[I] Catalyst and Catalysis

Berzelius (1835) found that the speed of a number of reactions is increased due to the presence of a small quantity of a foreign substance. He also found that these substances remain chemically unchanged at the end of the reaction. He termed these substances as **catalysts** and the phenomenon itself is known as **catalysts**. A familiar example is that of the decomposition of $KClO_3$. The decomposition of $KClO_3$ is very slow even at high temperatures, but a small quantity of MnO_2 increases the rate of decomposition to a very great extent and MnO_2 remains chemically unchanged at the end of the reaction.

$$2KClO_3 + [MnO_2] \longrightarrow 2KCl + 3O_2 + [MnO_2]$$

But later on it was observed that there are certain substances which can retard the rate of a chemical reaction. Hence, Ostwald defined that,

"A catalyst is a substance which influences the speed of a chemical reaction without itself undergoing any chemical change at the end of the reaction."

Catalysis is mainly divided into two types, *viz.*, homogeneous catalysis and heterogeneous catalysis.

[II] Homogeneous Catalysis

When the catalyst is present in the same phase as that of the reactants, the phenomenon is known as homogeneous catalysis.

(a) Examples of homogeneous catalysis in gas phase

(i) Oxidation of sulphur dioxide (SO_2) to sulphur trioxide (SO_3) with nitric oxide (NO) as catalyst,

$$\underset{\text{Gas}}{2SO_2} + \underset{\text{Gas}}{O_2} + \underset{\text{Gas}}{[NO]} \longrightarrow \underset{\text{Gas}}{2SO_3} + [NO]$$

(ii) Decomposition of acetaldehyde (CH_3CHO) with iodine (I_2) as catalyst,

$$\underset{\text{Vapour}}{CH_3CHO} + \underset{\text{Vapour}}{[I_2]} \longrightarrow \underset{\text{Gas}}{CH_4} + \underset{\text{Gas}}{CO} + [I_2]$$

(b) Examples of homogeneous catalysis in solution phase

Many reactions in solutions are catalysed by acids (H^+) and bases (OH^-).

(i) Decomposition of hydrogen peroxide (H_2O_2) in the presence of iodide ion (I^-) as catalyst,

$$2H_2O_2 \xrightarrow{I^-} 2H_2O + O_2$$

(ii) Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst,

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H_2SO_4} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

(iii) Hydrolysis of an ester in the presence of acid or alkali.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+/OH^-} \underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH}$$

[III] Heterogeneous Catalysis

When the catalyst is in a different phase than that of reactants, the phenomenon is known as heterogeneous catalysis.

Some examples of heterogeneous catalysis with reactants in the gas, liquid or the solid phase are given below.

(a) Heterogeneous catalysis with gaseous reactants (contact catalysis)

(i) Oxidation of ammonia to nitric oxide (NO) in the presence of a platinum gauze (a stage in the manufacture of nitric acid),

$$\underset{\text{Gas}}{4NH_3} + \underset{\text{Gas}}{5O_2} + \underset{\text{Solid}}{[Pt]} \longrightarrow 4NO + 6H_2O + [Pt]$$

(ii) Combination of sulphur dioxide (SO_2) and oxygen in the presence of finely divided platinum or vanadium pentoxide, V_2O_5, *(contact process for sulphuric acid).*

$$\underset{\text{Gas}}{2SO_2} + \underset{\text{Gas}}{O_2} + \underset{\text{Solid}}{[Pt]} \longrightarrow 2SO_3 + [Pt]$$

(iii) Hydrogenation reactions of unsaturated organic compounds are catalysed by finely divided nickel.

$$\underset{\text{Ethene (gas)}}{H_2C{=}CH_2} + \underset{\text{Gas}}{H_2} + \underset{\text{Solid}}{[Ni]} \longrightarrow \underset{\text{Ethane}}{H_3C-CH_3} + [Ni]$$

Vegetable oils are tri-esters of glycerol with higher unsaturated acid (oleic acid). When hydrogen is passed through the *vegetable oils* in presence of nickel, the carbon-carbon double bonds of the acid portion are hydrogenated to yield *solid fats (vanaspati ghee).*

(iv) Combination of nitrogen and hydrogen to form ammonia in the presence of finely divided iron, *(Haber's process for ammonia).*

$$\underset{\text{Gas}}{N_2} + \underset{\text{Gas}}{3H_2} + \underset{\text{Solid}}{[Fe]} \longrightarrow 2NH_3 + [Fe]$$

(b) Heterogeneous catalysis with liquid reactants

(i) The decomposition of aqueous solution of hydrogen peroxide (H_2O_2) is catalysed by manganese dioxide (MnO_2) or platinum in colloidal form.

$$\underset{\text{Liquid}}{2H_2O_2} + \underset{\text{Solid}}{[Pt]} \longrightarrow 2H_2O + O_2 + [Pt]$$

(ii) Benzene and ethanoyl chloride (CH_3COCl) react in the presence of anhydrous aluminium chloride to form phenyl methyl ketone ($C_6H_5COCH_3$).

$$\underset{\text{Liquid}}{C_6H_6} + \underset{\text{Liquid}}{CH_3COCl} + \underset{\text{Solid}}{[AlCl_3]} \longrightarrow C_6H_5COCH_3 + HCl + [AlCl_3]$$

(c) Heterogeneous catalysis with solid reactants

The decomposition of potassium chlorate ($KClO_3$) is catalysed by manganese dioxide (MnO_2).

$$\underset{\text{Solid}}{2KClO_3} + \underset{\text{Solid}}{[MnO_2]} \longrightarrow 2KCl + 3O_2 + [MnO_2]$$

The above reaction is heterogeneous, though both reactants are in the same phase (solid), because the solid forms a new phase.