more accurately calculable.

CATALYSIS

Berzelius (1836) realised that there are substances which increase the rate of a reaction without themselves being consumed. He believed that the function of such a substance was to loosen the bonds which hold the atoms in the reacting molecules together. Thus he coined the term **catalysis** (Greek *kata* = wholly, *lein* = to loosen).

There is no doubt that usually a catalyst accelerates a reaction as was originally thought by Berzelius. But a number of cases are now known where the catalyst definitely retards (slows down) the rate of a reaction.

Thus, a catalyst is now-a-days defined as a substance which alters the rate of a chemical reaction, itself remaining chemically unchanged at the end of the reaction. The process is called catalysis.

As evident from the above definition, a catalyst may increase or decrease the rate of a reaction.

A catalyst which enhances the rate of reaction is called a **Positive catalyst** and the process positive catalysis or simply **catalysis.**

For example potassium chlorate in the presence of MnO_2 decomposes rapidly. MnO_2 behaves as a positive catalyst.

$$2KClO_3 + (MnO_2) \rightarrow 2KCl + 3O_2 + (MnO_2)$$

A catalyst which retards the rate of a reaction is called a **Negative catalyst** and the process **Negative catalysis.**

For example hydrogen peroxide easily decomposes to give water and oxygen but presence of phosphoric acid reduces the rate of decomposition. Here phosphoric acid behaves as a negative catalyst.

$$2H_2O_2 \xrightarrow{H_3PO_4} 2H_2O + O_2$$

Types of Catalysis

There are two main types of catalysis :

(a) Homogeneous catalysis

(b) Heterogeneous catalysis

Also, there is a third type of catalysis known as **Enzyme catalysis** which is largely of biological interest.

(A) Homogeneous Catalysis

In homogeneous catalysis, **the catalyst is in the same phase as the reactants and is evenly distributed throughout.** This type of catalysis can occur in gas phase or the liquid (solution) phase.

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,

$$\underset{gas}{2SO_2} + \underset{gas}{O_2} + [NO] \rightarrow \underset{gas}{2SO_3} + \underset{gas}{[NO]}$$

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

$$\underset{gas}{CH_3CHO} + \underset{gas}{[I_2]} \rightarrow \underset{gas}{CH_4} + \underset{gas}{CO}$$

Examples of homogeneous catalysis in solution phase :

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

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

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H_2SO_4} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} + [H_2SO_4]$$

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

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

(B) Heterogeneous Catalysis

The catalysis in which the catalyst is in a different physical phase from the reactants is termed heterogeneous catalysis. The most important of such reactions are those in which the reactants are in the gas phase while the catalyst is a solid. The process is also called contact catalysis since the reaction occurs by contact of reactants with the catalyst surface. In contact catalysis, usually the catalyst is a finely divided metal or a gauze. This form of catalysis has greater industrial importance.

Examples of heterogeneous catalysis :

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

(1) Heterogeneous catalysis with gaseous reactans (Contact catalysis)

(i) 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*).

$$\underset{\text{gas}}{2SO_2} + \underset{\text{gas}}{O_2} + \underset{\text{solid}}{[Pt]} \rightarrow 2SO_3 + [Pt]$$

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

$$\underset{\text{gas}}{N_2} + \underset{\text{gas}}{3H_2} + \underset{\text{solid}}{[Fe]} \rightarrow 2NH_3 + [Fe]$$

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

$$\underset{\text{gas}}{4NH_3} + \underset{\text{gas}}{5O_2} + \underset{\text{solid}}{[Pt]} \rightarrow 4NO + 6H_2O + [Pt]$$

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

$$\underset{\text{Ethene (gas)}}{H_2C{=}CH_2} + \underset{\text{gas}}{H_2} + \underset{\text{solid}}{[Ni]} \rightarrow \underset{\text{Ethane}}{CH_3{-}CH_3} + [Ni]$$

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

(2) Heterogeneous catalysis with liquid reactants

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

$$\underset{\text{liquid}}{2H_2O_2} + \underset{\text{solid}}{[Pt]} \rightarrow 2H_2O + [Pt]$$

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

$$\underset{\text{liquid}}{C_6H_6} + \underset{\text{liquid}}{CH_3COCl} + \underset{\text{solid}}{[AlCl_3]} \rightarrow C_6H_5COCH_3 + HCl + [AlCl_3]$$

(3) Heterogeneous catalysis with solid reactants

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

$$\underset{\text{solid}}{2KClO_3} + \underset{\text{solid}}{[MnO_2]} \rightarrow 2KCl + 3O_2 + [MnO_2]$$

On the basis of catalytic reactions, they are of the following types :

1. Positive catalysis. *If a catalyst increases the rate of a reaction, it is called a positive and the phenomenon is called positive catalysis.* A few examples of positive catalysis are given below :

(i) Decomposition of potassium chlorate in the presence of MnO_2 as a catalyst

$$2KClO_3(s) \xrightarrow{MnO_2\ (s)} 2KCl(s) + 3O_2(g)$$

(ii) Oxidation of SO_2 to SO_3 using NO as a catalyst

$$SO_2(g) + \frac{1}{2}O_2 \xrightarrow{NO\ (g)} SO_3(g)$$

(iii) Manufacture of ammonia by Haber's process using finely divided iron as catalyst

$$N_2(g) + 3H_2(g) \xrightarrow{Fe} 2NH_3(g)$$

(iv) Hydrolysis of ethyl acetate in presence of an acid or an alkali as a catalyst

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H_3O^+ \text{ or } OH^-} CH_3COOH + C_2H_5OH$$

2. Negative catalysis. *If a catalyst decreases the rate of a reaction, it is called a* **negative catalyst** *and the phenomenon is called negative catalysis.* A few examples of negative catalysis are given below :

(i) Decomposition of H_2O_2 is retarded in the presence of traces of acetanilide

$$2H_2O_2 \xrightarrow{\text{Acetanilide}} 2H_2O + O_2$$

(ii) Oxidation of chloroform is retarded in the presence of a small quantity of ethyl alcohol

$$CHCl_3 + O_2 \xrightarrow{C_2H_5OH} 2COCl_2 + 2HCl$$

3. Auto-catalysis. When in a reaction, one of the products act as a catalyst for the reaction, the phenomenon is called autocatalysis. For example,

(i) In the titration of hot oxalic acid solution against acidified $KMnO_4$ solution, the pink colour is discharged first slowly and then rapidly as the reaction proceeds. This is because the Mn^{2+} ions formed during the reaction act as autocatalyst for the reaction.

$$5\begin{array}{l}COOH\\ |\\ COOH\end{array} + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

(ii) In hydrolysis of ethyl acetate, acetic acid and ethyl alcohol are formed. The reaction is initially very slow but gradually its rate increases. This is due to the formation of acetic acid which acts as an auto-catalyst in this reaction.

$$RCOOR' + H_2O \rightarrow RCOOH + R'OH$$

4. Induced catalysis. When one reaction influences the rate of other reaction, which does not occur under ordinary conditions, the phenomenon is known as **induced catalysis.** For example, sodium arsenite solution is not oxidised by air. If, however, air is passed through a mixture of the solution of sodium arsenite and sodium sulphite, both the them undergo simultaneous oxidation. The oxidation of sodium sulphite, thus, influences the oxidation of sodium arsenite.

General Characteristics of Catalytic Reactions

1. The catalyst remains unchanged in amount and chemical composition at the end of the reaction. The amount of the catalyst found at the end of the reaction is the same as before. However, it may undergo some physical change. For example, manganese dioxide catalyst used in the decomposition of potassium chlorate is found to have changed from granular state to the powder form. Similarly the surface of the platinum gauze used as a catalyst in the combination of hydrogen and oxygen to form water changes from smooth to rough.

2. Only a small quantity of the catalyst is generally needed. In many reactions only a small amount of the catalyst is required. For instance, such a low concentration as one gram of colloidal platinum in 106 litres can catalyse decomposition of hydrogen peroxide. Similarly, the concentration as low as one gram of cupric ion in 109 litres can catalyse the oxidation of sodium sulphite to sodium sulphate by atmospheric oxygen.

3. The catalyst does not alter the position of equilibrium in a reversible reaction. A catalyst can only hasten the approach of equilibrium in reversible reaction. It does not alter the concentrations of the products. For example, in the reaction.

$$2SO_2 + O_2 \rightarrow 2SO_3$$

The presence of platinised asbestos (catalyst) causes an appreciable increase in the rate of the reaction and hastens the approach of equilibrium but it does not in any way increase the yield of sulphur trioxide.

4. The catalyst does not initiate the reaction. The reaction is already occurring, though extremely slowly, in the absence of the catalyst. The function of the catalyst seems to be only to speed up the reaction considerably.

5. The catalyst is specific in its action. For example, manganese dioxide can catalyse the decomposition of potassium chlorate but not that of potassium perchlorate or potassium nitrate. However, transition metals like iron, cobalt, nickel, platinum and palladium can catalyse reactions of variuos types.

6. Catalysts cannot alter the nature of the products of the reaction. The combination of nitrogen and hydrogen under suitable conditions results invariably in the formation of ammonia whether a catalyst is added or not. Similarly potassium chlorate on decomposition gives potassium chloride and oxygen whether manganese dioxide is added or not.

However, there are a few exceptions. Carbon monoxide and hydrogen combine to form methane or methyl alcohol or formaldehyde depending upon the nature of the catalyst used :

$$CO + 3H_2 \xrightarrow{\text{Nickel}} CH_4 + H_2O$$

$$CO + 2H_2 \xrightarrow{ZnO + Cr_2O_3} CH_3OH$$

$$CO + H_2 \xrightarrow{Cu} HCHO$$

7. Optimum temperature. Every catalyst works properly at a definite temperature which is known as optimum temperature. On increasing the temperature activity of catalyst decreases due to change in physical state.

8. Catalytic activators or Promoters. It has been found that presence of some compounds enhance the strength of Catalyst. These compounds are called promoters or catalytic activators. For example molybdenum works as a promoter for iron catalyst in Haber's process.

$$N_2 + 3H_2 \xrightarrow[\text{Mo (promoter)}]{\text{Fe (catalyst)}} 2NH_3$$

9. A catalyst is poisoned by certain substances. It has been found that impurities of any type, even if present in small amounts, inhibit or retard the rate of catalysed reactions to a large extent. These impurities are, therefore, called **catalytic poisons**. For example, the combination of sulphur dioxide and oxygen in (in the contact process) is slowed down considerably if some arsenic compounds are present even in traces. Nowadays, vanadium pentoxide catalyst is preferred because it is much less sensitive to poisoning. Similarly traces of mercury reduce the catalytic activity of copper for the combination of ethylene and hydrogen to form ethane.

HOW DOES A CATALYST WORK ?

The presence of a catalyst provides an alternate path with lower energy barrier, as shown in Fig. 5.10. Thus the energy of activation is lowered and hence a greater number of molecules can cross the barrier and change over to products. According to Arrhenius equation $k = Ae^{-E_a/RT}$

As energy of activation E_a is lowered by the presence of catalyst, value of rate constant k (or rate of reaction) increases.

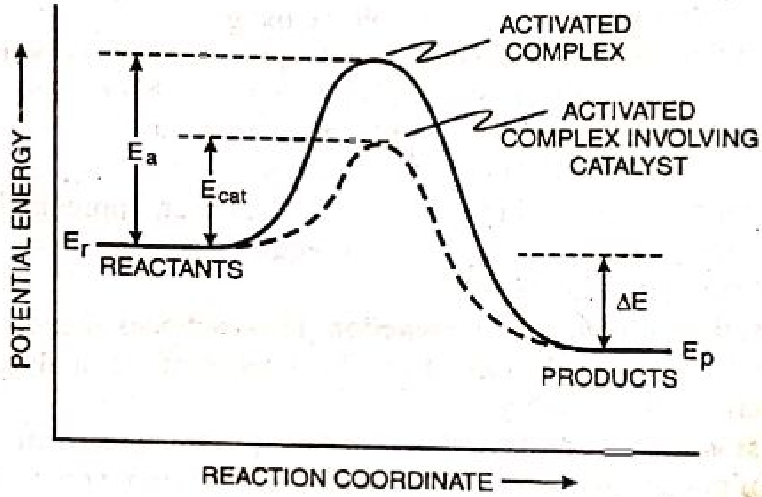

Fig. 5·13. Energy diagram for a catalysed and uncatalysed reaction showing the lowering of activation energy by a catalyst.

Further from Fig. 5.13, the following two additional results may be derived :

(a) ΔE (= $E_p - E_r$) for the catalysed reaction is the same as ΔE for the uncatalysed reaction.

(b) For reversible reactions, the energy of activation for the reverse reaction is lowered to the same extent as for the direct reaction. Hence the presence of the catalyst in such reactions increases the speed of the forward reaction and that of the backward reaction to the same extent. Consequently, the equilibrium is attained quickly otherwise remains undisturbed.

For explaining mechanism of catalysis, many theories have been proposed. Main theories are as follows :

Theories of catalysis (Mechanism of catalysis)

It is not possible to give a uniform explanation of the mechanism of the phenomenon of catalysis, as catalytic reactions are of varied nature. However, two broad theories of catalytic action have been proposed. First theory known as **intermediate compound formation theory** explains successfully the homogeneous catalysis while second theory termed as **adsorption theory** explains the heterogeneous catalysis.

(1) Intermediate Compound Theory

This theory was proposed by Clement and Desormes in 1806. According to this theory *the catalyst forms very reactive and unstable intermediate compound with reactants which* *immediately reacts with other reactants yielding the products of the reaction and liberating the catalyst in its original chemical composition.*

For example, a reaction of the type

$$A + B \longrightarrow AB$$

Which occurs in presence of a catalyst K, may take place as

$$\underset{}{A} + \underset{\text{Catalyst}}{K} \longrightarrow \underset{\text{Intermediate compound}}{AK}$$

$$AK + B \longrightarrow \underset{\text{Product}}{AB} + \underset{\text{Catalyst}}{K}$$

Many catalytic reactions can be explained on the basis of this theory.

(i) Catalytic action of NO in the manufacture of H_2SO_4 by Chamber's process :

$$\underset{\text{Catalyst}}{2NO} + \underset{\text{Reactant}}{O_2} \rightleftharpoons \underset{\text{Intermediate compound}}{2NO_2}$$

$$\underset{\text{(other reactant)}}{2SO_2} + 2NO_2 \rightleftharpoons 2SO_3 + 2NO$$

---

or $$[2NO] + 2SO_2 + O_2 \rightleftharpoons 2SO_3 + [2NO]$$

(ii) Preparation of O_2 from $KClO_3$ by heating in the presence of MnO_2 probably takes place as :

$$2KClO_3 + \underset{\text{Catalyst}}{2MnO_2} \longrightarrow 2KMnO_4 + O_2 + Cl_2$$

$$2KMnO_4 + Cl_2 \longrightarrow 2KCl + MnO_2 + O_2$$

∴ A little quantity of Cl_2 is found with O_2 and the residue is found to be pink coloured (due to $KMnO_4$) if only a small quantity of MnO_2 is used.

This theory, however **fails to explain** (i) the action of promoters and catalytic poisons, (ii) the function of catalyst in heterogeneous reactions where intermediate compound formation is not possible, *e.g.*, combination of SO_2 and O_2 in presence of platinised asbestos where catalyst is *solid* and reactants are *gases*.

(2) Modern Adsorption Theory

This theory mainly explains the mechanism of heterogeneous catalysts. In the first step molecules of reactants say A and B are adsorbed on the surface of catalyst. This increases local concentration of reactants. Since process of adsorption is exothermic, it decreases the value of activation energy. In the second step these adsrorbed molecules which are present on the active centres of the surface of catalyst react with atoms of free valencies to form 'Adsorbed Activated complex'.

$$A + B + S \text{ (Catalytic surface)} \rightarrow ABS \text{ (Adsorbed activated complex)}$$

Since potential energy of this complex is high, it decomposes therefore rapidly to products in third step.

$$ABS \rightarrow AB + S.$$

This released catalyst is again available for repeating the first step.

This theory explains why finely divided catalysts are more powerful. The surface area and free valencies are much more in rough and finely divided catalysts.

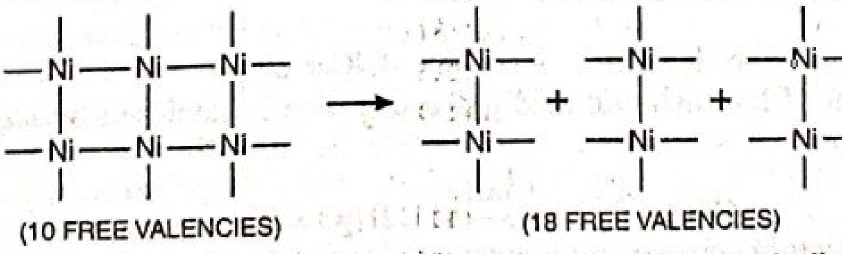

Fig. 5·14. Increase in free valencies as a result of sub-division

Zeolites—The most important oxide catalysts today are zeolites. Zeolites are microporous aluminosilicates of the general formula $M_{x/n}\,[AlO_2]_x\,(SiO_2)_y$. They are widely used in petrochemical industries for cracking of hydrocarbons and isomerization. Reactivity of zeolites depends on the size of cages (cavities) and apertures (pores) present in them. 'Shape selectivity' is the most remarkable feature of zeolite catalysis. Shape selective catalysis depends upon the pore structure. The pore size in zeolites generally varies between 260 pm and 760 pm. Reactions proceed in a specific manner depending on the size of the reactant and product molecules compared to size of the cages or pores of the zeolites. For example ZSM–5, a zeolite catalyst, converts alcohols into gasoline (petrol) by dehydrating alcohols.

APPLICATIONS OF CATALYSIS

Catalysis plays an important role in a large variety of laboratory and fermentation reactions.

1. Laboratory reaction. A few typical examples of laboratory reactions are given below :

(a) *Manganese dioxide* is used as a catalysts in the formation of oxygen on heating potassium chlorate.

(b) *Platinum* is used as a catalyst in the combination of hydrogen and oxygen gases to form water vapour.

(c) *Colloidal platinum* is used as a catalyst in the decomposition of hydrogen peroxide.

(d) *Hydrogen ions* (dilute acids) are used as catalysts in the inversion of cane-sugar.

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

2. Industrial reactions. Some of the important industrial reactions which take place in the presence of catalysts are given below :

(a) Combination of sulphur dioxide and oxygen in the *contact process* for the manufacture of sulphuric acid is catalysed by platinum deposited on asbestos (*platinised asbestos*) :

$$2SO_2 + O_2 \xrightarrow{Pt} \underset{\text{Sulphur trioxide}}{2SO_3}$$

(b) Combination of nitrogen and hydrogen to form *ammonia* (*Haber's process*) is catalysed by *iron* in the presence of *molybdenum* :

$$N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$$

(c) Hydrogenation of oils to produce *vanaspati* ghee is catalysed by finely divided *nickel* :

$$\underset{\substack{\text{Unsaturated compound}\\ \text{(oil)}}}{>C=C< + H_2} \xrightarrow{Ni} \underset{\substack{\text{Saturated compound}\\ \text{(fat)}}}{-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{H}{\overset{|}{\underset{|}{C}}}}$$

(d) Oxidation of ammonia to nitric oxide, (used in the manufacture of nitric acid) is catalysed by *platinum* (*Ostwald's process*) :

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O$$

(e) Oxidation of hydrochloric acid gas to chlorine is catalysed by *cupric chloride* (*Deacon's process*) :

$$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2$$

(f) The cracking of kerosene oil is catalysed by certain *silicates*.