Catalysis

MEANING OF THE TERM CATALYSIS

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

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

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

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

A catalyst which enhances the rate of 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.**

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

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

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

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

$$\underset{\text{vapour}}{CH_3CHO} + \underset{\text{vapour}}{[I_2]} \longrightarrow \underset{\text{gas}}{CH_4} + \underset{\text{gas}}{CO}$$

Examples of Homogeneous Catalysis in Solution phase

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

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

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

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

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+/OH} \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethanol}}{C_2H_5OH}$$

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

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

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)

(*i*) Combination of sulphur dioxide (SO_2) and oxygen in the presence of finely divided platinum or vanadium pentoxide, V_2O_5, *(Contact Process for Sulphuric acid).*

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

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

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

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

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

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

$$\underset{\text{ethane (gas)}}{H_2C{=}CH_2} + \underset{\text{gas}}{H_2} + \underset{\text{solid}}{[Ni]} \longrightarrow \underset{\text{ethane}}{H_3C-CH_3} + [Ni]$$

Vegetable oils are 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 (H_2O_2) is catalysed by manganese dioxide (MnO_2) or platinum in colloidal form,

$$\underset{\text{liquid}}{2H_2O_2} + \underset{\text{solid}}{[Pt]} \longrightarrow 2H_2O + O_2 + [Pt]$$

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

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

(3) Heterogeneous catalysis with solid reactants

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

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

CHARACTERISTICS OF CATALYTIC REACTIONS

Although there are different types of catalytic reactions, the following features or characteristics are common to most of them. These features are often referred to as the **Criteria of catalysis.**

(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 of chemical nature. However, it may undergo a physical change. Thus granular manganese dioxide (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,

$$C_6H_6 + C_2H_5Cl \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HCl$$

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,

$$\underset{\text{ester}}{RCOOR'} + H_2O \xrightarrow{H^+ \text{ or } OH^-} RCOOH + R'OH$$

the rate of reaction is proportional to the concentration of the catalyst (H^+ or 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,

$$C_2H_5OH \xrightarrow{Al_2O_3} \underset{\text{ethene}}{C_2H_4} + H_2O \qquad \textit{(Dehydration)}$$

but with hot copper it gives ethanal (CH_3CHO).

$$C_2H_5OH \xrightarrow{Cu} \underset{\text{ethanal}}{CH_3CHO} + H_2 \qquad \textit{(Dehydrogenation)}$$

(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.

$$H_2 + O_2 \xrightarrow{\text{room temp.}} \text{No reaction}$$

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

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 collisions 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

$$A + B \rightleftharpoons C + D$$

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. As 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.

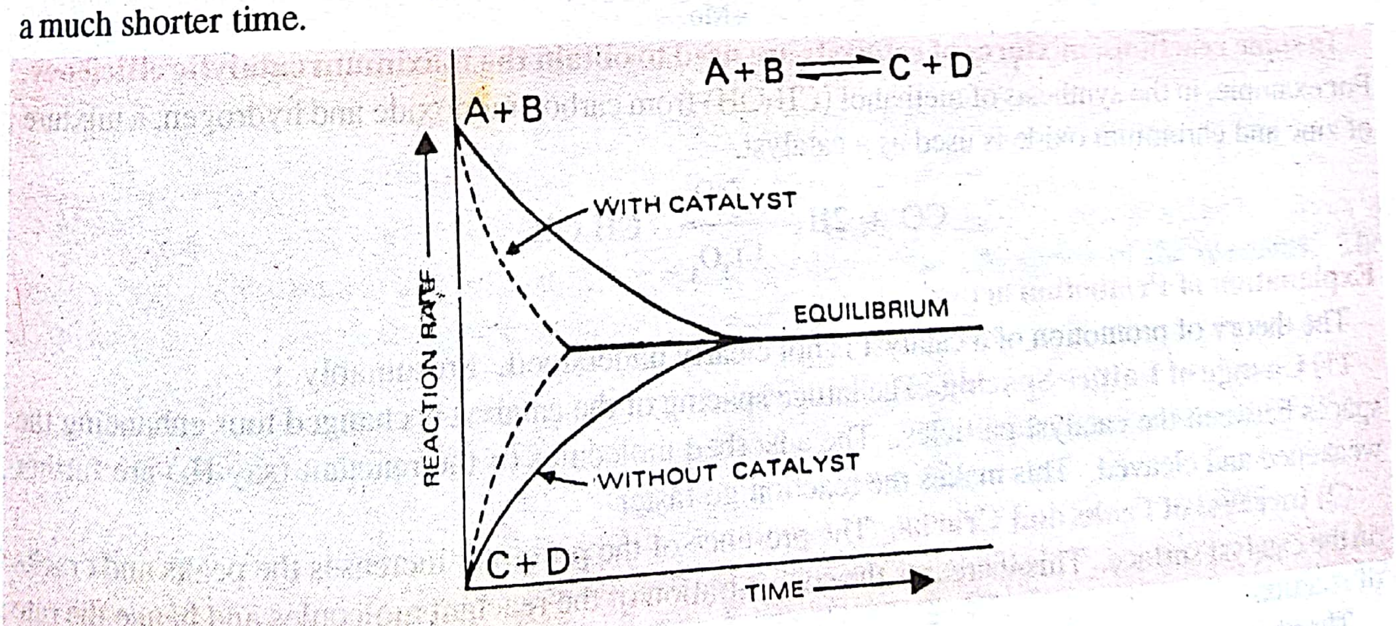


Fig. 21.1. The effect of a catalyst on the time required for the equilibrium to be established.

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

$$N_2 + 3H_2 \overset{Fe}{\rightleftharpoons} 2NH_3$$

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.

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 (Al_2O_3) promotes the activity of iron catalyst in the Haber synthesis for the manufacture of ammonia.

$$N_2 + 3H_2 \underset{+Mo}{\overset{Fe}{\rightleftharpoons}} 2NH_3$$

In some reactions, mixtures of catalysts are used to obtain the maximum catalytic efficiency. For example, in the synthesis of methanol (CH_3OH) from carbon monoxide and hydrogen, a mixture of zinc and chromium oxide is used as a catalyst.

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

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.

CATALYTIC POISONING

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

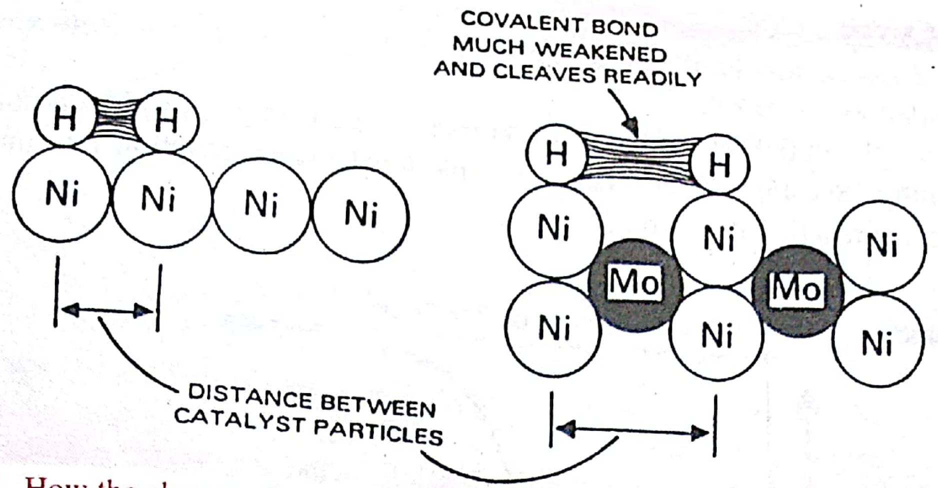


Fig. 21.2. How the change of crystal lattice spacing of catalyst makes the reaction go faster.

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)

$$SO_2 + O_2 \xrightarrow[\substack{\text{poisoned} \\ \text{by } As_2O_3}]{Pt} 2SO_3$$

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

$$N_2 + 3H_2 \xrightarrow[\substack{\text{poisoned} \\ \text{by } H_2S}]{Fe} 2NH_3$$

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

$$2H_2 + O_2 \xrightarrow[\substack{\text{poisoned} \\ \text{by CO}}]{Pt} 2H_2O$$

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.

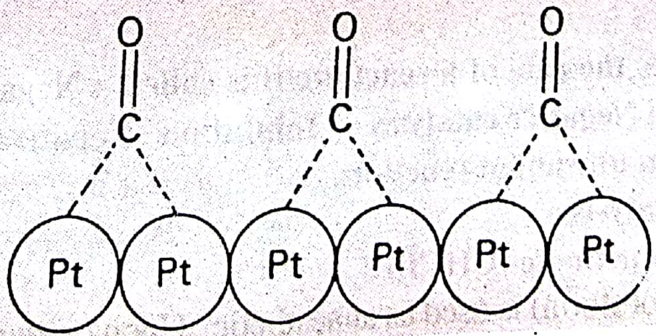


Fig. 21.3. Poisoning of platinum catalyst by carbon monoxide.

(2) **The catalyst may combine chemically with the impurity.** The poisoning of iron catalyst by H_2S falls in this class.

$$Fe + H_2S \longrightarrow FeS + H_2$$

AUTOCATALYSIS

When one of the products of a 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 (See Fig. 21.4). The curve plotted between reaction rate and time shows a maximum when the reaction is complete.

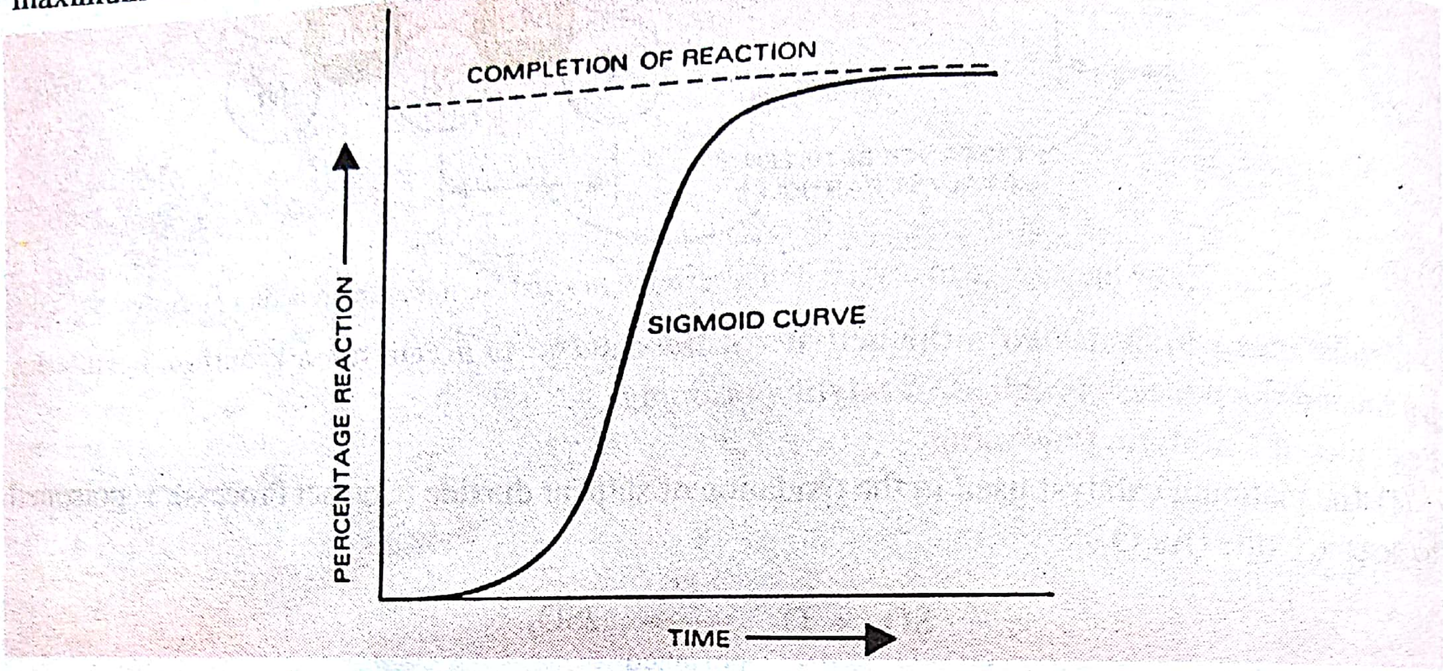


Fig. 21.4. Curve showing the rise of rate of reaction with time.

Examples of Autocatalysis

(1) Hydrolysis of an Ester. The hydrolysis of ethyl acetate forms acetic acid (CH_3COOH) and ethanol. Of these products, acetic acid acts as a catalyst for the reaction.

$$CH_3COOC_2H_5 + H_2O \longrightarrow \underset{\text{catalyst}}{CH_3COOH} + C_2H_5OH$$

(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.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow \underset{\text{catalyst}}{2MnSO_4} + K_2SO_4 + 8H_2O + 10CO_2$$

(3) Decomposition of Arsine. The free arsenic produced by the decomposition of arsine (AsH_3) autocatalyses the reaction.

$$2AsH_3 \longrightarrow \underset{\text{catalyst}}{2As} + 3H_2$$

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 ($CHCl_3$)

Trichloromethane (or chloroform) is used as anaesthetic. Upon oxidation by air it forms carbonyl chloride ($COCl_2$) which is a poisonous substance.

$$4CHCl_3 + 3O_2 \longrightarrow 4COCl_2 + 2H_2O + 2Cl_2$$

2 per cent of ethanol (C_2H_5OH) when added to chloroform acts as a negative catalyst and suppresses the formation of carbonyl chloride.

(2) Decomposition of Hydrogen peroxide

The decomposition of hydrogen peroxide,

$$2H_2O_2 \longrightarrow 2H_2O + O_2$$

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

(3) Tetraethyllead as Antiknock

When tetraethyllead, $Pb(C_2H_5)_4$, 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_2O_2). 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_2 and Cl_2, which is a chain reaction, is negatively catalysed by nitrogen trichloride (NCl_3).

$$Cl_2 \longrightarrow Cl\bullet + Cl\bullet$$

$$H_2 + Cl\bullet \longrightarrow HCl + H\bullet$$

$$H\bullet + Cl_2 \longrightarrow HCl + Cl\bullet$$

NCl_3 breaks the chain of reactions by absorbing the propagating species (Cl•), and the reaction stops.

$$NCl_3 + Cl\bullet \longrightarrow \tfrac{1}{2}N_2 + 2Cl_2$$

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.

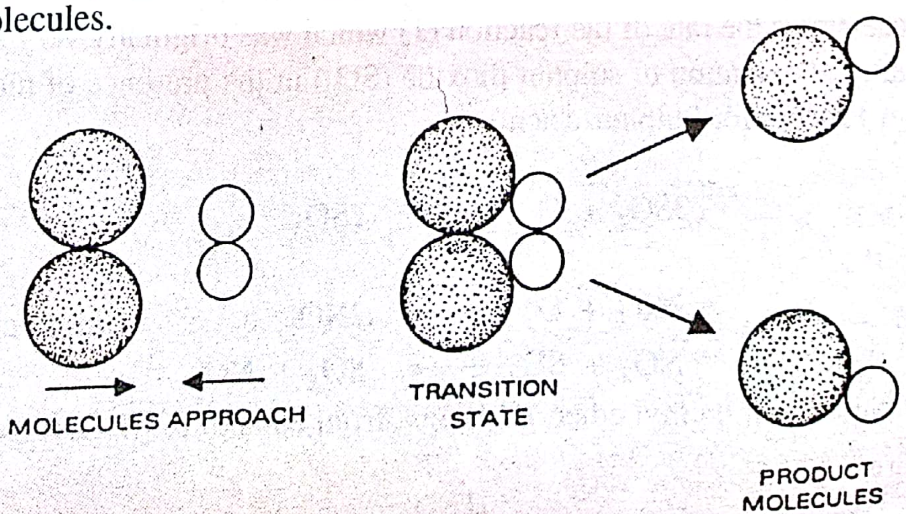


Fig. 21.5. Mechanism of a molecular reaction.

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.

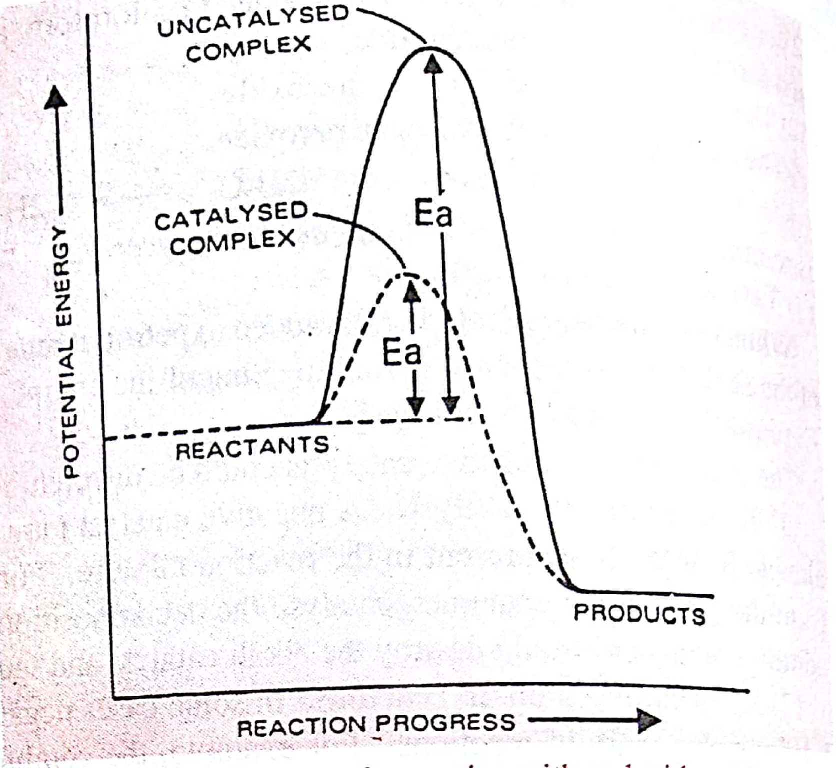


Fig. 21.6. Energy diagram of a reaction with and without the catalyst, showing clearly the lowering of activation energy by the catalyst.

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

$$A + B \xrightarrow{C} AB \qquad \text{... (1)}$$

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

$$A + C \longrightarrow \underset{\text{Intermediate}}{AC} \qquad \text{... (2)}$$

$$AC + B \longrightarrow AB + C \qquad \text{... (3)}$$

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 (SO_2) in the presence of nitric oxide (NO) as catalyst. (Chamber Process for Sulphuric acid)

$$2SO_2 + O_2 \xrightarrow{NO} 2SO_3$$

Mechanism :

$$2NO + O_2 \longrightarrow 2NO_2 \qquad \text{(Intermediate compound)}$$

$$NO_2 + SO_2 \longrightarrow SO_3 + NO$$

Example 2. Preparation of diethyl ether, $(C_2H_5)_2O$, from ethanol (C_2H_5OH) using sulphuric acid as catalyst.

$$C_2H_5OH + C_2H_5OH \xrightarrow{H_2SO_4} (C_2H_5)_2O + H_2O$$

Mechanism :

$$C_2H_5OH + H_2SO_4 \longrightarrow \underset{\substack{\text{Ethyl hydrogen sulphate} \\ \text{(Intermediate compound)}}}{C_2H_5HSO_4} + H_2O$$

$$C_2H_5HSO_4 + \underset{\substack{\text{(second} \\ \text{molecule)}}}{C_2H_5OH} \longrightarrow (C_2H_5)_2O + H_2SO_4$$

Example 3. Thermal decomposition of potassium chlorate ($KClO_3$) in the presence of manganese dioxide (MnO_2).

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

Mechanism :

$$2KClO_3 + 6MnO_2 \longrightarrow \underset{\substack{\text{Intermediate} \\ \text{compound}}}{6MnO_3} + 2KCl$$

$$6MnO_3 \longrightarrow 6MnO_2 + 3O_2$$

Example 4. Formation of methylbenzene, $C_6H_5CH_3$ by reaction between benzene, C_6H_6, and methyl chloride, CH_3Cl, using aluminium chloride, $AlCl_3$, as catalyst (Friedel-Crafts reaction),

$$C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl$$

Mechanism :

$$CH_3Cl + AlCl_3 \longrightarrow \underset{\substack{\text{Intermediate} \\ \text{compound}}}{[CH_3]^+ [AlCl_4]^-}$$

$$C_6H_6 + [CH_3]^+ [AlCl_4]^- \longrightarrow C_6H_5CH_3 + AlCl_3 + HCl$$

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 :

$$A(g) + B(g) \xrightarrow{\text{catalyst}} C(g) + D(g)$$

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 Waal's 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 a 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.

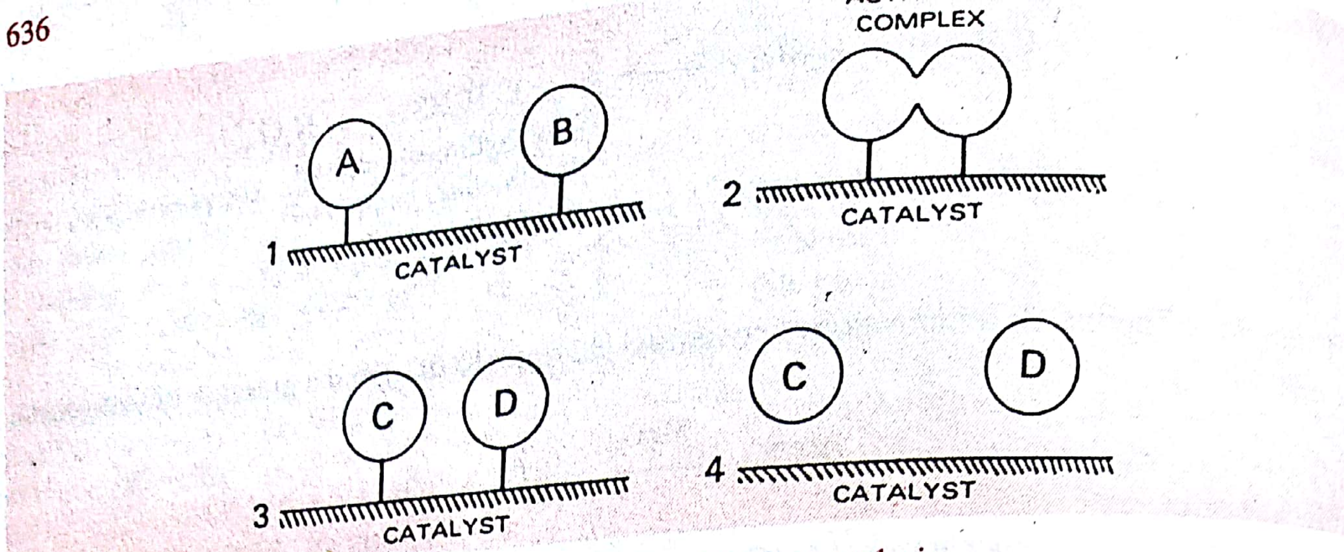


Fig. 21.7. Mechanism of Contact catalysis.

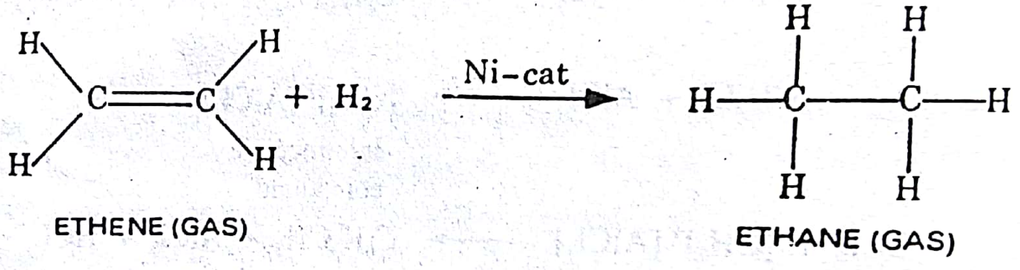
Step 4. Desorption of Products

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

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

HYDROGENATION OF ETHENE IN PRESENCE OF NICKEL

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



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 th nickel atoms.

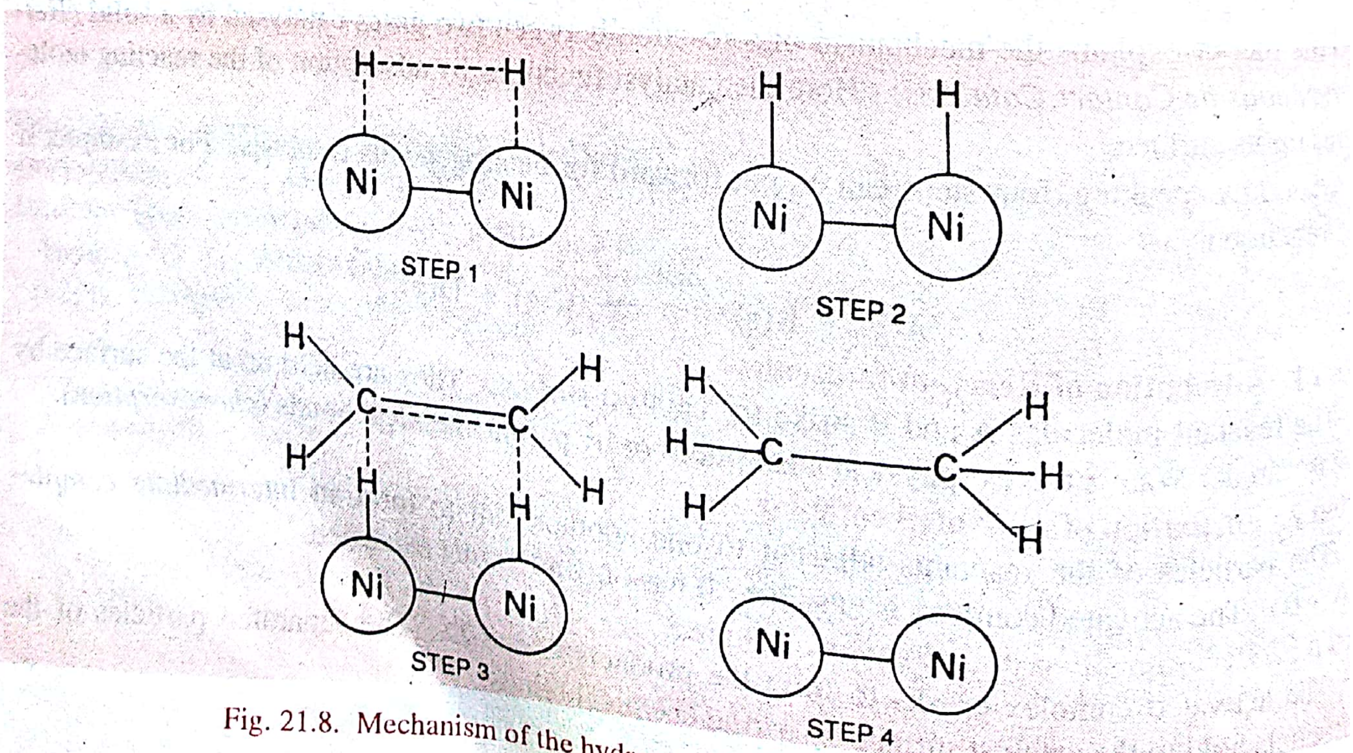


Fig. 21.8. Mechanism of the hydrogenation of ethene on nickel surface.

Step 2. H–H Bonds are broken

The H–H bond is smaller (0.74Å) 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 surface 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.**

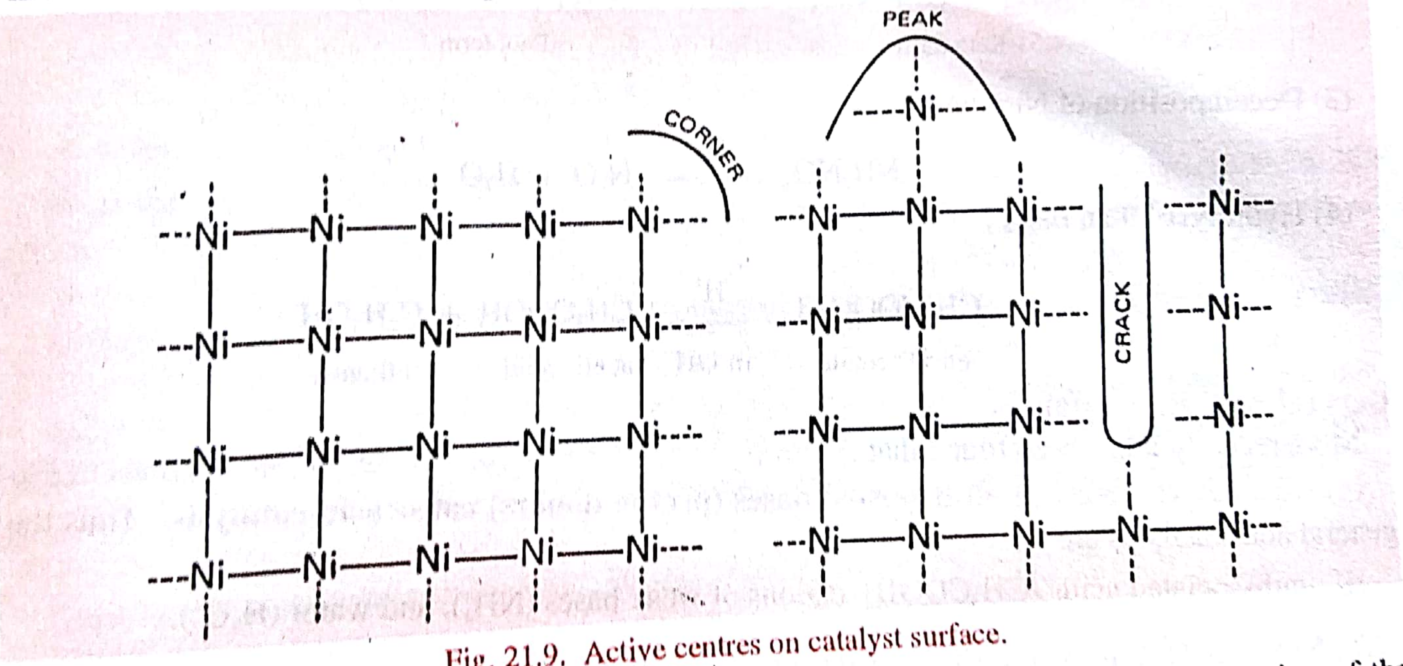


Fig. 21.9. Active centres on catalyst surface.

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.

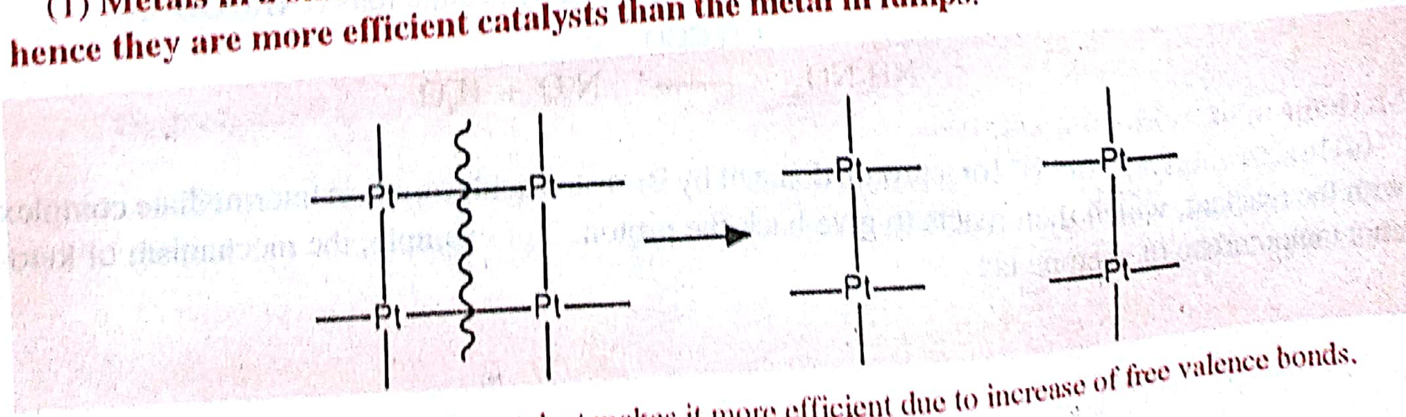


Fig. 21.10. Subdivision of a catalyst makes it more efficient due to increase of free valence bonds.

Table 23.1. Comparison of Physical adsorption and Chemisorption

Physical adsorption	Chemisorption
1. Caused by intermolecular van der Waals' forces.	1. Caused by chemical bond formation.
2. Depends on nature of gas. Easily liquefiable gases are adsorbed readily.	2. Much more specific than physical adsorption.
3. Heat of adsorption is small (about 5 kcal mol^{-1}).	3. Heat of adsorption is large (20–100 kcal mol^{-1}).
4. Reversible.	4. Irreversible.
5. Occurs rapidly at low temperature; decreases with increasing temperature.	5. Increases with increase of temperature.
6. Increase of pressure increases adsorption; decrease of pressure causes desorption.	6. Change of pressure has no such effects.
7. Forms multimolecular layers on adsorbent surface.	7. Forms unimolecular layer.

In chemisorption, the adsorbed layer of gas is one-molecule thick since chemical combination can take place with the adsorbent surface only directly.

ADSORPTION ISOTHERMS

The adsorption of a gas on a solid adsorbent in a closed vessel is a reversible process.

$$\text{Free gas} \rightleftharpoons \text{Gas absorbed on solid}$$

The amount of the gas adsorbed depends on equilibrium pressure (P) and temperature. **The relationship between the equilibrium pressure of a gas and its amount adsorbed on the solid adsorbent at any constant temperature is called an Adsorption isotherm.** It may be given in the form of an equation or graphical curve.

Freundlich Adsorption isotherm

Freundlich proposed an empirical relation in the form of a mathematical equation

$$\frac{w}{m} = k\,P^{1/n}$$

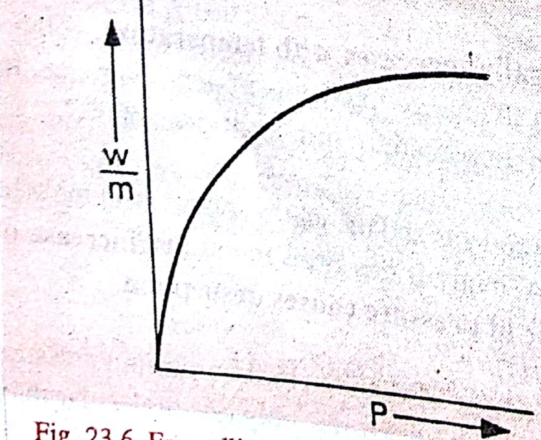


Fig. 23.6. Freundlich isotherm : a plot of mass of adsorbed gas per unit mass of adsorbent.

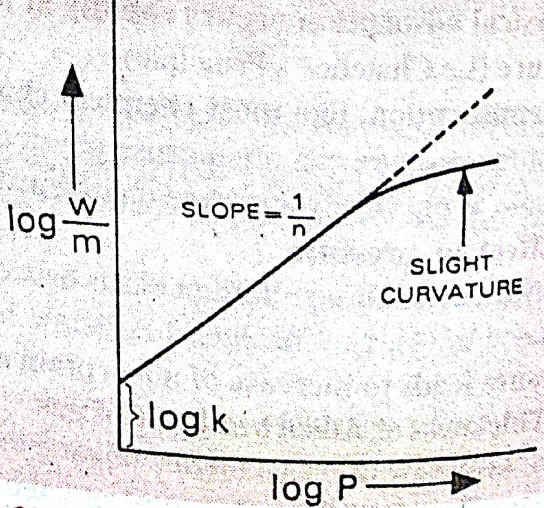


Fig. 23.7. Plot of log w/m against log P shows slight curvature at higher pressures.

where w is the mass of the gas adsorbed on a mass m of adsorbent at a pressure P; k and n are constants depending on the nature of the gas and the adsorbent and on temperature. This relation is generally represented in the form of a curve obtained by plotting the mass of the gas adsorbed per unit mass of adsorbent (w/m) against equilibrium pressure.

Freundlich isotherm is not applicable at high pressures. Taking logarithms on both sides of Freundlich equation, we have

$$\log \frac{w}{m} = \log k + \frac{1}{n} \log P$$

This is equation for a straight line. Thus a plot of log (w/m) against log P should be a straight line with slope $1/n$ and intercept log k. However, it is actually found that the plots were straight lines at low pressures, while at higher pressures they showed a slight curvature, especially at low temperatures. This indicated that Freundlich equation is approximate and does not apply to adsorption of gases by solids at higher pressures.

LANGMUIR ADSORPTION ISOTHERM

Langmuir (1916) derived a simple adsorption isotherm based on theoretical considerations. It was named after him.

Assumptions

Langmuir made the following assumptions.

(1) The layer of the gas adsorbed on the solid adsorbent is one-molecule thick.

(2) The adsorbed layer is uniform all over the adsorbent.

(3) There is no interaction between the adjacent adsorbed molecules.

Derivation of Langmuir isotherm

Langmuir considered that the gas molecules strike a solid surface and are thus adsorbed. Some of these molecules then evaporate or are 'desorbed' fairly rapidly. A dynamic equilibrium is eventually established between the two opposing processes, adsorption and desorption.

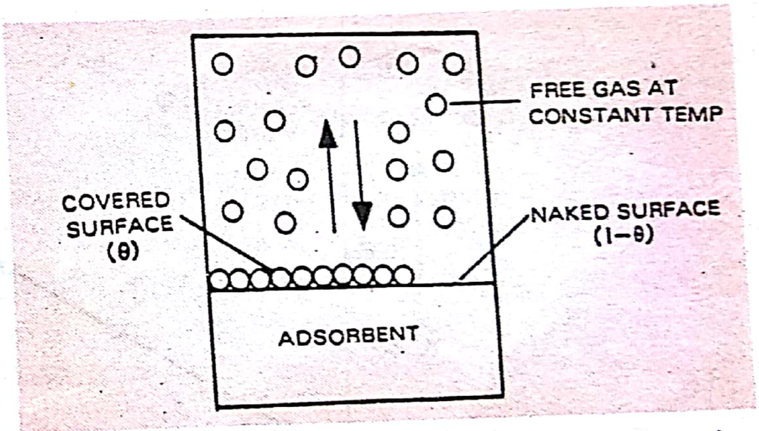


Fig. 23.8. Dynamic equilibrium exists between free molecules and those adsorbed on the fraction of adsorbent surface.

If θ is the fraction of the total surface covered by the adsorbed molecules, the fraction of the naked area is (1 – θ). **The rate of desorption (R_d) is proportional to the covered surface θ.** Therefore,

$$R_d = k_d\,\theta$$

where k_d is the rate constant for the desorption process.

The rate of adsorption (R_a) is proportional to the available naked surface (1 – θ) and the pressure (P) of the gas.

$$R_a = k_a(1-\theta)P$$

where k_a is rate constant for the adsorption process.

At equilibrium the rate of desorption is equal to the rate of adsorption. That is,

$$k_d\theta = k_a\,(1-\theta)\,P$$

$$\theta = \frac{k_a P}{K_a + K_a P}$$

or

$$\theta = \frac{(k_a/k_d)\,P}{1 + (k_a/k_d)\,P}$$

or

$$\theta = \frac{KP}{1 + KP}$$

or

where K is the equilibrium constant and is referred to as the **adsorption coefficient**.

The amount of the gas adsorbed per gram of the adsorbent, x, is proportional to θ.

Hence,

$$x \propto \frac{KP}{1 + KP}$$

or

$$x = K'\,\frac{KP}{1 + KP} \qquad \ldots(1)$$

where K' is a new constant. Equation (1) gives the relation between the amount of gas adsorbed to the pressure of the gas at constant temperature and is known as **Langmuir Adsorption isotherm.**

In order to test the Langmuir isotherm, equation (1) is rearranged so that

$$\frac{P}{x} = \frac{1}{K'} + \frac{P}{K''} \qquad \ldots(2)$$

where K'' constant = K'/K.

The equation (2) is similar to an equation for a straight line. Thus if P/x is plotted against P, we should get a straight line with slope $1/K''$ and the intercept $1/K'$. It was found in most cases that the actual curves were straight lines. Thus Langmuir isotherm stood verified.

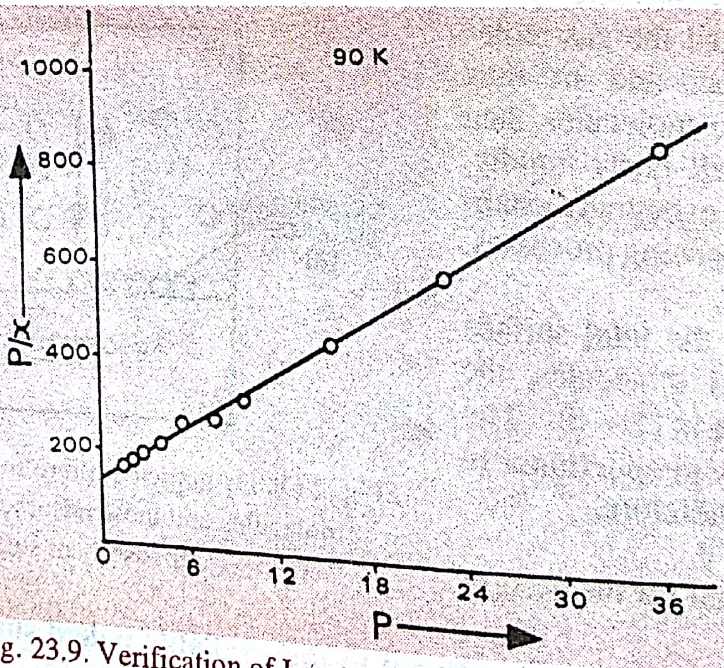


Fig. 23.9. Verification of Langmuir isotherm for adsorption of N_2 on mica at 90°K.

Langmuir Isotherm holds at low pressures but fails at high pressures

As stated above, Langmuir Adsorption isotherm may be written as

$$\frac{P}{x} = \frac{1}{K'} + \frac{P}{K''}$$

If the pressure (P) is very low, the factor P/K'' may be ignored and the isotherm assumes the form

$$x = K'P \qquad \text{(at low pressure)}$$

If the pressure (P) is very high, the factor $1/K'$ may be ignored and the isotherm becomes