B.Sc. (Honours) Part-II
Paper-III

Topic: Catalysis
UG
Subject-Chemistry

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CATALYSIS

13.9 INTRODUCTION

Potassium chlorate when strongly heated decomposes slowly giving oxygen. The decomposition occurs in the temperature range of 380–600°C.

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

However, when a little of manganese dioxide is added, the decomposition takes place at a considerable lower temperature range, *i.e.*, 200–360°C at a much accelerated rate. The manganese dioxide added remains unchanged with regard to its mass and composition.

In a similar manner, the rates of a number of chemical reactions can be altered by the mere presence of a foreign substance. The systematic study of the effect of various foreign substances on the rates of chemical reactions was first made by **Berzelius,** in 1835. He suggested the name **catalyst,** for such substances.

Substances which thus alter the velocity of a reaction, themselves remaining chemically and quantitatively unchanged after the reaction, are known as **catalysts** and the phenomenon is known as **catalysis.** Ostwald (1895), defined a catalyst as: *a substance which changes the reaction rate without affecting the overall energetics of the reaction.*

13.10 HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

Catalytic reactions can be broadly divided into two groups:

1. Homogeneous catalysis: When the reactants and the catalyst are in the same phase, *i.e.*, solid, liquid or gas, the catalysis is said to be **homogeneous.** The following are some of the examples of homogeneous catalysis:

(i) Oxidation of sulphur dioxide into sulphur trioxide with oxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process.

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

The reactants sulphur dioxide and oxygen are in gaseous state. The catalyst nitric oxide is also in gaseous state, *i.e.*, all are in the same phase.

(ii) Hydrolysis of methyl acetate is catalysed by H^+ ions furnished by hydrochloric acid.

$$CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(l) + CH_3OH(l)^*$$

Both the reactants and catalyst are in the same phase.

(iii) Hydrolysis of sugar is catalysed by H^+ ions furnished by sulphuric acid.

$$\underset{\text{Solution}}{C_{12}H_{22}O_{11}(l)} + H_2O(l) \xrightarrow{H_2SO_4(l)} \underbrace{\underset{\text{Glucose}}{C_6H_{12}O_6(l)} + \underset{\text{Fructose}}{C_6H_{12}O_6(l)}}_{\text{Solution}}$$

Both the reactants and the catalyst are in the same phase.

2. Heterogeneous catalysis: The catalytic process in which the reactants and the catalyst are in different phases is known as **heterogeneous catalysis.** Some of the examples of heterogeneous catalysis are given below:

(i) Oxidation of sulphur dioxide into sulphur trioxide in the presence of platinum metal or vanadium pentoxide as catalyst in the contact process for the manufacture of sulphuric acid.

$$2SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$$

The reactants are in gaseous state while the catalyst is in solid state.

(ii) Combination between nitrogen and hydrogen to form ammonia in the presence of finely divided iron in Haber process.

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

The reactants are in gaseous state while the catalyst is in solid state.

(iii) Oxidation of ammonia into nitric oxide in the presence of platinum gauze as a catalyst in Ostwald's process.

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt(s)} 4NO(g) + 6H_2O(g)$$

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*(l) represents liquid or solution in chemical reactions.

The reactants are in gaseous state while the catalyst is in the solid state.

(iv) Hydrogenation of vegetable oils in the presence of finely divided nickel as catalyst.

$$\text{Vegetable oils }(l) + H_2(g) \xrightarrow{Ni(s)} \text{Vanaspati ghee}(s)$$

One of the reactants is in liquid state and the other in gaseous state while the catalyst is in solid state.

13.11 TYPES OF CATALYSIS

Catalytic reactions are of the following types:

1. Positive catalysis: When the rate of reaction is accelerated by the foreign substance, it is said to be a **positive catalyst** and the phenomenon as **positive catalysis.**

Examples of positive catalysis:

(i) Decomposition of H_2O_2 in presence of colloidal platinum.

$$2H_2O_2(l) \xrightarrow{Pt} 2H_2O(l) + O_2(g)$$

(ii) Decomposition of $KClO_3$ in presence of manganese dioxide.

$$2KClO_3(s) \xrightarrow[270°C]{MnO_2(s)} 2KCl(s) + 3O_2(g)$$

(iii) Oxidation of ammonia in presence of platinum gauze.

$$4NH_3(g) + 5O_2(g) \xrightarrow[300°C]{Pt(s)} 4NO(g) + 6H_2O(g)$$

(iv) Oxidation of sulphur dioxide in presence of nitric oxide.

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

(v) Oxidation of sulphur dioxide in presence of platinized asbestos or vanadium pentoxide.

$$2SO_2(g) + O_2(g) \xrightarrow[\text{or } Pt(s)]{V_2O_5(s)} 2SO_3(g)$$

(vi) Oxidation of hydrochloric acid into chlorine by Deacon's process in presence of $CuCl_2$.

$$4HCl(g) + O_2(g) \xrightarrow[450°C]{CuCl_2(s)} 2Cl_2(g) + 2H_2O(g)$$

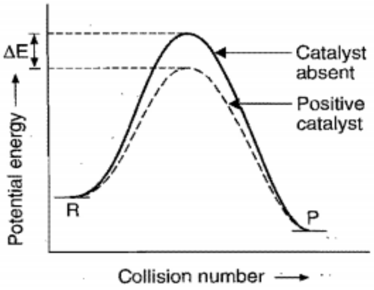


Fig. 13.6

(vii) Hydrogenation of vegetable oil in presence of nickel.

$$\text{Vegetable oil}(l) + H_2(g) \xrightarrow{Ni(s)} \text{Vanaspati ghee}(s)$$

(viii) Synthesis of ammonia by Haber process in presence of a mixture of iron and molybdenum.

$$N_2(g) + 3H_2(g) \xrightarrow[450\text{-}500°C]{Fe(s)} 2NH_3(g)$$

(ix) Manufacture of methyl alcohol in presence of ZnO/Cr_2O_3.

$$CO(g) + 2H_2(g) \xrightarrow[Cr_2O_3(s)]{ZnO(s),\ 250°C} CH_3OH(g)$$

(x) Formation of methane in presence of nickel.

$$CO(g) + 3H_2(g) \xrightarrow{Ni(s)} CH_4(g) + H_2O(g)$$

Positive catalyst increases the rate by lowering activation energy of reaction. Catalyst changes the mechanism by changing the intermediate, *i.e.*, an intermediate of low energy is formed. It increases the rate by converting some inactive molecules into active ones.

From chemical kinetics:

$$\frac{k_p}{k_a} = e^{\Delta E/RT}$$

where, k_p = rate constant in presence of catalyst, k_a = rate constant in absence of catalyst.

ΔE = Lowering of activation energy

$$\log_e\left(\frac{k_p}{k_a}\right) = \frac{\Delta E}{RT}$$

$$\frac{k_p}{k_a} = \text{antilog}\left[\frac{\Delta E}{2.303\,RT}\right]$$

2. Negative catalysis: There are certain substances which, when added to the reaction mixture, retard the reaction rate instead of increasing it. These are called **negative catalysts** or **inhibitors** and the phenomenon is known as **negative catalysis.**

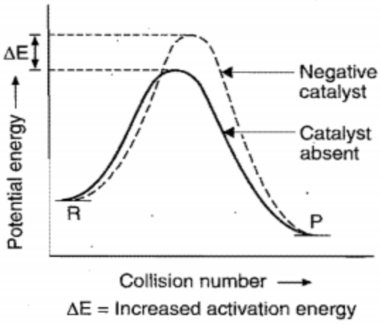


Fig. 13.7

Examples of negative catalysis:

(i) The oxidation of sodium sulphite by air is retarded by alcohol.

$$2Na_2SO_3(s) + O_2(g) \xrightarrow{\text{Alcohol}(l)} 2Na_2SO_4(s)$$

Alcohol acts as a negative catalyst.

(ii) The decomposition of hydrogen peroxide decreases in presence of glycerine. Thus, in this reaction glycerine acts as a negative catalyst.

$$2H_2O_2(l) \xrightarrow{\text{Glycerine}(l)} 2H_2O(l) + O_2(g)$$

(iii) The oxidation of chloroform by air is retarded if some alcohol is added to it.

$$2CHCl_3(l) + O_2(g) \xrightarrow{\text{Alcohol}(l)} 2COCl_2(g) + 2HCl(g)$$

(iv) The oxidation of benzaldehyde is retarded if some diphenyl amine is added. It acts as a negative catalyst.

$$2C_6H_5CHO(l) + O_2(g) \xrightarrow{\text{Diphenyl amine}(l)} 2C_6H_5COOH(l)$$

(v) Tetraethyl lead (TEL) acts as an antiknocking agent in the case of petrol. Thus, it decreases knocking of petrol and acts as a negative catalyst.

(vi) Addition of small amount of acetanilide shows slow decomposition of hydrogen peroxide.

Negative catalysts decrease the rate by increasing the activation energy of reaction. Mechanism is altered by altering the intermediate; the new intermediate lies at high energy state.

3. Autocatalysis: In certain reactions, one of the products acts as a catalyst. In the initial stages the reaction is slow but as soon as the products come into existence, the reaction rate increases. This type of phenomenon, in which one of the products itself acts as a catalyst, is known as **autocatalysis.**

Examples of autocatalysis:

(i) The rate of oxidation of oxalic acid by acidified potassium permanganate increases as the reaction progresses. This acceleration is due to the presence of Mn^{2+} ions which are formed during reaction. Thus, Mn^{2+} ions act as autocatalyst.

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

(ii) When nitric acid is poured on copper, the reaction is very slow in the beginning; gradually the reaction becomes faster due to the formation of nitrous acid during the reaction which acts as an autocatalyst.

(iii) 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 autocatalyst in this reaction.

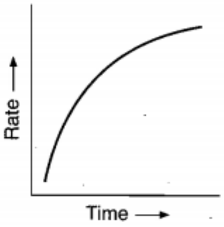


Fig. 13.8

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

In the case of homogeneous autocatalytic reactions, rate increases with passage of time because in such cases rate of reaction is directly proportional to concentration of catalyst, *e.g.*,

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

$$\text{Rate} = k\,\underset{\text{Reactant}}{[CH_3COOC_2H_5]}\,\underset{\text{Catalyst}}{[CH_3COOH]}$$

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.**

Examples of induced catalysis:

(i) 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 of them undergo simultaneous oxidation. The oxidation of sodium sulphite, thus, induces the oxidation of sodium arsenite.

$$Na_2SO_3 + \frac{1}{2}O_2 \longrightarrow Na_2SO_4$$

$$Na_3AsO_3 + \frac{1}{2}O_2 \longrightarrow Na_3AsO_4$$

(ii) The reduction of mercuric chloride ($HgCl_2$) with oxalic acid is very slow, but potassium permanganate is reduced readily with oxalic acid. If, however, oxalic acid is added to a mixture of potassium permanganate and mercuric chloride, both are reduced simultaneously. The reduction of potassium permanganate, thus, induces the reduction of mercuric chloride.

13.12 CHARACTERISTICS OF CATALYSIS

The following are the characteristics which are common to most of the catalytic reactions:

(i) A catalyst remains unchanged in mass and chemical composition at the end of the reaction: The amount of the catalyst found at the completion of the reaction is the same as taken at the start of the reaction. There is also no change in its composition. However, it is observed that in some cases the physical state may change. For example, manganese dioxide used in the granular form as a catalyst in the decomposition of $KClO_3$ is left as a fine powder at the completion of the reaction.

(ii) A small quantity of the catalyst is generally sufficient to catalyse almost unlimited reaction: For example, in the decomposition of hydrogen peroxide, one gram of colloidal platinum can catalyse 10^8 litre of hydrogen peroxide. One mole of Cu^{2+} in 10^6 litre can catalyse the oxidation of sodium sulphite by atmospheric oxygen.

However, in some reactions the rate of the reaction is proportional to the concentration of the catalyst. For the acid and alkaline hydrolysis of an ester, the rate of reaction is proportional to the concentration of H^+ or OH^- ions.

$$RCOOR'(l) + H_2O(l) \xrightarrow[OH^-]{H^+ \text{ or}} RCOOH(l) + R'OH(l)$$

In Friedel-Crafts reaction, anhydrous aluminium chloride is required in relatively large amount to the extent of 30% of the mass of benzene.

$$C_6H_6(l) + C_2H_5Cl(l) \xrightarrow{AlCl_3(s)} C_6H_5C_2H_5(l) + HCl(l)$$

It is also observed that in certain heterogeneous reactions, the rate of reaction increases with the increase of area of the catalytic surface.

(iii) The catalyst cannot initiate the reaction: The function of a catalyst is to alter the speed of the reaction rather than to start it. The reaction in presence of a positive catalyst adopts some alternative path which requires less amount of activation energy.

However, there are certain instances where it is observed that the reaction cannot be started in absence of a catalyst. For example, there is no reaction between H_2 and O_2 at room temperature but the reaction occurs very readily in presence of platinum black.

$$2H_2(g) + O_2(g) \xrightarrow{\text{Room temp.}} \text{No reaction}$$

$$2H_2(g) + O_2(g) \xrightarrow{\text{Pt black}} 2H_2O(g)$$

Similarly, combination of dry chlorine with dry hydrogen is not possible unless water vapours are added. Water vapours which act as a catalyst might be thought to start the reaction.

$$H_2(g) + Cl_2(g) \xrightarrow{\text{Water vapour}} 2HCl(g)$$

The concept is still disputed.

(iv) The catalyst is generally specific in nature: A substance, which acts as a catalyst for a particular reaction, fails to catalyse the other reactions. Different catalysts for the same reactants may form different products. Manganese dioxide which acts as a catalyst for the decomposition of potassium chlorate fails to catalyse the decomposition of potassium perchlorate. Ethanol yields ethene when passed over alumina but in presence of hot copper, acetaldehyde is formed.

$$C_2H_5OH(l) \begin{cases} \xrightarrow{Al_2O_3} C_2H_4(g) + H_2O(g) \text{ (Dehydration)} \\ \xrightarrow{Cu} CH_3CHO(g) + H_2(g) \text{ (Dehydrogenation)} \end{cases}$$

Similarly, in the case of formic acid, different products are formed using Cu or Al_2O_3 as catalysts.

$$HCOOH(l) \begin{cases} \xrightarrow{Cu} CO_2(g) + H_2(g) \text{ (Dehydrogenation)} \\ \xrightarrow{Al_2O_3} CO(g) + H_2O(g) \text{ (Dehydration)} \end{cases}$$

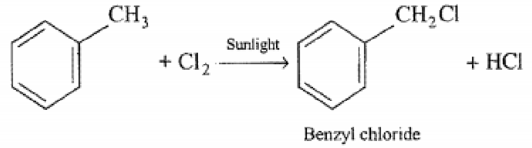
Carbon monoxide and hydrogen combine to form CH_4, CH_3OH, HCHO depending on the nature of the catalyst used.

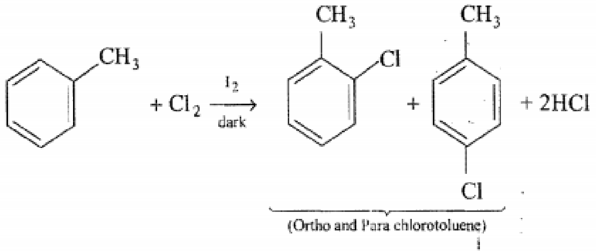
$$CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O$$

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

$$CO(g) + H_2(g) \xrightarrow{Cu} HCHO$$

Sometimes catalyst may alter the reaction product:





Enzymes have also specific action. However, transition metals like Fe, Co, Ni, Pt, Pd, etc., can catalyse reactions of various types.

(v) The catalyst cannot change the position of equilibrium: In the case of reversible reactions, the concentrations of the products and reactants cannot be affected by the catalyst if the equilibrium has been established. However, the use of a catalyst can help to achieve the equilibrium state in lesser time as forward and backward reactions are influenced to the same extent by the catalyst.

Let us consider a reversible reaction,

$$A + BC \rightleftharpoons AB + C$$

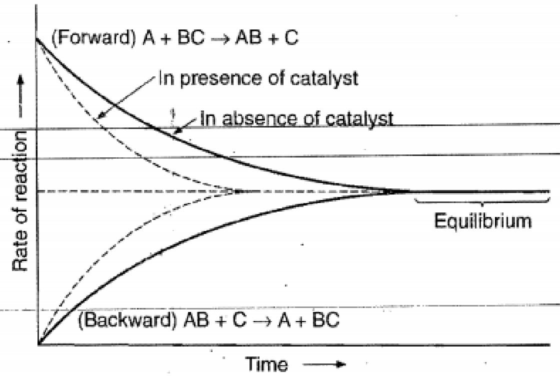


Fig. 13.9 Equilibrium state and catalyst

(vi) Catalytic promoters: Substances which themselves are not catalysts, but when mixed in small quantities with the catalysts increase their efficiency, are called as **promoters** or **activators.** Some examples of the promoters are given below:

(a) In the Haber process for the synthesis of ammonia, traces of molybdenum increase the activity of finely divided iron which acts as a catalyst. Oxides of aluminium and thorium are also used as promoter in this reaction.

(b) In the manufacture of methyl alcohol from water gas ($CO + H_2$), chromic oxide (Cr_2O_3) is used as a promoter with the catalyst zinc oxide (ZnO).

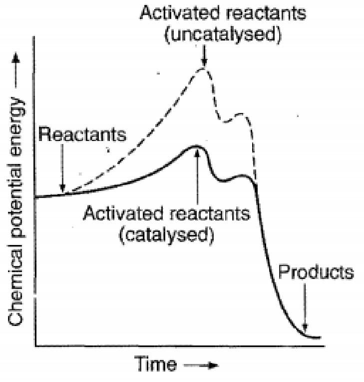


Fig. 13.10

(c) In the hydrogenation of oils, the activity of the catalyst nickel increases on adding small amount of copper and tellurium.

(vii) Catalytic poisons: Substances which destroy the activity of the catalyst by their presence are known as **catalytic poisons.** Some of the examples are:

(a) The presence of traces of arsenious oxide (As_2O_3) in the reacting gases reduces the activity of platinized asbestos which is used as catalyst in contact process for the manufacture of sulphuric acid.

(b) The activity of iron catalyst is destroyed by the presence of H_2S or CO in the synthesis of ammonia by Haber process.

(c) The platinum catalyst used in the oxidation of hydrogen is poisoned by CO.

The poisoning of a catalyst is probably due to the preferential adsorption of poison on the surface of the catalyst, thus reducing the space available for the adsorption of reacting molecules.

(viii) Change of temperature alters the rate of catalytic reaction as it does for the same reaction in absence of a catalyst: By increasing the temperature, there is an increase in the catalytic power of a catalyst but after a certain temperature its power begins to decrease. A catalyst has, thus, a particular temperature at which its catalytic activity is maximum. This temperature is termed as **optimum temperature.**

However, in the case of colloidal solutions acting as catalysts, the catalytic activity decreases by the rise of temperature as it may cause coagulation of the colloidal solution.

(ix) A positive catalyst lowers the activation energy: According to collision theory, a reaction occurs on account of effective collisions between the reacting molecules. For effective collision, it is necessary that the molecules must possess a minimum amount of energy known as activation energy (E_a). Under this condition, molecules after collision form an activated complex which dissociates to yield the product molecules.

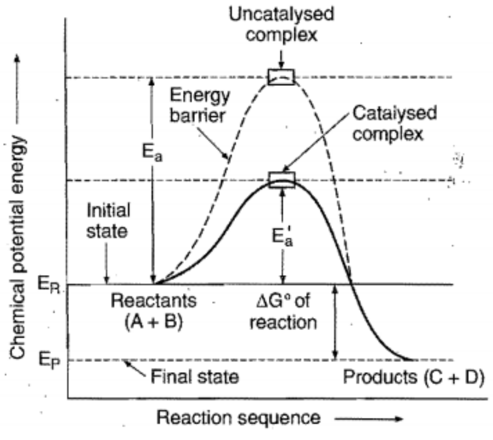


Fig. 13.11 (a)

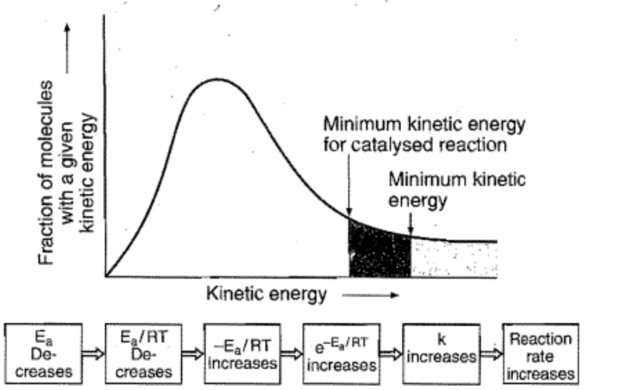


Fig. 13.11 (b) Lowering of energy barrier by the catalyst

The catalyst provides a new pathway involving lower amount of activation energy. Thus, larger number of effective collisions occur in the presence of a catalyst in comparison to effective collisions at the same temperature in absence of a catalyst. Hence, the presence of a catalyst makes the reaction to go faster.

Fig. 13.11 (a) shows that activation energy, E_a, in absence of a catalyst is higher than the activation energy, E'_a, in presence of a catalyst. E_R and E_P represent the average energies of reactants and products. The difference gives the value of ΔG, *i.e.*,

$$\Delta G = E_R - E_P$$

13.13 THEORIES 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 formation theory: This theory was proposed by **Clement** and **Desormes** in 1806.

According to this theory, **the catalyst first forms an intermediate compound with one of the reactants. The intermediate compound is formed with less energy consumption than needed for the actual reaction. The intermediate compound being unstable combines with other reactant to form the desired product and the catalyst is regenerated.**

For example, a reaction of the type

$$A + B \overset{K}{=\!=} AB$$

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

$$A + \underset{\text{Catalyst}}{K} = \underset{\substack{\text{Intermediate}\\\text{compound}}}{AK} \qquad \text{(Slow reaction)}$$

$$AK + B = \underset{\text{Product}}{AB} + \underset{\text{Catalyst}}{K} \quad \text{(Fast reaction)}$$

$$\text{Rate} = K'[A][K \text{ catalyst}]$$

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

(i) The catalytic oxidation of sulphur dioxide to sulphur trioxide in the lead chamber process probably takes place as:

$$\underset{\text{Catalyst}}{2NO} + O_2 \longrightarrow \underset{\text{Intermediate product}}{2NO_2}$$

$$NO_2 + SO_2 \longrightarrow \underset{\text{Product}}{SO_3} + \underset{\text{Catalyst}}{NO}$$

(ii) The catalytic action of manganese dioxide on the decomposition of $KClO_3$ was proposed by McLeod. The reaction probably takes place as follows:

$$\begin{array}{l} 2MnO_2 + 2KClO_3 \longrightarrow 2KMnO_4 + Cl_2 + O_2 \\ 2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2 \\ K_2MnO_4 + Cl_2 \longrightarrow 2KCl + MnO_2 + O_2 \\ \hline 2KClO_3 + [2MnO_2] \longrightarrow 2KCl + 3O_2 + [2MnO_2] \end{array}$$

The reaction accounts for the fact that oxygen given out is often contaminated with a little of chlorine.

(iii) The formation of methyl benzene (toluene) from benzene and methyl chloride in presence of a catalyst anhydrous aluminium chloride can be explained in the following way:

$$\underset{\text{Catalyst}}{AlCl_3} + CH_3Cl \longrightarrow \underset{\text{Intermediate compound}}{(CH_3)^+(AlCl_4)^-}$$

$$C_6H_6 + (CH_3)^+(AlCl_4)^- \longrightarrow \underbrace{C_6H_5CH_3 + HCl}_{\text{Products}} + \underset{\text{Catalyst}}{AlCl_3}$$

(iv) The formation of diethyl ether from ethyl alcohol using sulphuric acid as a catalyst can be explained as:

$$C_2H_5OH + \underset{\text{Catalyst}}{H_2SO_4} \longrightarrow \underset{\text{Intermediate compound}}{C_2H_5HSO_4}$$

$$C_2H_5HSO_4 + HOC_2H_5 \longrightarrow \underset{\text{Product}}{C_2H_5OC_2H_5} + \underset{\text{Catalyst}}{H_2SO_4}$$

(v) The decomposition of acetaldehyde which occurs as follows,

$$CH_3CHO \xrightarrow{I_2} CH_4 + CO$$

can be explained as shown below:

$$\begin{array}{l} CH_3CHO + \underset{\text{Catalyst}}{I_2} \longrightarrow \underset{\text{Intermediate}}{CH_3I} + HI + CO \\ CH_3I + HI \longrightarrow CH_4 + I_2 \\ \hline CH_3CHO \longrightarrow CH_4 + CO \end{array}$$

This theory explains why a catalyst remains unchanged in mass and chemical composition at the end of the reaction and is effective even in small quantities. The scope of this theory is, however, limited as the formation of intermediate compound is possible in the case of homogeneous catalysis only. It also fails to explain the action of catalytic promoters, catalytic poisons and action of finely divided catalysts.

(vi) Variable oxidation state of transition metals makes them efficient catalysts. For example, Fe^{3+} catalyses the reaction between iodide and persulphate ions.

$$2I^- + S_2O_8^{2-} \xrightarrow{Fe^{3+}} I_2 + 2SO_4^{2-}$$

The catalytic action can be explained as,

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$

2. Adsorption theory: This theory explains the mechanism of heterogeneous catalysis. The old point of view was that when a catalyst is in solid state and the reactants are in gaseous state or in solutions, the molecules of the reactants are adsorbed on the surface of the catalyst. The increased concentration of the reactants on the surface influences the rate of reaction (law of mass action). Adsorption being an exothermic process, the heat of adsorption is taken up by the surface of the catalyst which is utilised in enhancing the chemical activity of the reacting molecules. The view does not explain the specificity of a catalyst.

Adsorption is broadly of two types: physical and chemical. The chemical adsorption is specific and involves chemical combination on the surface of the catalyst. The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory. The catalytic activity is localised on the surface of the catalyst. The mechanism involves five steps:

(i) Diffusion of reactants to the surface of the catalyst.

(ii) Some form of association between the catalyst surface and the reactants occurs. This is assumed to be adsorption.

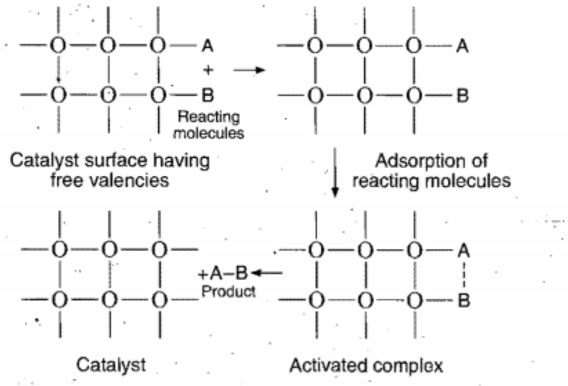


Fig. 13.12 Adsorption of reacting molecules, formation of activated complex and adsorption of products

(iii) Occurrence of chemical reaction on the catalyst surface.

(iv) Desorption of reaction products away from the catalyst surface.

(v) Diffusion of reaction products away from the catalyst surface.

The catalyst surface is a seat of chemical forces of attraction. There are free valencies on the surface of a catalyst. When a gas comes in contact with such a surface, its molecules are held up there due to loose chemical combination. If different molecules are adsorbed side by side, they may react and new molecules so formed may evaporate leaving the way for the fresh reactant molecules (Fig. 13.12).

In case, free valencies are responsible for the catalytic activity, it follows that with the increase of these valencies on the surface of a catalyst, the catalytic activity will be greatly enhanced. The free valencies can be increased in the following two ways:

(a) Sub-division of the catalyst,

(b) Rough surface of the catalyst.

(a) Sub-division of the catalyst: The number of free valencies increases on disintegration. Finely powdered or colloidal catalyst particles having large surface area are very rich in free valencies.

Actually, it is observed that finely divided nickel and colloidal platinum act as efficient catalysts.

(b) Rough surface of the catalyst: There are a number of active spots in the form of edges, corners, cracks and peaks on a rough surface. They give rise to an increase in number of free valencies. These active spots enhance the adsorption and thereby increase the catalytic efficiency of the catalyst.

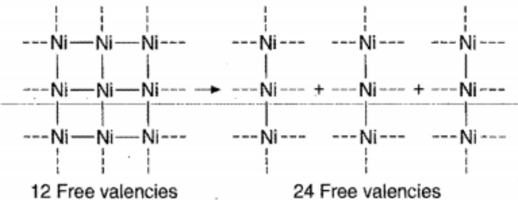


Fig. 13.13 Increase in number of free valencies

The adsorption theory explains the following facts of heterogeneous catalysis:

(i) The surface of the catalyst is used again and again due to alternate adsorption and desorption. **Thus, a small quantity of a catalyst can catalyse large amounts of reactants.**

(ii) Chemical adsorption depends on the nature of the adsorbent and adsorbate. Hence, catalysts are specific in action.

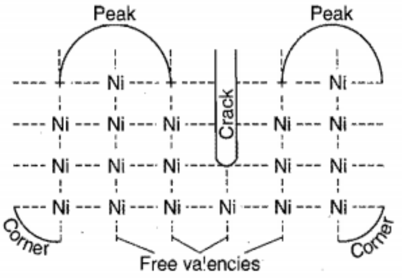


Fig. 13.14

(iii) Desorption leaves the catalytic surface unchanged. Thus, the catalyst at the end of reaction remains same in mass and composition.

(iv) The energy of adsorption compensates the activation energy of the reacting molecules to some extent. Thus, the reactions occur at faster rate.

(v) Greater efficiency of the catalyst in finely divided state and rough surface.

(vi) It adequately explains the poisoning of catalysts. The poisons are preferentially adsorbed at the active centres of the catalyst. This effect reduces the free valencies for the reacting molecules and, thus, the catalytic activity decreases.

(vii) Promoters are responsible for increasing the roughness of the surface of a catalyst. This effect increases the free valencies for the reacting molecules and, thus, the catalytic activity of the catalyst is increased.

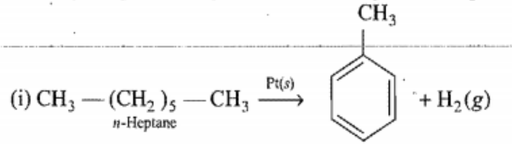
Activity and Selectivity of Heterogeneous Catalysis

Activity is the ability of a catalyst to accelerate chemical reactions. In certain cases the activity can be as high as 10^{10}, *i.e.*, the catalysed reaction is 10^{10} times faster than the uncatalysed reaction.

$$H_2(g) + O_2(g) \longrightarrow \text{No reaction}$$

$$2H_2(g) + O_2(g) \xrightarrow[\Delta]{Pt} 2H_2O(g)$$

Selectivity of a catalyst is its ability to direct the reaction in such a way as to yield particular products excluding others, *e.g.*,



n-Heptane is catalysed by Pt to toluene.

(ii) Propylene and oxygen selectively give acrolein over bismuth molybdate as catalyst.

$$CH_3-CH=CH_2+O_2 \xrightarrow[BiMoO_4]{\text{Bismuth molybdate}} \underset{\text{Acrolein}}{CH_2=CH-CHO} + H_2O$$

(iii) Acetylene on hydrogenation in presence of Pt or Ni or Pd catalyst gives ethane.

$$H-C\equiv C-H+2H_2(g) \xrightarrow{Pt/Pd/Ni} \underset{\text{Ethane}}{CH_3-CH_3}$$

Hydrogenation of acetylene in presence of Lindlar's catalyst gives ethylene.

$$H-C\equiv C-H + H_2 \xrightarrow[\text{Sulphur or quinoline}]{Pd\text{-}BaSO_4} \underset{\text{Ethylene}}{CH_2=CH_2}$$

13.14 ACID-BASE CATALYSIS

Generally, homogeneous catalysis in solution is brought about by acids and bases. On the basis of studies done by Arrhenius and Ostwald in the hydrolysis of esters and nitrites, it was established that in acid-base catalysis, it is the hydrogen ion or hydroxyl ion which acts as catalyst.

Examples of acid-base catalysis:

(i) Hydrolysis of an ester:

$$CH_3COOC_2H_5(l) + H_2O(l) \xrightarrow[OH^-]{H^+ \text{ or}} CH_3COOH(l) + C_2H_5OH(l)$$

(ii) Inversion of cane sugar:

$$C_{12}H_{22}O_{11}(l) + H_2O(l) \xrightarrow{H^+} C_6H_{12}O_6(l) + C_6H_{12}O_6(l)$$

(iii) Conversion of acetone into diacetone alcohol:

$$CH_3COCH_3\,(l) + CH_3COCH_3\,(l) \xrightarrow{OH^-} CH_3COCH_2 \cdot C(CH_3)_2OH(l)$$

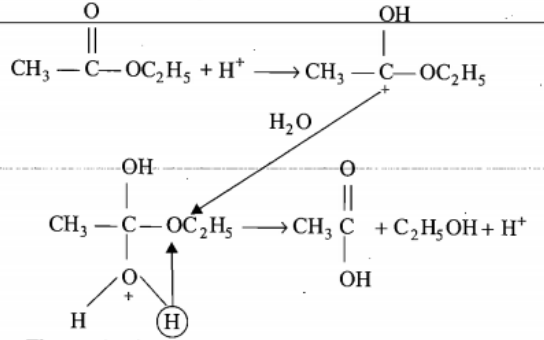
(iv) Decomposition of nitramide:

$$NH_2 \cdot NO_2\,(l) \xrightarrow{OH^-} N_2O(g) + H_2O(l)$$

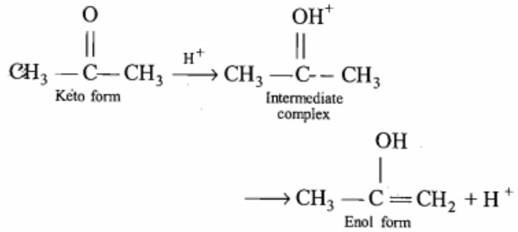
The recent work has shown that all substances which have a tendency to lose or to gain protons can show catalytic activity, *i.e.*, all Bronsted acids and bases act as acid-base catalysts.

Mechanism of Acid-Base Catalysis

(a) In acid catalysis, the proton given by Bronsted acid forms an intermediate complex with the reactant which then reacts to give back the proton (H^+). For example, the hydrolysis of ester occurs in the following manner:



The mechanism of keto-enol tautomerism of acetone is:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow{H^+} CH_3-\overset{\overset{\displaystyle OH^+}{\|}}{C}-CH_3 \longrightarrow CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2 + H^+$$

(b) In base catalysed hydrolysis, the OH^- ion or any Bronsted base accepts a proton from the reactant to form an intermediate complex which then reacts or decomposes to regenerate the OH^- or Bronsted base. In presence of OH^- ions, the decomposition of nitroamine can be shown as:

$$NH_2NO_2 + OH^- \longrightarrow NHNO_2^- + H_2O$$
$$\downarrow$$
$$N_2O + OH^-$$

or in presence of CH_3COO^- ions,

$$NH_2NO_2 + CH_3COO^- \longrightarrow NHNO_2^- + CH_3COOH$$
$$\downarrow$$
$$N_2O + OH^-$$
$$OH^- + CH_3COOH \longrightarrow CH_3COO^- + H_2O$$

13.15 ENZYME CATALYSIS

Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. Enzymes are actually high molecular mass protein molecules. Enzymes form colloidal solutions in water and are very effective catalysts. They catalyse numerous reactions, especially those connected with natural processes. Numerous reactions occur in the bodies of animals and plants to maintain the life process. These reactions are catalysed by enzymes. The enzymes are thus termed as **biochemical catalysts** and the phenomenon is known as **biochemical catalysis.**

Many enzymes have been obtained in pure crystalline state from living cells. However, the first enzyme was synthesised in the laboratory in 1969. The following are some of the examples of enzyme catalysis:

(i) Inversion of cane sugar: The invertase enzyme converts cane sugar into glucose and fructose.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}\,(l)} + H_2O(l) \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6\,(l)} + \underset{\text{Fructose}}{C_6H_{12}O_6\,(l)}$$

(ii) Conversion of glucose into ethyl alcohol: The zymase enzyme converts glucose into ethyl alcohol and carbon dioxide.

$$\underset{\text{Glucose}}{C_6H_{12}O_6\,(l)} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH(l)} + 2CO_2\,(g)$$

(iii) Conversion of starch into maltose: The diastase enzyme converts starch into maltose.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n\,(l)} + nH_2O(l) \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}\,(l)}$$

(iv) Conversion of maltose into glucose: The maltase enzyme converts maltose into glucose.

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}\,(l)} + H_2O(l) \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6\,(l)}$$

(v) Decomposition of urea into ammonia and carbon dioxide: The enzyme urease catalyses this decomposition.

$$NH_2CONH_2\,(l) + H_2O(l) \xrightarrow{\text{Urease}} 2NH_3\,(g) + CO_2\,(l)$$

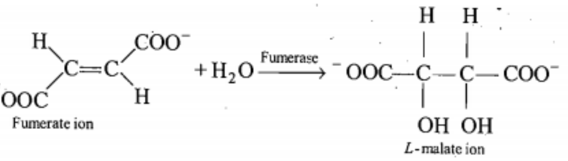
(vi) In stomach, the pepsin enzyme converts proteins into peptides while in intestine, the pancreas trypsin converts proteins into amino acids by hydrolysis.

(vii) Conversion of ethyl alcohol into acetic acid: The *Mycoderma aceti* enzyme converts dilute solutions of alcohol into acetic acid and water.

$$C_2H_5OH(l) + O_2\,(g) \xrightarrow{\textit{Mycoderma aceti}} CH_3COOH(l) + H_2O(l)$$

(viii) Conversion of milk into curd: It is an enzymatic reaction brought about by *lactic bacilli* enzyme present in curds.

(ix) The enzyme **fumerase** catalyses the hydration process of fumerate ion.



This reaction shows selectivity of enzymes because fumerase enzyme is unable to catalyse '*Cis*' isomer, *i.e.*, malate ion.

(x) In our body, the enzyme **carbonic anhydrase** catalyses the following reaction:

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

Forward process takes place when CO_2 goes to tissues from blood, whereas backward process takes place when CO_2 gas is released from the blood to the lungs.

Carbonic anhydrase has very high efficiency, one molecule of it catalyses 10^6 substrate molecules.

(xi) Lysozyme is found in the tear of our eyes. It protects our eyes from bacteria. It breaks down the cell wall of bacteria and then it ruptures due to endo-osmosis.

(xii) Nitrogenase enzyme is found in the bacteria of the root nodules of leguminous plants such as peas and beans. It catalyses the nitrogen fixation, *i.e.*, conversion of N_2 from atmosphere to the NH_3 in the soil.

Table 13.1 gives the summary of some important enzymatic reactions:

Table 13.1 Some enzymatic reactions

	Enzyme	Source	Enzymatic reaction
1.	Invertase	Yeast	Sucrose ⟶ Glucose and fructose
2.	Zymase	Yeast	Glucose ⟶ Ethyl alcohol and carbon dioxide
3.	Diastase	Malt	Starch ⟶ Maltose
4.	Maltase	Yeast	Maltose ⟶ Glucose
5.	Urease	Soyabean	Urea ⟶ Ammonia and carbon dioxide
6.	Pepsin	Stomach	Proteins ⟶ Amino acids
7.	Trypsin	Intestine	Proteins ⟶ Amino acids
8.	Amylase	Saliva	Starch ⟶ Glucose
9.	*Lactic bacilli*	Curd	Fermentation of milk
10.	*Mycoderma aceti*	Vinegar	Ethyl alcohol ⟶ Acetic acid
11.	Lipase	Castor seed	Fat ⟶ Glycerol
12.	Ptylin	Saliva	Starch ⟶ Sugar

Characteristics of Enzyme Catalysis

Enzyme catalysis is intermediate between homogeneous and heterogeneous catalysis. In general, it is similar to inorganic heterogeneous catalysis and sometimes it is called microheterogeneous catalysis. However, it is unique in its efficiency and high degree of specificity. The following characteristics are exhibited by enzyme catalysts:

(i) Most efficient catalysts: The enzyme-catalysed reactions are very fast in comparison to the reactions catalysed by inorganic substances. This is due to the fact that activation energy of a reaction in presence of an enzyme is low. One molecule of an enzyme may transform one million molecules of the reactant per minute.

(ii) High specific nature: Each enzyme is specific for a given reaction, *i.e.*, one catalyst cannot catalyse more than one reaction. For example, the enzyme urease catalyses the hydrolysis of urea only. It does not catalyse any other amide, not even methyl urea.

(iii) Temperature dependence: The rate of an enzyme reaction depends on the temperature. The enzyme activity rises rapidly with temperature and becomes maximum at a definite temperature, called the **optimum temperature.** Beyond the optimum temperature, the enzyme activity decreases and ultimately becomes zero. The enzyme activity is destroyed at about 70° C. The optimum temperature of enzyme reactions occurring in the human body is 37° C. At higher temperatures (fever), the enzyme activity becomes less. The favourable temperature range for enzymatic activity is 25–37° C.

(iv) pH dependence: The rate of an enzyme-catalysed reaction varies with pH of the system. The enzyme activity is maximum at a particular pH called optimum pH. The optimum pH of enzyme reactions occurring in human body is 7.4. The favourable pH range for enzymatic reactions is 5–7.

Activity of enzyme decreases above and below the optimum pH. Effect of pH on enzymatic rate may reflect denaturation.

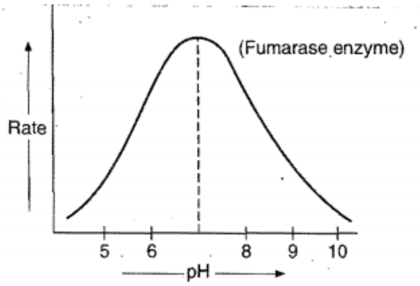


Fig. 13.15

(v) No effect on equilibrium state: Like ordinary catalysts, enzymes cannot disturb the final state of equilibrium of a reversible reaction.

(vi) Colloidal nature: Enzymes form colloidal solutions in water. Their efficiency is retarded in presence of large quantities of electrolytes. Enzymes are destroyed by ultraviolet rays.

(vii) Activators or coenzymes: The enzymatic activity is increased in the presence of certain substances, known as **coenzymes.** It has been observed that when a small non-protein

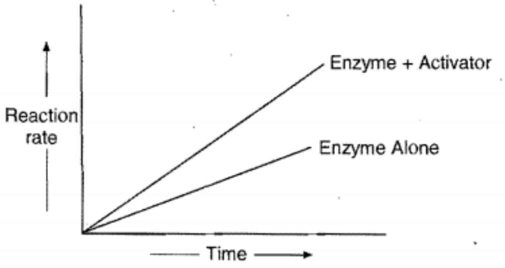


Fig. 13.16 Effect of activators on the rate of enzyme catalysis