

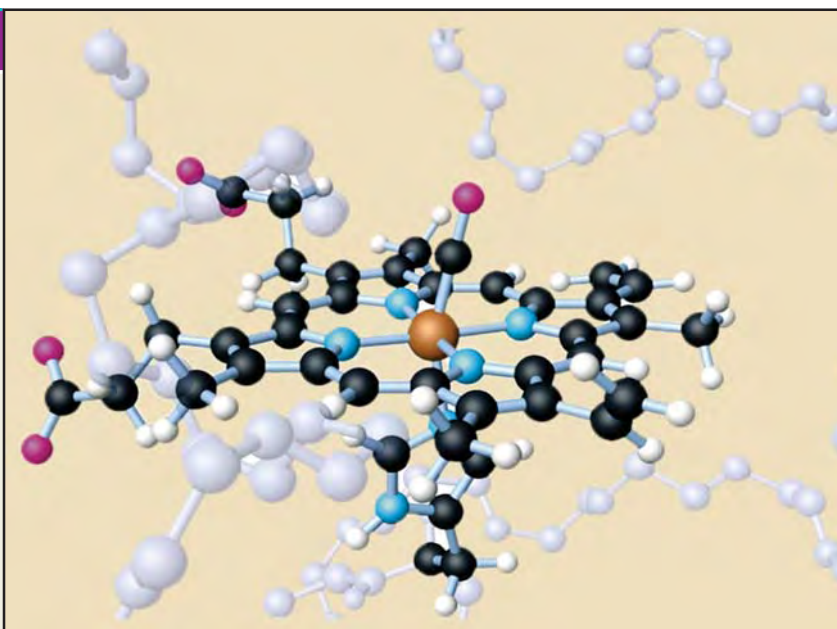
## 21

## Catalysis

## CHAPTER

## CONTENTS

WHAT IS CATALYSIS
TYPES OF CATALYSIS
HOMOGENEOUS CATALYSIS
HETEROGENEOUS CATALYSIS
CHARACTERISTICS OF CATALYTIC REACTIONS
PROMOTERS
CATALYTIC POISONING
AUTOCATALYSIS
NEGATIVE CATALYSIS
ACTIVATION ENERGY AND CATALYSIS
THEORIES OF CATALYSIS
The Intermediate Compound Formation Theory
The Adsorption Theory
HYDROGENATION OF ETHENE IN PRESENCE OF NICKEL
ACID-BASE CATALYSIS
Mechanism of Acid catalysis
ENZYME CATALYSIS
MECHANISM OF ENZYME CATALYSIS
CHARACTERISTICS OF ENZYME 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 through by Berzelius. But a number of cases are now known where the catalyst definitely retards (slows down) the rate of reaction.

**A catalyst is 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 a reaction is called a **Positive catalyst** and the process **Positive catalysis** or simply **Catalysis**.

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

## JÖNS JAKOB BERZELIUS

Jöns Jakob Berzelius (1779-1848), Swedish chemist, considered one of the founders of modern chemistry.

Berzelius was born near Linköping. While studying medicine at the University of Uppsala, he became interested in chemistry. After practicing medicine and lecturing, he became a professor of botany and pharmacy at Stockholm in 1807. From 1815 to 1832 he was professor of chemistry at the Caroline Medico-Chirurgical Institute in Stockholm. He became a member of the Stockholm Academy of Sciences in 1808 and in 1818 became its permanent secretary. For his contributions to science, Berzelius was made a baron in 1835 by Charles XIV John, king of Sweden and Norway.



Berzelius's research extended into every branch of chemistry and was extraordinary for its scope and accuracy. He discovered three chemical elements—cerium, selenium, and thorium—and was the first to isolate silicon, zirconium, and titanium. He introduced the term catalyst into chemistry and was the first to elaborate on the nature and importance of catalysis. He introduced



Statue of Berzelius in the center of Berzelii Park, Stockholm

the present system of chemical notation, in which each element is represented by one or two letters of the alphabet. In addition, Berzelius was primarily responsible for the theory of radicals, which states that a group of atoms, such as the sulphate group, can act as a single unit through a series of chemical reactions. He developed an elaborate electrochemical theory that correctly stated that chemical compounds are made up of negatively and positively charged components. All of his theoretical work was supported by elaborate experimental measurements. His greatest achievement was the measurement of atomic weights.

We will first proceed to discuss 'positive catalysis' or catalysis as it is commonly designated.

### TYPES OF CATALYSIS

There are two main types of catalysis :

- (a) Homogeneous catalysis
- (b) Heterogenous catalysis

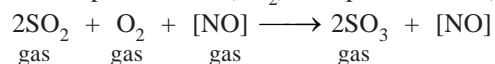
Also, there is a third types of catalysis known as **Enzyme catalysis** which is largely of biological interest. This will be discussed separately at a later stage.

### HOMOGENEOUS CATALYSIS

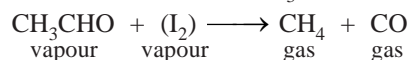
In homogeneous catalysis, **the catalyst is in the same phase as the reactants and is evenly distributed throughout.** This type of catalysis can occur in gas phase or the liquid (solution) phase.

#### Examples of Homogeneous Catalysis in Gas Phase

- (a) Oxidation of sulphur dioxide ( $\text{SO}_2$ ) to sulphur trioxide ( $\text{SO}_3$ ) with nitric oxide (NO) as catalyst,



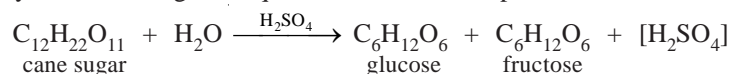
(b) Decomposition of acetaldehyde ( $\text{CH}_3\text{CHO}$ ) with iodine ( $\text{I}_2$ ) as catalyst,



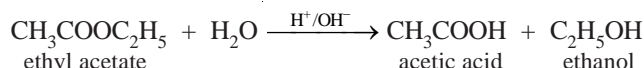
### Examples of Homogeneous Catalysis in Solution Phase

Many reactions in solutions are catalysed by acids ( $\text{H}^+$ ) and bases ( $\text{OH}^-$ ).

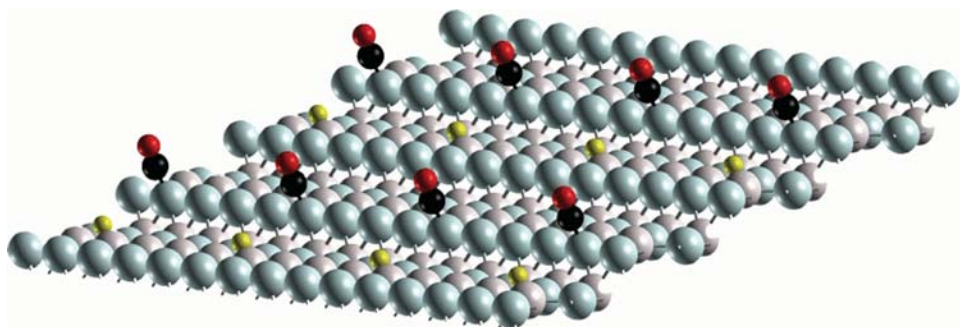
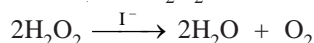
(a) Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst,



(b) Hydrolysis of an ester in the presence of acid or alkali,



(c) Decomposition of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in the presence of iodide ion ( $\text{I}^-$ ) as catalyst,



### HETEROGENEOUS CATALYSIS

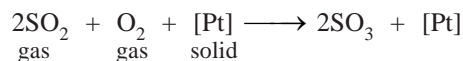
The catalysis in which the catalyst is in a different physical phase from the reactants is termed **Heterogeneous catalysis**. The most important of such reactions are those in which the reactants are in the gas phase while the catalyst is a solid. The process is also called **Contact catalysis** since 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 great industrial importance.

#### Examples of Heterogeneous Catalysis

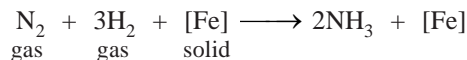
Some examples of heterogeneous catalysis with reactants in the gas, liquid or the solid phase are listed below.

(1) **Heterogeneous catalysis with gaseous reactants (Contact catalysis)**

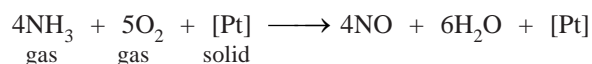
(a) Combination of sulphur dioxide ( $\text{SO}_2$ ) and oxygen in the presence of finely divided platinum or vanadium pentoxide,  $\text{V}_2\text{O}_5$ , (*Contact Process for Sulphuric acid*).



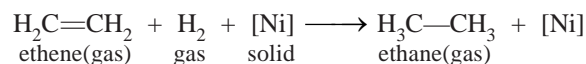
(b) Combination of nitrogen and hydrogen to form ammonia in the presence of finely divided iron, (*Haber Process for Ammonia*).



(c) Oxidation of ammonia to nitric oxide ( $\text{NO}$ ) in the presence of platinum gauze (a stage in manufacture of Nitric acid).



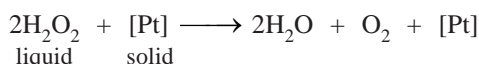
(d) Hydrogenation reactions of unsaturated organic compounds are catalysed by finely divided nickel.



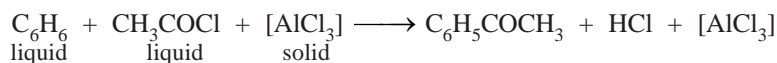
Vegetable oils are triesters of glycerol with higher unsaturated acid (oleic acid). When hydrogen is passed through the *vegetable oils* in the presence of nickel, the carbon-carbon double bonds of the acid portions are hydrogenated to yield *solid fats* (*Vanaspati ghee*).

### (2) Heterogeneous catalysis with liquid reactants

(i) The decomposition of aqueous solutions of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is catalysed by manganese dioxide ( $\text{MnO}_2$ ) or platinum in colloidal form,

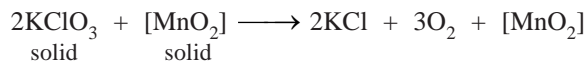


(ii) Benzene and ethanoyl chloride ( $\text{CH}_3\text{COCl}$ ) react in the presence of anhydrous aluminum chloride to form phenyl methyl ketone ( $\text{C}_6\text{H}_5\text{COCH}_3$ ),



### (3) Heterogeneous catalysis with solid reactants

The decomposition of potassium chlorate ( $\text{KClO}_3$ ) is catalysed by manganese dioxide ( $\text{MnO}_2$ ).



## CHARACTERISTICS OF CATALYTIC REACTIONS

Although there are different types of catalytic reactions, the following features or characteristics are common to most of them.

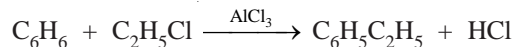
### (1) A catalyst remains unchanged in mass and chemical composition at the end of the reaction

Qualitative and quantitative analysis show that a catalyst undergoes no change in mass or chemical nature. However, it may undergo a physical change. Thus granular manganese dioxide ( $\text{MnO}_2$ ) used as a catalyst in the thermal decomposition of potassium chlorate is left as a fine powder at the end of the reaction.

### (2) A small quantity of catalyst is generally needed to produce almost unlimited reaction

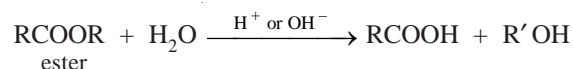
Sometimes a trace of a metal catalyst is required to affect very large amounts of reactants. For example, one ten-millionth of its mass of finely divided platinum is all that is needed to catalyse the decomposition of hydrogen peroxide.

On the other hand, there are catalysts which need to be present in relatively large amount to be effective. Thus in Friedel-Crafts reaction,



anhydrous aluminium chloride functions as a catalyst effectively when present to the extent of 30 per cent of the mass of benzene.

For the acid and alkaline hydrolysis of an ester,



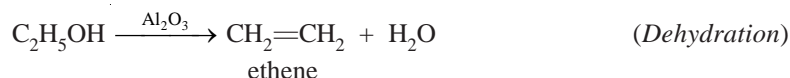
the rate of reaction is proportional to the concentration of the catalyst ( $\text{H}^+$  or  $\text{OH}^-$ ).

**(3) A catalyst is more effective when finely divided**

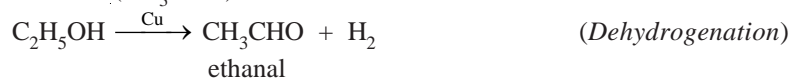
In heterogeneous catalysis, the solid catalyst is more effective when in a state of fine subdivision than it is used in bulk. Thus a lump of platinum will have much less catalytic activity than colloidal or platinised asbestos. Finely divided nickel is a better catalyst than lumps of solid nickel.

**(4) A catalyst is specific in its action**

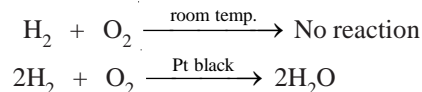
While a particular catalyst works for one reaction, it will not necessarily work for another reaction. Different catalysts, moreover, can bring about completely different reactions for the same substance. For example, ethanol ( $C_2H_5OH$ ) gives ethene ( $C_2H_4$ ) when passed over hot aluminium oxide,



but with hot copper it gives ethanal ( $CH_3CHO$ ).

**(5) A catalyst cannot, in general, initiate a reaction**

In most cases a catalyst speeds up a reaction already in progress and does not initiate (or start) the reaction. But there are certain reactions where the reactants do not combine for very long period (perhaps years). For example, a mixture of hydrogen and oxygen, which remains unchanged almost indefinitely at room temperature, can be brought to reaction by the catalyst *platinum black* in a few seconds.

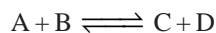


Thus it is now considered that the catalyst can initiate a reaction. According to this view, the reacting molecules (in the absence of catalyst) do not possess minimum kinetic energies for successful collisions. The molecules rebound from collision without reacting at all.

**(6) A catalyst does not affect the final position of equilibrium, although it shortens the time required to establish the equilibrium**

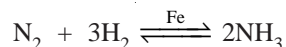
It implies that in a reversible reaction the catalyst accelerates the forward and the reverse reactions equally. Thus the ratio of the rates of two opposing reactions *i.e.*, the equilibrium constant, remains unchanged.

The effect of a catalyst on the time required for equilibrium to be established for the reaction

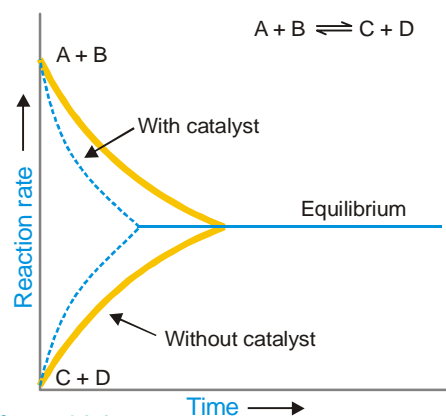


is illustrated in Fig. 21.1. To start with the concentrations of A and B are at the maximum and hence the rate of forward reaction is maximum. As the time passes the rate of the reaction decreases till the equilibrium is established. For the reverse reaction the initial concentrations of C and D are zero and the rate of reaction is lowest. At the time passes, the rate of reaction increases till the equilibrium is established. Similar curves of the rates of reactions with the catalyst show that the rates of the forward reaction and the reverse reaction are altered equally but the equilibrium is established in a much shorter time.

For example, in the **Haber Process for ammonia**,



the reaction is very slow. In the presence of the catalyst, the equilibrium is reached much sooner but the percentage yield remains unchanged. The iron catalyst shortens the time to attain equilibrium but cannot alter the percentage yield.



■ **Figure 21.1**  
The effect of a catalyst on the time required for the equilibrium to be established.

Energy considerations also show that the final state of equilibrium cannot be changed by the catalyst. Suppose the catalyst accelerates the forward reaction more than the reverse reaction. This will shift the equilibrium point, which cannot happen without the supply of energy to the system. But a catalyst unchanged in mass and composition at the end of the reaction, cannot supply the required energy.

(7) **Change of temperature alters the rate of a catalytic reaction as it would do for the same reaction without a catalyst**

We have already studied the effect of temperature change on reversible reactions under Le Chatelier principle.

Some catalysts are, however, physically altered by a rise in temperature and hence their catalytic activity may be decreased. This is particularly true with colloidal solutions like that of platinum, since a rise in the temperature may cause their coagulation. In such a case the rate of reaction increases up to a certain point and then gradually decreases. **The rate of reaction is maximum at a particular temperature called the optimum temperature.**

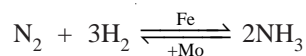
### PROMOTERS

The activity of a catalyst can often be increased by addition of a small quantity of a second material. This second substance is either not a catalyst itself for the reaction or it may be a feeble catalyst.

**A substance which, though itself not a catalyst, promotes the activity of a catalyst is called a promoter.**

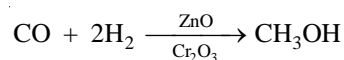
#### Example of Promoters

Molybdenum (Mo) or aluminium oxide ( $\text{Al}_2\text{O}_3$ ) promotes the activity of iron catalyst in the Haber synthesis for the manufacture of ammonia.



**In some reactions, mixtures of catalysts are used to obtain the maximum catalytic efficiency.**

For example, in the synthesis of methanol ( $\text{CH}_3\text{OH}$ ) from carbon monoxide and hydrogen, a mixture of zinc and chromium oxide is used as a catalyst.



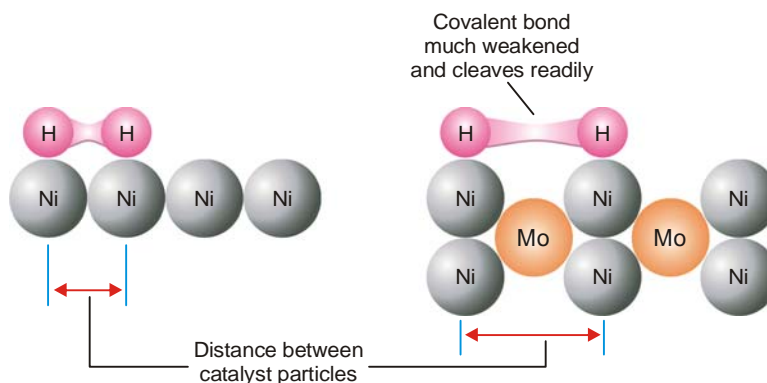
### Explanation of Promotion Action

The theory of promotion of a catalyst is not clearly understood. Presumably :

(1) **Change of Lattice Spacing.** The lattice spacing of the catalyst is changed thus enhancing the spaces between the catalyst particles. The adsorbed molecules of the reactant (say  $H_2$ ) are further weakened and cleaved. This makes the reaction go faster.

(2) **Increase of Peaks and Cracks.** The presence of the promoter increases the peaks and cracks on the catalyst surface. This increases the concentration of the reactant molecules and hence the rate of reaction.

The phenomenon of promotion is a common feature of heterogeneous catalysis.



■ **Figure 21.2**  
How the change of crystal lattice spacing of catalyst makes the reaction go faster.

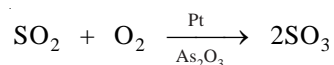
### CATALYTIC POISONING

Very often a heterogeneous catalyst is rendered ineffective by the presence of small amounts of impurities in the reactants.

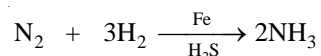
**A substance which destroys the activity of the catalyst to accelerate a reaction, is called a poison and the process is called Catalytic poisoning.**

#### Examples of Catalytic Poisoning

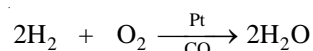
(1) The platinum catalyst used in the oxidation of sulphur dioxide (Contact Process), is poisoned by arsenic oxide ( $As_2O_3$ )



(2) The iron catalyst used in the synthesis of ammonia (Haber Process) is poisoned by  $H_2S$ .

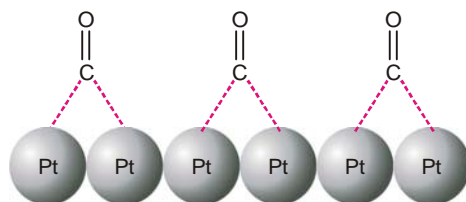


(3) The platinum catalyst used in the oxidation of hydrogen is poisoned by carbon monoxide.



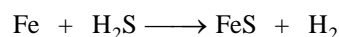
### Explanation of Catalytic Poisoning

**The poison is adsorbed on the catalyst surface in preference to the reactants.** Even a monomolecular layer renders the surface unavailable for further adsorption of the reactants. The poisoning by  $As_2O_3$  or CO appears to be of this kind.



■ **Figure 21.3**  
Poisoning of platinum catalyst by carbon monoxide.

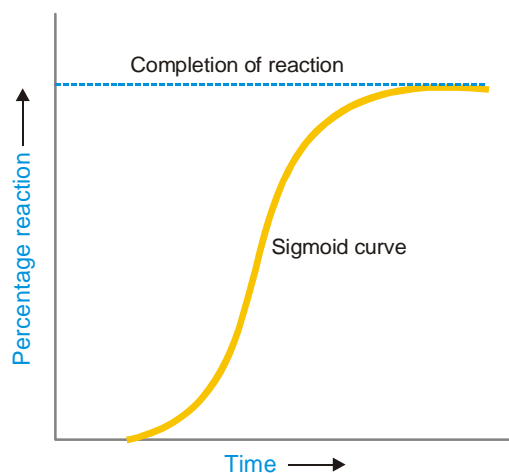
(2) **The catalyst may combine chemically with the impurity.** The poisoning of iron catalyst by  $\text{H}_2\text{S}$  falls in this class.



### AUTOCATALYSIS

**When one of the products of reaction itself acts as a catalyst for that reaction the phenomenon is called Autocatalysis.**

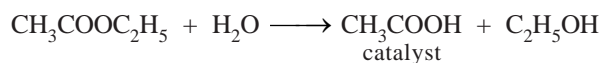
In autocatalysis the initial rate of the reaction rises as the catalytic product is formed, instead of decreasing steadily (Fig. 21.4). The curve plotted between reaction rate and time shows a maximum when the reaction is complete.



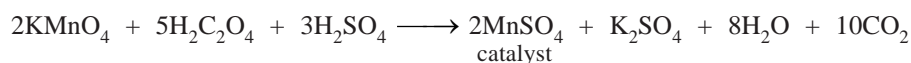
■ **Figure 21.4**  
Curve showing the rise of rate of reaction with time.

### Examples of Autocatalysis

(1) **Hydrolysis of an Ester.** The hydrolysis of ethyl acetate forms acetic acid ( $\text{CH}_3\text{COOH}$ ) and ethanol. Of these products, acetic acid acts as a catalyst for the reaction.

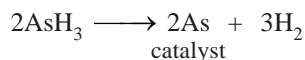


(2) **Oxidation of Oxalic acid.** When oxalic acid is oxidised by acidified potassium permanganate, manganous sulphate produced during the reaction acts as a catalyst for the reaction.



(3) **Decomposition of Arsine.** The free arsenic produced by the decomposition of arsine ( $\text{AsH}_3$ ) autocatalyses the reaction.





### NEGATIVE CATALYSIS

When a catalyst reduces the rate of a reaction, it is called a **Negative catalyst or Inhibitor**. This phenomenon is called **Negative catalysis or Inhibition**. Negative catalysis is useful to slow down or stop altogether an unwanted reaction.

#### Examples of Negative Catalysis

(1) **Oxidation of Trichloromethane (CHCl<sub>3</sub>)**

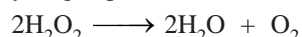
Trichloromethane (or chloroform) is used as anaesthetic. Upon oxidation by air it forms carbonyl chloride (COCl<sub>2</sub>) which is a poisonous substance.



2 per cent of ethanol (C<sub>2</sub>H<sub>5</sub>OH) when added to chloroform acts as a negative catalyst and suppresses the formation of carbon chloride.

(2) **Decomposition of Hydrogen peroxide**

The decomposition of hydrogen peroxide,



is retarded by the presence of *dilute acids* or *glycerol*.

(3) **Tetraethyllead as Antiknock**

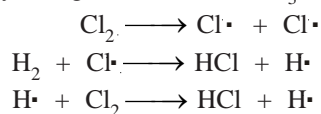
When tetraethyllead, Pb(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, is added to petrol, it retards the too rapid or explosive combustion of the fuel which is responsible for knocking of the engine.

#### Explanation of Negative Catalysis

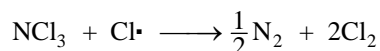
The mechanism of negative catalysis could be different for different reactions.

(1) **By poisoning a catalyst.** A negative catalyst may function by poisoning a catalyst which already happens to be present in the reaction mixture. For example, the traces of alkali dissolved from the glass of the container, catalyse the decomposition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). But the addition of an acid would destroy the alkali catalyst and thus prevent decomposition.

(2) **By breaking a chain reaction.** In some cases negative catalysts are believed to operate by breaking the chain of reactions. For example, the combination of H<sub>2</sub> and Cl<sub>2</sub>, which is a chain reaction, is negatively catalysed by nitrogen trichloride (NCl<sub>3</sub>).

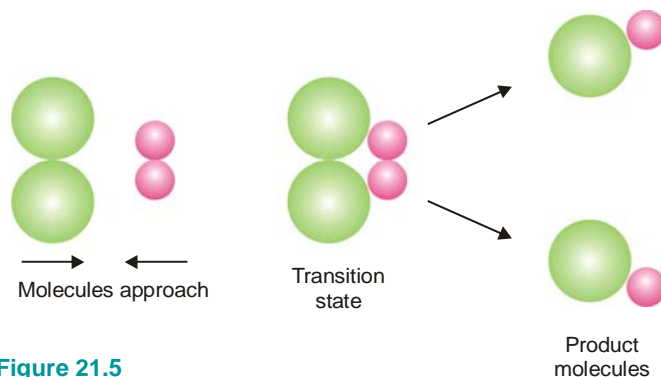


NCl<sub>3</sub> breaks the chain of reactions by absorbing the propagating species (Cl), and the reaction stops.



### ACTIVATION ENERGY AND CATALYSIS

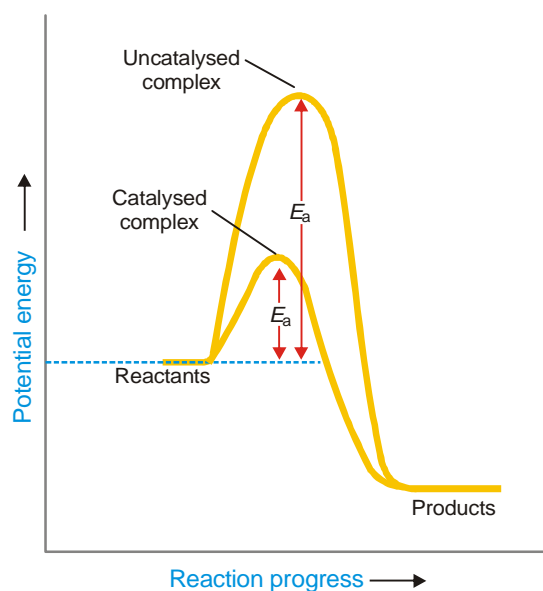
According to the collision theory, a reaction occurs by the collisions between the reactant molecules (or ions). At ordinary temperature, the molecules do not possess enough energy and hence the collisions are not effective. However, when the temperature of the system is raised, the kinetic energy of the molecules increases. But the molecules do not react unless they attain a minimum amount of energy. **The minimum amount of energy required to cause a chemical reaction is known as the Activation Energy.** The activated molecules on collision first form an **Activated Complex**. As a result of breaking and forming of new bonds, the activated complex dissociates to yield product molecules.



■ **Figure 21.5**  
Mechanism of a molecular reaction.

A catalyst lowers the activation energy of the reaction by providing a new pathway (mechanism).

Thus larger number of effective collisions occur in the presence of the catalyst than would occur at the same temperature without the presence of the catalyst. In this way the presence of the catalyst makes the reaction go faster, other conditions remaining the same.



■ **Figure 21.6**  
Energy diagram of a reaction with and without the catalyst, showing clearly the lowering of activation energy by the catalyst.

## THEORIES OF CATALYSIS

There are two main theories of catalysis :

- (1) Intermediate Compound Formation theory
- (2) The Adsorption theory.

In general, the Intermediate Compound Formation theory applies to homogeneous catalytic reactions and the Adsorption theory applies to heterogeneous catalytic reactions.

### The Intermediate Compound Formation Theory

As already discussed a catalyst functions by providing a new pathway of lower activation

energy. In homogeneous catalysis, it does so by forming an intermediate compound with one of the reactants. The highly reactive intermediate compound then reacts with the second reactant to yield the product, releasing the catalyst. Let us illustrate it by taking the general reaction

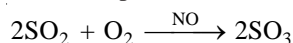


where C acts as catalyst. The reaction proceeds through the reactions :

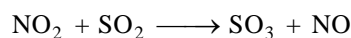
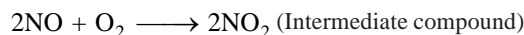


The activation energies of the reactions (2) and (3) are lower than that of the reaction (1) Hence the involvement of the catalyst in the formation of the intermediate compound and its subsequent decomposition, accelerates the rate of the reaction (1) which was originally very slow.

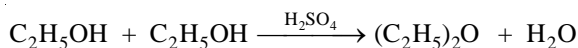
**Example 1.** Catalytic oxidation of sulphur dioxide ( $\text{SO}_2$ ) in the presence of nitric oxide (NO) as catalyst. (Chamber Process of Sulphuric acid)



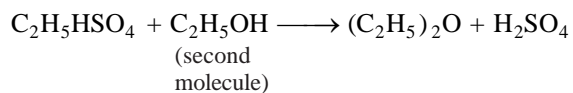
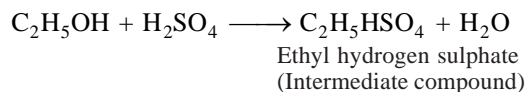
**Mechanism :**



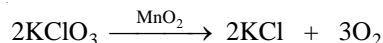
**Example 2.** Preparation of diethyl ether,  $(\text{C}_2\text{H}_5)_2\text{O}$ , from ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) using sulphuric acid as catalyst.



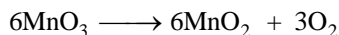
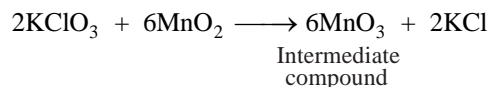
**Mechanism :**



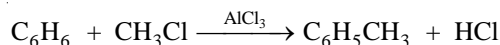
**Example 3.** Thermal decomposition of potassium chlorate ( $\text{KClO}_3$ ) in the presence of manganese dioxide ( $\text{MnO}_2$ ).



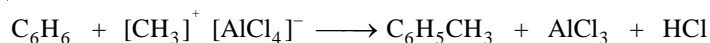
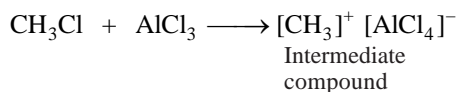
**Mechanism :**



**Example 4.** Formation of methylbenzene,  $\text{C}_6\text{H}_5\text{CH}_3$  by reaction between benzene,  $\text{C}_6\text{H}_6$ , and methyl chloride,  $\text{CH}_3\text{Cl}$ , using aluminium chloride  $\text{AlCl}_3$ , as catalyst (Friedel-Crafts reaction),



**Mechanism :**

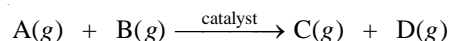


It may be noted that the actual isolation of intermediate compounds which would prove their existence is very difficult. As already stated, by their very nature they are unstable. In general, the intermediate compounds suggested as being formed are usually plausible rather than proved.

### The Adsorption Theory

This theory explains the mechanism of a reaction between two gases catalysed by a solid (*Heterogeneous or Contact Catalysis*). Here the catalyst functions by adsorption of the reacting molecules on its surface.

Generally speaking, four steps can be put forward for heterogeneous catalysis. For example, if the reaction is :



#### Step 1. Adsorption of Reactant molecules

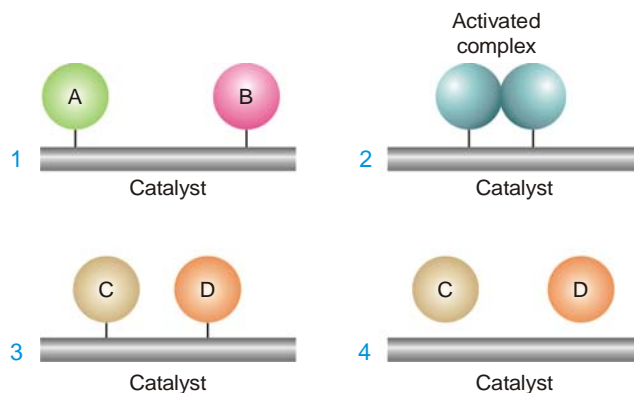
The reactant molecules A and B strike the catalyst surface. They are held up at the surface by weak van der Waals forces (*Physical adsorption*) or by partial chemical bonds (*Chemisorption*).

#### Step 2. Formation of Activated complex

The particles of the reactants adjacent to one another join to form an *intermediate complex* (A – B). The activated complex is unstable. It has only fleeting existence.

#### Step 3. Decomposition of Activated complex

The activated complex breaks to form the products C and D. The separated particles of the products hold to the catalyst surface by partial chemical bonds.



■ **Figure 21.7**  
Mechanism of Contact catalysis.

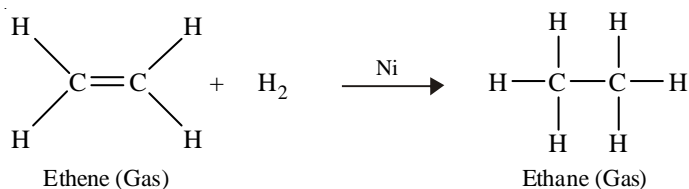
#### Step 4. Desorption of Products

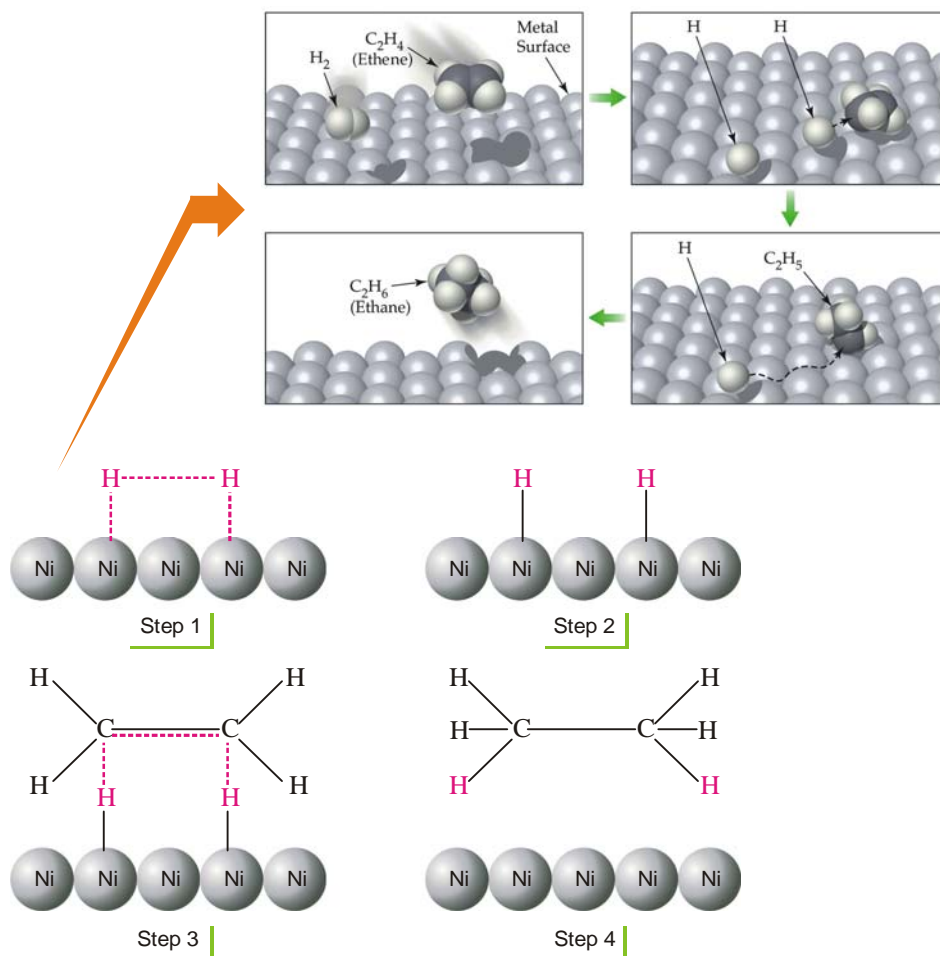
The particles of the products are *desorbed* or released from the surface. They are stable and can lead an independent existence.

The mechanism of contact catalysis may vary in details, depending on the nature of the reactants.

### HYDROGENATION OF ETHENE (ETHYLENE) IN PRESENCE OF NICKEL

Ethene adds hydrogen in the presence of nickel as a catalyst to yield ethane.





■ **Figure 21.8**  
**Mechanism of the hydrogenation of ethene on nickel surface.**

The catalyst operates by the following steps.

**Step 1. Adsorption of Hydrogen molecules**

Hydrogen molecules are adsorbed on the nickel surface due to the residual valence bonds of the nickel atoms.

**Step 2 H–H Bonds are broken**

The H–H bond is smaller ( $0.74\text{\AA}$ ) than Ni–Ni bond. Therefore, the H–H bond of the adsorbed hydrogen molecule is stretched and weakened. The weakened bond breaks, separating the hydrogen atoms. The separated hydrogen atoms are held to the nickel surface by chemical bonds.

**Step 3. Formation of the Activated complex**

The chemisorbed hydrogen atoms then attach to ethene molecule by partial chemical bonds. The unstable activated complex is thus formed.

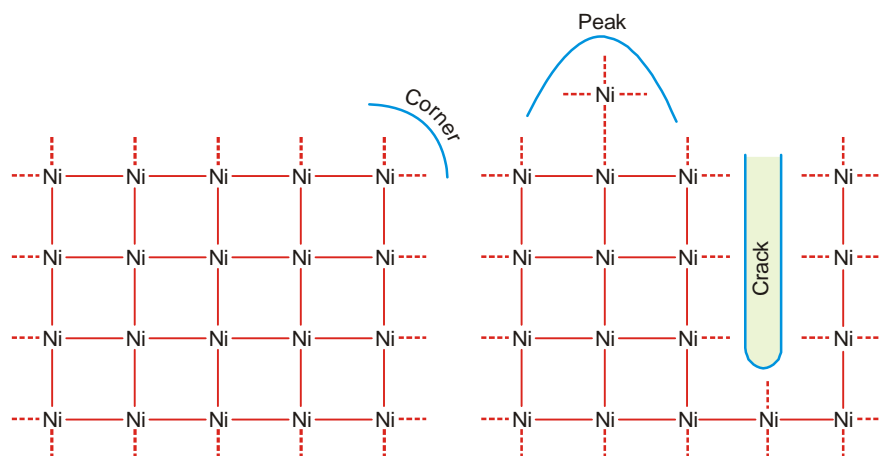
**Step 4. Decomposition of the Activated complex and desorption of ethane molecules**

The unstable activated complex decomposes to release ethane molecules. The freed catalyst surface is again available for further action.

### Active Centres on Catalyst Surface

Just like surface tension, the catalyst has unbalanced chemical bonds on it. The reactant gaseous molecules are adsorbed on the surface by these free bonds. This accelerates the rate of the reaction.

The distribution of free bonds on the catalyst surface is not uniform. These are crowded at the 'peaks', 'cracks' and 'corners' of the catalyst. The catalytic activity due to adsorption of reacting molecules is maximum at these spots. These are, therefore, referred to as the **active centres**.

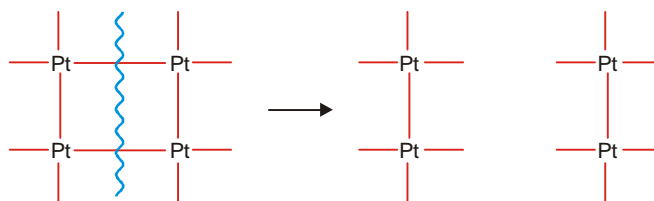


■ **Figure 21.9**  
Active centres on catalyst surface.

The active centres increase the rate of reaction not only by increasing the concentration of the reactants but they also activate the molecule adsorbed at two such centres by stretching it.

### The Adsorption Theory Explains Catalytic Activity

- (1) Metals in a state of fine subdivision or colloidal form are rich in free valence bonds and hence they are more efficient catalysts than the metal in lumps.



■ **Figure 21.10**  
Subdivision of a catalyst makes it more efficient due to increase of free valence bonds.

- (2) Catalytic poisoning occurs because the so-called poison blocks the free valence bonds on its surface by preferential adsorption or by chemical combination.
- (3) A promoter increases the valence bonds on the catalyst surface by changing the crystal lattice and thereby increasing the active centres.

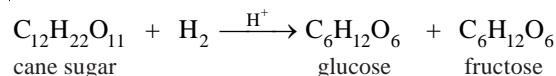
### ACID-BASE CATALYSIS

A number of homogeneous catalytic reactions are known which are catalysed by acids or bases, or both acids and bases. These are often referred to as **Acid-Base catalysts**.

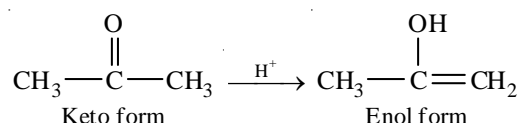
Arrhenius pointed out that acid catalysis was, in fact, brought about by  $H^+$  ions supplied by strong acids, while base catalysis was caused by  $OH^-$  ions supplied by strong bases.

### Examples of Acid-Base catalysis

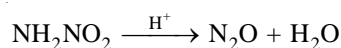
(1) Inversion of Cane sugar :



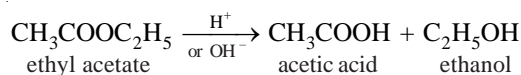
(2) Keto-Enol tautomerism of Acetone :



(3) Decomposition of Nitramide :



(4) Hydrolysis of an Ester :



### General Acid-Base catalysis

More recently it has been found that :

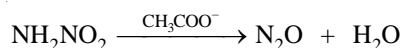
(a) **Not only H<sup>+</sup> ions but all Bronsted bases (proton donors) cause acid catalysis.** Thus the general acid catalysts are :

H<sup>+</sup>, undissociated acids (CH<sub>3</sub>COOH), cations of weak bases (NH<sub>4</sub><sup>+</sup>), and water (H<sub>2</sub>O).

(b) **Not only OH<sup>-</sup> ions but all Bronsted bases (proton acceptors) act as base catalyst.** Thus the general base catalysts are :

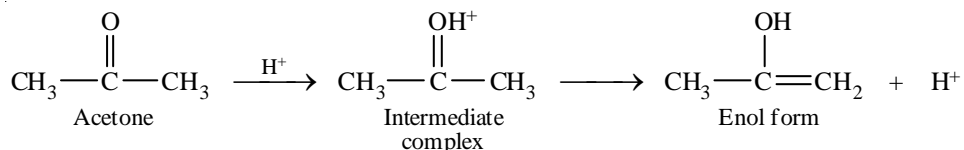
OH<sup>-</sup>, undissociated bases, anions of weak acids (CH<sub>3</sub>COO<sup>-</sup>) and water (H<sub>2</sub>O).

The catalysis brought about by general acids and bases is termed **General Acid-Base catalysis**. For elucidation, decomposition of nitramide is also catalysed by acetate ions (CH<sub>3</sub>COO<sup>-</sup>).



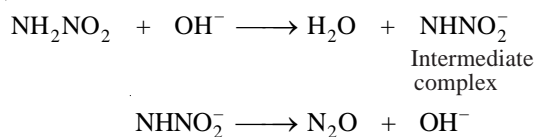
### Mechanism of Acid-Base catalysis

(a) In **acid catalysis**, the H<sup>+</sup> (or a proton donated by Bronsted acid) forms an intermediate complex with the reactant, which then reacts to give back the proton. For example, the mechanism of keto-enol tautomerism of acetone is :

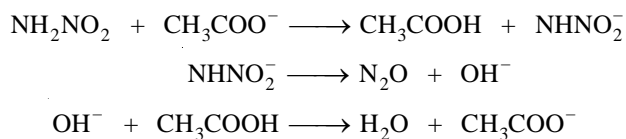


(b) In **base catalysis**, the OH<sup>-</sup> ion (or any Bronsted base) accepts a proton from the reactant to form an *intermediate complex* which then reacts or decomposes to regenerate the OH<sup>-</sup> (or Bronsted base). For example, the decomposition of nitramide by OH<sup>-</sup> ions and CH<sub>3</sub>COO<sup>-</sup> ions may be explained as follows :

(i) **By OH<sup>-</sup> ions :**



(ii) By  $\text{CH}_3\text{COO}^-$  ions :



### ENZYME CATALYSIS

Numerous organic reactions are taking place in the body of animals and plants to maintain the life process. These reactions being slow remarkably catalysed by the organic compounds known as **Enzymes**. All enzymes have been found to be complex protein molecules. Thus :

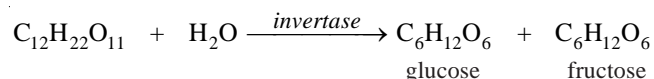
Enzymes are protein molecules which act as catalysts to speed up organic reactions in living cells. **The catalysis brought about by enzymes is known as Enzyme Catalysis.**

Each enzyme is produced in a particular living cell to catalyse a reaction occurring in that cell. Many enzymes have been identified and obtained in pure crystalline state from the cells to which they belong. However the first enzyme as prepared by synthesis in the laboratory in 1969.

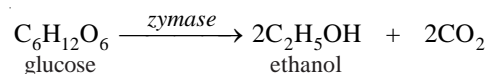
#### Examples of Enzyme Catalysis

Some common examples of the biochemical reactions catalysed by enzymes are :

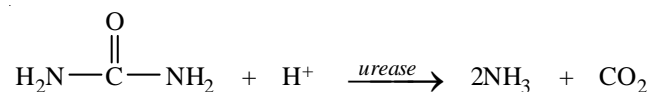
(1) **Inversion of cane sugar** ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) by *Invertase present in yeast*,



(2) **Conversion of glucose into ethanol** by *Zymase present in yeast*,



(3) **Hydrolysis of urea** ( $\text{H}_2\text{N}-\text{CO}-\text{NH}_2$ ) by *Urease present in soya bean*,



### MECHANISM OF ENZYME CATALYSIS

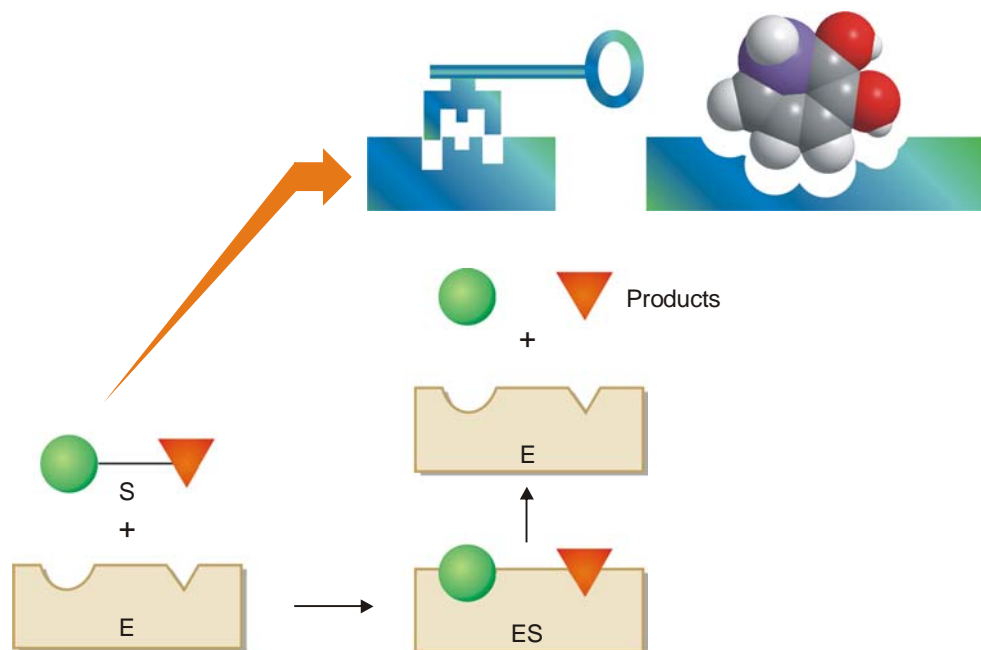
The long chains of the enzyme (protein) molecules are coiled on each other to make a rigid colloidal particle with cavities on its surface. These cavities which are of characteristic shape and abound in active groups ( $\text{NH}_2$ ,  $\text{COOH}$ ,  $\text{SH}$ ,  $\text{OH}$ ) are termed **Active centres**. The molecules of substrate which have complementary shape, fit into these cavities just as key fits into a lock (**Lock-and-Key theory**). By virtue of the presence of active groups, the enzyme forms an activated complex with the substrate which at once decomposes to yield the products. Thus the substrate molecules enters the cavities, forms complex and reacts, and at once the products get out of the cavities.

Michaelis and Menten (1913) proposed the following mechanism for enzyme catalysis (Fig. 21.11).



where E = enzyme; S = substrate (reactant); ES = activated complex; P = products.





■ **Figure 21.11**  
Illustration of the lock-and-key model of enzyme catalysis.

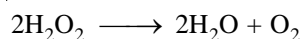
### CHARACTERISTICS OF ENZYME CATALYSIS

In general, enzymes behave like inorganic heterogeneous catalysts. However, they are unique in their efficiency and high degree of specificity. Some more important features of enzyme catalysis are listed below.

#### (1) Enzymes are the most efficient catalysts known

The enzyme catalysed reactions proceed at fantastic high rates in comparison to those catalysed by inorganic substances. Thus one molecule of an enzyme may transform one million molecules of the substrate (reactant) per minute.

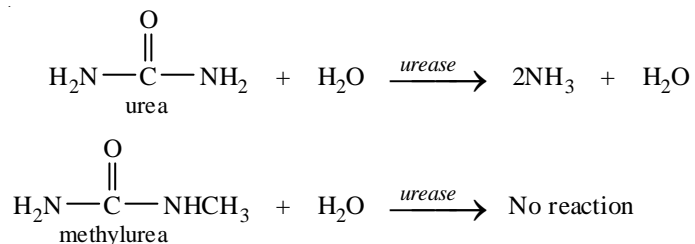
Like inorganic catalysts, enzymes function by lowering the activation energy of a reaction. For example, the activation energy of the decomposition of hydrogen peroxide,

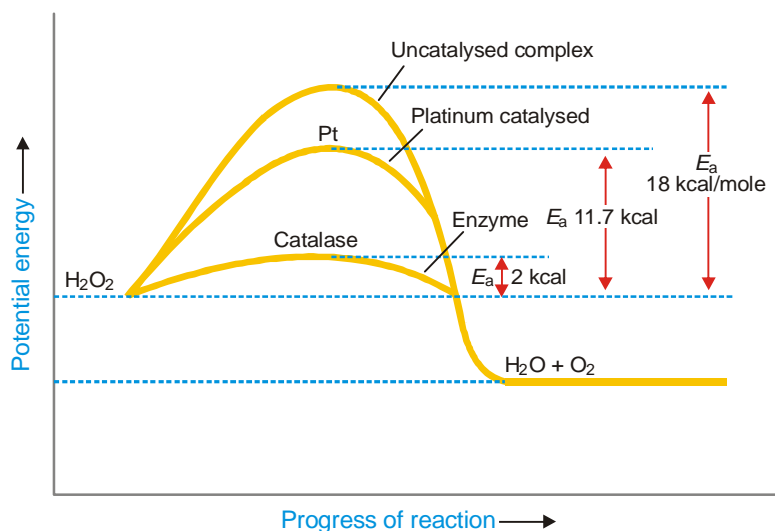


without a catalyst is 18 kcal/mole. With colloidal platinum (inorganic catalyst), the activation energy is lowered by 11.7 kcal/mole. The enzyme *catalase* lowers the activation energy of the same reaction to less than 2 kcal/mole.

#### (2) Enzyme catalysis is marked by absolute specificity

An enzyme as a rule catalyses just one reaction with a particular substance. For example, *urease* (an enzyme derived from soya bean) catalyses the hydrolysis of urea and no other amide, not even methylurea.



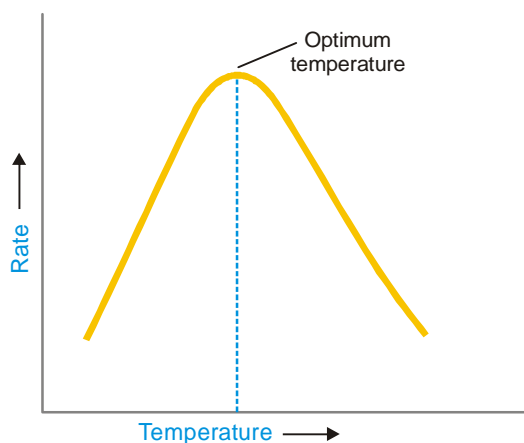


■ **Figure 21.12**  
Enzyme lowers the activation energy of the decomposition of  $\text{H}_2\text{O}_2$  by maximum which explains for their extremely high catalytic efficiency.

Enzyme catalysed reactions are often marked by absolute specificity. Thus where a compound can exist in optically active isomers (identical in every respect except the space arrangement of groups), an enzyme which can act on one of the isomers is unable to act on the other. For example, the enzyme present in ordinary mould (*Penicillium glaucum*) when added to a ( $\pm$ )-mixture of tartaric acid, decomposes the (+)-form only, leaving the (–)-form behind.

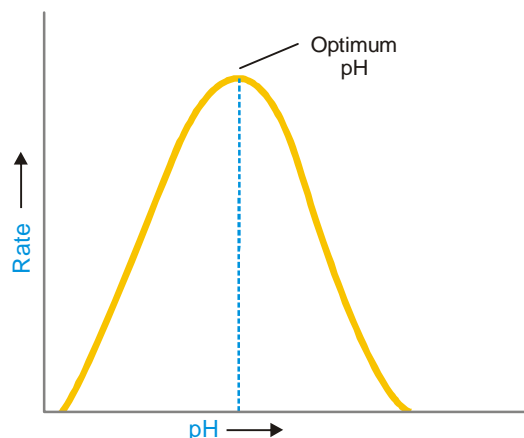
### (3) The rate of enzyme catalysed reactions is maximum at the optimum temperature

The rate of an enzyme catalysed reaction is increased with the rise of temperature but up to a certain point. Thereafter the enzyme is denatured as its protein structure is gradually destroyed. Thus the rate of reaction drops and eventually becomes zero when the enzyme is completely destroyed. The rate of an enzyme reaction with raising of temperature gives a bell-shaped curve. The temperature at which the reaction rate is maximum is called the **optimum temperature**.



■ **Figure 21.13**  
The variation of rate of an enzyme catalysed reaction with rise of temperature.

For example, the optimum temperatures, of enzyme reactions occurring in human body is 37°C (98.6°F). At much higher temperatures, all physiological reactions will cease due to loss of enzymatic activity. This is one reason why high body temperature (fever) is very dangerous.



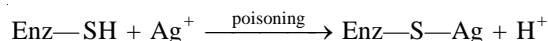
■ **Figure 21.14**  
The variation of rate of an enzyme catalysed reaction with increase of pH.

#### (4) Rate of enzyme catalysed reactions is maximum at the optimum pH

The rate of an enzyme catalysed reaction varies with pH of the system. The rate passes through a maximum at a particular pH, known as the **optimum pH**. The enzyme activity is lower at other values of pH. Thus many enzymes of the body function best at pH of about 7.4, the pH of the blood and body fluids.

#### (5) Enzymes are markedly inhibited or poisoned

The catalytic activity of an enzyme is often reduced (*inhibited*) or completely destroyed (poisoned) by addition of other substances. These inhibitors or poisons interact with the active functional groups on the enzyme surface. For example, heavy metal ions ( $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ) react with the  $-\text{SH}$  groups of the enzyme and poison it.



The physiological activity of many drugs is related to their action as enzyme inhibitors in the body. Thus sulpha drugs, penicillin, and streptomycin inhibit the action of several bacteria and have proved effective in curing pneumonia, dysentery, cholera, and many other infectious diseases.

#### (6) Catalytic activity of enzymes is greatly enhanced by the presence of Activators or Coenzymes

Activators are metal ions  $\text{Na}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{CO}^{2+}$ ,  $\text{Cu}^{2+}$ , etc., which get weakly bonded to enzyme molecules and promote their catalytic action. Thus it has been found that the addition of sodium chloride ( $\text{Na}^+$ ) makes *amylase* catalytically very active.

Often, a small nonprotein (*vitamin*) termed a **coenzyme** when present along with an enzyme, promotes the catalytic activity of the latter.

**EXAMINATION QUESTIONS**

- Define or explain the following terms :
  - Catalyst
  - Homogeneous catalysis
  - Heterogeneous catalysis
  - Activation energy
- What is meant by the term catalyst? Give general characteristics of catalytic reactions.
- What effect does a catalyst have on an equilibrium system? Explain from the point of view of Kinetics and the Law of mass action.
- Discuss the mechanism of enzyme catalysed reactions. Deduce Michaelis Menten equation and give conditions under which an enzyme catalysed reaction changes its order.
- Give examples of heterogeneous catalysis in which reactants taking part are
    - solid,
    - liquid and
    - gaseous state
  - Discuss the theories of heterogeneous catalysis and illustrate with examples.
- Give characteristics of enzyme catalysis. Discuss Michaelis and Menten's enzyme mechanism in detail to express the rate of reaction. Derive the required equation.
- Discuss intermediate compound formation theory of catalysis.
  - Define the following :
    - Catalyst promoter
    - Catalyst inhibitor
    - Catalytic poison

*(Kerala BSc, 2000)*
- Derive Michaelis-Menten equation for enzyme catalysed reaction.
  - Explain the mechanism of heterogeneous catalysis by taking a suitable example.
 

*(Madras BSc, 2000)*
- Under what conditions an enzyme catalysed reaction follows
  - Second order kinetics
  - First order kinetics
  - Zero order kinetics

*(Nagpur BSc, 2000)*
- Explain the important characteristics of enzyme catalysis. *(Assam BSc, 2000)*
- What is catalysis? Derive the Michaelis-Menten equation to explain enzyme catalysis. *(Kathmandu BSc, 2001)*
- What is heterogeneous catalysis? Explain giving one example. *(Guru Nanak Dev BSc, 2002)*
- By considering one example each of catalytic promoters and inhibitor, distinguish between the action of these promoters and inhibitors.
  - What mechanism would you suggest for heterogeneous catalytic reactions? Clarify it with one example. *(MD Rohtak BSc, 2002)*
- What are characteristic of catalytic reactions?
  - Explain with examples autocatalysis. *(Arunachal BSc, 2002)*
- Derive an expression for the rate of an acid catalysed reaction. *(Jamia Millia BSc, 2002)*
- Explain the important characteristics of enzyme catalysis. *(Punjabi BSc, 2002)*
- Discuss the theories of heterogeneous catalysis.
  - Give an account of enzyme catalysis. *(Purvanchal BSc, 2002)*
- Write notes on :
  - Catalyst and energy of activation
  - Specificity of catalytic action *(Mizoram BSc, 2002)*
- What is the function of catalytic promoters and inhibitors in chemical reactions?
  - Explain the important characteristics of enzyme catalysis. *(Punjabi BSc, 2003)*

20. Explain the following with example:
- |                        |                    |
|------------------------|--------------------|
| (i) Negative catalyst  | (ii) Autocatalysis |
| (iii) Catalytic poison | (iv) Promoters     |
- (v) Specificity of a catalyst (Purvanchal BSc, 2003)
21. Derive an expression for the kinetics of enzyme catalysis of Michaelis equation. What will be the effect of very high substance concentrations? (Arunachal BSc, 2003)
22. Write the Michaelis-Menten equation for an enzyme-catalysed reaction and define/explain all symbols used in it. (Guru Nanak Dev BSc, 2004)
23. Explain how a catalyst increases the speed of a reaction. (Agra BSc, 2001; Sambalpur BSc, 2003; Delhi BSc, 2004)
24. Write down the mechanism of enzyme catalysis suggested by Michaelis and Menten. (Meerut BSc, 2004)
25. (a) Give an example each for enzyme catalysis and acid-base catalysis.  
 (b) Describe the theory of homogeneous and heterogeneous catalysis. (Baroda BSc, 2004)
26. Explain the difference between homogeneous and heterogeneous catalysis. Discuss the theories of catalysis. (Madurai BSc, 2004)
27. Write notes on :
- |                             |                    |
|-----------------------------|--------------------|
| (i) Heterogeneous catalysis |                    |
| (ii) Homogeneous catalysis  | (Madras BSc, 2005) |
28. Write notes on :
- |                      |                         |
|----------------------|-------------------------|
| (i) Enzyme catalysis |                         |
| (ii) Autocatalysis   | (Bundelkhand BSc, 2006) |

### MULTIPLE CHOICE QUESTIONS

- A catalyst
  - does not react
  - reacts and is produced in one of the later steps of a reaction
  - reacts in an early step and is produced in a later step
  - reacts but is not produced

**Answer.** (c)
- A catalyst
  - changes the free energy change of a reaction
  - is included in the balanced chemical equation for a reaction
  - changes the mechanisms for a reaction
  - slows down the rate of a reaction

**Answer.** (c)
- A catalyst can be described as a substance that:
  - undergoes change to accelerate the rate of the reaction
  - increases the kinetic energy of the reactants
  - provides a path of lower activation energy for the reaction
  - lowers the potential energy of the products with respect to the energy of the reactants

**Answer.** (c)
- The minimum amount of energy needed to bring about a non-spontaneous change is the

- (a) free energy (b) activation energy  
(c) entropy (d) enthalpy

**Answer:** (b)

5. A catalyst will affect the rate of the forward reaction by changing the  
(a) activation energy (b) heat of reaction  
(c) heat of formation (d) potential energy of the products

**Answer:** (a)

6. Which of the following is most likely to increase the rate of a reaction?  
(a) decreasing the temperature  
(b) increasing the volume of the reaction vessel  
(c) reducing the activation energy  
(d) decreasing the concentration of the reactant in the reaction vessel

**Answer:** (c)

7. All of the following are true statements concerning catalysts except  
(a) a catalyst will speed the rate-determining step  
(b) a catalyst will be used up in a reaction  
(c) a catalyst may induce steric strain in a molecule to make it react more readily  
(d) a catalyst will lower the activation energy of a reaction

**Answer:** (b)

8. At equilibrium  
(a) the forward reaction will continue  
(b) a change in reaction conditions may shift the equilibrium  
(c) the reverse reaction will not continue  
(d) both (a) and (b)

**Answer:** (d)

9. Which statement is not correct regarding the function of a catalyst?  
(a) it affects the rate of a chemical reaction  
(b) it lowers the energy of the product, causing the reaction to be more exothermic  
(c) it changes the mechanism of a reaction  
(d) it lowers the activation energy

**Answer:** (b)

10. Which of the following will lower the activation energy for a reaction?  
(a) increasing the concentrations of reactants  
(b) raising the temperature of the reaction  
(c) adding a suitable catalyst  
(d) there is no way to lower the activation energy of a reaction

**Answer:** (c)

11. Which of the following reactions occurs at the fastest rate?  
(a) one which is exothermic by 15 kcal/mole and has an activation energy of 20 kcal/mole  
(b) one which is endothermic by 5 kcal/mole and has an activation energy of 30 kcal/mole  
(c) one which is exothermic by 30 kcal/mole and has an activation energy of 15 kcal/mole  
(d) one which is exothermic by 20 kcal/mole and has an activation energy of 20 kcal/mole

**Answer:** (c)

12. At which temperature does an aqueous solution of LiCl have the highest average kinetic energy?  
(a) 100°C (b) 200°C  
(c) 273 K (d) 373 K

**Answer:** (b)

13. The minimum amount of energy required to start a chemical reaction is called  
(a) entropy (b) enthalpy  
(c) free energy (d) activation energy  
**Answer.** (d)
14. Which one of the following statements is incorrect?  
(a) activation energies of simple reactions can be negative  
(b) more molecules in a gas have energies above some threshold value as the temperature is increased  
(c) the rate does not depend on the magnitude of the  $\Delta E$   
(d) the lower the activation energy, the faster the rate if equal numbers of collisions are always involved  
**Answer.** (a)
15. Which one of the following statements is incorrect?  
(a) catalysts speed up a reaction by lowering the activation energy  
(b) heterogeneous catalysts are often found on a solid in contact with gaseous reactants  
(c) an automotive catalytic converter uses a catalyst to burn gasoline better for higher gas mileage  
(d) enzymes are biological catalysts  
**Answer.** (c)
16. The energy needed to overcome for a reaction to occur is called:  
(a) activation energy (b) energy of vaporization  
(c) specific heat (d) potential energy  
**Answer.** (a)
17. When a catalyst is added to a reaction system,  
(a) the reaction rate is changed (b) the equilibrium position of the reaction is shifted  
(c) the  $\Delta H$  of the reaction is changed (d) all of these  
**Answer.** (a)
18. As a good rule of thumb, many reactions double in speed for a  $10^\circ\text{C}$  increase in T at room temperature. Taking the two temperatures to be  $20^\circ\text{C}$  and  $30^\circ\text{C}$ , the activation energy for such reactions would be:  
(a)  $148\text{ kJ mol}^{-1}$  (b)  $0.35\text{ kJ mol}^{-1}$   
(c)  $6.12\text{ kJ mol}^{-1}$  (d)  $51\text{ kJ mol}^{-1}$   
**Answer.** (d)
19. A catalyst  
(a) may be in same phase with the reactants or in a different phase  
(b) may accelerate a reaction  
(c) affects a reaction without being consumed in the process  
(d) all of the above  
**Answer.** (d)
20. For any chemical reaction at equilibrium, the rate of the forward reaction is  
(a) less than the rate of the reverse reaction  
(b) greater than the rate of the reverse reaction  
(c) equal to the rate of the reverse reaction  
(d) unrelated to the rate of the reverse reaction  
**Answer.** (c)
21. A reaction requires the presence of a strip of metal in the reaction vessel, when the reactants are gases. This is an example of what kind of catalysis?  
(a) homogeneous (b) heterogeneous  
(c) equilibrium (d) thermodynamic  
**Answer.** (b)
22. Which of the following steps occur in heterogeneous catalysis at a solid/gas surface?





(d) increases the rate of backward and forward reaction to equal extent

**Answer.** (d)

31. A catalyst is a substance which

(a) increases the equilibrium concentration of the products

(b) changes the equilibrium constant of the reaction

(c) supplies energy to the reactions

(d) shortens the time to reach the equilibrium

**Answer.** (d)

32. The enzyme which can catalyse the conversion of glucose to ethanol is

(a) maltase

(b) diastase

(c) invertase

(d) zymase

**Answer.** (d)

33. The decomposition of Nitroglycerine is an example of

(a) self catalytic reaction

(b) enzyme catalysed reaction

(c) autocatalytic reaction

(d) induced catalysis

**Answer.** (c)

34. Enzymes are

(a) finely divided metals

(b) transition metal ions

(c) auto-catalysts

(d) proteins

**Answer.** (d)

35. Which of the following processes does not involve the use of a catalyst

(a) Contact process

(b) Ostwald process

(c) Lead chamber process

(d) Thermite process

**Answer.** (d)

36. In Haber's process for the synthesis of ammonia, the use of finely divided iron (a catalyst) increases:

(a) the rate of formation of  $\text{NH}_3$  as well as amount of ammonia formed

(b) the rate of formation of  $\text{NH}_3$  without changing the amount of ammonia formed

(c) the rate of formation of  $\text{NH}_3$  but decreases the amount of ammonia formed

(d) the amount of ammonia formed without increasing the rate of formation

**Answer.** (b)

37. Which of the following statements is incorrect

(a) enzymes are catalysts

(b) urease is an enzyme

(c) enzymes can catalyse any reaction

(d) enzymes are in colloidal state

**Answer.** (a)

38. The efficiency of an enzyme in catalysing a reaction is due to its capacity

(a) to change the shape of the substrate molecule

(b) to lower the activation energy of the reaction

(c) to form a strong enzyme substrate complex

(d) to decrease the bond energy of the substrate molecule

**Answer.** (b)

39. A promoter is a substance which

(a) lowers the kinetic energy of reactants

(b) lowers the activation energy of reaction

(c) enhances the activity of the catalyst

(d) enhances the concentration of the catalyst

**Answer.** (c)

40. Catalytic poisoning

(a) reduces the activity of the catalyst

(b) reduces the reaction rate of the reaction

- (c) increases the activation energy of the reaction
- (d) increases the temperature of the reaction

**Answer:** (a)

41. Arsenic oxide ( $As_2O_3$ ) acts in the Contact process as

- (a) a catalyst
- (b) a promoter
- (c) a poison
- (d) an enzyme

**Answer:** (c)

42. In the synthesis of ammonia by Haber's process, the substance which acts as catalytic poison is

- (a) platinum
- (b) iron
- (c)  $As_2O_3$
- (d)  $H_2S$

**Answer:** (d)

43. Tetraethyl lead,  $Pb(C_2H_5)_4$ , when added to petrol acts as

- (a) a catalyst
- (b) a promoter
- (c) an inhibitor
- (d) auto catalyst

**Answer:** (c)

44. An example of acid-base catalysis is

- (a) inversion of cane sugar
- (b) keto-enol tautomerism
- (c) decomposition of nitramide
- (d) all the above

**Answer:** (d)

45. Which is true?

- (a) Metals in a state of fine sub-division are more efficient catalysts than metal in lumps
- (b) catalytic poisoning occurs due to blockage of free valence bonds on the surface
- (c) A promoter increases the valence bonds on the catalyst surface by changing the crystal lattice
- (d) all the above

**Answer:** (d)

46. In intermediate compound formation theory of catalysis, the intermediate complex formed has

- (a) lesser activation energy than uncatalysed complex
- (b) more activation energy than uncatalysed complex
- (c) lesser kinetic energy than the reactants
- (d) lesser kinetic energy than the products

**Answer:** (a)

47. The intermediate compound formation theory generally applies to

- (a) homogeneous catalytic reactions
- (b) heterogeneous catalytic reactions
- (c) auto catalytic reactions
- (d) all of these

**Answer:** (a)

48. Which of the following processes is an example of heterogenous catalysis

- (a) Contact process
- (b) Haber's process
- (c) Hydrogenation of vegetable oils
- (d) all of these

**Answer:** (d)

49. The phenomenon of negative catalysis is also known as

- (a) auto catalysis
- (b) self catalysis
- (c) inhibition
- (d) enzyme catalysis

**Answer:** (c)