1}_{0}n$$

(iii) (p-d) reactions

$$^{7}_{3}\mathrm{Li} + ^{1}_{1}\mathrm{H} \longrightarrow ^{6}_{3}\mathrm{Li} + ^{2}_{1}\mathrm{H}$$

$$^{9}_{4}\mathrm{Be} + ^{1}_{1}\mathrm{H} \longrightarrow ^{8}_{4}\mathrm{Be} + ^{2}_{1}\mathrm{H}$$

(iv) (p-γ) reactions

$$^{12}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H} \longrightarrow ^{13}_{7}\mathrm{N} + \gamma$$

$$^{27}_{13}\mathrm{Al} + ^{1}_{1}\mathrm{H} \longrightarrow ^{28}_{14}\mathrm{Si} + \gamma$$

4. Deuteron as projectile:

(i) (d-α) reactions

$$^{6}_{3}\mathrm{Li} + ^{2}_{1}\mathrm{H} \longrightarrow ^{8}_{4}\mathrm{Be} \longrightarrow ^{4}_{2}\mathrm{He} + ^{4}_{2}\mathrm{He}$$

$$^{16}_{8}\mathrm{O} + ^{2}_{1}\mathrm{H} \longrightarrow ^{18}_{9}\mathrm{F} \longrightarrow ^{14}_{7}\mathrm{N} + ^{4}_{2}\mathrm{He}$$

(ii) (d-p) reactions

$$^{12}_{6}\mathrm{C} + ^{2}_{1}\mathrm{H} \longrightarrow ^{14}_{7}\mathrm{N} \longrightarrow ^{13}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H}$$

$$^{31}_{15}\mathrm{P} + ^{2}_{1}\mathrm{H} \longrightarrow ^{33}_{16}\mathrm{S} \longrightarrow ^{32}_{15}\mathrm{P} + ^{1}_{1}\mathrm{H}$$

(iii) (d-n) reactions

$$^{2}_{1}\mathrm{H} + ^{2}_{1}\mathrm{H} \longrightarrow ^{3}_{2}\mathrm{H} + ^{1}_{0}n$$

$$^{12}_{6}\mathrm{C} + ^{2}_{1}\mathrm{H} \longrightarrow ^{14}_{7}\mathrm{N} \longrightarrow ^{13}_{7}\mathrm{N} + ^{1}_{0}n$$

5. α-particle as projectile:

(i) (α-p) reactions

$$^{10}_{5}\mathrm{B} + ^{4}_{2}\mathrm{He} \longrightarrow ^{14}_{7}\mathrm{N} \longrightarrow ^{13}_{6}\mathrm{C} + ^{1}_{1}\mathrm{H}$$

$$^{23}_{11}\mathrm{Na} + ^{4}_{2}\mathrm{He} \longrightarrow ^{27}_{13}\mathrm{Al} \longrightarrow ^{26}_{12}\mathrm{Mg} + ^{1}_{1}\mathrm{H}$$

(ii) (α-n) reactions

In general, α-n reaction is represented as:

$$^{A}_{Z}\mathrm{X} + ^{4}_{2}\mathrm{He} \longrightarrow ^{A+4}_{Z+2}\mathrm{Cn} \longrightarrow ^{A+3}_{Z+2}\mathrm{Y} + ^{1}_{0}n$$

Examples :

$$^{7}_{3}\text{Li} + ^{4}_{2}\text{He} \longrightarrow ^{11}_{5}\text{B} \longrightarrow ^{10}_{5}\text{B} + ^{1}_{0}n$$

$$^{9}_{4}\text{Be} + ^{4}_{2}\text{He} \longrightarrow ^{13}_{6}\text{C} \longrightarrow ^{12}_{6}\text{C} + ^{1}_{0}n$$

In many cases, in addition to the emission of neutrons, γ-rays are also emitted by the excited nuclei. Moreover, neutrons also possess very high energy.

6.5. CONSERVATION LAWS IN NUCLEAR REACTIONS

Broadly, the following conservation laws are obeyed in nuclear reactions.

(*i*) **Conservation of number of nucleons.**

(*ii*) **Conservation of charge.** In a reaction, the total electric charge is conserved. This ultimately means that the total Z number, the atomic number is conserved.

(*iii*) **Conservation of linear momentum.** Like all physical processes involving collisions, the total momentum along any direction, before and after the event, is always conserved.

(*iv*) **Conservation of angular momentum.**

(*v*) **Conservation of mass-energy.** According to mass-energy equivalence in the theory of relativity, mass and energy are equivalent. So the principle of conservation of energy in mechanics has to be extended to the conservation of mass-energy in nuclear reactions. The mass-energy equation for the nuclear reaction may be written as :

$$m_1c^2 + \text{E}_{k_1} + m_2c^2 + \text{E}_{k_2} = m_3c^2 + \text{E}_{k_3} + m_4c^2 + \text{E}_{k_4}$$

where m_1, m_2, m_3 and m_4 are the rest masses and E_{k_1}, E_{k_2}, E_{k_3} and E_{k_4} are their respective kinetic energies.

Nuclear Fission

In 1939, German Scientists Otto Hahn and Strassmann while studying nuclear reactions, discovered that when a uranium nucleus is bombarded with a neutron, it explodes into two nearly equal fragments, Barium and Krypton. Since this process somewhat resembles fission of cells in biology, therefore this phenomenon of nuclear disintegration was also called fission.

Nuclear fission *is defined as a type of nuclear disintegration in which a heavy nucleus splits up into two nuclei of nearly comparable masses with liberation of energy.*

The fission is accompanied by the release of three neutrons and radiation energy in the form of γ-rays. The reaction is represented as :

$$ {}^{1}_{0}n + {}^{235}_{92}\mathrm{U} \longrightarrow [{}^{236}_{92}\mathrm{U}] \longrightarrow {}^{141}_{56}\mathrm{Ba} + {}^{92}_{36}\mathrm{Kr} + 3\,{}^{1}_{0}n + \gamma $$

The diagrammatic sketch is given in Fig. 6.6. A neutron strikes the ^{235}U nucleus and in the process two nuclides ^{141}Ba and ^{92}Kr are formed with the release of 3 neutrons as shown. The wavy lines indicate the energy released in the form of γ-radiations. An important point to note here is that a *slow* neutron is used to cause fission. Further whereas one neutron is lost in the process to produce fission, three neutrons are produced as a product of the fission. This fact has a tremendous significance in the construction of nuclear bomb.

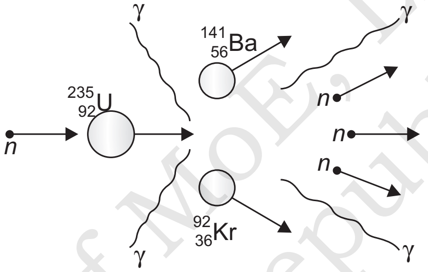


Fig. 6.6. Nuclear fission

Energy released in fission. The fission fragments Barium, Krypton and neutrons are released with high velocities. Also energy is released in the form of γ-rays. An estimate can be made as in the example given below :

Before the reaction:

Mass of ${}^{235}_{92}\mathrm{U}$ = 235.0439 amu ; Mass of ${}^{1}_{0}n$ = 1.0087 amu

Total mass = 236.0526 amu ...(*i*)

After the reaction:

Mass of ${}^{141}_{56}\mathrm{Ba}$ = 140.9129 amu ; Mass of ${}^{92}_{36}\mathrm{Kr}$ = 91.8973 amu

Mass of three ${}^{1}_{0}n$ = 3.0261 amu

Total mass = 235.8363 amu ...(*ii*)

Mass defect = 0.2163 amu [(*i*) – (*ii*)]

Since 1 amu = 931 MeV,

$\therefore$ The energy released = 931 × 0.2163 = 201.37 MeV ≈ 200 MeV

This is a huge figure. Calculations reveal that 235 g of Uranium, on complete fission, releases energy equivalent to the burning of about

600 tonnes of coal. However, this 200 MeV consists of K.E. of fission fragments, of released neutrons and of the γ-rays. Eventually, it is transferred to the surrounding matter appearing as heat.

Nuclear Fission Explained on the Basis of Liquid-drop Model

Nuclear fission can be understood on the basis of the liquid-drop model of the nucleus. When a liquid-drop is suitably excited, it may oscillate in a variety of ways. A simple one is shown in Fig. 6.7. The drop in turn becomes a prolate spheroid, a sphere, an oblate spheroid, a sphere, a prolate spheroid again, and so on. The restoring force of its surface tension always returns the drop to spherical shape, but the inertia of the moving liquid molecules causes the drop to overshoot sphericity and go to the opposite extreme of distortion.

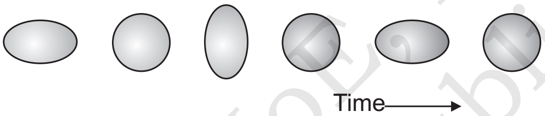


Fig. 6.7. The oscillation of a liquid-drop.

Nuclei exhibit surface tension, and so can vibrate like a liquid-drop when in an excited state. They also are subject to disruptive forces due to the mutual repulsion of their protons. When a nucleus is distorted from a spherical shape, the short-range restoring force of surface tension must cope with the long-range repulsive force as well as with the inertia of the nuclear matter. If the degree of distortion is small, the surface tension can do this, and the nucleus vibrates back and forth until it eventually loses its excitation energy by gamma decay. If the degree of distortion is too great, however, the surface tension is unable to bring back together the now widely separated groups of protons and the nucleus splits into two parts. This picture of fission is illustrated in Fig. 6.8.

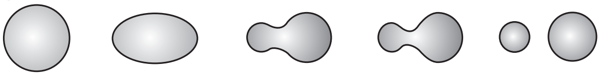


Fig. 6.8. Nuclear fission according to the liquid-drop model

Chain Reaction

If the energy available per reaction is large and one reaction can trigger reaction in other nuclei, then the nuclear reaction will act as a real source of energy.

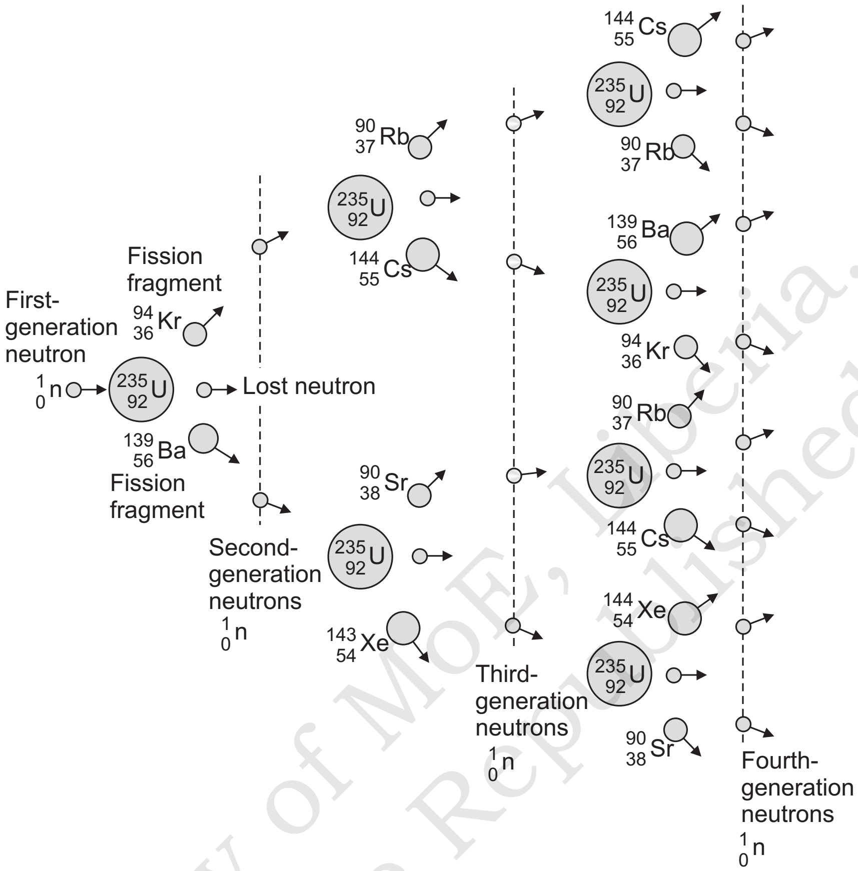


Fig. 6.9. Chain reaction.

When a single Uranium nucleus undergoes fission, it releases a number of neutrons. Some of them are absorbed in the body of the material and some in air. At least, two may be capable of having the right speed to cause further fission. The number of neutrons produced and available for further fission divided by the number of neutrons present initially before the reaction is called the *reproduction factor.* This reproduction factor k should be at least equal to one so that the nuclear reaction may be sustained. It may be > 1. A case when $k = 2$ is shown as a sketch in Fig. 6.9. Here one single neutron is absorbed to cause a nuclear reaction. And in so doing, it releases two neutrons which take over this job further. Under suitable circumstances, these secondary neutrons cause the fission of more nuclei and yield more secondary neutrons. Thus, the whole process takes place in a *geometric progression* and the reaction once started continues to gather momentum rapidly. This is known as a *chain reaction.* Every time a ^{235}U splits, 200 MeV energy is released. Partly it goes to give the K.E. to the fragments but quite a sizeable portion of this is released in the form of γ-rays. It has been calculated that a neutron takes about 10^{-8} second from its release from a nucleus to cause the splitting of another nucleus. Thus, 200 MeV energy is released in just 10^{-8} s. Thus, in about a μs (10^{-6} s), the total energy released in a chain reaction would be about 2×10^{13} J. This is really a large quantity of energy and if left uncontrolled, it would cause a violent explosion. This uncontrolled chain reaction is utilised in the nuclear bomb-popularly known as atom bomb.

Critical size. For chain reaction to occur, the size of the material must be within certain limits. The neutrons produced as a result of one fission may (*i*) be straying out due to leakage from the surface ; or (*ii*) be absorbed in the non-fissionable part in the system ; or (*iii*) be absorbed in the system itself if the size of the system is so large that the velocity of the neutron becomes very small ; and is of too low energy to cause further fission. It has been estimated that a released neutron must travel about 10 cm so that it is now properly slowed down to cause further fission. If the size of the material is less than 10 cm in any direction, the neutron simply crosses it and goes out without doing any further fission. So *if the material is too small, no fission is possible.* Thus, there has to be an optimum size of the material such that the neutrons once released would be slowed down in the material to the right speed and further chain reaction may get going. This optimum size of the material is called the **critical size.** The corresponding mass is called the **critical mass.** If the size of ^{235}U piece is equal to the critical size, then number of neutrons lost is just equal to the number of neutrons produced.

It is thus to be noted that if the size of the fissionable material is less than the critical size, a chain reaction is simply not possible and the material is quite safe to handle. But if the material is of a size greater than the critical size, it may capture a stray neutron and start an uncontrolled chain reaction, resulting in a violent spontaneous explosion, and consequent release of energy.

Nuclear Fusion

We know 'fission' to be a process in which a heavy nucleus breaks up into two lighter nuclei. Fusion, on other hand, is the reverse of fission. Thus, fusion *is a process in which lighter nuclei merge into one another to form a heavier nucleus.* As in fission, fusion also is accompanied by a release of energy.

The binding energy per nucleus thus formed is greater than the binding energy per nucleon of the lighter elements, which fuse to form the single nucleus. Taking an example, let us consider the fusion of the deuterium nuclei to form a single helium nucleus :

We know that mass of a deuteron = 2.01471 amu

$\therefore$ Mass of two deuterons = 4.02942 amu

Mass of α-particle (*i.e.*, a Helium nucleus) = 4.00388 amu

$\therefore$ Δm, mass defect = 0.02554 amu

Since 1 amu = 931 MeV,

$\therefore$ The energy liberated = 0.02554 × 931 MeV

= 23.78 MeV ≈ 24 MeV

Thus, a single helium nucleus formed out of fusion of two deuterons (*i.e.*, deuterium nuclei) releases 24 MeV energy. In case a large number of helium nuclei are fused, we readily see that a tremendous amount of energy is released.

Since both the deuterons are similarly charged (+ 1), therefore, we require a large amount of energy to bring the two together for fusion against Coulomb repulsion. Though theoretically this energy may be given to them by accelerating them through strong electric field, practically it is not easy or convenient. The other alternative is to give them high thermal energies. In the Sun and the stars, such high temperatures (≈ 10 Million K) are available which impart enough energy to the fusing particles which are protons or deuterons. Thus, such a fusion process is called a *thermonuclear fusion.*

Energy Source of Stars and Sun

(*i*) Proton-Proton Cycle. The interior of Sun is at about 27 million K. The thermonuclear reactions taking place are as follows :

$$^{1}_{1}\text{H} + {}^{1}_{1}\text{H} \xrightarrow{\qquad} {}^{2}_{1}\text{H} + {}^{0}_{1}e + 0.4\ \text{MeV} \qquad \ldots(i)$$

$$^{1}_{1}\text{H} + {}^{2}_{1}\text{H} \xrightarrow{\qquad} {}^{3}_{2}\text{He} + 5.5\ \text{MeV} \qquad \ldots(ii)$$

$$^{3}_{2}\text{He} + {}^{3}_{2}\text{He} \xrightarrow{\qquad} {}^{4}_{2}\text{He} + 2{}^{1}_{1}\text{H} + 12.9\ \text{MeV} \qquad \ldots(iii)$$

The reactions (*i*) and (*ii*) occur twice. So, the net reaction is :

$$4{}^{1}_{1}\text{H} \xrightarrow{\qquad} {}^{4}_{2}\text{He} + 2{}^{0}_{1}\text{e} + 24.7\ \text{MeV}$$

Thus at that high temperature available in the core of the Sun, four protons fuse into a Helium nucleus with the release of two positrons and 24.7 MeV of energy.

(*ii*) Carbon-Nitrogen Cycle. It is understood that for stars whose interior temperatures are greater than that of Sun, a Carbon-Nitrogen cycle takes place to produce the desired thermonuclear fusion reactions. It takes place as indicated below:

$$^{12}_{6}\text{C} + {}^{1}_{1}\text{H} \longrightarrow {}^{13}_{7}\text{N} + h\nu \text{ (energy)}; \quad {}^{13}_{7}\text{N} \longrightarrow {}^{13}_{6}\text{C} + {}^{0}_{1}\text{e} \text{ (positron)}$$

$$^{13}_{6}\text{C} + {}^{1}_{1}\text{H} \longrightarrow {}^{14}_{7}\text{N} + h\nu \text{ (energy)}; \quad {}^{14}_{7}\text{N} + {}^{1}_{1}\text{H} \longrightarrow {}^{15}_{8}\text{O} + h\nu \text{ (energy)}$$

$$^{15}_{8}\text{O} \longrightarrow {}^{15}_{7}\text{N} + {}^{0}_{1}\text{e} \text{ (positron) + energy}; \quad {}^{1}_{1}\text{H} + {}^{15}_{7}\text{N} \longrightarrow {}^{12}_{6}\text{C} + {}^{4}_{2}\text{He}$$

The net result of this complete cycle of reactions is that four protons fuse into one helium nucleus with the emission of positrons and release of energy.

Hydrogen Bomb

We know that a thermonuclear fusion reaction involving the fusion of four protons into a helium nucleus or two deuterons into a helium nucleus releases tremendous energy. This energy is produced by the Sun for peaceful purposes to sustain our life. But man has made use of this very energy to create a weapon of destruction—the hydrogen bomb.

Fusion cannot take place at ordinary temperatures. So, initially in the hydrogen bomb, we have a small fission bomb, which on explosion, causes the temperature to rise very high to about 10^7 K. At this temperature, a fusion of lighter nuclei takes place and helium nuclei are formed with the release of tremendous energy in an uncontrolled manner. Since proton is a hydrogen nucleus, we in a layman's language call this instrument of destruction as a hydrogen bomb. It is obvious that its explosive power is greater than that for a fission bomb ; because in reality the hydrogen bomb is a combination of both the processes-fission to produce the desired initial high temperature and fusion to produce the extra energy for devastation.

Radiation Hazards

After the invention of the nuclear reactions as a pure scientific study, man developed the atomic and hydrogen bombs in an attempt to gain supremacy over other men. But in this process, the large amount of radiated energy to which mankind as a whole is exposed is really posing a problem even for human existence. These radiations are causing great dangers to human organism.

For instance, let us see how γ-ray acts on a human system. When γ-ray or any high energy nuclear particle passes through any material, it knocks out electrons from its atoms and ionises them. With the atom thus broken and ionised, the complex molecular structure of the organism becomes weak and may break up. This breaking up of the molecules disrupts the entire normal functioning of the biological system. This leads to a permanent damage of the tissues, and ultimately leads to death.

The extent to which a human organism is damaged depends upon (*i*) the dose and the rate at which the radiation is being given, (*ii*) the part of the body exposed to it. Our hands and feet, not being vital organs, can receive much greater dose than other parts of the body. The damage itself can be either (*i*) **pathological** or (*ii*) **genetic.**

In the **pathological damage,** the organism exposed to the radiation may ultimately die. This happens when the body is exposed to about 600 *r*. Smaller dose of 100 *r* approximately may cause a start of leukemia (death of red blood corpuscles in the blood) or cancer, which on spreading causes death ultimately.

The **genetic damage** is still worse. The radiations cause injury to genes in the reproductive cells. This gives rise to mutations which pass on from generation to generation. Mutations are always harmful and are irreversible. There is no way to escape from the results of this damage. In a simple language, it may mean that a person exposed to such damage may have a certain disorder; and all his subsequent generations will continue having the same disorder in their systems. The only hope and prayer is that when one is exposed to these radiations, the exposure is too small to cause any serious damage.

When an atom bomb explodes nearby, the radiations are extremely intense and sudden. This causes immediate death and destruction of life, pathologically, and damage to the heredity, by genetic damage.

Nuclear holocast: Large scale destruction and devastation caused by nuclear weapons is known as nuclear holocast.

Types and Nature of Radiations

In natural radioactive decay, three common emissions are observed. As scientists were unable to identify them as some already known particles hence name them alpha particles (α), beta particles (β) and gama rays (γ) using first three letters of Greek alphabet. Later alpha particles were identified as H^{-4} nuclei, Beta particles as electrons and gama rays as electromagnetic radiations.

Alpha Particles: Alpha particles are identical to helium nucleus. Alpha particles are positively charged particled made up of two protons and two neutrons from an atom's nucleus. Heaviest radioactive elements like uranium, radium and polonium. Because of two protons and two neutrons, alpha particles are heavy particles so they move only up to short distances even if they are very energetic. They are unable to travel very far from the atom.

Alpha particles are unable to penetrate even the outer layer of the skin. Hence exposure to alpha particles is not problem, but alpha particles can damage soft tissues inside our body if swallowed, inhaled or enter into our body through a cut. They are more dangerous as they cause more severe damage to cells and DNA. They are able to release all their energy in few cells. For example uranium$^{238}_{92}$decays to form thorium$^{234}_{90}$

$^{238}_{92}U \longrightarrow Th + ^{4}_{2}He$ equation for alpha decay is $^{A}_{Z}X \longrightarrow ^{A-4}_{Z-2}Y + ^{4}_{2}He$

Alpha decay occurs in heaviest elements and have energy level upto 5 MeV and speed of amount 5% of light.

Beta Particles β: Beta particles are small, fast moving, negatively charged electrical particles emitted from an atoms nucleus during radioactive decay. β-particles are emitted by certain unstable atoms such as hydrogen–3 (tritium), carbon-14 and strontium-90 and sulphur-35. β particles are more penetrating but less damaging to living tissues than alpha particles because they produced widely spaced ionizations. They move farther in air than alpha particles but can be stopped by a layer of clothings or by a thin layer of aluminium. Some β particles are capable of penetrating the skin and causing damage such as skin burns. β emitters are more harmful and dangerous than alpha emitter if they are inhaled or swallowed. Beta particles is 1/7000th the size of an alpha particle.

Gama Rays γ: Gama rays are weightless particles of energy. Unlike alpha and beta particles which have both mass and energy, gama rays are pure energy. Gama rays are emitted immediately after the ejection of alpha or beta particles during radio active decay. Gama rays are like visible light but have much energy.

Gama rays are hazardous for our entire body. They are more penetrating than alpha and beta particles. They can penetrate clothes as well as skin. Gama rays pass through several inches thick dense material like lead and 1–2 feet of concrete even. Gama rays can pass through complete human body and cause ionisation as a result of which tissues and DMA can be damaged.

X-rays: X rays are just like gama rays as they are photons of pure energy. X rays and gama rays have same basic properties but originate from different parts of atoms. Gama rays are emitted from inside of the nucleus while X rays are emitted from outside the nucleus. X rays have less energy and are less penetrating than gama rays. X rays can be produced both naturally and by machines using electricity.

X rays are publically known because of their use in medicines. X ray machines are used world wide in medical field. Computerised tomography (CT or CT scan) use specialised X ray machine to make high resolution images of bones and soft tissues in the body. X-rays are also in use for inspection and control processes in industries.

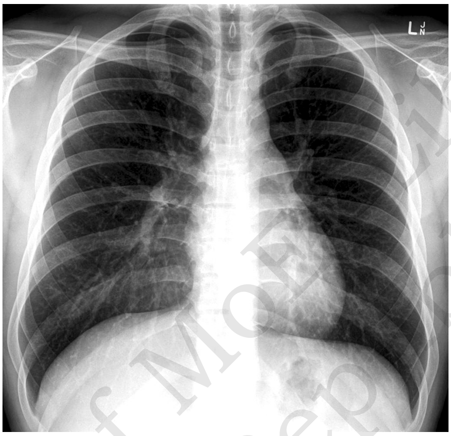


Fig. 6.10. Picture of X ray

Natural Radiations: Radiations are present naturally all around us. We have been adapted to these natural radiations as we have evolved in a world containing significant level of ionizing radiations.

The United Nations Scientific Committee on the effect of Atomic Radiation (UNSCER) identifies four major sources of public exposure to natural radiation.

(*a*) Cosmic radiation
(*b*) Terrestrial radiation
(*c*) Inhalation
(*d*) Ingestion

(*a*) **Exposure from cosmic radiations:** Our planet's atmosphere is continuously bombarded by cosmic radiations coming from sun, and other celestial bodies and events in the space. Cosmic radiations consist of fast moving particles, protons, or wave energy. Such ionising radiations which enter earth's environment are absorbed by human beings which results in natural radiation exposure. High altitudes receive more radiations.

(*b*) **Exposure from Terrestrial Radiations:** Deposits of uranium, thorium and potassium found as natural deposits in earths crust, release small amount of ionizing radiations which become the cause of exposure to natural radiations.

(*c*) **Exposure through inhalations:** Gases like radon and thoron are produced by uranium 238 and thorium found in the soil and bedrock. These gases when released in air get accumulated in houses in the mining areas and cause exposure to human beings through inhalation.

(*d*) **Exposure through ingestion:** Traces of radioactive mineral are found in vegetables, grains and ground water. Once ingested these minerals result in internal exposure to natural radiation. Naturally occurring radioisotopes like K^{40} and carbon 14 are such radioactive minerals.

Table 6.2. Radioactive isotropes in Body (70 kg adult)

Isotope	*Amount of radio activity in Bq.*
Uranium	2.3
Thorium	0.21
Potassium 40	4000
Radium 266	1.1
Carbon 14	3700
Polonium 210	40

Artificial Sources of Radiation: Radiation are also emitted by the way of following:

(*a*) **Atmospheric testing:** We receive smaller doses of fall out of radioactive material because of testing of atomic weapons by different countries. Radioactive material having short half life do not exist for longer time but those with more half life decay slowly and exist for longer time.

(*b*) **Medical sources:** X ray, CT scanners, MRI machines release radiations. Nuclear medicines containing radioactive isotopes used in the treatment of diseases like cancer are also the source of radiations.

(*c*) **Industrial sources:** Radioactive materials used in nuclear gauges (used to build roads), density gauges (used to measure flow of material through pipes), spread radiation in the environment, smoke detectors glow signs and some of the sterilizers spread radiations.

(*d*) **Nuclear power plants:** Nuclear power plants use uranium which being radioactive elements spreads radiations around nuclear power plant inspite of best checks and controls.

Ionizing Power of Radiations

When radiation particles attack the atoms, the impact causes atoms to loose electrons to form ions. Alpha particles have highest ionizing power and greatest ability to damage tissue.

The process in which electron is given enough energy to break away from atoms is called ionisation which results in the formation of two charged ions, the molecule with net positive charge and a free electron with negative charge.

Gama radiations have least ionizing power, beta radiations have 100 times the ionising strength of game radiations and alpha radiations have 1000 times the ionizing power of gama radiations.

Penetrating Power: Penetrating power is defined as the power of the radiation to pass through the matter. The more material the radiation can pass through, the greater the penetrating power and the more dangerous they are. The greater the mass of radiation particles, greater the ionizing power and lower the penetrating power.

6.6. EFFECTS AND APPLICATIONS OF RADIOACTIVITY

Radiations interact with matter to produce exitation and ionization of atoms and molecules and cause physical and biological effects. Radiations have effects on human life also. Radiation have some uses and applications also. Radiations also have played a significant role in improving the quality of human life. Radio isotopes are useful in the field of, tracing, radiography, food preservations, sterilization, eradication of insects and pests, medical diagnosis and therapy, and new variety of crops in agricultural field.

Effects of Radioactivity

Radiations emitted by radioactive isotopes release much energy and produce physical chemical and biological changes. Damage is caused by interaction of this energy with nuclei or orbiting electrons resulting in change of material structure and properties.

(*a*) **Effect on Metals:** Radiations effect on metals was first recognised by Wigner in 1946. Effect of radiation depend on type and duration of radiations. Ionising radiations have two types of effects on metals

(*i*) By displacing the atoms from original position in lattice structure causing displacement damage production.

(*ii*) Chemical composition of the target can be changed by ion implantation or transmutation.

Neutrons released by radioactive elements cause increase in electrical and thermal resistance, hardness and tensile strength and decrease in ductibility. Thermal neutrons (the neutrons at high temperature have very less significant effect on mechanical properties of metals.

(*b*) **Effect on non metals:** Radiations increase the viscosity of oils and greese and make them gummy, tar like polymers. Rubber may be come harder or softer. Concavate heats up under radiation exposure resulting in swelling, cracking and spalling.

(*c*) **Effect on polymers:** When polymers are exposed to radiations, their ionised and excited species are formed due to bond rearrangement, chain scission radical formation etc. As a result chemical, electrical, mechanical, properties of polymers are changed leading to their applications in different scientific and technology fields.

(*d*) **Cross linking:** Due to radiation polymerisation two free radical monomers combine to form three dimensional network of cross linked high molecular polymer which possess high thermal resistance and strong mechanical strength.

(*e*) **Radiation grafting:** Radiations cause, grafting changes the surface of polymeric materials. Radiation induced grafting is used in a variety of applications biomedical environmental and industrial.

(*f*) **Degradation:** Radiation induced degradation is used to develop viscose, pulp, paper, food preservation, pharmaceutical production, and natural bio-active agent industries.

(*g*) **Biological effects of radiations:** Radiation may cause harmful health effects in human beings. Radiation cause damage to DNA of the tissues of human beings.

Applications of Radioactivity

1. **In medical field**

(*i*) Radio isotope Iodine 131 is used for determining. Cardiac output, plasma volume, fat metabolism and to measure the activity of thyroid gland.

(*ii*) Phophorus 32 is used for identifying malignant tumours cancer cells accumulate phosphorus more than normal cells.

(*iii*) Technetium 99 is used with radiographic scanning devices and for examining the anatomic structure of organs.

(*iv*) Radio isotopes cobalt-60 and cesium-137 are used to treat cancer.

2. **Industrial uses**

(*i*) Fission energy of uranium is used in nuclear power stations.

(*ii*) Radio isotopes are used to density of metals and plastic sheets.

(*iii*) Radio active substances are used to stimulate cross linking of polymers.

(*iv*) Radioactive substances are used to induce mutations in plants to develop harder seeds.

(*v*) Used to kill microbes that cause spoilage of tools.

(*vi*) Radio isotopes are used in tracer applications.

(*vii*) Radio isotypes are used in motor oils which increase the life of piston and ring alloys.

(*viii*) Radiometric dating is used to find out the age of rocks and rock formation.

3. **Carbon dating:** Carbon 14 dating is used to find out the age of fossils, old structures, rocks etc.

4. Radio isotopes are used to measure deep water currents and snow water content in water sheds.

5. Radioactive substances are used to sterlize mass reared insects so that they are not able to increase their progeny as a result life of crop is preserved and production is increased.

6. Radiation ^{60}Co and ^{137}Cs, X rays and electrobeams are used for food irradication and saved from attack of pests, insects, bacteria and fungi.

SUMMARY

- Discovery of radioactivity in uranium by French physicist **Henri Becquerel** in 1896 forced scientist to radically changed their ideas about atomic structure.
- The nuclear stability bond shows various combinations of neutrons/ protons combinations that give rise to different types of observable nuclei with measurable half lives.

- **Half life** of a radioactive isotope is the amount of time it takes for one half of the radioactive isotope to decay. Half life of a specific radio active isotope is constant, and it is independent of the initial amount of that isotope.
- The activity or rate of decay of a sample is defined as the number of radioactive disintegrations taking place per second in the sample.
- In 1939, German Scientists Otto Hahn and Strassmann while studying nuclear reactions, discovered that when a uranium nucleus is bombarded with a neutron, it explodes into two nearly equal fragments, Barium and Krypton.
- **Nuclear fission** *is* defined as a type of nuclear disintegration in which a heavy nucleus splits up into two nuclei of nearly comparable masses with liberation of energy.

EVALUATION

I. Multiple Choice Questions

1. The half-life of a certain radioactive element is such that 7/8 of a given quantity decays in 12 days. What fraction remains undecayed after 24 days?

(a) 0 (b) $\frac{1}{128}$

(c) $\frac{1}{64}$ (d) $\frac{1}{32}$

2. β-decay means emission of electron from

(a) innermost electron orbit. (b) a stable nucleus.

(c) outermost electron orbit. (d) radioactive nucleus.

3. A radioactive isotope has a half-life to T years. How long will it take the activity to reduce to 1% of its original value?

(a) 3.2T years (b) 4.6T years

(c) 6.6T years (d) 9.2T years

4. Fusion reaction takes place at high temperature because

(a) nuclei break up at high temperature.

(b) atoms get ionised at high temperature.

(c) kinetic energy is high enough to overcome the coulomb repulsion between nuclei.

(d) molecules break up at high temperature.

5. The half-life of an old rock element is 5800 years. In how many years its sample of 25 gm is reduced to 6.25 gm.

(a) 2900 years (b) 5800 years

(c) 11600 years (d) 23200 years

6. The fusion reaction in the sun is a multi-step process in which the

(a) helium is burned into deuterons.

(b) helium is burned into hydrogen.

(c) deutron is burned into hydrogen.

(d) hydrogen is burned into helium.

(e) helium is burned into neutrons.

7. A nuclear fission is said to be critical when multiplication factor or K

(a) K = 1 (b) K > 1

(c) K < 1 (d) K = 0

8. What amount of original radioactive materials is left after 3 half-lines?

(a) 6.5% (b) 12.5%

(c) 25.5% (d) 33.3%

9. Nuclear fusion is not found in

(a) thermonuclear reactor (b) hydrogen bomb

(c) energy production in sun (d) atom bomb

(e) energy production in stars.

10. During β-emission

(a) a neutron in the nucleus decays emitting an electron.

(b) an atomic electron is ejected.

(c) an electron already present within the nucleus is ejected.

(d) a part of the binding energy of the nucleus is converted into an electron.

(e) a proton in the nucleus decays emitting an electron.

II. Descriptive Questions

1. Write one equation representing nuclear fusion reaction.

2. Name two radioactive elements which are not found in observable quantities in nature. Why is it so?

3. Write down the radioactive rays in the order of increasing penetrating power.

4. Very high temperature as those obtained in the interior of the sun are required for fusion reaction to take place.

5. The half-lives of radioactive nuclides that emit α-rays vary from microsecond to billion year. What is the reason for this large variation in the half-life of α-emitters?

6. An element emits in succession 2 α-particles and 1 β-particle. What is the change in mass number?
7. Why α-particles have a high ionising power?
8. What is the mass in g of a radioactive element whose activity is equal to 1 curie?

III. Numerical Questions

1. Explain with the help of a nuclear reaction in each of the following cases. How the neutron to proton ratio changes during (*i*) alpha decay (*ii*) beta decay.
2. A radioactive material is reduced to 1/10th of original amount in 4 days. How much material should one begin with so that 4×10^{-3} kg of the material is left over?

   (Ans. Original amount = $4 \times 10^{-3} \times 64$ kg = 0.256 kg)
3. A radioactive isotope has a half life of 10 years. How long will it take for the activity to reduce to 3.125%? (**Ans.** Required Time = 50 years)
4. A radioactive isotope has a half life of T year. How long will it take the activity to reduce to 3.125%. (**Ans.** t = 5T years)
5. Half life of $^{90}_{38}\text{Sr}$ is 28 years. What is the disintegration rate of 15 mg of this isotope? (**Ans.** 2.129 Ci, 7.878×10^{10} Bq)

SEMESTER–II (Period–VI)

7

TOPIC

Chemical Equilibrium

C11CH7

Learning Objectives

Upon completion of this topic, learners will:

- Discuss the general principles of equilibrium
- Explain the Le Chatelier's Principle as it relates to factors influencing equilibrium
- Explain the nature of equilibrium constant, performing simple related calculations and
- Demonstrate the mathematical relationship between K_p and K_c.

It is generally observed that many of the chemical reactions do not proceed to completion when they are carried out in a closed container. This implies that the reactants are not completely converted into the products. Instead, after some time *concentrations* of the reactants do not undergo further decrease and the reaction appears to have stopped. This state of the system in which no further net change occurs is called a **state of equilibrium.**

Equilibrium can be attained for both physical and chemical processes. The equilibrium achieved in physical processes such as dissolution of salt, evaporation of water, etc., is called **physical equilibrium,** whereas the equilibrium achieved in chemical processes such as decomposition of calcium carbonate or reaction between hydrogen and iodine is called **chemical equilibrium.**

The equilibrium situation raises many interesting questions such as:

(*a*) What is the equilibrium state and how is it recognised?

(*b*) What is the molecular behaviour when state of equilibrium is reached?

(*c*) What are the factors which alter the state of equilibrium?

In this unit, we shall seek answers to these questions.

7.1. EQUILIBRIUM IN PHYSICAL PROCESSES

In order to understand the characteristics of systems in equilibrium state let us study some physical changes in a state of equilibrium. Some common physical equilibria are:

$$\text{Solid} \rightleftharpoons \text{Liquid}$$

$$\text{Liquid} \rightleftharpoons \text{Gas}$$

$$\text{Solid} \rightleftharpoons \text{Gas}$$

Solid-Liquid Equilibrium

When a pure solid substance is heated, it starts changing into liquid at a certain temperature. At this temperature, the solid and liquid states of the substance coexist under the given conditions of pressure.

For any pure substance, at atmospheric pressure, the temperature at which the solid and liquid states can coexist is called the normal melting point or the normal freezing point of the substance.

At melting point the solid substance is in equilibrium with liquid state of the substance. If heat energy is added to a mixture of solid and liquid at equilibrium, the solid is gradually converted to liquid while the temperature remains constant. If a solid-liquid system at melting point is taken in a well-insulated container then this constitutes a system in which solid is in dynamic equilibrium with liquid.

For example, let us consider ice and water at 273 K (melting point of ice), taken in a perfectly insulated thermos flask. It may be noted that the temperature as well as the masses of ice and water remain constant. This represents a dynamic equilibrium between ice and water.

$$\text{Ice} \rightleftharpoons \text{Water}$$

or

$$H_2O(s) \rightleftharpoons H_2O(l)$$

Since there is no change in mass of ice and water the number of molecules going from ice into water is equal to the number of molecules of water going into ice. Thus, at equilibrium,

Rate of melting = Rate of freezing.

Liquid-Vapour Equilibrium

In order to illustrate the liquid-vapour equilibrium, let us consider evaporation of water in a closed vessel. When a small amount of water is taken in an evacuated vessel at room temperature it starts evaporating. A pressure is built up gradually within the vessel due to the formation of water vapours. This process continues for some time as indicated by the *gradually increasing pressure* recorded on the manometer attached to the vessel (Fig. 7.1).

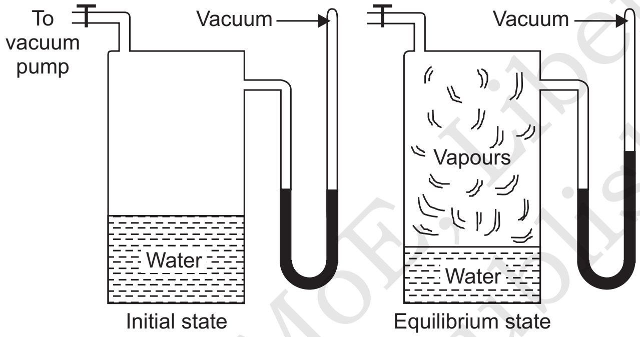


Fig. 7.1. Evaporation of water in a closed vessel.

After some time it is observed that *pressure becomes constant* indicating that no more water is evaporating, although liquid water is still present in the vessel. This indicates that a *state of equilibrium has been attained* between water and water vapour.

$$H_2O(l) \rightleftharpoons H_2O(g).$$

Equilibrium from Molecular Point of View

Now let us examine this equilibrium state from **molecular point of view.** In the evaporation of water in a closed evacuated vessel, at first the pressure inside the vessel increases. As the number of molecules in the gas phase increases the molecules of water in gas phase may strike the liquid surface and may be captured by the liquid. This process is called **condensation** and it acts in a direction opposite to evaporation. The rate of condensation is less than rate of evaporation in the beginning (Fig. 7.2) but with increase in population of molecules in gas phase the rate of condensation continues to increase and eventually the two rates become equal. At this state the equilibrium is said to be established. Thus, *at equilibrium the number of molecules entering the gas phase at any time is equal to the number of molecules returning to the liquid* *phase i.e., evaporation and condensation occur at the same rate.* Thus, at equilibrium,

Rate of evaporation = Rate of condensation.

The pressure exerted by the vapours in equilibrium with the liquid at a particular temperature is called the equilibrium vapour pressure or just vapour pressure of the liquid.

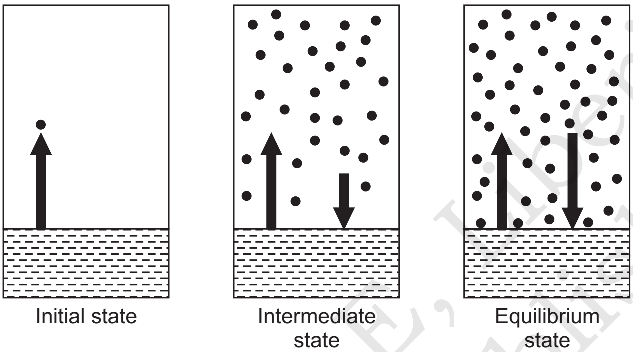


Fig. 7.2. Equilibrium state in evaporation: a dynamic balance between evaporation and condensation.

The vapour pressure of a liquid is constant at a given temperature. It does not depend upon the amount of the liquid or size of the vessel.

The vapour pressure of a liquid increases with increase in temperature. The vapour pressure of a liquid also depends on nature of the liquid. A liquid having weaker interparticle forces has higher vapour pressure. For example, acetone has higher vapour pressure than water. A liquid having greater vapour pressure is more volatile.

A liquid having greater vapour pressure has lower boiling point because for such a liquid vapour pressure becomes equal to atmospheric pressure at lower temperature. For example, consider the two liquids, water and ethanol. Vapour pressures of water and ethanol at 293 K are 2.34 kPa and 5.85 kPa respectively. This indicates that ethanol is more volatile than water. Water will have higher boiling point than ethanol because it has lower vapour pressure. Vapour pressure of water will become equal to atmospheric pressure at higher temperature.

It may be emphasized that **the equilibrium between the vapours and the liquid is attained only in a closed vessel.** If the vessel is open, the vapours leave the vessel and get dispersed. As a result, the rate of condensation can never become equal to the rate of evaporation.

Dissolution of Solids in Liquids

We know that it is not possible to dissolve just any amount of a solute in a given amount of solvent. **For example**, when we add sugar to water, the crystals of sugar keep on going into solution in the beginning. But after some time no more of sugar dissolves.

A solution in which no more solute can be dissolved is called a saturated solution. The amount of solute required to prepare a saturated solution in a given quantity of solvent is known as solubility of the solute at a particular temperature.

The saturated solution corresponds to the *state of equilibrium*. Now let us see how equilibrium is established in this case. When we add sugar crystals to water, molecular vibration tends to dislodge molecules from the surface of the crystals. The molecules of sugar which go into solution are free to move through the water. In the beginning, the rate at which molecules leave the crystal is much greater than the rate of their return. As the number of molecules in solution increases, the rate at which molecules return to the crystal also increases. Soon a balance between the two rates *i.e.*, the rate of dissolution and the rate of precipitation, is established and this corresponds to the state of equilibrium. Thus, in a saturated solution, a dynamic equilibrium exists between the molecules of sugar in the solid state and the molecules of sugar in the solution.

$$\text{Sugar } (\textit{in solution}) \rightleftharpoons \text{Sugar } (\textit{solid})$$

The **dynamic nature of equilibrium** can be demonstrated by adding radioactive sugar into a saturated solution of non-radioactive sugar (Fig. 7.3). It is observed that the solution and the rest of the non-radioactive sugar also becomes radioactive. This shows that even at equilibrium, the processes of dissolution and precipitation are taking place. This means that equilibrium is dynamic in nature. Thus, at equilibrium,

Rate of dissolution = Rate of precipitation.

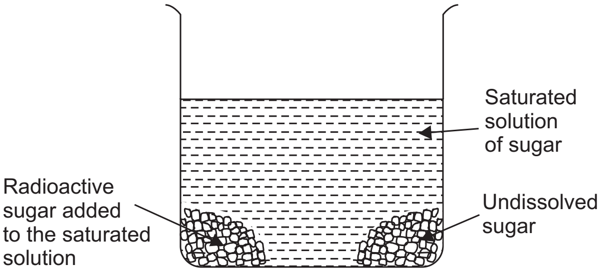


Fig. 7.3. Demonstration of dynamic nature of physical equilibrium.

Solubility of a solid in any liquid depends upon temperature. Pressure does not have any significant effect on the solubilities of solid in liquids.

Dissolution of Gases in Liquids

We know that when a **soda water** bottle is opened, the carbon dioxide dissolved in it fizzes out rapidly. At a given pressure, there is an equilibrium between the molecules of the carbon dioxide (solute) in gaseous state and the molecules dissolved in the liquid. This may be expressed as:

$$CO_2\ (gas) \rightleftharpoons CO_2\ (in\ solution)$$

Effect of pressure on the solubility of a gas in a liquid is given by **Henry's Law.** This law states that:

The mass of a gas dissolved in a given mass of a solvent, at a given temperature, is directly proportional to the pressure of the gas above the solvent.

$$m \propto p$$
$$m = kp$$

Solid-Vapour Equilibrium

In case of a solid which undergoes sublimation at room temperature, a solid-vapour equilibrium exists when such a solid is enclosed in a closed vessel. For example, when solid iodine crystals are placed in a closed vessel, it is observed that the vessel gets filled up with violet vapours of iodine. The intensity of colour increases for sometime and then becomes constant. At this stage vapours of iodine are in dynamic equilibrium with solid iodine. The equilibrium may be represented as:

$$I_2\ (solid) \rightleftharpoons I_2\ (vapour)$$

or

$$I_2\ (s) \rightleftharpoons I_2\ (g)$$

Some more examples showing solid-vapour equilibrium are,

$$\text{Naphthalene}\ (solid) \rightleftharpoons \text{Naphthalene}\ (vapour)$$
$$\text{Camphor}\ (solid) \rightleftharpoons \text{Camphor}\ (vapour)$$
$$NH_4Cl\ (solid) \rightleftharpoons NH_4Cl\ (vapour)$$

General Characteristics of Equilibria Involving Physical Processes

In the physical equilibria discussed above, it may be noted that:

1. In the case of *liquid* $\rightleftharpoons$ *gas equilibrium,* the vapour pressure of the liquid is constant at equilibrium at a particular temperature. **For example**, for the equilibrium,

$$H_2O(l) \rightleftharpoons H_2O(g)$$

vapour pressure of water, p_{H_2O}, is constant at a given temperature.

2. For *solid* $\rightleftharpoons$ *liquid equilibrium*, there is only one temperature at which the two phases can co-exist at a particular pressure. This temperature is known as melting point. For example, the equilibrium

$$H_2O(s) \rightleftharpoons H_2O(l)$$

or

$$\text{Ice} \rightleftharpoons \text{Water}$$

exists at 273 K at 1.0 atm pressure. At the melting point the masses of the two phases remain constant provided no exchange of heat takes place between the system and the surroundings.

3. For dissolution of solids in liquids, the solubility (concentration of solid solute in solution) is constant at a given temperature.

For example, for the equilibrium,

$$\text{Sugar}(s) \rightleftharpoons \text{Sugar}(aq)$$

concentration of sugar in solution is constant at a given temperature.

4. For dissolution of gases in liquids, the concentration of a gas in liquid, at a given temperature, is directly proportional to the pressure of the gas over the liquid. For example, for the equilibrium,

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

$$CO_2(aq) \propto p_{CO_2} \quad \text{or} \quad [CO_2(g)]$$

or $\dfrac{[CO_2(aq)]}{[CO_2(g)]}$ is constant at a given temperature.

From the physical equilibria discussed above the **general characteristics of the equilibria involving physical processes** may be stated as follows:

1. At equilibrium, the measurable properties of the system become constant.

   For example, in case of evaporation of water, the vapour pressure of liquid becomes constant at equilibrium.

2. At equilibrium, there is a dynamic balance between the two opposite processes.

   For example, in case of evaporation of water, the rate of evaporation is equal to the rate of condensation at equilibrium.

3. The equilibrium is attained only in a system which cannot gain matter from the surroundings or lose matter to the surroundings (*i.e.*, a closed system).

For example, if evaporation of water takes in an open vessel, no equilibrium is attained and whole of the water evaporates.

4. When equilibrium is attained, there exists an expression involving the concentration of substances involved in equilibrium which reaches a constant value at a given temperature.

   For example, for the dissolution of CO_2 in water, $\frac{[CO_2(aq)]}{[CO_2(g)]}$ is constant at a given temperature. Similarly, for the dissolution of sugar in water, concentration of sugar in water (solubility of sugar) is constant at a given temperature.

5. The magnitude of the constant value of the concentration-related expression indicates the extent to which the process proceeds before reaching equilibrium.

   For example, for the dissolution of CO_2 in water greater the value of $\frac{[CO_2(aq)]}{[CO_2(g)]}$, greater is the extent to which CO_2 dissolves in water.

Equilibrium in Chemical Processes

When a piece of sodium is dropped into water, a violent reaction occurs resulting in the formation of sodium hydroxide and hydrogen gas.

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

However, it is not possible to carry out the reverse reaction under any known experimental conditions, *i.e.*, reduction of aqueous sodium hydroxide by hydrogen to form sodium and water cannot be achieved.

The reactions in which the products do not react under any condition to give back reactants are called irreversible reactions.

On the other hand, let us consider the reaction between metallic iron and steam. Again, hydrogen gas is formed but at much slower rate than in the case of sodium. The iron is converted into iron oxide Fe_3O_4.

$$3Fe(s) + 4H_2O(g) \longrightarrow Fe_3O_4(s) + 4H_2(g) \qquad ...(7.1)$$

If this reaction is carried out in an open vessel, then the hydrogen gas escapes and the reaction proceeds to completion provided the sufficient amount of steam is supplied. The reverse of this reaction, *i.e.*, reduction of iron oxide (Fe_3O_4) to iron by hydrogen gas can also be achieved rather easily in the laboratory.

$$Fe_3O_4(s) + 4H_2(g) \longrightarrow 3Fe(s) + 4H_2O(g) \qquad ...(7.2)$$

To carry out this reaction hydrogen gas is passed over heated iron oxide. Again, if this reaction is carried out in an open vessel the whole of Fe_3O_4 is reduced to iron because one of the products, *i.e.*, water escapes as steam. Now if we combine the reactants of equation (7.1) in stoichiometric ratio in a *closed vessel* at constant temperature, Fe_3O_4 and hydrogen are formed. As the products accumulate, occasional collisions of these species are effective and the reduction of Fe_3O_4 begins to occur. Eventually, a stage is reached at which no further net change occurs. This state is called *equilibrium state.*

The reactions in which products under suitable conditions react to give back reactants are called reversible reactions.

A reversible reaction is represented by putting two arrows pointing in opposite directions between the formulae of the reactants and the products as shown below:

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

Some more examples of reversible reactions are

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Since, in a reversible reaction both forward as well as backward reactions are feasible, therefore, if such a reaction is carried in a closed vessel then both the reactions occur simultaneously and before whole of the reactants are converted into products a state of equilibrium is established. In the state of equilibrium, the reaction appears to be stopped even though the reactants are still present. Therefore, reversible reactions do not proceed to completion. On the other hand, irreversible reactions are feasible only in one direction and hence, go to completion.

Let us illustrate the state of equilibrium in some reversible processes and see how it is recognised.

1. Decomposition of Calcium Carbonate. Calcium carbonate when heated to 1073 K in a closed evacuated vessel, starts decomposing to yield calcium oxide and carbon dioxide gas. Carbon dioxide builds up pressure within the vessel which can be recorded on a manometer, as shown in Fig. 7.4. The pressure goes on increasing as the reaction proceeds and *finally becomes constant* and remains so *as long as the* *temperature remains constant.* It appears as if the reaction has come to a stop although $CaCO_3$ is still present. This indicates that the system has attained the equilibrium state.

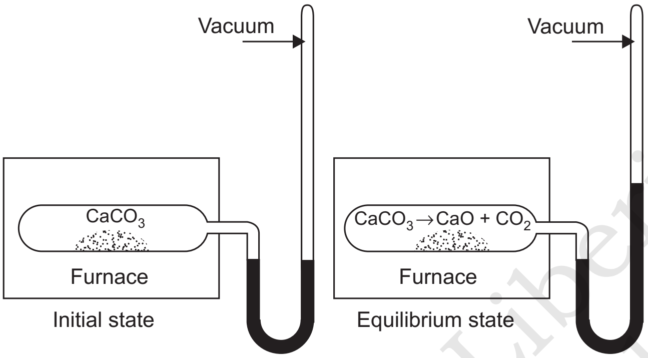


Fig. 7.4. Attainment of equilibrium in the thermal decomposition of $CaCO_3$.

2. Reaction between Hydrogen and Iodine. When hydrogen and iodine are heated in a closed vessel at 717 K, they react to form hydrogen iodide. The colour of the reaction mixture is deep violet in the beginning due to the presence of iodine. As the reaction progresses the intensity of colour decreases due to the formation of hydrogen iodide which is colourless.

After sometime, it is observed that *intensity of colour becomes constant* indicating that the reaction has stopped although hydrogen and iodine are still present. Actually the system acquires a state of equilibrium.

Concept of Equilibrium State

From the study of the reversible processes discussed earlier, it may be noticed that when such a process is carried out in a closed container, it appears to stop after sometime although the reactants are not completely consumed. This state of the system is referred to as *state of equilibrium.* The attainment of equilibrium is recognised by constancy of *certain observable properties.* **For example**, in the case of dissociation of calcium carbonate, we recognised the attainment of equilibrium by observing that pressure of carbon dioxide had become constant. In this case, *attainment of equilibrium has been recognised by observing constancy of pressure*. In case of reaction between hydrogen and iodine the attainment of equilibrium is recognised by observing *constancy of intensity of colour* of the reaction mixture.

Sometimes, concentration of one of the reactants or products is measured to recognise the state of equilibrium. Thus:

The state of equilibrium is a state in which the measurable properties of the system do not undergo any noticeable change under a particular set of conditions.

EXPERIMENT 1

Aim: Perform an experiment to demonstrate reversible and irreversible chemical reactions

Theory:

$$\underset{\text{Reactant}}{PCl_5} \longrightarrow \underset{\text{Product}}{\underline{PCl_3 + Cl_2}}$$

$$\underset{\text{Products}}{\underline{PCl_3 + Cl_2}} \longrightarrow \underset{\text{Reactants}}{\underline{PCl_5}}$$

Reversible reactions are those reactions where products react again under suitable conditions to for reactants again. For example, if we heat PCl_5 it decomposes to PCl_3 and Cl_2. If PCl_3 and Cl_2 are given suitable conditions of temperature and pressure, they react to form PCl_5 again. such reactions are reversible reactions.

If products are not able to form reactants again the reaction is called irreversible.

Requirements: Beaker, Water, Common salt (NaCl), Paper, Raw egg, Burner, Stirrer, Wire gauge.

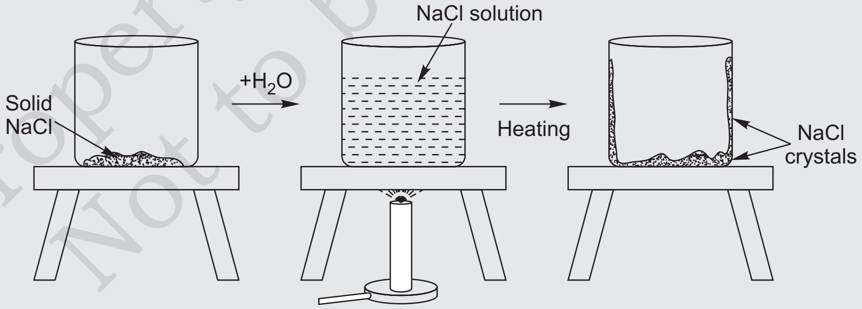


Fig. 7.5. Reversible reaction showing solid NaCl → NaCl solution → NaCl Crystals evaporation

Procedure: Reversible Reaction:

1. Take a beaker and pour 100 ml of water in it.
2. Now add 35 gm of common salt and dissolve it with a stirrer.
3. Heat the aqueous solution of NaCl to evaporate water.

4. We get crystals of NaCl again.
5. Hence this is a reversible reaction.

Other examples:

1. Same experiment can be done with copper sulphate solution
2. Freezing of water to ice, then melting of ice water again.
3. $2KClO_3 \rightleftharpoons 2KCl + 3O_2$. This is a reversible reaction.
4. Take copper sulphate in a test tube, heat the test tube. the blue copper sulphate looses water and becomes white. Now left the test tube cool again. The anhydrous copper sulphate absorbs water vapours from the air and turns blue again.

Irreversible reaction:

1. Here reactants change to product permanently and do not give back the reactants again.
2. Take flour, egg, and sugar. Mix them and add water to it. Now take it in an oven. It becomes a cake. This cake can not be changed again to initial ingredients (Reactants) *e.g.* flour, egg, sugar and water.

Other Characteristics of Chemical Equilibrium

It has already been discussed that chemical equilibrium is dynamic in nature. In addition to this, other characteristics of chemical equilibrium are:

1. ***The observable properties of the system, such as pressure, colour, concentration, etc., become constant at equilibrium and remain unchanged thereafter.*** **For example**, for the reaction between hydrogen and iodine to form hydrogen iodide, the colour of the reaction mixture becomes constant at equilibrium.

2. ***The equilibrium can be approached from either direction.*** This can be proved with the help of a very simple experiment of the equilibrium between dinitrogen tetraoxide, N_2O_4 (colourless gas) and nitrogen dioxide, NO_2 (a reddish brown gas).

$$\underset{\text{Colourless}}{N_2O_4(g)} \rightleftharpoons \underset{\text{Reddish brown}}{2NO_2(g)}$$

It is observed that at ordinary temperature, say 298 K, two gases exist as equilibrium mixture having pale brown colour. At very low temperature (273 K), N_2O_4 is stable and exists almost as pure N_2O_4 (colourless gas). When temperature is increased, it decomposes to NO_2. At 373 K, it decomposes almost completely to NO_2, which is dark brown in colour.

Let us take two identical flasks A and B. Fill both of them with nitrogen dioxide and seal them. Place the flask A in an ice bath and the flask B in boiling water as shown in Fig. 7.6.

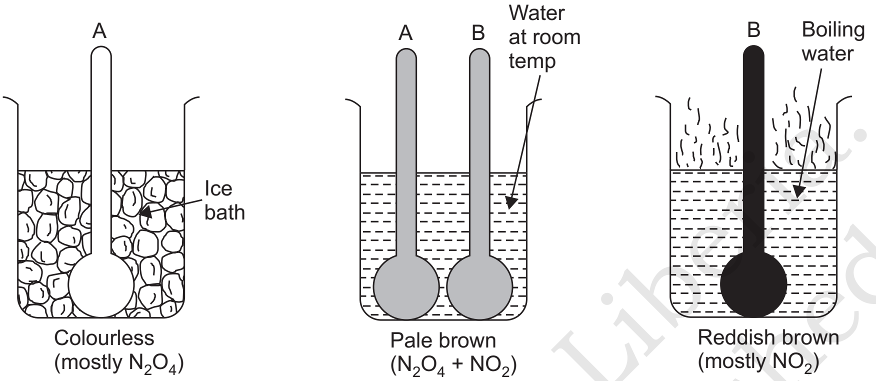


Fig. 7.6. Study of the equilibrium, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.

The gas in a flask A becomes almost colourless and consists of mostly N_2O_4 molecules. On the other hand, the gas in flask B becomes reddish brown and consists of mainly NO_2 molecules.

Now transfer both the flasks into a bath maintained at 298 K and observe the change in colour. The colour of the gas in flask A starts changing into brown colour indicating the gradual conversion of N_2O_4 into NO_2.

$$\underset{\text{Colourless}}{N_2O_4(g)} \longrightarrow \underset{\text{Reddish brown}}{2NO_2(g)} \qquad \text{(Flask A)}$$

On the other hand, the reddish brown colour in flask B begins to fade and becomes pale brown indicating the gradual decomposition of N_2O_4. This may be represented as:

$$\underset{\text{Reddish brown}}{2NO_2(g)} \longrightarrow \underset{\text{Colourless}}{N_2O_4(g)} \qquad \text{(Flask B)}$$

After some time, when both the flasks attain the temperature of the bath, the colour in the two flasks becomes identical and no further change in colour occurs. This constancy of colour indicates that equilibrium has been attained in both the flasks and both contain mixture of NO_2 and N_2O_4 of the same composition.

This experiment clearly demonstrates that the equilibrium can be approached from either direction.

Similarly, let us consider the reaction between hydrogen and iodine to form hydrogen iodide.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Suppose 1 mol each of H_2 and I_2 is taken in a closed container and heated to 730 K. The forward reaction starts. As a result concentrations of H_2 and I_2 start decreasing while that of HI starts increasing. Finally, all the concentrations become constant and the reaction attains equilibrium. The colour of the reaction mixture becomes constant at this stage. Now take 2 mol of HI in the closed container of the same size and heat to 730 K. The backward reaction starts taking place. As a result, concentration of HI starts decreasing while that of H_2 and I_2 start increasing and finally become constant when the equilibrium is attained.

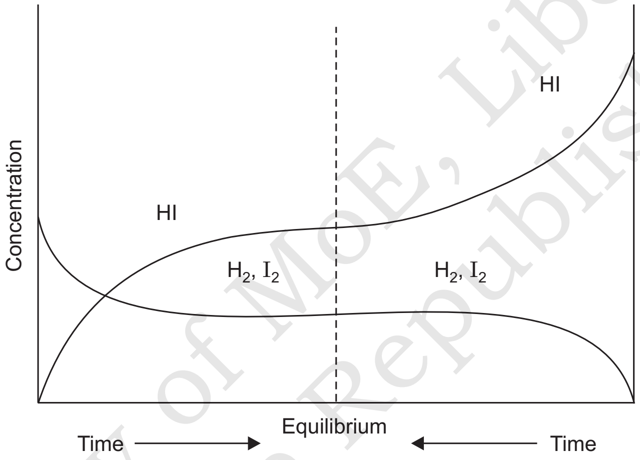


Fig. 7.7. Chemical equilibrium can be attained from either direction.

If we compare the intensity of purple colour in the two containers we find that it is identical. It indicates that same equilibrium is attained in both cases, in one case starting with H_2 and I_2 and in the other case starting with HI. It shows that equilibrium can be attained from either direction.

3. ***The equilibrium can be attained only if the system is closed.*** For the establishment of equilibrium, it is necessary that the system should be close one. If the system is not closed, the products may escape from the container and, therefore, backward reaction may not take place.

4. ***A catalyst does not alter the equilibrium point.*** In a reversible reaction, catalyst increases the rate of forward as well as backward reaction to the same extent. Therefore, equilibrium point is not altered. However, the equilibrium is attained earlier in the presence of a catalyst.

EXPERIMENT 2

Aim: Demonstrate an experiment by heating $Pb(NO_3)_2$ and dinitrogen tetra oxide to explain the variation of K_c/K_p.

$$N_2O_4 \rightleftharpoons NO_2$$

Theory: The $K_c = \frac{[CNO_2]^1}{[N_2O_4]^1}$ when temperature increases number of molecules/moles of NO_2 increase as a result K_c will increase.

Same way $K_p = \frac{[PNO_2]^1}{[PN_2O_4]^1}$ one increasing of temperature pressure created by NO_2 molecules will increase hence K_p will increase on increase of temperature.

Requirements: Beaker, ice, water, flask, N_2O_4, burner, tripod stand.

Procedure:

1. Take a flask containing N_2O_4 (dinitrogen)tetra oxide at low temperature (273 K). The N_2O_4 gas is colourless.
2. Now put the flask in another beaker at 298 K. At this temperature, the flask contains a mixture of N_2O_4 and NO_2. Hence the flask shows a pale brown colour.
3. Now heat the flask upto 373 K. At this temperature the whole of N_2O_4 changes to NO_2 resulting in change of colour to pure brown as NO_2 is brown in colour.
4. Hence it is observed that on increasing the temperature both K_c and K_p will increase.

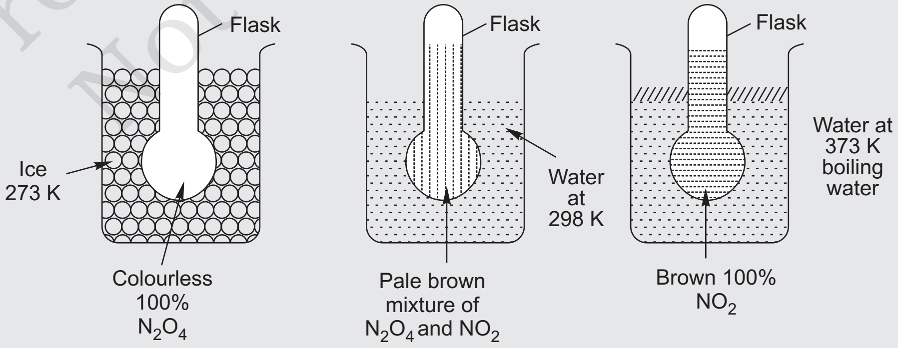


Fig. 7.8

Observation:

1. At 273 K (0°C) the flask contains only N_2O_4 which is colourless. The formation of NO_2.
2. At 298 K (20°C) the flask contains a mixture of N_2O_4 and NO_2 resulting in pale brown colour in the flask.
3. At 373 K (100°C) whole of N_2O_4 changes to NO_2 showing 100% brown colour in the brown.

Result: K_p and K_c increases with increase in temperature.

7.2. LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

Law of Mass Action

On the basis of observations of many equilibrium reactions, two Norwegian chemists Cato Guldberg and Peter Waage (1864) suggested a qualitative relationship between rates of reaction and the concentration of the reacting species. The relationship is known as ***Law of Mass Action.*** This law states that:

At constant temperature the rate of a chemical reaction is directly proportional to the product of the molar concentrations of reacting species with each concentration term raised to the power equal to the numerical co-efficient of that species in the chemical equation.

Let us apply mass action to a hypothetical reaction.

$$A + B \longrightarrow \text{Products}$$

According to law of mass action,

Rate of reaction, $r \propto [A][B] = k\,[A][B]$

where [A] and [B] are the molar concentrations of the reactants A and B respectively, k is a constant of proportionality called rate constant.

For any general reaction,

$$aA + bB \longrightarrow \text{Products}$$

The law of mass action may be written as

$$\text{Rate} = k\,[A]^a[B]^b$$

Application of Law of Mass Action to Chemical Equilibrium

By applying law of mass action to a reversible reaction, at equilibrium, it is possible to derive a simple mathematical expression known as **law of chemical equilibrium.**

Let us consider a simple reversible reaction,

$$A + B \rightleftharpoons C + D$$

in which an equilibrium exists between the reactants A and B and the products C and D. According to law of mass action:

Rate of forward reaction $\propto [A][B]$

$$= k_f [A][B]$$

where $\boldsymbol{k_f}$ is the rate constant for the forward reaction. [A] and [B] are molar concentrations of reactants A and B respectively.

Similarly, the rate of backward reaction

$$\propto [C][D]$$

$$= k_b[C][D]$$

where $\boldsymbol{k_b}$ is the rate constant for the backward reaction and [C] and [D] are molar concentrations of products C and D respectively.

At equilibrium the rates of two opposing reactions become equal. Therefore, at equilibrium,

Rate of forward reaction = Rate of backward reaction

$$\therefore \quad k_f [A][B] = k_b[C][D]$$

or

$$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

Since k_f and k_b are constants, therefore, the ratio k_f/k_b is also constant and is represented by K_c.

$$K_c = \frac{k_f}{k_b} = \frac{[C][D]}{[A][B]} \quad ...(7.3)$$

The constant K_c is called **equilibrium constant.** The subscript '*c*' indicates that K_c is expressed in terms of concentrations (mol L^{-1}) of reactants and products. The concentrations in the expression 7.3 are the equilibrium concentrations.

For a general reaction of the type:

$$aA + bB \rightleftharpoons C + dD$$

The expression of equilibrium constant can be written as:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad ...(7.4)$$

The equilibrium constant, K_c, may be defined as the ratio of product of the equilibrium concentrations of the products to that of the reactants with each concentration term raised to the power equal to the stoichiometric co-efficient of the substance in the balanced chemical equation.

Equations (7.3) and (7.4) are the expressions for law of chemical equilibrium.

Law of chemical equilibrium may be stated as :

At a given temperature, the ratio of product of equilibrium concentrations of the products to that of the reactants with each concentration term raised to the power equal to the respective stoichiometric co-efficients in the balanced chemical has a constant value.

$$\text{The concentration ratio} = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

is called **concentration quotient** and is denoted by Q_c. According to law of chemical equilibrium,

$$Q_c = K_c \text{, at equilibrium.}$$

Equilibrium Constant in Gaseous Systems

If an equilibrium involves gaseous species, then the concentrations in the concentration quotient may be replaced by partial pressures because at a given temperature the partial pressure of a gaseous component is proportional to its concentration. If the above mentioned reaction has all the gaseous species, then

$$Q_p = \frac{[p_{\mathrm{C}}]^c[p_{\mathrm{D}}]^d}{[p_{\mathrm{A}}]^a[p_{\mathrm{B}}]^b} = K_p$$

The equilibrium constant, K_p, defined in terms of partial pressures is not the same as the equilibrium constant, K_c, defined in terms of concentrations.

7.3. RELATIONSHIP BETWEEN K_p AND K_c

K_p	K_p is the equilibrium constant in terms of partial pressure of gaseous reactants and products.
K_c	K_c is the equilibrium constant in terms of concentration of reactants and products.

For an ideal gas, $PV = nRT$

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

$$\therefore \quad p_{\mathrm{A}} = C_{\mathrm{A}}RT$$

$$p_{\mathrm{B}} = C_{\mathrm{B}}RT$$

$$p_C = C_C RT$$

$$p_D = C_D RT$$

$$K_p = \frac{[C_C RT]^c [C_D RT]^d}{[C_A RT]^a [C_B RT]^b}$$

$$= \frac{[C_C]^c [C_D]^d}{[C_A]^a [C_B]^b} \cdot (RT)^{(c+d)-(a+b)}$$

$$\mathbf{K_p = K_c (RT)^{\Delta n}}$$

where $$\Delta n = \begin{pmatrix}\text{Sum of the exponents in}\\ \text{the numerator of } Q_c\end{pmatrix} - \begin{pmatrix}\text{Sum of the exponents in}\\ \text{the denominator of } Q_c\end{pmatrix}$$

For the reactions such as $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ and $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ for which $\Delta n = 0$, the value of $K_p = K_c$. However, this is not true for all equilibria.

It is necessary that while calculating the value of K_p, pressures should be expressed in bar because standard state is 1 bar. The value of R in the relation $K_p = K_c\,(RT)^{\Delta n}$ is 0.083 bar litre/mol K.

Homogeneous and Heterogeneous Equilibria

The equilibrium in which all the substances are present in the same phase is known as homogeneous equilibrium.

For example,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

The equilibrium in which the substances involved are present in different phases is called heterogeneous equilibrium.

For example,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$H_2O(l) \rightleftharpoons H_2O(g)$$

$$AgCl(s) + (aq) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$Fe(OH)_3(s) + (aq) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$$

Characteristics of Equilibrium Constant (K)

Some important characteristics of equilibrium constant are as follows:

1. *The equilibrium constant has a definite value for every chemical reaction at a particular temperature. The value of equilibrium constant is independent of initial concentrations of the reacting species.*

For example, the equilibrium constant for the reaction,

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeSCN^{2+}(aq),$$

at 298 K is

$$K = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^{-}]} = 138.0$$

Whatever may be the initial concentrations of the reactants, Fe^{3+} and SCN^{-} ions, the value of K comes out to be 138.0 at 298 K.

2. *The value of equilibrium constant, K changes with change in temperature.*

The value of K may increase or decrease with increase in temperature depending upon whether the reaction is endothermic or exothermic in nature. The values of K_p at different temperatures for an endothermic reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$) and for an exothermic reaction ($N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$) are given in Table 7.1.

Table 7.1. Variation of K_p with Temperature for Some Reactions

Reactions	*Temperature (K)*	K_p
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	298	0.98
	400	47.9
	500	1700
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	298	6.8×10^5
	400	41
	500	3.6×10^{-2}

3. *For a reversible reaction, the equilibrium constant for the backward reaction is inverse of the equilibrium constant for the forward reaction.*

For example, equilibrium constant, K, for the reaction of combination between hydrogen and iodine at 717 K is 48.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g);\ K = \frac{[HI]^2}{[H_2][I_2]} = 48$$

The equilibrium constant for the decomposition of hydrogen iodide at the same temperature is the inverse of the above equilibrium constant.

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

$$K_1 = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{K} = \frac{1}{48}$$

4. *The equilibrium constant is independent of the presence of catalyst.*

This is so because the catalyst does not affect the equilibrium state, at a particular temperature.

5. *If the equilibrium constant is expressed in terms of concentration, it has different units for different reactions.*

This can be illustrated by following examples:

(*a*) If the number of moles of the product is same as the number of moles of reactants, K has no units (*i.e.*, it is dimensionless). Thus, in the reaction between hydrogen and iodine to form hydrogen iodide, K has no units as illustrated below:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(\text{mol L}^{-1})^2}{(\text{mol L}^{-1})(\text{mol L}^{-1})}$$

(*b*) If the number of moles of the products is *not the same as* that of reactants, K will have certain units depending upon the change in the number of moles. Thus, for the reaction between nitrogen and hydrogen to form ammonia, K would have the units $L^2\ mol^{-2}$ as shown below:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(\text{mol L}^{-1})^2}{(\text{mol L}^{-1})(\text{mol L}^{-1})^3}$$

$$= \frac{1}{(\text{mol L}^{-1})^2}$$

Thus, K will have the units $L^2\ mol^{-2}$.

Similarly, K_p for this reaction has units bar^{-2}.

Equilibrium Constants for a General Reaction and its Multiples

It may be noted that the value of K changes if the co-efficients of various species in the equation representing equilibrium are multiplied by some number. For example, equilibrium constant for the equation

$$H_2 + I_2 \rightleftharpoons 2HI$$

$$K_1 = \frac{[HI]^2}{[H_2][I_2]} = 49 \text{ at } 711 \text{ K}$$

is different from the equilibrium constant for the equation

$$\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightleftharpoons HI$$

$$K_2 = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} = \sqrt{K_1} = 7 \text{ at } 711 \text{ K}$$

In general, if K_1 is the equilibrium constant for a particular equation then equilibrium constant K_2 for some new equation which is obtained by multiplying the first equation by n is given by the following relation:

$$K_2 = (K_1)^n$$

Thus, when the equation for an equilibrium is multiplied by a factor, the equilibrium constant must be raised to the power equal to the factor.

Table 7.2. Relations Between Equilibrium Constants for a General Reaction and its Multiples

Chemical Equation	*Equilibrium Constant*
$aA + bB \rightleftharpoons cC + dD$	K_c
$cC + dD \rightleftharpoons aA + bB$	$K_c' = (1/K_c)$
$naA + nbB \rightleftharpoons ncC + ndD$	$K_c'' = (K_c)^n$

6. *When addition of two equilibria leads to another equilibrium then, the product of their equilibrium constants gives the equilibrium constant of the resultant equilibrium.*

For example, consider the following three equilibria:

(*i*) $N_2 + O_2 \rightleftharpoons 2NO; \quad K_1$

(*ii*) $2NO + O_2 \rightleftharpoons 2NO_2; \quad K_2$

(*iii*) $N_2 + 2O_2 \rightleftharpoons 2NO_2; \quad K_3$

Now, addition of (*i*) and (*ii*) gives (*iii*), then

$$K_1 \times K_2 = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$= \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3$$

Thus, $\mathbf{K_1 \times K_2 = K_3}$.

Temperature Dependence of Equilibrium Constant

At equilibrium the rates of forward and backward reactions are equal. On increasing the temperature, the rates of reactions, in general, increase. However, the extents of increase in rates of forward and backward reactions are different. This is because of different values of activation energies for forward and backward reactions. In other words, the values of k_f and k_b will change with the increase in temperature but to a different extent. Consequently, the ratio k_f / k_b *i.e.*, equilibrium constant will change with the rise in temperature. Some important facts to be noted are :

- *K for endothermic reaction increases with rise in temperature.*
- *K for exothermic reaction decreases with rise in temperature.*

If K_1 and K_2 are equilibrium constants of the reactions at two temperatures T_1 and T_2 and ΔH is the enthalpy change of the reaction, then

$$\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

7.4. APPLICATIONS OF EQUILIBRIUM CONSTANT

The knowledge of equilibrium constant helps us in

1. Predicting the extent of a reaction.
2. Predicting the direction in which the net reaction is taking place.
3. Calculation of equilibrium concentrations and equilibrium pressures.

1. Prediction of Extent of Reaction

The magnitude of equilibrium constant tells us about the extent to which the reactants are converted into the products before the equilibrium is attained.

Larger the value of K, greater is the extent to which the reactants are converted into the products. On the other hand, if the value of K is small it indicates that equilibrium is mainly in favour of reactants and that only a small fraction of the reactants is converted into products.

We can make the following generalisations concerning the composition of equilibrium mixtures:

- If $K_c > 10^3$, products predominate over reactants. If K_c is very large, the reaction proceeds nearly to completion.
- If $K_c < 10^{-3}$, reactants predominate over products. If K_c is very small, the reaction hardly proceeds.
- If K_c is in the range of 10^{-3} to 10^3, appreciable concentrations of both reactants and products are present.
- For example, consider the following reaction:

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$$

$$K = 2.2 \times 10^{22} \text{ at } 1000 \text{ K}$$

K for this reaction is given by the expression:

$$K = \frac{[CO_2]^2}{[CO]^2\,[O_2]}$$

Large value of K in this indicates that at equilibrium, concentration of CO_2 is quite high. In other words, this indicates that the reaction between CO and O_2 to form CO_2 is almost complete under the given conditions.

Similarly, the value of K is very large for the reaction:

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

$$K = 4.0 \times 10^{31} \text{ at } 300 \text{ K.}$$

This indicates that the formation of HCl from H_2 and Cl_2 goes to almost completion at 300 K.

Let us now consider another reaction:

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

$$K = 4.1 \times 10^{-48} \text{ at } 500 \text{ K}$$

The expression for equilibrium constant of this reaction is

$$K = \frac{[H_2]^2[O_2]}{[H_2O]^2}$$

Since the value of K in this case is very small, it indicates that at equilibrium, the concentrations of H_2 and O_2 are very small. In other words, under the given conditions only a small fraction of H_2O dissociates into H_2 and O_2. Now let us consider some reactions in which the value of K_c is neither too small nor too large. In such reactions there are appreciable concentrations of both reactants and products at equilibrium. The two such equilibria are given as follows:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K_c = 57 \text{ at } 700 \text{ K}$$

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$K_c = 4.64 \times 10^{-3} \text{ at } 298 \text{ K}$$

Relationship between K_c and the extent of reaction is illustrated in Fig. 7.9.

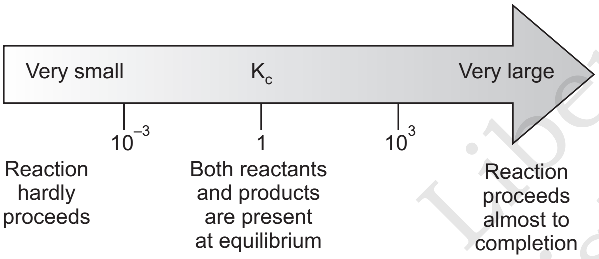


Fig. 7.9. Relationship between K_c and the extent of reaction.

The value of K also gives us an idea about the relative stabilities of reactants and products. If value of K is large, the products are more stable whereas if K is small, the reactants are more stable.

2. Predicting the Direction of the Net Reaction

From the knowledge of equilibrium constant, it is possible to predict the direction in which the net reaction is taking place at a given concentrations or partial pressures of reactions and products.

From the given concentrations, the concentration quotient Q_c for the reaction is calculated. By comparing the value of Q_c with the equilibrium constant, K_c the direction of reaction can be predicted.

- If $Q_c > K_c$, the net reaction is taking place in backward direction *i.e.*, direction of reactants.
- If $Q_c < K_c$, the net reaction is taking place in forward direction *i.e.*, direction of products.
- If $Q_c = K_c$, the reaction is at equilibrium *i.e.*, no net reaction is taking place.

For example, for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the value of K_c at 717 K is 48. If at a particular instant, the concentrations of H_2, I_2 and HI are 0.2 mol L^{-1}, 0.3 mol L^{-1} and 0.6 mol L^{-1} respectively then the concentration quotient of the reaction at this stage would be

$$Q_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.6)^2}{(0.2)(0.3)} = 6$$

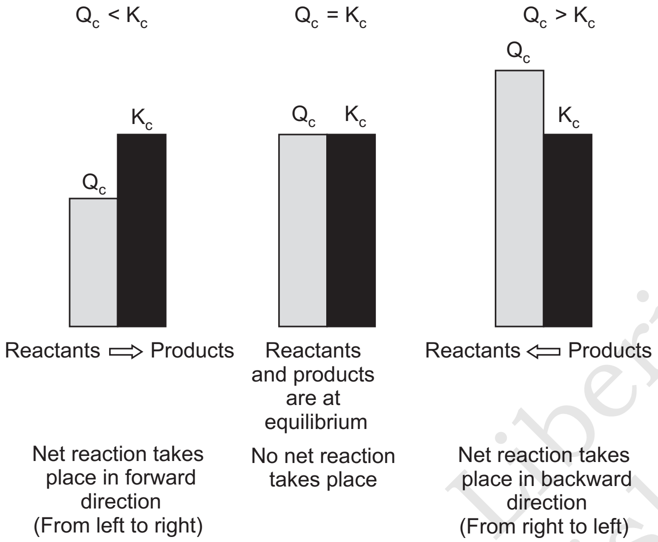


Fig. 7.10. Relation between Q_c, K_c and the direction of net reaction.

At this stage Q_c is less than K_c, therefore the net reaction will occur in the forward direction, resulting in the formation of more of HI.

3. Calculation of Equilibrium Concentrations and Equilibrium Pressures

If the equilibrium concentrations of various reactants and products are known in a reaction, the equilibrium constant can be calculated. On the other hand, if the equilibrium constant is known, then equilibrium concentration can be calculated.

Steps for Calculating Equilibrium Concentrations and Equilibrium Pressures

Step I. Write chemical equation for the equilibrium.

Step II. Write equilibrium constant expression for the reaction.

Step III. Express all unknown concentrations or partial pressures in terms of a single variable x.

Step IV. Substitute the equilibrium concentrations or partial pressures (in terms of x) in the equilibrium constant expression.

Step V. Solve the equation for x.

Step VI. Substitute the value obtained for x in the expressions in step III to calculate equilibrium concentrations or equilibrium partial pressures.

7.5. FACTORS AFFECTING EQUILIBRIA—Le Chatelier's Principle

Le Chatelier, a French chemist, made a generalization to explain the effect of changes in concentration, temperature or pressure on the state of system in equilibrium. The generalization is known as **Le Chatelier's Principle.** It states that:

If a system in equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect of the change.

Let us consider the effect of these variables in the light of Le Chatelier's principle, in the case of a few well known equilibria.

Effect of Change of Concentration

According to Le Chatelier's principle, when the concentration of one of the substance in a system at equilibrium is increased, then the equilibrium will shift so as to use up the substance added. Suppose at equilibrium one of the reactants is added, the equilibrium will shift in the direction that consumes reactants, *i.e.*, the forward direction. In other words, more of the reactants would be converted into products. On the other hand, if one of the products is added, the equilibrium will shift in the backward direction because it consumes the products.

In order to understand the effect of change of concentration on equilibrium, let us consider the reaction,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

If H_2 is added to the reaction mixture at equilibrium, then the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a directions wherein H_2 is consumed, *i.e.*, more of H_2 and I_2 react to form HI and finally the equilibrium is re-established. Thus, addition of H_2 shifts the equilibrium in forward direction. In the new equilibrium mixture, the concentration of H_2 would be less than it was after addition of H_2 but more than what it was in the original equilibrium has been shown Fig. 7.11.

The same point can be understood in terms of the reaction quotient, Q_c.

$$Q_c = [HI]^2/[H_2]\,[I_2]$$

If concentration of H_2 is increased, the value of Q_c decreases and it is no longer equal to K_c. In order to attain new equilibrium, the reaction proceeds in forward direction resulting in decrease in concentrations of H_2 and I_2 and increase in concentration of HI. Finally, new equilibrium is attained.

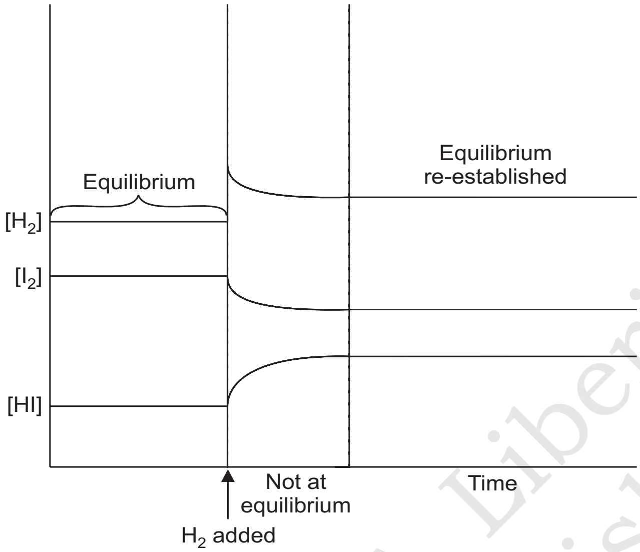


Fig. 7.11. Effect of addition of H_2 on change of concentration for the reactants and products in the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.

Similarly, we can say that removal of a product also favours the forward reaction and increases the concentration of the products. **For example**, in the manufacture of NH_3 by Haber's process, ammonia is liquefied and removed from the reaction mixture so that reaction keeps moving in forward direction. Similarly, in the large scale production of CaO, by calcination of lime stone ($CaCO_3$), CO_2 is continuously removed from the klin to shift the reaction in forward direction. Continuous removal of one of the products maintains Q_c at a value less than K_c and thus reaction keeps on proceeding in the forward direction.

The effect of concentration on equilibrium can be demonstrated with the help of the following reaction:

$$\underset{\text{(yellow)}}{Fe^{3+}(aq)} + \underset{\text{(colourless)}}{SCN^{-}(aq)} \rightleftharpoons \underset{\text{(deep red)}}{[FeSCN]^{2+}(aq)}$$

$$K_c = \frac{[Fe(SCN)^{2+}\ (aq)]}{[Fe^{3+}(aq)]\,[SCN^{-}\ (aq)]}$$

A reddish colour appears on adding 2 – 3 drops of 0.002 M potassium thiocynate solution to 5 mL of 0.2 M iron (III) nitrate solution due to the formation of $[Fe(SCN)]^{2+}$. The intensity of the red colour becomes constant when equilibrium is attained. This equilibrium can be shifted in either forward or backward directions depending on our choice of adding a reactant or a product.

Suppose, some ferric salt (say, ferric chloride) is added to this equilibrium. The colour of the solution deepens immediately showing that there is increase in the concentration of the coloured complexion $[FeSCN]^{2+}$. This change is in accordance with Le-Chatelier's principle. Addition of more of Fe^{3+} ions has resulted in increasing the concentration of the complex $[FeSCN]^{2+}$ ions. The change imposed on the system meant to raise the concentration of one of the *reactants* (Fe^{3+} ions) but it has resulted in raising the concentration of the *product.* Similarly, if some potassium thiocyanate is added at the equilibrium, the colour deepens again due to the formation of more of the $[FeSCN]^{2+}$ ions. Here again the addition of one of the *reactants* had led to the formation of more of the *products.*

The above equilibrium can be shifted in the backward direction by adding reagents that remove Fe^{3+} or SCN^- ions. For example, oxalic acid ($H_2C_2O_4$), reacts with Fe^{3+} ions to form the stable complex ion $[Fe(C_2O_4)_3]^{3-}$, thus decreasing the concentration of Fe^{3+} ions. In accordance with the Le Chatelier's principle, the decrease in the concentration of Fe^{3+} ions, leads to the decrease in concentration of $[FeSCN]^{2+}$ ions which is indicated by the fact that colour of the solution becomes lighter.

Addition of $HgCl_2$ solution also decreases red colour because Hg^{2+} ions reacts with SCN^- ions to form stable complex ion $[Hg(SCN)_4]^{2-}$. Removal of free SCN^- ions shifts the equilibrium in backward direction to increase the concentration of SCN^- ions. The colour again becomes lighter due to decrease in concentration of $[Fe(SCN)]^{2+}$ ions.

Let us study some **examples** illustrating the effect of change of concentration on equilibrium.

(*i*) **Clothes dry quicker when there is breeze.** Clothes get dried quickly in breeze or by shaking them in air. It is because, the water vapours of nearby air are removed and the clothes lose water vapours to re-establish the equilibrium with surrounding air.

(*ii*) **On a humid day we sweat more.** The sweating on a humid day is more because surrounding air has large amount of water vapours and our body cannot lose water as water vapours.

(*iii*) **Transport of oxygen by haemoglobin in blood.** The haemoglobin, Hb, in the red corpuscles of our blood carries oxygen to the tissues. The equilibrium may be represented as

$$Hb(s) + O_2(g) \rightleftharpoons HbO_2(s)$$

The blood that is in equilibrium with the oxygen of the air in the lungs finds a situation in the tissues where partial pressure of oxygen is low and hence the equilibrium readjusts itself by some of the oxyhaemoglobin releasing the oxygen. When the blood returns to the lungs the partial pressure of the oxygen is higher and more oxyhaemoglobin is formed.

(*iv*) **Removal of CO_2 from tissues by blood.** The blood removes the CO_2 from the tissues in the similar way. The equilibrium is :

$$\begin{aligned} CO_2(g) + H_2O(l) &\rightleftharpoons H_2CO_3(aq) \\ &\rightleftharpoons H^+(aq) + HCO_3^-(aq) \end{aligned}$$

Here, CO_2 dissolves in the blood in the tissues since its partial pressure is high; in the lungs where the partial pressure of CO_2 is low, it is released from the blood.

(*v*) **Formation of ammonia.** The reaction involving formation of ammonia is :

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

If at equilibrium more H_2 or N_2 is added to the above reaction, equilibrium shifts in the forward direction resulting in the formation of more NH_3. The equilibrium can also be shifted in forward direction by removing ammonia by liquifying. In general, it may be concluded that if concentration of one or all the reactant species is increased, the equilibrium shifts in the forward direction and more of the products are formed. Alternatively, if the concentration of one or all the product species is increased, the equilibrium shifts in the backward direction forming more of the reactants.

Effect of Change in Pressure

The change of pressure has effect only on those equilibria which involve gaseous substances and proceed with a change in the number of moles of the gases. According to Le Chatelier's principle, increase of external pressure should affect the equilibrium in such a way as to reduce the pressure. This implies that the equilibrium will shift in the direction which has smaller number of moles of the gaseous substances. This can be easily understood from the following equilibrium representing the formation of ammonia.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

On increasing the pressure, the volume occupied by the system will decrease. As such there will be greater number of moles per unit volume. The effect of this change can be counteracted if the equilibrium shifts in the direction involving a decrease in the number of moles. This can happen only if nitrogen and hydrogen combine to form ammonia. Thus, increase in pressure in this case will favour the forward reaction.

This can also be understood in terms of reaction quotient Q_c. Suppose pressure of the reaction mixture is doubled and volume is reduced to half. The partial pressures and concentrations of various species in the reaction mixture would become double. We obtain Q_c by replacing each equilibrium concentration by double its value.

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = \frac{(a)^2}{(b)\,(c)^3} = \frac{a^2}{bc^3}$$

$$Q_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = \frac{(2a)^2}{(2b)\,(2c)^3} = \frac{a^2}{4bc^3}\,.$$

As the value of Q_c is less than K_c, the reaction proceeds in the forward direction.

Let us now consider the equilibrium in the following reaction :

$$C(s) + CO_2(g) \rightleftharpoons 2CO(g)$$

Here backward reaction takes place with a decrease in the number of moles of gaseous species. As the pressure is increased, the volume decreases and the number of moles per unit volume increases. Therefore, the equilibrium shifts in the backward direction. In this way, the number of moles of gases decreases and the effect of increase of pressure is counteracted to some extent. On the other hand, decrease in pressure shifts the equilibrium in the favour of forward reaction.

Now, let us consider some reactions which do not involve any change in number of moles of gaseous species :

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

In such reactions pressure does not have any effect on equilibrium.

Let us explain the effect of pressure on solubility of gases in liquid solvents on the basis of **Le Chatelier's principle**. As an example, let us study the equilibrium involving dissolution of CO_2 in water. The equilibrium may be represented as :

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

On increasing the pressure of CO_2 the equilibrium shifts in the direction which results in the decrease in pressure of CO_2. The pressure of CO_2 will be lowered only if $CO_2(g)$ dissolves in water to form $CO_2(aq)$. Thus, *solubility of a gas in some liquid is directly proportional to the pressure of the gas in equilibrium with the solution.*

Effect of Temperature

A chemical equilibrium involves two opposing reactions, one favouring the products and the other favouring the reactants. If one of the reactions is exothermic the other must be endothermic. **For example**, let us consider the equilibrium representing the formation of ammonia:

$$N_2(g) + 3H_2(g) \underset{\text{Endothermic}}{\overset{\text{Exothermic}}{\rightleftharpoons}} 2NH_3(g)\ ; \quad \Delta H = -\ \mathbf{93.6\ kJ.}$$

In this equilibrium, the forward reaction is exothermic while the backward reaction is endothermic. Now, if the temperature is increased, the equilibrium will shift in the direction of endothermic reaction, which tends to undo the effect of added heat. Since the backward reaction is endothermic, so the equilibrium shifts in favour of backward reaction. In other words, it will result into lesser amount of ammonia. On the other hand, if temperature is decreased, the equilibrium will shift towards exothermic reaction. So low temperature favours the formation of ammonia.

In the case of reaction between nitrogen and oxygen, the forward reaction is endothermic while the backward reaction is exothermic.

$$N_2(g) + O_2(g) \underset{\text{Exothermic}}{\overset{\text{Endothermic}}{\rightleftharpoons}} 2NO(g)\ ; \quad \Delta H = \mathbf{180\ kJ.}$$

According to **Le Chatelier's principle**, the increase in temperature will favour the forward (endothermic) reaction. This is because, the equilibrium shifts towards the direction in which heat is absorbed to relieve the system of the stress of added heat. On the other hand, decrease in temperature shifts the equilibrium in the direction of exothermic reaction, *i.e.*, in favour of reactants in the above **example**.

The effect of temperature on equilibrium can be demonstrated with the help of a simple endothermic reaction.

$$\underset{\text{Pink}}{[Co(H_2O)_6]^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{Blue}}{[CoCl_4]^{2-}(aq)} + 6H_2O(l)\ ;\ \Delta H = +\text{ve}$$

At room temperature, the above equilibrium mixture is blue in colour due to the presence of $[CoCl_4]^{2-}$. When the reaction mixture is cooled in a freezing mixture the colour becomes pink due to formation of $[Co(H_2O)_6]^{2+}$, indicating that equilibrium has shifted in favour of reactants. On heating, the colour again becomes blue indicating that the equilibrium has shifted in favour of products.

It may be emphasized here that whenever an equilibrium is disturbed by a change in the concentration or pressure or volume, the reaction quotient, Q_c changes and no longer equals the equilibrium constant, K_c. However, when a change in temperature occurs, the value of equilibrium constant, K_c changes and Q_c is no longer equal to K_c.

In general, the temperature dependence of the K_c depends on whether the reaction is exothermic or endothermic.

- The equilibrium constant for an exothermic reaction decreases as the temperature increases.
- The equilibrium constant for an endothermic reaction increases as the temperature increases.

Effect of Temperature on Solubility of the Substances

We can also explain the effect of temperature on solubility of solids in liquids with the help of Le-Chatelier's principle. If during the dissolution **heat is absorbed,** the solubility **increases** with increase in temperature. NH_4Cl and $NaNO_3$ are examples of such substances. On the other hand, substances such as $CaCl_2$, Li_2CO_3, Li_2SO_4 and NaI **liberate heat** during dissolution. The solubility of such substances **decreases** with increase in temperature.

Dissolution of **gases in liquids** is always **exothermic.** Therefore, solubility of gases in liquids decreases with increase in temperature.

Effect of Catalyst

The presence of catalyst does not disturb the state of equilibrium because it increases the rate of forward as well as backward reaction to the same extent. It simply hastens the attainment of equilibrium by providing a new pathway having low activation energy. Catalyst does not disturb the equilibrium composition of the reaction mixture.

Certain reactions such as formation of ammonia from nitrogen and hydrogen cannot be carried out at high temperatures because high temperature favours the backward reaction. So such reactions give poor yields at high temperatures and therefore, have to be carried out at low temperature. But at low temperature the rate of reaction becomes very slow and it takes very long time to attain the equilibrium. In order to increase the rates of such reactions, generally, catalysts are used so that equilibrium is attained early. For example, in case of formation of ammonia, a catalyst consisting of iron to catalyse the reaction is used.

Effect of Addition of Inert Gas

The effect of addition of inert gas (*i.e.*, a gas which does not react with any of species involved in equilibrium) can be discussed under different conditions as described below :

(*a*) **Addition of inert gas at constant volume.** When inert gas is added to the equilibrium system at constant volume, it will cause the increase in the total pressure of the system. But the partial pressure of each of the reactant as well as product species will not be affected and will remain the same. Hence, under these conditions, *there will be no effect on the equilibrium.*

(*b*) **Addition of inert gas at constant pressure.** When inert gas is added to the system at constant pressure, it will result in the increase in volume. As a consequence of this, the number of moles per unit volume of various reactants and products will decrease. To counterbalance this stress, *the equilibrium will shift to the side where number of moles are increased.*

For example, for an equilibrium,

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

the addition of inert gas at constant pressure will push the equilibrium to the backward direction.

Similarly, for an equilibrium,

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

the addition of inert gas at constant pressure will push the equilibrium to the forward direction.

The effect of change of concentration, pressure and temperature has been summed up in the following table :

Stress	*Direction in which Equilibrium Shifts*
• Increase in the concentration of one or more reactants	Forward direction
• Increase in the concentration of one or more products	Backward direction
• Increase in temperature	Towards endothermic reaction

• Decrease in temperature	Towards exothermic reaction
• Increase of pressure	Towards lesser number of gaseous moles
• Decrease of pressure	Towards large number of gaseous moles
• Addition of catalyst	No effect
• Addition of inert gas : (*a*) at constant volume (*b*) at constant pressure	No effect Towards larger number of gaseous moles.

EXPERIMENT 3

Aim: Explain Le Chaterlier's principle using the reaction of $FeCl_3$, KCN and H_2O.

Theory: According to Le Chaterlier's principle the equilibrium is subjected to change of concentration, pressure or temperature, the equilibrium shifts in the dirrection that tends to undo the effect of change.

$$FeCl_3 + KSCN_{(aq)} \rightleftharpoons FeSCN_{(aq)} + KCl_{(aq)}$$

$$K_c = \frac{\left[Fe(SCN)^{2+}_{aq}\right]}{\left[FeCl_3\right] + [KSCN]}$$

Procedure: Take 25 ml 0.2 m $FeCl_3$ solution in a beaker, now add few drops of KSCN (pottassium thiocynate). The colour of the solution starts becoming dark red because of the formation of potassium thiocynate. Soon the stage of equilibrium comes. Now if we add any of the reactants like $FeCl_3$ or KSCN, it will lead to shift of equilibrium in forward direction resulting in formation of more feric thiocynate hence deepening of red colour. If we add water to the solution. The H_2O will react with Fe^{3+} ions decreasing the concentration of $FeCl_2$ in the solution resulting is lightening of red colour. It means decrease in concentration of Fe^{3+} ions result in decrease of product concentration also (FeSCN). Means equilibrium is shifting to left in order to undo the change of concentration.

Observation:

1. Adding of potassium thiosulphate causes increasing of concentration of reactant resulting in formation of more feric thiocynate due to shifting of equilibrium towards product side.

2. Adding of water causes decreases in concentration of reactant resulting in shifting of equilibrium towards reactant side hence decreasing the concentration of product (ferric thiocynate) which is visibly seen as lightening of colour. This experiment proves the Le Chaterlier's principle.

Precautions:

1. Can should he taken that temperature and pressure should remain constant.

SUMMARY

- **Equilibrium State.** A state of the system when its observable properties do not change at a given set of conditions. At equilibrium, the forward and backward reactions proceed at same rate.
- **Physical Equilibrium.** Equilibrium achieved in physical processes.
- **Chemical Equilibrium.** Equilibrium achieved in chemical processes.
- **Homogeneous Equilibrium.** Equilibrium in which reactants and products are in same phase.
- **Heterogeneous Equilibrium.** Equilibrium in which various substances involved have different phases.
- **Law of Mass Action.** A theoretical concept which states that rate of reaction is directly proportional to the product of molar concentrations of reactants with each concentration term raised to the power equal to stoichiometric co-efficient of that species in the balanced equation.
- **Velocity Constant or Rate Constant.** It is the rate of reaction when concentration of each of reacting species is unity.
- **Equilibrium Constant (K).** It is the ratio of the velocity constants of forward reaction to that of backward reaction.
- **Applications of Equilibrium Constant**
  - To predict the extent of a reaction on the basis of its magnitude.
  - To predict the direction of the reaction.
  - To calculate equilibrium concentrations.
- If $K_c > 10^3$, products predominate over reactants, and the reaction proceeds nearly to completion.

  If $K_c < 10^{-3}$, reactants predominate over products, and the reaction proceeds rarely.

If K_c is in the range 10^3 to 10^{-3} appreciable concentrations of both the reactants and products are present.

- **Le Chatelier's Principle.** When an equilibrium is subjected to any kind of stress (change in concentration, temperature or pressure) it shifts in a direction so as to undo the effect of stress.

EVALUATION

I. Multiple Choice Questions

1. In a chemical reaction, equilibrium is established when:
   (a) opposing reaction ceases
   (b) concentrations of reactants and products are equal
   (c) velocity of the opposing reaction is same as that of forward reaction
   (d) forward reaction ceases.

2. Application of Le Chatelier's principle indicates that synthesis of ammonia (represented by
   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -92.4$ kJ mol^{-1})
   is favoured by
   (a) low pressure (b) high temperature
   (c) presence of catalyst (d) removal of ammonia.

3. According to Le Chatelier's principle, adding heat to a solid and liquid in equilibrium will cause the
   (a) amount of solid to decrease (b) amount of liquid to decrease
   (c) temperature to rise (d) temperature to fall.

4. Which of the following is not a general characteristic of equilibria involving physical processes?
   (a) All the physical processes stop at equilibrium.
   (b) Equilibrium is possible only in a closed system at a given temperature.
   (c) All measurable properties of the system become constant.
   (d) The opposing processes occur at the same rate.

5. Which of the following equilibria will have the same values for K_p and K_c?
   (a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ (b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
   (c) $A(s) + 2B(g) \rightleftharpoons 2C(g)$ (d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

6. For the reaction,

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g),$$

at a given temperature, the equilibrium amount of $CO_2(g)$ can be increased by

(a) adding a suitable catalyst
(b) adding an inert gas
(c) decreasing the volume of container
(d) increasing the amount of $CO(g)$.

7. The equilibrium constant for the reaction,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

is 4×10^{-4} at 2000 K. In presence of a catalyst, equilibrium is attained ten times faster. Therefore, the equilibrium constant, in presence of the catalyst, at 2000 K is

(a) 40×10^{-4} (b) 4×10^{-4}
(c) 4×10^{-3}
(d) difficult to compute without more data.

8. Which of the following statements is correct about the equilibrium constant?

(a) Its value increases by increase in temperature
(b) Its value decreases by decrease in temperature
(c) Its value may increase or decrease with increase in temperature
(d) Its value is constant at all temperatures.

9. The units of equilibrium constant for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{heat},$$

will be

(a) $mol^{-2}\,L^{2}$ (b) $mol\,L^{-1}$
(c) $mol^{2}\,L^{-2}$ (d) $L\,mol^{-1}$.

10. In which of the following equilibria K_c and K_p are not equal?

(a) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$
(b) $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
(c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(d) $2C(s) + O_2(g) \rightleftharpoons 2CO_2(g) + O_2(g)$.

II. Fill in the Blanks

1. An equilibrium can be achieved only in _________ reactions.

2. For the reaction,

$$N_2 + O_2 \rightleftharpoons 2NO;\ \Delta H = 180\text{ kJ},$$

the increase in temperature shifts the equilibrium in _________ direction.

3. For a certain equilibrium reaction $K_p = K_c$. It indicates the equilibrium is _________ pressure variation.
4. The temperature at which solid $\rightleftharpoons$ liquid equilibrium exist is known as _________ of the substance.
5. With increase in concentrations of the reactants, the value of equilibrium constant _________ .

III. Descriptive Questions

1. What is the meaning of notation $[A]^x$ as used in the expression of equilibrium?
2. What is meant by concentration quotient of chemical reaction? Under what conditions, it is equal to equilibria constant?
3. Write expression and units of K_p for the reaction

$$A_2(g) + 3B_2(g) \rightleftharpoons 2AB_3(g).$$

4. Equilibrium constants for certain reactions for certain reactions at two temperatures 20°C and 50°C are respectively 1×10^{-2} and 1×10^{-3}, can it help in predicting the exothermic and endothermic nature of the forward reaction?
5. Two equilibria $A + B \rightleftharpoons C + D$

$$P + Q \rightleftharpoons R + S$$

have values of K at 25°C as 1×10^{-2} and 1×10^{20}. What do they tells us about reaction?

6. For reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the value of equilibrium constant is 80 atm at 100°C. What is the behaviour of the mixture of NO_2 and N_2O_4 with respective partial pressure as 4×10^{-3} atm each?
7. Can equilibrium be achieved between water and its vapours in an open beaker?
8. On dissolving ammonium chloride in water cooling effect is caused. Predict on the basis of Le Chatelier's principle the effect of temperature on the solubility of ammonium chloride.
9. Why do we sweat more on humid day?
10. Name the factors on which equilibrium constant depends.
11. Why solubility of CO_2 decreases with rise in temperature?
12. What is the effect of catalyst on equilibrium state?
13. Explain the following:
    (i) Normal freezing point
    (ii) Vapour pressure of a liquid.
    (iii) Henery's Law.

14. What is the effect of temperature and pressure on the solubility of

(*i*) a solid in liquid

(*ii*) a gas in liquid.

IV. Numerical Questions

1. For reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ the value of K_p is 3.6×10^{-3} at 500 K. Calculate the value of K_c for the reaction at the same temperature.

2. At 700 K, the equilibrium constant K_p of the reaction

$$2SO_2(g) \longrightarrow 2SO_2(g) + O_2(g)$$

is 1.8×10^{-3} kPa. What is the numerical value in moles per litre K_c for this reaction at the same temperature.

3. A gaseous reaction $e + f \rightleftharpoons g$ at 373 K, the partial pressure of e,f,g at equilibrium are 0.30 atm and 0.60 atm respectively. Calculate K_p and K_c for the reaction.

4. Consider the reaction $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$ at 373 K. Suppose at a particular moment concentration of N_2O_4 and NO_2 are 1 mol L^{-1} each. In which direction the reaction will proceed to establish equilibrium? K for the reaction is 0.36.

5. The value of K_c for the reaction

$$3O_2(g) \rightleftharpoons 2O_3(g)$$

is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2}. What is the concentration of O_3?

SEMESTER–II (Period–VI)

8

TOPIC

Chemical Kinetics

C11CH8

Learning Objectives

Upon completion of this topic, learners will:

- Discuss the Rate Laws
- Demonstrate the reaction mechanism
- Discuss Activation Energy
- Explain the concept of Collision Theory

The extent to which a reaction will proceed can be determined from ***chemical equilibrium*** whereas the feasibility of a chemical reaction can be predicted by thermodynamics ($\Delta G < 0$). The knowledge of ***free energy*** change of a reaction however gives us no idea about the rate and the factors controlling the rate of a reaction.

How quickly a chemical reaction occurs is a crucial factor in how the reaction affects its surroundings. Therefore, **knowing the rate of a chemical reaction is integral to understanding the reaction.**

All these questions can be answered by the branch of chemistry known as ***chemical kinetics.***

The kinetic studies deals with the study of reaction rates or velocity or speed of a reaction. It describes the conditions by which the reaction rates can be altered. The kinetic data is used to predict the mechanism governing the reactions.

Types of Reaction Based on Rates

1. **Very fast Reactions:** These are instantaneous reaction. It is very difficult to find rate of such reactions

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

2. **Very slow reactions:** These reactions occur at a very slow rate and take years to complete. e.g. rusting of iron, weathering or rock.

3. **Moderately slow reactions:** Their rate is between very fast and very slow reactions.

8.1. RATE OF A CHEMICAL REACTION

The ***rate of a chemical reaction*** is the speed or velocity at which a reaction takes place.

It may be expressed in any of the following ways:

(*i*) *The rate of decrease in concentration of any one of the reactant,* or

(*ii*) *The rate of increase in concentration of any one of the product at a given temperature.*

For **example**, for a hypothetical reaction,

$$R \longrightarrow P$$

If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2 then,

Time required for change in conc.,

$$\Delta t = t_2 - t_1$$

Change in concentration of reactants,

$$\Delta[R] = [R]_2 - [R]_1$$

Change in concentration of products,

$$\Delta[P] = [P]_2 - [P]_1$$

Rate of disappearance of reactant R

$$= \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t}\ .$$

Rate of appearance of product P

$$= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = +\frac{\Delta[P]}{\Delta t}$$

The expressions for rate in terms of reactants carry a negative sign.

Significance of Negative Sign

The negative sign in first expression does not mean that the rate is negative, rather it indicates the decrease in concentration of the reactant. As we know that with passage of time the concentrations of reactants decrease, therefore, the change in concentration, Δ[*R*] = (Final conc. – Initial conc.) will have a negative value. Since the rate of a reaction is a positive quantity, thus, to get a positive rate we put a –ve sign in the rate expression.

Note: *The square brackets in the above expressions are used to express molar concentration.*

Thus, *rate of reaction = Rate of disappearance of R = Rate of appearance of P* $= -\dfrac{\Delta[\mathrm{R}]}{\Delta t} = +\dfrac{\Delta[\mathrm{P}]}{\Delta t}$

Mathematical Expression for Rates of Reaction

1. **Reactions Involving Same Stoichio-metric Coefficients of all the Reactants and Products**

Let us consider the gaseous reaction between nitrogen dioxide and carbon monoxide.

$$\mathrm{NO_2}(g) + \mathrm{CO}(g) \longrightarrow \mathrm{CO_2}(g) + \mathrm{NO}(g)$$

In this case, as the reactants and products appear in ***same stoichiometric proportions,*** therefore, the rate of the reaction may be expressed in terms of rate of disappearance of nitrogen dioxide or carbon monoxide or ***alternatively***, by the rate of appearance of carbon dioxide or nitric oxide whichever may be convenient.

Thus, rate of reaction is mathematically given as,

$$= -\frac{\Delta[\mathrm{NO_2}]}{\Delta t} = -\frac{\Delta[\mathrm{NO_2}]}{\Delta t} = +\frac{\Delta[\mathrm{CO_2}]}{\Delta t} = +\frac{\Delta[\mathrm{NO}]}{\Delta t}$$

2. **Reactions Involving Different Stoichiometric Coefficients of Reactants and Products**

Let us take an example of simple reaction,

$$\mathrm{H_2}(g) + \mathrm{I_2}(g) \longrightarrow 2\mathrm{HI}(g)$$

Now, in the present case, as the reactants (H_2 and I_2) and products (HI) have ***different stoichiometric coefficients,*** this means that for every mole of H_2 or I_2 reacting, we get two moles of HI. Thus, the rate of formation of HI will be twice the rate of disappearance or H_2 or I_2. *In such cases, we divide the rate of change of concentration by the stoichiometric coefficient of reactants or products involved in the reaction.* Thus, we have

$$\text{Rate of reaction} = -\frac{\Delta[\mathrm{H_2}]}{\Delta t} = -\frac{\Delta[\mathrm{I_2}]}{\Delta t}$$

$$= +\frac{1}{2}\,\frac{\Delta[\mathrm{HI}]}{\Delta t}$$

Similarly, for the reaction,

$$5Br^- (aq) + BrO_3^- (aq) + 6H^+ (aq) \longrightarrow 3\ Br_2(aq) + 3H_2O(l)$$

$$\text{Rate of reaction} = \frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[Br_3^-]}{\Delta t}$$

$$= -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t}$$

$$= +\frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = +\frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

Units of Rate of Reaction

The units of rate of reaction are units of concentration divided by units of time. As concentration of substance is expressed in *mol* L^{-1} and the time is expressed in ***seconds (s)*** or ***minutes (min)*** or ***hours (h)*** then, the units for reaction rate will be **moles litre^{-1} sec^{-1} (mol L^{-1} s^{-1})** or **moles litre^{-1} min^{-1} (mol L^{-1} min^{-1})** or **moles litre^{-1} hr^{-1} (mol L^{-1} h^{-1}) respectively.**

For gaseous reactions, whose concentrations are given in terms of partial pressures, the units of rate of reaction will be **atm min^{-1}** or **bar min^{-1}** or **atm s^{-1}** or **bar s^{-1}** or **atm h^{-1}** or **bar h^{-1}.**

Interconversion of units. The partial pressure can also be converted into units of concentration, *i.e.*, moles per litre, by using the following equation:

$$pV = nRT \quad \text{or} \quad p = \frac{n}{V}RT = cRT \quad \text{or} \quad c = \frac{p}{RT}.$$

$$\text{Rate in terms of change in pressure} = \frac{\Delta(p)}{\Delta t}$$

If $\Delta(p)$ and Δt are known then
rate in terms of conc. units (mol L^{-1})

$$= \frac{\text{rate in terms of pressure units}}{RT}$$

8.2. AVERAGE RATE AND INSTANTANEOUS RATE

Average Rate

The **average rate** of a reaction is defined as the *rate of change of concentration per unit time.* It is calculated by dividing the total change in concentration of any one of the reactant or product by the total time taken to do so. For a reaction.

$$\underset{(\textit{reactant})}{\mathrm{R}} \longrightarrow \underset{(\textit{product})}{\mathrm{P}}$$

Average rate

$$= \frac{\text{Change in concentration in given time}}{\text{Time taken}}$$

i.e.,
$$= -\frac{\Delta \mathrm{R}}{\Delta t} \text{ or } = +\frac{\Delta \mathrm{P}}{\Delta t} \text{ or } = \frac{\Delta x}{\Delta t}$$

The Average rate of reaction changes with passage of time hence to know the true rate, it is expressed as instant rate.

Instantaneous Rate

The **instantaneous rate** of a reaction is defined as the *decrease in concentration of any one of the reactants or increase in concentration of any one of the product at a particular instant of time for a given temperature.*

Mathematically, the instantaneous rate may be written as,

$$r_{\text{inst}} = -\frac{d[\mathrm{R}]}{dt} \text{ or } + \frac{d[\mathrm{P}]}{dt} \text{ or } = \frac{dx}{dt}^{*}$$

Here, dt is the infinitesimally small time interval and dx is the change in concentration of any of the species in time interval dt.

To **sum up**, the expression $-\frac{\Delta[\mathrm{R}]}{\Delta t}$ or $\frac{\Delta[\mathrm{P}]}{\Delta t}$ or $\frac{\Delta x}{\Delta t}$ becomes $-\frac{d[\mathrm{R}]}{dt}$ or $\frac{d[\mathrm{P}]}{dt}$ or $\frac{dx}{dt}$ as Δt approaches zero. The average rate approaches the instantaneous rate as Δt becomes smaller and approaches zero, *i.e.*,

$$\left(\frac{\Delta x}{\Delta t}\right)_{\Delta t \to 0} = \frac{dx}{dt}$$

For **example,** for the gaseous reaction,

$$2\mathrm{N_2O_5} \longrightarrow 4\mathrm{NO_2} + \mathrm{O_2},$$

the ***instantaneous rate*** will be expressed as,

$$r_{\text{inst}} = -\frac{1}{2}\frac{d[\mathrm{N_2O_5}]}{dt} = \frac{1}{4}\frac{d[\mathrm{NO_2}]}{dt} = \frac{d[\mathrm{O_2}]}{dt}.$$

Experimental Determination of Reaction Rate

The rate of a reaction is determined by measuring the concentration of any of the reactants or products after definite intervals of time. The common practice to find the change in concentration is, to withdraw a small amount of reaction mixture ($2\ cm^3$ to $5\ cm^3$) at different intervals of time. The withdrawn sample is then placed in the freezing mixture of ice and sodium chloride. It is called **freezing of reaction.** The concentration at the given interval is then determined by a suitable method. On the basis of kinetic data, a graph is plotted between **concentration** and **time** (Fig. 8.1) and the rate is calculated, *i.e.*, average rate or instantaneous rate, as illustrated in next topic.

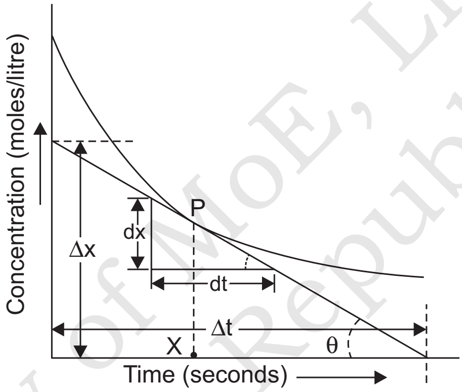


Fig. 8.1. Determination of rate of a reaction.

EXPERIMENT 1

Aim: To study the effect of concentration on the rate of reaction.

Theory: According to the **law of mass action**, *rate of a chemical reaction is directly proportional to the product of the molar concentration of the reactants.* In other words the rate of reaction increases with the increase in the concentration of the reactants. The effect of concentration of reactants on rate of a reaction can be studied easily by the reaction between sodium thiosulphate and hydrochloric acid.

$$Na_2S_2O_3 + 2HCl \longrightarrow S(s) + 2NaCl(aq) + SO_2(g) + H_2O(l)$$

The insoluble sulphur, formed during the reaction, gives a milky appearance and makes the solution opaque. Therefore, rate of the reaction can be studied by measuring the time taken to produce enough sulphur to make some mark invisible on a paper kept under the conical flask in which the reaction is carried out.

Requirements: Stop-watch, two burettes and five conical flasks (100 ml).

Materials Required: 0.1 M $Na_2O_2O_3$ solution and 1 M HCl solution.

Procedure:

1. Wash the conical flasks with water and label them as 1, 2, 3, 4 and 5 respectively.
2. With the help of a burette, add 10, 20, 30, 40 and 50 ml of 0.1 M $Na_2S_2O_3$ solution to the flasks 1, 2, 3, 4 and respectively.
3. Now add 40, 30, 20 and 10 ml of distilled water to the flask 1, 2, 3 and 4 respectively so that volume of solution in each flask is 50 ml.
4. Take 10 ml of 1 M HCl in a test tube with the help of a burette.
5. Add 10 ml of hydrochloric acid taken in a test tube to the conical flask No. 1 containing 10 ml of 0.1 M $Na_2S_2O_3$ and 40 ml of distilled water and start the stop-watch. When half of the hydrochloric acid solution has been added. Shake the contents of the conical flask and place it on the tile with a cross mark as shown in Fig. 8.2.
6. Go on observing from top to downwards in the flask and stop the stop-watch when the cross mark just becomes invisible. Not down the time.
7. Repeat the experiment by adding 10 ml of 1 M HCl to flasks 2, 3, 4 and 5 record the time taken in each case for the cross to become just invisible.

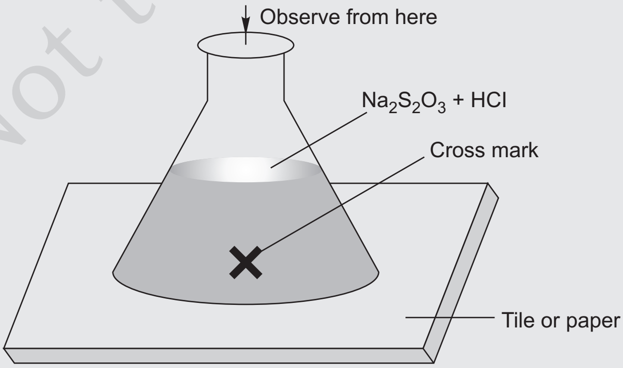


Fig. 8.2. Study of rate of reaction

Observations:

Flask No.	*Volumes of $Na_2S_2O_3$ solution in ml*	*Volume of water in ml*	*Total volume of solution in ml*	*Concentration of $Na_2S_2O_3$ solution*	*Volume of 1 M HCl (ml)*	*Time taken for cross to become just invisible (t)*	$\frac{1}{t}$ (s^{-1})
1.	10	40	50	0.02 M	10	......s	
2.	20	30	50	0.04 M	10	......s	
3.	30	20	50	0.06 M	10	......s	
4.	40	10	50	0.08 M	10	......s	
5.	50	0	50	0.10 M	10	......s	

Plotting of graph: Plot a graph between $\frac{1}{t}$ (in seconds) and the conc. of sodium thiosulphate by taking $\frac{1}{t}$ along ordinate (vertical axis) and conc. of $Na_2S_2O_3$ along abcissa (horizontal axis). It should be a straight sloping line.

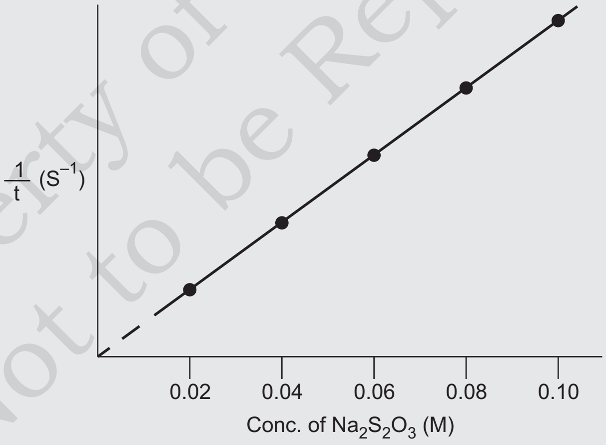


Fig. 8.3. A graph of conc. $Na_2S_2O_3$ vs $\frac{1}{t}$.

Result: From the graph, it is clear that $\frac{1}{t}$ is directly proportional to the conc. of $Na_2S_2O_3$ solution. But $\frac{1}{t}$ is a direct measure of rate of the reaction, therefore, rate of the reaction between $Na_2S_2O_3$ and HCl is directly proportional to the conc. of $Na_2S_2O_3$ solution taken. Hence, rate of this reaction is directly proportional to the concentration of $Na_2S_2O_3$, which is one of the reactants.

Note: It may be noted that the reaction rate also increases when the amount of sodium thiosulphate is kept constant but the concentration of hydrochloric acid is increased.

Precautions:

1. The apparatus must be thoroughly clean. If the same conical flask is to be used again and again, it should be thoroughly washed with conc. HNO_3 and then with water.
2. Measure the volumes of sodium thiosulphate solution, hydrochloric acid and distilled water very accurately.
3. Use the same tile with the same cross-mark for all observation.
4. Complete the experiment at one time only so that there is not much temperature variation.
5. Start the stop-watch immediately when half of the hydrochloric acid solution has been added to sodium thiosulphate solution.
6. View the cross-mark through the reaction mixture from top to bottom from same height for all observations.

EXPERIMENT 2

Aim: To study the effect of change in temperature on the rate of reaction.

Theory: The rate of a chemical reaction depends to a great extent upon temperature. The rate of reaction increases with increase in temperature. Increase in temperature increase kinetic energy of the molecules. Therefore, the fraction of molecules having energy greater than its threshold energy increases which results in the increase in number of effective collisions per second. It has been observed that in most of the cases *for every 10°C rise in temperature, the rate of the reaction becomes almost double.* The rate of reaction between sodium thiosulphate and hydrochloric acid increase with increase in temperature.

Requirements: Conical flask (250 ml) measuring cylinders (50 ml and 5 ml), stop-watch, thermometer, tripod stand, wire-gauze and burner.

Materials Required: 0.1 M $Na_2S_2O_3$ solution, 1 M HCl, distilled water and conc. HNO_3.

Procedure:

1. Take 50 ml of 0.1 M $Na_2S_2O_3$ solution in a 100 ml conical flask and note its temperature with the help of a thermometer.

2. Add 10 ml of 1 M HCl to it and start the stop-watch immediately when half of the hydrochloric acid solution has been added.
3. Shake the contents of the flask gently and place it on the tile with a cross-mark.
4. Observe the cross-mark from the top and note the time taken for the mark to become just invisible.
5. Empty the flask and clean it thoroughly with conc. HNO_3 and then with water.
6. Take again 50 ml of 0.1 M $Na_2S_2O_3$ in conical flask and heat it so that the temperature of the solution become (T + 10°)C.
7. Remove the flask from the tripod-stand and add 10 ml of 1 M HCl to it and start the stop-watch.
8. Shake the contents gently and place it on the tile having a cross-mark.
9. Note the time taken for the mark to become just invisible.
10. Repeat the experiment at (T + 20)°C, (T + 30)°C and (T + 40)°C temperatures and record the observations as given below.

Other examples: Volume of 0.1 M $Na_2S_2O_3$ solution taken each time = 50 ml

Volume of 1 M HCl added each time = 10 ml.

S. No.	*Temperature*	*Time taken for cross to become just invisible (t)*	$\frac{1}{t}$
1.			
2.			
3.			
4.			
5.			

Plotting of Graph: Plot a graph by taking $\frac{1}{t}$ along the ordinate (vertical axis) and temperature along the abscissa (horizontal axis).

Result: Rate of reaction between sodium thiosulphate and hydrochloric acid increases with the increase in temperature.

Precautions: Same as in experiment 1.

8.3. FACTORS INFLUENCING RATE OF A REACTION

The rate of reactions is influenced by the following factors:

(*i*) *Concentration of the reactants,*

(*ii*) *Temperature of the reactants,*

(*iii*) *Nature of the reacting substances,*

(*iv*) *Presence of catalyst, and*

(*v*) *Exposure to radiations.*

8.4. DEPENDENCE OF RATE ON CONCENTRATION

When a chemical reaction occurs, the reactants change over to products. It is observed that with the passage of time the concentrations of reactants decrease while those of products increase. It is graphically shown in Fig. 8.4.

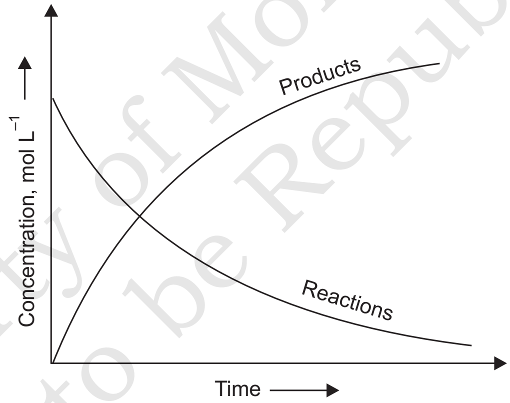


Fig. 8.4. Time dependence of the concentrations of reactants and products in a reaction.

Now, if we assume that other factors are constant then the rate of a chemical reaction decreases with the decrease in concentration of the reactants. Conversely, rates generally increase when reactant concentrations increase. For **example,** *we find that a piece of wood burns at a much faster rate in oxygen than in air. It is because of higher concentration of oxygen in the former.*

The representation of the rate of reaction in terms of concentration of reactants is known as **rate law**. It is also called **rate equation.**

Rate Expression and Rate Constant

Consider a general reaction

$$aA + bB \longrightarrow cC + dD$$

(*Here, a, b, c and d are stoichiometric coefficients*)

The rate equation for the reaction is

$$\text{Rate} \propto [A]^x [B]^y$$

$$= k [A]^x [B]^y \qquad \text{...(1)}$$

or $$-\frac{d[R]}{dt} = k [A]^x [B]^y \qquad \text{...(2)}$$

Note: *x and y may or may not be equal to stoichiometric coefficients a and b.*

The equation (1) is called **rate law** or **rate expression**. Thus, *rate law is the mathematical expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.*

The equation (2) is known as **differential rate equation.**

The constant k is a proportionality constant and is known as **rate constant** or **velocity constant** or **specific reaction rate.**

If the concentration of all reacting species is taken as unity then,

$$\text{rate} = k \qquad [\because \quad [A] = [B] = 1 \text{ mol L}^{-1}]$$

Hence, **rate constant** is defined as *the rate of reaction when the concentration of each reactant is taken as unity*. It is for this reason that the rate constant is also called **specific reaction rate.**

Deriving the Rate Expression from Data

There are many different ways and methods to determine the rate expression for a reaction. One experimental method that is used to determine rate laws of chemical reactions is the ***method of initial reaction rate.***

Initial Rate Method

The initial rate of a reaction is the instantaneous rate determined just after the reaction begins ($t \approx 0$).

In this method the basic idea is to determine the instantaneous rate before the initial concentrations of reactants have changed significantly. Several experiments are carried out using different initial concentrations, and the initial rate is determined for each experimental run. The results are then compared to see how the initial rate depends on the initial concentrations. On the basis of kinetic data the rate law is determined.

Let us **illustrate** the method of initial rates using the following equation:

$$NH_4^+\,(aq) + NO_2^-\,(aq) \longrightarrow N_2(g) + H_2O(l)$$

The general form of the rate law for this reaction is,

$$\text{rate} = -\frac{d\left[NH_4^+\right]}{dt} = k\,[NH_4^+]^m\,[NO_2^-]^n$$

On the basis of experimental studies, the following table giving initial rates is formulated from three experiments involving different concentration of reactants.

Experiment	*Initial [NH_4^+]* *(mol L^{-1})*	*Initial [NO_2^-]* *(mol L^{-1})*	*Initial rate* *(mol L^{-1} s^{-1})*
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}

The above data is used to determine the values of the rate exponents, *m* and *n*. The strategy is to find two experiments in which only one of the initial concentrations is changing while the other is kept constant. Accordingly, we can find the dependence of the rate on the change in initial concentration.

In the given kinetic data table, in experiments 1 and 2, the initial concentration of NH_4^+ remains the same but the initial concentration of NO_2^- doubles. Using the rate expression, we get

$$\text{rate}_{\text{exp 1}} = k\,[0.1]^m\,[0.005]^n \qquad \ldots(i)$$

$$\text{rate}_{\text{exp 2}} = k\,[0.1]^m\,[0.010]^m \qquad \ldots(ii)$$

Dividing eqn. (*ii*) with eqn. (*i*)

$$\frac{\text{rate}_{\text{exp 2}}}{\text{rate}_{\text{exp 1}}} = \frac{k\,[1.0]^m\,[0.010]^n}{k\,[1.0]^m\,[0.005]^n} = \left[\frac{0.010}{0.005}\right]^n = (2)^n$$

or

$$\frac{2.70 \times 10^{-7}}{1.35 \times 10^{-7}} = (2)^n$$

or

$$2 = (2)^n. \quad \text{Hence } n = 1$$

In a similar manner the results of experiment 2 and 3 yield the ratio.

$$\frac{\text{rate}_{\text{exp } 3}}{\text{rate}_{\text{exp } 2}} = \frac{5.40 \times 10^{-7}}{2.70 \times 10^{-7}} = \frac{k\,[0.2]^m\,[0.01]^n}{k\,[0.1]^m\,[0.01]^n} = (2)^m$$

or $$2 = 2^m, \text{ Hence } m = 1$$

Conclusion

- The value of exponents, $m = 1$ and $n = 1$
- The rate expression of the reaction is therefore

$$\text{rate} = k[NH_4^+]\,[NO_2^-]$$

- The differential form of this rate expression is given as

$$-\frac{d[R]}{dt} = k\,[NH_4^+]\,[NO_2^-]$$

Characteristics of Rate Constant

(*i*) The value of rate constant gives an idea about the rate of a reaction, *i.e.*, greater is the value of rate constant faster is the reaction.

(*ii*) Each reaction has a definite value of the rate constant at a particular temperature.

(*iii*) The value of rate constant depends on the temperature *i.e.*, changes with change in temperature.

(*iv*) The value of rate constant is independent of the concentration of reacting species.

(*v*) The units of rate constant depend on the order of reaction.

Difference Between Rate of Reaction and Rate Constant

The important differences between the ***rate*** of the reaction and ***rate constant*** of the reaction are being given as follows in tabular form.

Rate of Reaction	*Rate Constant of Reaction*
1. It is the speed at which the reactants are converted into the products at any moment of time.	1. It is constant of proportionality in the rate law expression.
2. It depends upon the concentration of reactant species at that moment of time.	2. It refers to the rate of reaction at the specific point when concentration of every reacting species is unity.
3. It generally decreases with the progress of reaction.	3. It is constant and does not depend on the progress of the reaction.

8.5. RATE LAW OR RATE EQUATION

A very curious question arises here that how could we know the rate equation or rate expression of a complex reaction? Which of the steps in the mechanism can be choosen as rate determining step. It must be noted that the determination of the rate law expression of a complex reactions is not an easy task. Its determination requires.

- *Information about the number of moles of reactants consumed during the reaction.*
- *A knowledge of the intermediates produced during the reaction and how much they accumulate during the early period of reaction.*
- *The rate data to be supplemented by different techniques so that the certain elementary steps are verified to the maximum.*

In complex reactions the rate expression written on the basis of the overall balanced equation has no significance at all. The rate expression for such complex reactions can be written on the basis of the experimental evidence like detection of the presence of some short lived intermediates, etc.

Illustration

Let us consider the gaseous reaction,

$$2NO_2(g) + F_2(g) \longrightarrow 2\ NO_2F(g)$$

- The rate expression on the basis of balanced equation is:

$$\text{rate} = k\,[NO_2]^2\,[F_2]$$

- The rate expression on the basis of experimental results is:

$$\text{rate} = k\,[NO_2]\,[F_2]$$

"A mathematical expression written in terms of concentration of reactants, which actually influence the rate, is called Rate Law."

8.6. ORDER OF REACTION

It is an important parameter for every chemical reaction. It is always determined experimentally and cannot be written from the balanced chemical equation.

It may be defined as, *"the sum of powers or exponents to which the concentration terms are raised in the rate law expression."*

For a hypothetical reaction,

$$aA + bB \longrightarrow \text{Products}$$

if the rate law expression for this reactions is,

$$\text{Rate} = k[\text{A}]^m [\text{B}]^n$$

- The **order** of the above reaction is equal to (**m** + **n**).
- The powers or exponents, *i.e.*, m and n have no relation to the stoichiometric coefficients a and b of the balanced chemical equation.
- Order of the reaction with respect to A is m and that with respect to B is n.
- If the sum of the power is equal to *one*, the reaction is called **first order reaction.**
- If the sum of the powers is **two or three,** the reaction is **second order or third order** reaction respectively.

The order of a reaction can also be ***zero*** *or* ***fractional.***

First Order Reaction

First order reaction can be defined a chemical reaction in which the rate of reaction is directly proportional to the concentration of only one reactant. If the concentration of that reactant is doubled the rate of reaction is also doubled.

In other words the sum of power to which the concentration terms are raised in the rate law equation is one then reaction is first order reaction.

Rate of reaction = $k[\text{A}]^1 \Rightarrow k[\text{A}]$

Second Order Reaction

Second order reaction is defined as a chemical reaction which depend on either the concentration of two first order or the concentration of one second order reactant.

In other words second order reactions are those reactions where in the sum of exponent in the corresponding rate law of the chemical reaction is equal to 0.2.

The rate of second order reaction is either as

$$r = k[\text{A}]^2 \text{ or as } r = k[\text{A}]\,[\text{B}]$$

8.7. REACTION MECHANISM

Reaction mechanism is the sequence of elementary steps (reaction) by which the overall chemical reaction occurs leading to the formation of final product. Reaction mechanism is the sequential account of each step describing details of electron movement, energies during bond dissociation and bond formation and rates of transformation of reactants and products. The first test of reaction mechanism is that it must give the experimental rate law, but it does not guarantee the correctness of rate mechanism.

Some reaction occur in two steps.

For example:

$$2NO + 2H_2 \rightarrow N_2 + H_2O$$

First step. $2NO + H_2 \rightarrow N_2 + H_2O_2$

Second step. $H_2O_2 + H_2 \rightarrow 2H_2O$

Here the first step is intermediate step.

The product formed in first step (intermediate step) is consumed in next elementary step so that it does not appear as final product. The first being the slow step determines the rate. The rate determining step is termolecular hence the overall order of reaction is 3.

$$\text{rate}_1 = k_1\ [NO]^2\ [H_2].$$

8.8. INTEGRATED RATE EQUATIONS

We have already learnt that the concentration dependence of rate is called ***differential rate equation.*** It is not always convenient to determine the instantaneous rate, as it is measured by determination of slope of the tangent at point '*t*' in concentration vs time plot. This makes it difficult to determine the rate law and hence the order of the reaction. *In order to avoid this difficulty, we can integrate the differential rate equation. The integrated rate equation gives a relation between directly measured experimental quantities, i.e., concentrations at different times and the rate constant.*

For a general reaction, $aA + bB \longrightarrow$ Products the differential rate law equation is,

$$\frac{dx}{dt} = k[A]^a\ [B]^b$$

Zero Order Reaction

A *reaction is zero order if its rate is independent of the concentration of reactants* or *the rate of reaction is proportional to zero power of the concentration of reactants*. Consider a general zero order reaction:

$$R \longrightarrow P$$

For this reaction,

$$\text{Rate} = -\frac{d[\text{R}]}{dt} = k[\text{R}]^{\circ} \qquad \ldots(8.1)$$

(Here, [R] is the concentration of reactant and k is the rate constant of zero order reaction)

As any quantity raised to power zero is unity

$$\therefore \qquad \text{Rate} = -\frac{d[\text{R}]}{dt} = k \times 1$$

or $$d[\text{R}] = -\,kdt$$

Integrating both sides, we get

$$\int d[\text{R}] = -\,k\int dt$$

$$[\text{R}] = -\,kt + \text{I} \qquad \ldots(8.2)$$

where, *I is the constant of integration*

At $t = 0$, $\quad [\text{R}] = [\text{R}]_0$,

(where $[R]_0$ is initial concentration of reactant).

Hence, $\quad \text{I} = [\text{R}]_0$

Substituting this value in equation (8.2), we get

$$[\text{R}] = -\,kt + [\text{R}]_0 \quad \text{or} \quad kt = [\text{R}]_0 - [\text{R}]$$

or $$k = \frac{1}{t}\Big[[\text{R}]_0 - [\text{R}]\Big] \qquad \ldots(8.3)$$

Significance of Integrated Rate Equation

(*i*) All zero order reactions obey the equation 8.3.

(*ii*) The value of k can be evaluated if $[\text{R}]_0$ and [R] at time t are known.

(*iii*) The expression, $[\text{R}] = -\,kt + [\text{R}]_0$, is comparable to straight line equation, $y = mx + \text{C}$, and therefore the value of k can be evaluated by **graphical method.**

The above equation can be written as:

$$[\text{R}] = [\text{R}]_0 - kt$$

On plotting a graph of [R] vs. t we get a straight line as shown in the figure below. The slope of the line is given as:

$$\text{slope} = -\,k$$

The intercept on the concentration axis = $[\text{R}]_0$

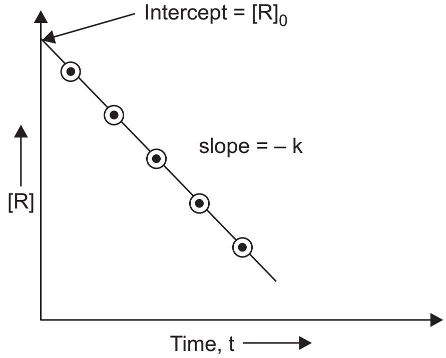


Fig. 8.5

First Order Reaction

Let us assume a simple hypothetical first order reaction as,

$$R \longrightarrow P$$

If the initial concentration of R is $[R]_0$, k is the rate constant and [R] is conc. at time t then the differential form of this first order reaction will be

$$\frac{-\,d[R]}{dt} = k[R]$$

Rearranging the equation, we get

$$\frac{d[R]}{[R]} = -\,kdt \qquad \text{...(8.4)}$$

On integrating equation (8.4),

$$\int \frac{d[R]}{[R]} = -\int kdt$$

We get, $\ln [R] = -\,k\,t + \text{constant}$ ...(8.5)

$$\left[\text{Integral of } \frac{d[R]}{[R]} \text{ is } \ln [R]\right]$$

At $t = 0$, $[R] = [R]_0$

therefore eqn. 8.5 reduces to form

$$\ln [R]_0 = -\,k \times 0 + \text{constant}$$

or $\text{constant} = \ln [R]_0$

Substituting this value in Eqn. (8.5), we get

$$\ln [R] = -\,k\,t + \ln [R]_0$$

or $k\,t = \ln [R]_0 - \ln [R]$

$$k\,t = \ln \frac{[R]_0}{[R]} = \ln [R]_0 - \ln [R] \qquad \text{...(8.6)}$$

Changing the above expression to common log ($\ln_e x = 2.303 \log_{10} x$) we get,

$$k\,t = 2.303 \log \frac{[R]_0}{[R]}$$

or

$$\mathbf{k} = \frac{\mathbf{2.303}}{\mathbf{t}} \,\mathbf{log}\, \frac{\mathbf{[R]_0}}{\mathbf{[R]}} \qquad \text{...(8.7)}$$

Equation (8.7) is the **Integrated Rate Equation** for the first order reaction.

Physical significance of k. It represents the fraction of the reactant decomposed per unit time of constant concentration. For example, if k for a given reaction is 0.00674 s^{-1}. It means that $0.00674 \times 100 = 0.674\%$ of substance would dissociate per second provided initial concentration is kept constant.

8.9. HALF LIFE OF A REACTION

It is defined as *the time during which the concentration of the reactants is reduced to half of the initial concentration or it is the time required for the completion of half of the reaction.* It is denoted by $t_{1/2}$ or $t_{0.5}$

Half Life of Zero Order Reaction

The integrated equation for zero order reaction is;

$$[R] = [R]_0 - kt$$

Now at $t_{1/2}$,

$$[R] = \frac{[R]_0}{2}$$

$\therefore$

$$\frac{[R]_0}{2} = [R]_0 - kt$$

or

$$kt_{1/2} = [R]_0 - \frac{[R]_0}{2} = \frac{[R]_0}{2}$$

or

$$\mathbf{t_{1/2}} = \frac{\mathbf{[R]_0}}{\mathbf{2k}} \qquad \text{...(8.8)}$$

From the eqn. 8.8 it is clear that the half life of a zero order reaction is directly proportional to initial concentration.

i.e., $t_{1/2} \propto [R]_0$

The plot of $t_{1/2}$ *vs.* $[R]_0$ is shown below:

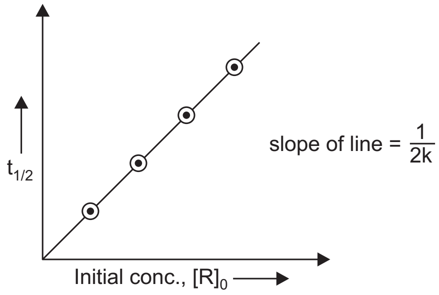


Fig. 8.6

Half Life of First Order Reaction

For first order reaction, we know that

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \quad \text{or} \quad t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

when $t = t_{1/2}$ then $[R] = \frac{[R]_0}{2}$,

therefore, $$t_{1/2} = \frac{2.303}{k} \log \frac{[R]_0}{[R]_0/2} = \frac{2.303}{k} \log 2$$

$$\mathbf{t_{1/2} = \frac{0.693}{k}} \qquad [\because \log 2 = 0.3010]$$

The above expression does not carry conc. term hence the *half life period or half change time for first order reaction does not depend upon initial concentration of the reactants. Similarly, the time required to reduce the concentration of the reactant to any fraction of the initial concentration for the first order reaction is also independent of the initial concentration.*

Plots of Half Lives vs. Initial Concentration

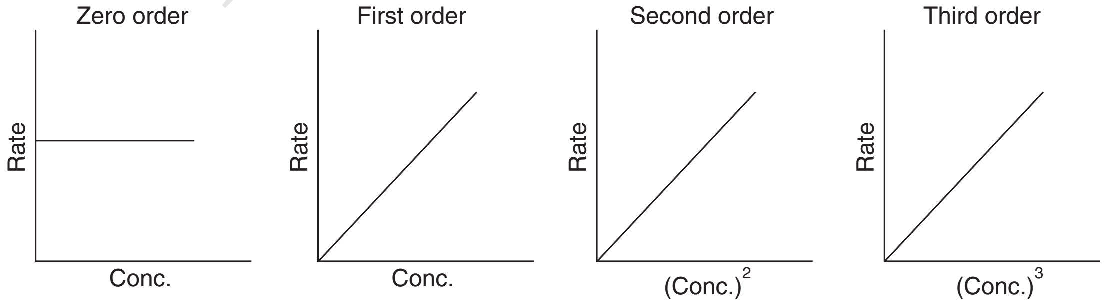


Fig. 8.7

8.10. ACTIVATION ENERGY

A reaction can occur when molecules of reactants collide with each other to form an unstable intermediate. The intermediate exists for a very short time and then breaks up to form product molecules.

The energy required to form this intermediate, called ***activated complex (C),*** is known as ***activation energy (E_a).*** In a given sample of gas, at a given temperature, all the molecules of the reacting species do not have the same kinetic energy. Since it is difficult to predict the behaviour of individual molecule with precision, Ludwig Boltzmann and James Clerk Maxwell used statistics to predict the behaviour of large number of molecules. According to them, the distribution of kinetic energy may be described by ***plotting the fraction of molecules (N_E / N_T)*** with a given kinetic energy (E) ***vs kinetic energy*** (Fig. 8.8).

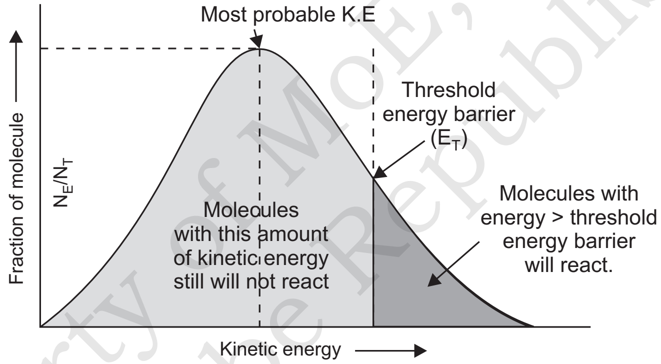


Fig. 8.8. Distribution of energies of gaseous molecules.

Here, N_E is the number of molecules with energy E and N_T is the total number of molecules.

The peak of the curve corresponds to the **most probable kinetic energy** *i.e.,* kinetic energy of maximum fraction of molecules. Only those collisions result in the formation of products which possess energy equal to or more than the certain minimum energy called ***threshold energy***. Collisions of the molecules possessing energy less than threshold energy do not form products. In between the reactants and the products there is an energy barrier which must be crossed before the reactants are converted into products. The energy required for crossing this energy barrier is called **activation energy.** It is defined as,

"The minimum extra energy over and above the average potential energy of the reactants which must be supplied to the reactants to enable them

to cross over the energy barrier between reactants and products is called Activation energy".

Activation energy = (*Threshold energy*) – (*Average energy of the reactants*)

or $$E_a = E_T - E_R$$

The idea of activation energy and the energy barrier involved in a reaction is represented graphically in Fig. 8.9.

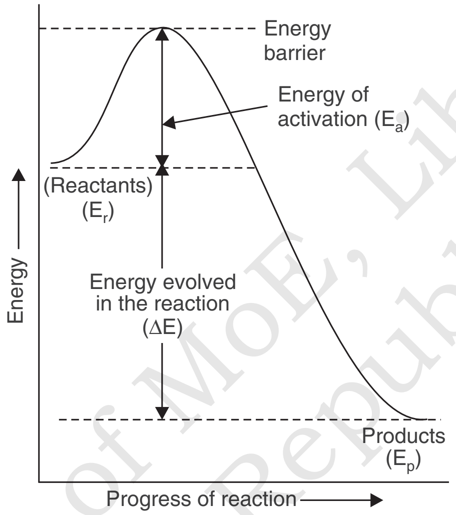


Fig. 8.9. Illustration of activation energy and energy barrier involved in a reaction.

Each reaction has a definite value of E_a and this decides the fraction of total collisions which are effective. Obviously,

(*i*) if the activation energy for a reaction is low, large number of molecules can have this energy and the ***fraction of effective collision, f,*** will be large. Such a reaction proceeds at high rate.

(*ii*) if the activation energy is high, then ***f*** will be small and the reaction may be quite slow.

Activated Complex or Transition State

In a chemical reaction certain bonds are broken and certain new bonds are formed. The breaking of bonds requires absorption of energy whereas the formation of bonds results in the release of energy.

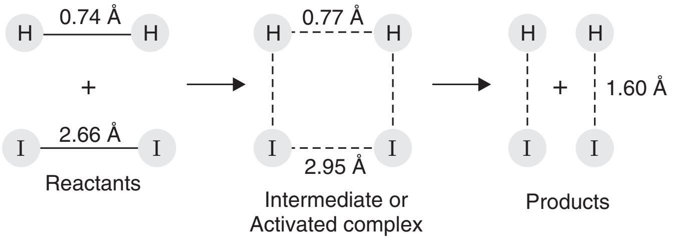


Fig. 8.10. Formation of activated complex during the reaction of H_2 and I_2 from HI.

For example, in the reaction of hydrogen with iodine to form hydrogen iodine, when a molecule of hydrogen approaches that of iodine, H—H and I—I bonds start breaking and H—I bonds start forming. In the beginning, breaking of bonds predominates and therefore, energy of the system starts increasing till it reaches a maxima (corresponding to threshold energy). After this, the energy starts decreasing because the process of bond formation predominates and finally leads to the product hydrogen iodide. ***The arrangement of atoms corresponding to energy maxima*** *(threshold energy)* **is called transition state or activated complex.** In transition state, the system has partial reactant character and partial product character as shown in Fig. 8.10 and Fig. 8.11.

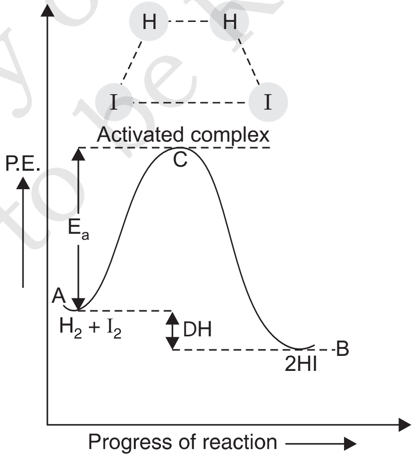


Fig. 8.11. Transition state or activated complex.

The difference between energy of the transition state and energy of the reactants is equal to activation energy.

$$\mathbf{E}_{\textbf{transition state}} - \mathbf{E}_{\textbf{reactants}} = \mathbf{E}_{\textbf{activation}}$$

The difference of energy between reactants (E_R) and products (E_P) at constant temperature and pressure is called enthalpy of reaction *i.e.*, ΔH.

Explanation of Effect of Temperature

Let us now consider the effect of increase in temperature on the number of effective collisions (*f*).

When the temperature increases the kinetic energy of molecules increases ($\because$ K.E. $\propto$ T) therefore, the maximum of the energy distribution curve gets flattened and shifts towards higher energy value *i.e.,* shifts to right as there is now greater proportion of molecules with much higher energies. On the basis of probability consideration Fig. 8.12 is drawn to give the energy distribution curves at temperatures T_1 and T_2 (where $T_2 = T_1 + 10$). A close examination of the curves in the graph clearly reveals that the fraction of the molecules possess higher kinetic energy i.e., energy greater than thressed energy, as indicated by shaded portion becomes almost double and therefore **the rate of reaction almost doubles for 10° rise of temperature**.

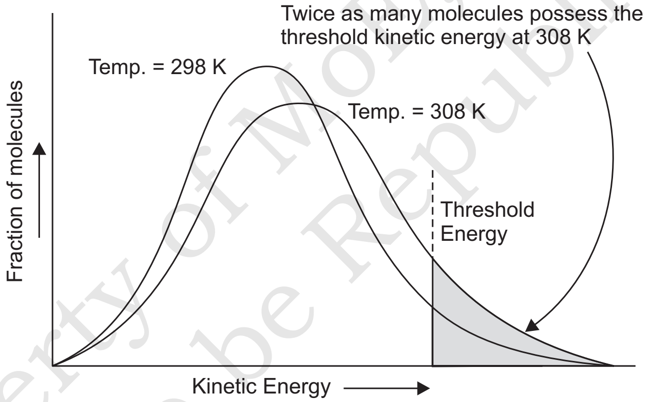


Fig. 8.12. Energy distribution at different temperatures.

Thus increase in the rate of reaction with increase in temperature is mainly due to increase in number of collisions **which are energetically** effective.

Effect of Catalyst

A catalyst is a substance that alters rate of a chemical reaction without itself being permanently chemically changed.

Never state things like "it doesn't react, just speeds it up". It must take part in the reaction and it must change chemically, albeit on a temporary basis. A catalyst provides a different 'pathway' or mechanism that makes the bond breaking processes (or other electronic changes in the reactants) occur more readily. In general,

- *A catalyst speeds up a reaction, but it must be involved 'chemically', however temporarily, in some way, and is continually changed and reformed as the reaction proceeds.*
- *Catalysts work by providing an alternative reaction pathway of lower activation energy.*

Thus, the function of a catalyst is to lower down the activation energy *i.e.,* greater is the decrease in the activation energy caused by the catalyst, higher will be the reaction rate. ***In the presence of a catalyst, the reaction follows a path of lower activation energy.*** Under this condition, a large number of reacting molecules are able to cross over the energy barrier and thus the rate of reaction increases. The energy profile diagram for the catalysed and uncatalysed reactions are as shown in the Fig. 8.13. Where dotted curve represents the progress of catalysed reaction and solid curve represents the uncatalysed reaction.

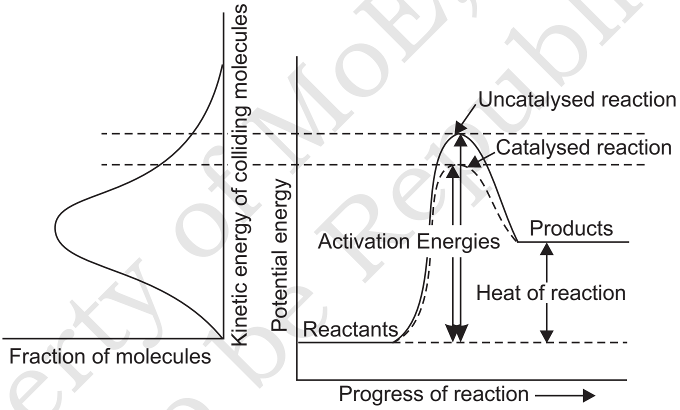


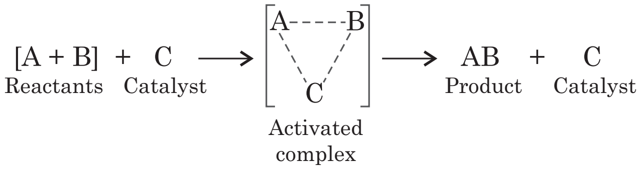
Fig. 8.13. Potential energy curves for catalysed and uncatalysed reactions.

For a general reaction of the type, A + B ⟶ AB the course of uncatalysed and catalysed reaction may be represented as:

(*a*) *Uncatalysed reaction:*

$$A + B \longrightarrow \underset{\text{Activated complex}}{[A......B]} \longrightarrow AB$$

(*b*) *Catalysed reaction:*



Though the catalyst increases the rate of the reaction, yet it does not effect the state of equilibrium in case of reversible reactions. It is because the activation energy for the forward reaction and backward reaction is reduced to the same extent.

EXPERIMENT 3

Aim: To study the effect of catalyst on the rate of reaction.

Theory: A catalyst speeds up the rate of reaction. A catalyst lowers the activation energy (the energy required to initiate the reaction) hence facilitate the reaction.

Requirements: Conical flask, delivery tube, measuring cylinder, trough, plug, $H_2O_2(l)$, catalyst (manganese (IV) oxide), lead (III) oxido, iron (III) oxide and copper (II) oxide).

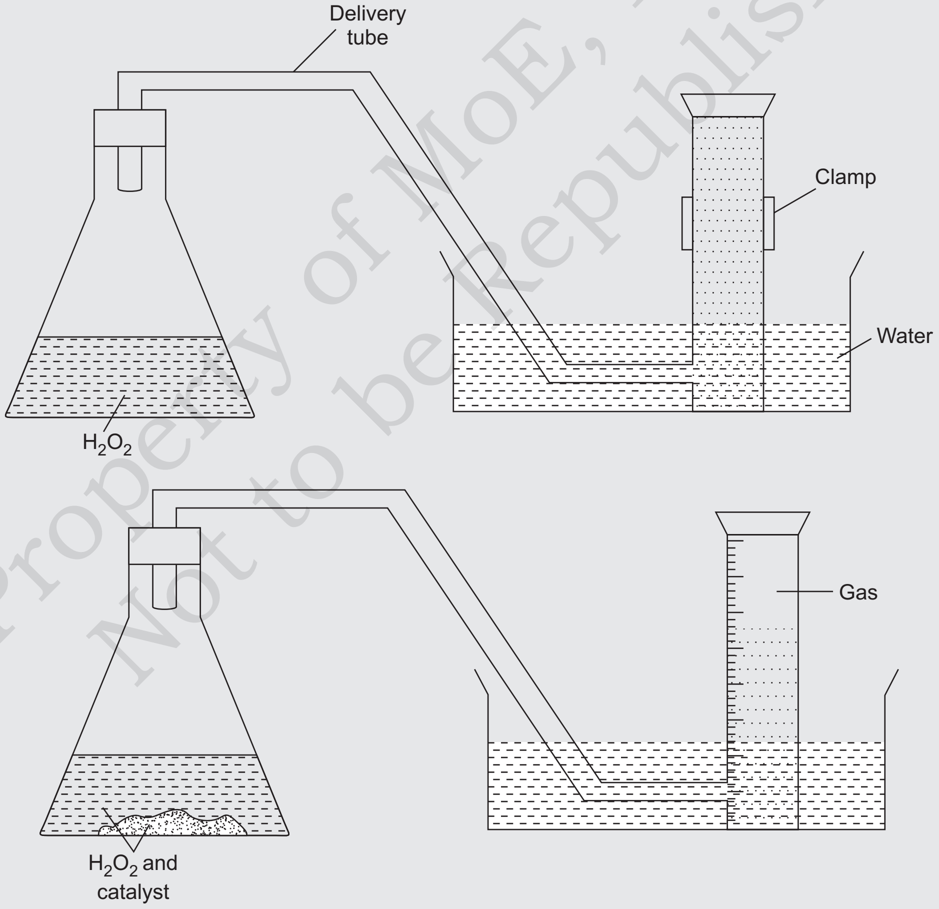


Fig. 8.14. Effect of catalyst on reaction rate

Procedure:

1. Add H_2O_2 in a conical flask.
2. Connect conical flask to a measuring cylinder put inverted in a water trough.
3. Add a catalyst in to conical flask and close the plug.
4. Measure the volume of gas produced using a fixed interval of time, in the measuring cylinder.
5. Repeat the experiment with different catalysts and compare the volume produced, hence the rate of reaction.

Precautions:

1. Plug should be tightly put on the mouth of conical flask
2. Conical flask and water trough should the put at same level.

Result:

1. Volume of gas collected after 2 minutes will he different with different catalyst.
2. Compare the data and plot the data for different catalysts on the same graph.

8.11. COLLISION THEORY OF CHEMICAL REACTIONS

Though, Arrhenius equation is applicable under a wide range of circumstances but **collision theory,** which was developed by Max Trautz and William Lewis in 1916–18, provides a greater insight into the energetic and mechanistic aspects of reactions. *It is based on kinetic theory of gases*. According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. Thus, the reaction rate shall be dependent upon:

(*i*) *Collision frequency (Z)* (*ii*) *Effective collisions* and (*iii*) *Activation energy.*

Postulates of Collision Theory

(*i*) *A reaction occurs on collision of two molecules only if they possess a certain minimum amount of energy in excess of the normal energy of molecules.*

(*ii*) *The minimum energy which molecules must possess before collision should be equal to or greater than the activation energy.*

Expression for Rate Constant of a Bimolecular Reaction

Say we have an elementary bimolecular reaction

$$A + B \longrightarrow \text{Products}$$

According to collision theory the reaction takes place as a result of collisions between A and B. **The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z_{AB}).** As all the collisions between A and B are not effective therefore, the rate of reaction is equal to the rate of collisions per unit volume per unit time multiplied by the fraction of collisions that have sufficient relative kinetic energy to overcome the energy barrier, *i.e.*, molecules with energies equal to or greater than E_a. Thus, the rate constant (or rate) is given as:

k ∝ rate of collisions or frequency of collisions (Z_{AB}) ∝ energy factor (given by Boltzmann factor, $e^{-Ea/RT}$)

Thus, the rate of a reaction would be mathematically expressed as:

$$\text{Rate} = Z_{AB} \cdot e^{-Ea/RT} \qquad \text{...(8.9)}$$

The above equation predicts the value of rate constants fairly accurately for the reactions that involve atomic species or simple molecules but for complex molecules significant deviations are observed. The *reason could be that all the collisions between A and B will not lead to reaction even if the energy requirement is satisfied. It is because the colliding molecules should also have* ***proper orientation***. In simple words all colliding molecules having sufficient energy but no proper orientation will bounce back without any reaction.

Similarly, it can be predicted that the, formation of methanol from bromoethane depends upon the orientation of reactant molecules as shown in Fig. 8.15. ***The proper orientation of reactants molecules leads to bond formation whereas improper orientation makes them simply bounce back and no products are formed.***

$$CH_2Br + \bar{O}H \longrightarrow CH_3OH + \bar{B}r$$

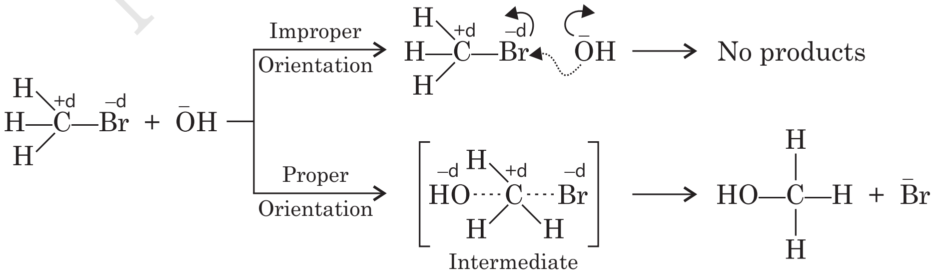


Fig. 8.15. Diagram showing molecules having proper and improper orientation.

ASSIGNMENTS/EXERCISES

1. Describe the speed of certain natural reactions

(*a*) explosions (*b*) food decay

(*c*) rusting of iron (*d*) ripening of fruits

Students can be explained following topics in the laboratory with the help of some example demonstration of the following natural reactions.

(*a*) **Explosions:** Explosions are the conclusion reactions of explosive chemicals like TNT (Trinitrotouline). Explosive chemicals when undergo rapid oxidation with the production of large quantity of gases. The shock waves produced by expanding gases cause much damage with lots of sound and heat.

(*b*) **Food decay:** The food kept for long time at a temperature range of 25–40°C smells foul and looks rotten making it unsuitable for eating. This food decay may be due to light, oxygen, heat, humidity bacterial growth, protozoa, fungi, like yeasts and moulds. Food decay can be identified by change in colour, change in texture, unpleasant odour or undesirable taste. Food can be prevented from decay by any means which stops on control the growth of germs like bacterial fungi etc. Freezing, boiling. Using preservatives (as for pickles and fish), by adding excess sugar (james, jellies, murabbas etc.) and dehydration are the ways to protect fruits from decaying.

(*c*) **Rusting of Iron:** Rusting is slow oxidation that occurs on the surface of iron in the presence of oxygen and moisture resulting in the formation of plucky brown layer that accumulates on the iron surface. It results in formation of oxide (Fe_3O_4).

$$Fe + 3O_2 + H_2O \longrightarrow Fe_3O_4 + H_2O.$$

(*d*) **Ripening of fruits:** Ripening of fruits is a process in which fruit attains more sweatiness, desirable colour and flavour and become palatable in nature. On ripening level of ethylene increases in fruits. During ripening fruit flash, softens, sugar content rises, acid level reduced because of formation of esters from organic acids. The production of ethelene in fruits causes increase in production of ethelene. So ethylene has autocatalytic effect in ripening of fruits.

SUMMARY

- **Rate of Reaction:** It is the rate of change of concentration of any of the reactant or product with time at any particular moment of time.
- **Average Rate:** The rate of reaction measured over a long time interval is called average rate. It is given as $\Delta x/\Delta t$.

- **Instantaneous Rate:** It is the rate of a reaction at a given instant of time *i.e.*, $\frac{\Delta x}{\Delta t}$ (average rate) becomes $\frac{dx}{dt}$ when Δt approaches zero.
- **Initial Rate:** The rate at the beginning of a reaction when the conc. have not changed appreciably.
- **Law of Mass Action:** The rate of a reaction is directly proportional to the product of conc. of reactants with each term raised to power number of times it is present in a balanced equation at a given temperature.
- **Rate Constant (k):** It is the rate of the reaction when the concentration of each of reacting species is unity. It is also called *velocity constant* or *specific reaction rate* of the reaction.
- **Rate Law:** The mathematical expression based on experimental fact, which describes the reaction rate in terms of concentrations of reacting species. It cannot be written from the balanced equation.
- **Integrated Rate Equation:** The differential rate equations which are integrated to give a relationship between rate constant and concentrations at different times.
- **Order of Reaction:** The sum of the exponents of the concentration terms in the experimental rate law of reaction. It can be zero, 1, 2, 3 or and any fractional value.
- **First Order Reaction:** A reaction in which the rate of reaction is directly proportional to the conc. of reacting substance, *i.e.*, $r = k[A]$

  or $kt = 2.303 \log [A]_0/[A]$
- **Half-life Period of Reaction ($t_{1/2}$):** The time taken for the concentration of reactants to be reduced to half of their initial concentration.
- **Activation Energy (E_a):** The additional energy required by reacting species over and above their average PE to enable them to cross the energy barrier between reactants and products.
- **Catalyst:** A substance which enhances the rate of a reaction.
- **Mechanism of Reaction:** The sequence of elementary steps leading to overall stoichiometry of a reaction.
- **Threshold Energy:** The minimum energy that a reacting species must possess in order to undergo effective collisions.

- **Collision Theory:** A chemical reaction takes place due to collisions between reacting molecules. For a bimolecular reaction, Rate = $Z_{AB} \cdot e^{-Ea/RT}$. Here Z is collision frequency and $e^{-Ea/RT}$ is fraction of molecules with energy equal to or greater than E*a*.

EVALUATION

I. Multiple Choice Questions

1. The rate of a chemical reaction can be expressed in

(*a*) grams per mole

(*b*) energy consumed per mole

(*c*) volume of gas per unit time

(*d*) moles formed per liter of solution

2. The addition of a catalyst to a reaction causes ....

(*a*) an increase in the Gibb's energy of the reaction.

(*b*) a decrease in the enthalpy of the reaction.

(*c*) a change in the activation energy of the reaction.

(*d*) an increase in the equilibrium constant of the reaction.

3. When a catalyst is added to an exothermic reaction, the heat evolved during the reaction ....

(*a*) increases (*b*) decreases

(*c*) remains unchanged (*d*) may increase or decrease

4. Which of the following factors affects the rate of heterogeneous reaction only?

(*a*) Nature of reactants (*b*) Temperature of system

(*c*) Surface area of reactants (*d*) Concentration of reactants

5. The addition of a catalyst to a reaction provides an alternative mechanism with

(*a*) lower activation energy and lower reaction rate

(*b*) lower activation energy and higher reaction rate

(*c*) higher activation energy and lower reaction rate

(*d*) higher activation energy and higher reaction rate

6. Collision theory states that

(*a*) all collisions lead to chemical reactions

(*b*) most collisions lead to chemical reactions

(*c*) very few reactions involves particle collisions

(*d*) effective collisions lead to chemical reactions.

7. When a lit match stick is touched to the wick of a candle, the candle begins to burn. When the match is removed, the candle continues to burn. In this reaction, the lit match stick

(*a*) acts as a catalyst

(*b*) supplies activation energy

(*c*) touched to wick is the rate-determining step

(*d*) lowers the activation energy barrier

8. To have successful collisions the reactants must have

(*a*) favourable geometry only

(*b*) sufficient heat of reaction only

(*c*) sufficient potential energy only

(*d*) sufficient kinetic energy and favorable geometry

9. The half-life period for a certain first order reaction is 30 minutes. How long will it take for 1/32 of the reactant to be left behind?

(*a*) 60 minute (*b*) 120 minute

(*c*) 90 minute (*d*) 150 minute

10. How does the addition of a catalyst increase the reaction rate of an endothermic reaction?

(*a*) It reduces the ΔH of the reaction.

(*b*) It increase the ΔH of the reaction.

(*c*) It reduces the required activation energy.

(*d*) It causes the reaction to become exothermic.

II. Descriptive Questions

1. Write a chemical reaction in which the units of rate and rate constant are same.

2. Define order of a reaction.

3. Define 'activation energy' of a reaction.

4. What is the effect of adding a catalyst on activation energy (E_a) of a reaction.

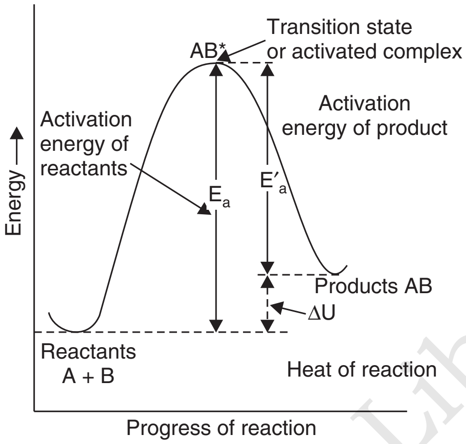
5. What do you understand by the rate of a chemical reaction? Name the factor on which it depends.

6. Why the rate of a chemical reaction do not remain uniform throughout the reaction? Is it possible to have reactions with a uniform rate?

7. A chemical reaction has zero activation energy. What is the effect of temperature on rate constant of reaction?

8. How a catalyst only changes the speed of a reaction whereas a photosensitizer initiates the reaction?

9. State the role of activated complex in a reaction and state its relation with activation energy.



Potential energy diagram of an endothermic reaction

10. The rate constant of a zero order reaction is 1×10^{-3} mol L^{-1} s^{-1}. Starting with 50 moles, calculate the time in minutes in which the concentration decreases to 10 moles.

III. Numerical Questions

1. Rate of formation of nitric oxide (NO) in the following reaction is 3.6×10^{-3} mol^{-1} s^{-1}.

$$4NH_3(g) + SO_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Find the rate of disappearance of oxygen.

2. Calculate the overall order of the reaction which has the rate expression.

(a) Rate = $k[A]^{1/2} [B]^{3/2}$

(b) Rate = $k[A]^{3/2} [B]^{-1}$

3. A first order reaction has rate constant of 10^{-2} sec^{-1}. Calculate the half life period for this reaction.