

Catalysis

Catalyst and catalysis:

Rate of the chemical reaction may be influenced considerably in the presence of small amount of specific substance such substance are called catalyst and the phenomena referred to as catalysis

Catalyst

It is a substance which alter the rate of the chemical reaction without being used up in the reaction and can be recovered chemically unchanged at the end of the reaction



Positive catalyst

Negative catalyst

Positive catalyst:

The catalyst which increases the rate of the reaction is called positive catalyst and phenomena is known as positive catalysis

e.g.



Negative catalyst:

The catalyst which decreases the rate of the reaction

The phenomena is negative catalysis

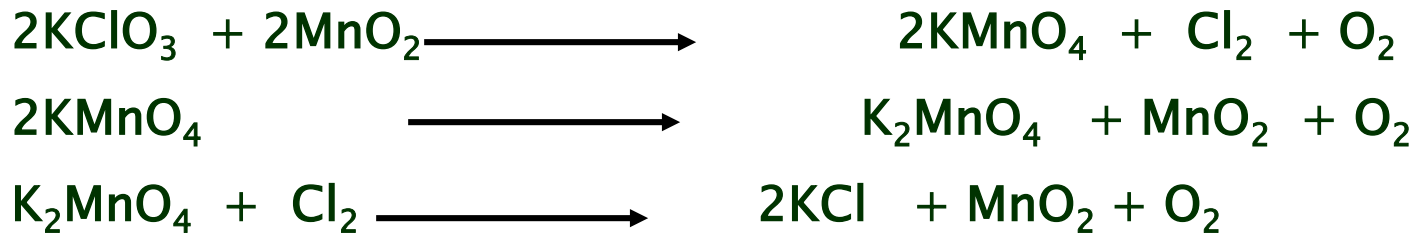
e.g. The oxidation of chloroform in the presence of air is retarded in the presence of alcohol

Tetra ethyl lead decreases the knocking of petrol. Thus acts as negative catalyst

Characteristics of catalysts

1. A catalyst remains unchanged in mass and chemical composition at the end of the reaction

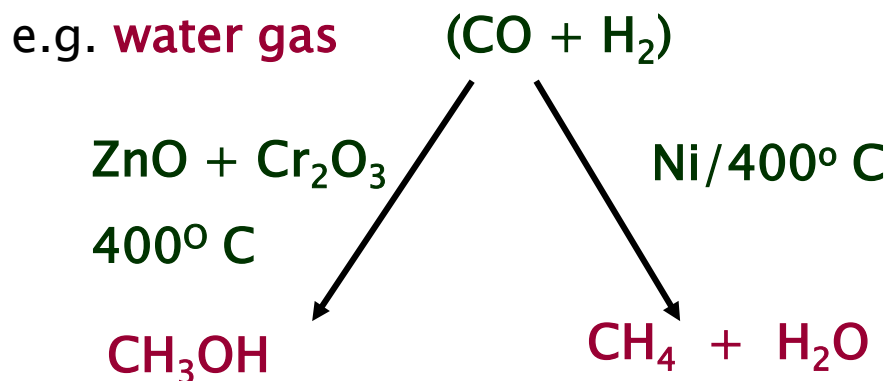
e.g. Granular MnO_2 used as a catalyst during the decomposition of KClO_3 is recovered as a fine powder after the reaction



2. A small amount of catalyst is sufficient to bring about an appreciable change in the velocity of reaction

e.g. Presence of even 1 mg of fine Pt powder is enough to catalyse the combination of 2.5 lit of a mixture of H_2 and O_2 to form H_2O

3. A catalyst can exert a selective action, like a key can open a particular lock



4. A catalyst does not alter the position of the equilibrium in a reversible reaction

Since catalyst help in the equilibrium state being reached more quickly through increasing rate of forward and reverse reaction in the same proportions, the value of equilibrium constant is same whether a catalyst is used or not.

5. A catalyst is most active at particular temperature called optimum temperature

6. The activity of a catalyst substance can be changed by the presence of small amount of foreign substances. These foreign substances can be called *promoters* which increase the activity of a catalyst or *anticatalyst* or *catalytic poisons* which inhibit or completely destroy the activity

e.g. promoters

In the manufacture of NH_3 by Haber's process, finely divided Fe acts as a catalyst; while molybdenum (or a mixture of $\text{Al}_2\text{O}_3 + \text{K}_2\text{O}$) acts as a promoter.

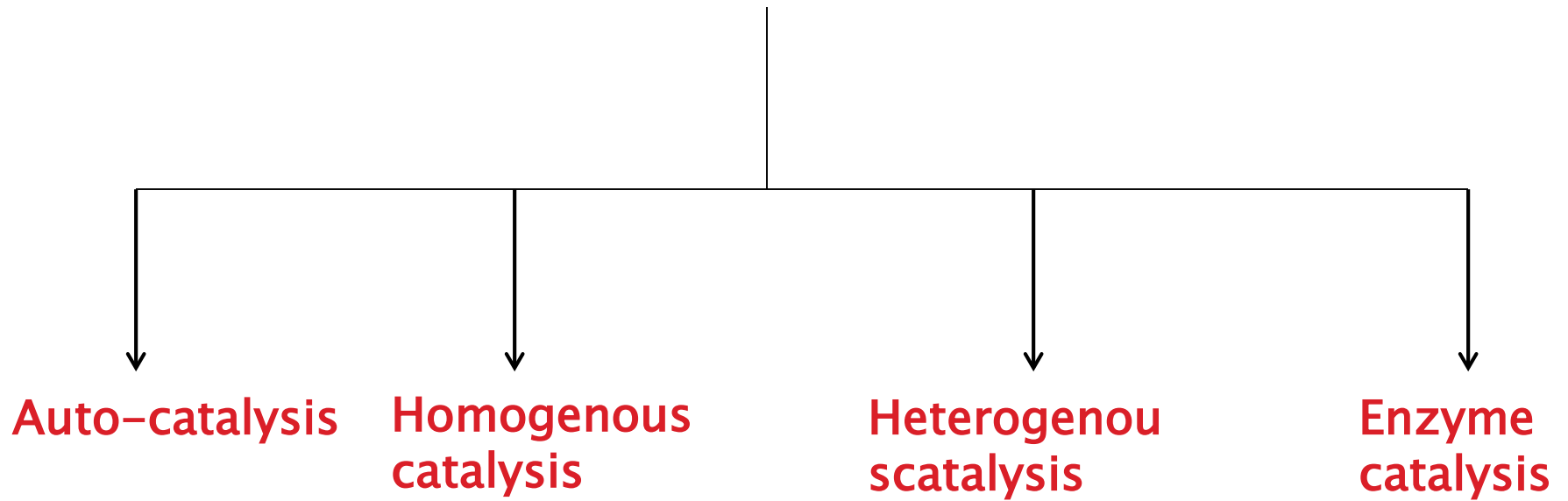
In the manufacture of CH_3OH from CO and H_2 the activity of the catalyst ZnO is greatly enhanced by the presence of chromium sesquioxide, the promoter.

e.g. Poisons

In the manufacture of H_2SO_4 by the contact process, a trace of As_2O_3 destroys the catalytic efficiency of spongy platinum.

Catalytic poisons like HCN, As_2O_3 , CO, H_2S , etc are remarkably poisonous to organisms.

Types of catalysis

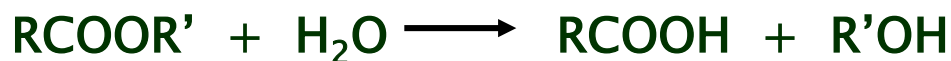


Auto-catalysis

When a product formed in the course of reaction enhances the velocity of the reaction (or acts as a catalyst) the phenomenon, is called auto-catalysis

Example.

1. Hydrolysis of ester by water



The acid liberated as a result of hydrolysis catalyse the reaction

2. Titration of warm solution of oxalic acid by KMnO_4 solution

First few drops take appreciable time before they are decolorised, since the reaction is initially very slow, but after some time the decolorisation goes rapidly as the Mn^{2+} ions formed in the course of the reaction catalyse the reaction



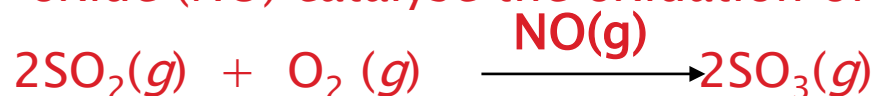
Homogenous catalysis

In this, the catalyst is present in the same phase as the reacting substances

Examples

a) In gas phase:

(i) In the lead chamber process for the manufacture of H_2SO_4 , nitric oxide (NO) catalyse the oxidation of sulphur dioxide



(ii) Decomposition of acetaldehyde is catalysed by iodine vapours



(iii) Nitric oxide acts as a catalyst in the combination of carbon monoxide and oxygen



b) In liquid phase

e.g. Inversion of cane sugar



Assignment

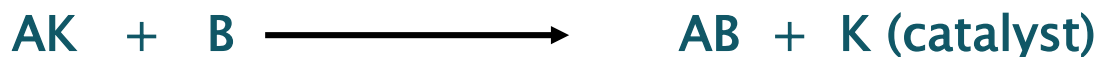
1. What is catalysis and catalyst? Mention different type of catalyst.
2. Give example of positive and negative catalysis.

Mechanism of catalytic action

Unstable intermediate compound formation theory

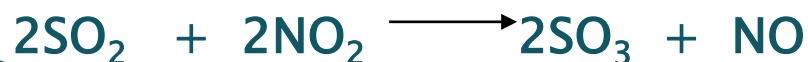
Forwarded by Clement and Desormes in 1806

According to this the catalyst forms a very reactive and unstable intermediate compound with reactants, which immediately reacts with other reactants yielding the products of the reaction and liberating the catalyst in its original chemical composition



Many reactions can be explained by this mechanism

Example: Catalytic action of NO in the manufacture of H_2SO_4 by Chamber's process:



Limitations of Unstable intermediate compound formation theory

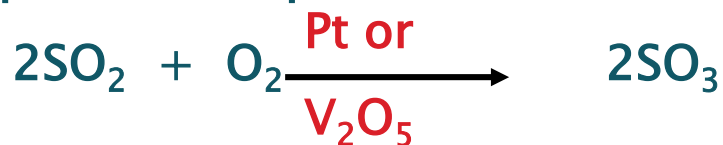
1. The action of promoters and catalytic poisons
2. The function of catalyst in heterogenous reactions, where intermediate compound formation is not possible,
e.g. Combination of SO_2 and O_2 in presence of platinised asbestos, where catalyst is solid and the reactants are gases

Heterogenous Catalysis

In such reactions, the catalyst is present in a different phase from the reacting substances.

Examples

- (i) In contact process for the manufacture of H_2SO_4 , sulphur dioxide is directly oxidized to sulphur trioxide by atmospheric oxygen in the presence of platinum or vanadium pentoxide as catalyst



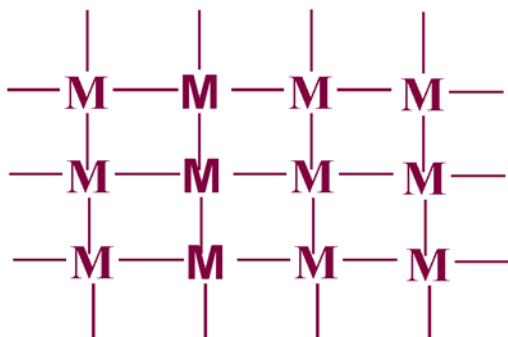
- (ii) In Haber's process for the manufacture of NH_3 , nitrogen and hydrogen in the volume ratio of 1:3 are passed over heated iron catalyst, which contains a promoter (molybdenum)



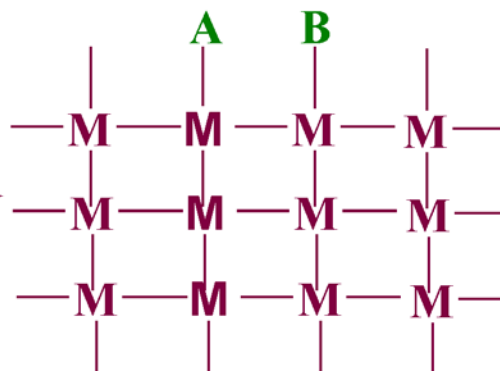
Adsorption or contact theory

- 1) The surface of the solid catalyst possesses some isolated active spots (or centres) having residual affinity or free unsatisfied valency forces
- 2) Due to these free unsatisfied valency forces on the catalyst surface, the molecules of the gaseous reactants get adsorbed in unimolecular thickness layer.
- 3) The adsorbed molecules react due to their close proximity, forming products. The latter then fly off; leaving the surface for fresh action
- 4) The chemical action is accelerated on account of increased concentration of the reacting substances on the surface of the solid catalyst, and no definite intermediate compound formation takes place
- 5) The forces which keep the molecules of reactants intact with catalyst also attract the reacting molecules. The distorted molecules of a catalyst, being under more strain are more active

A B

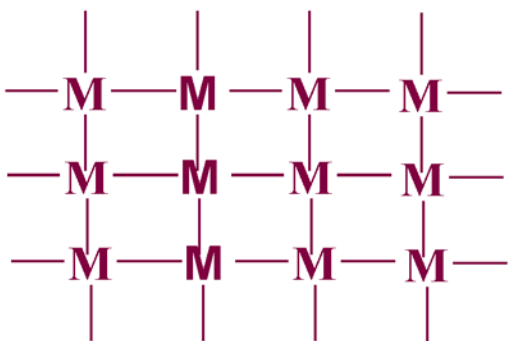


a) reactant molecules A and B near the catalyst

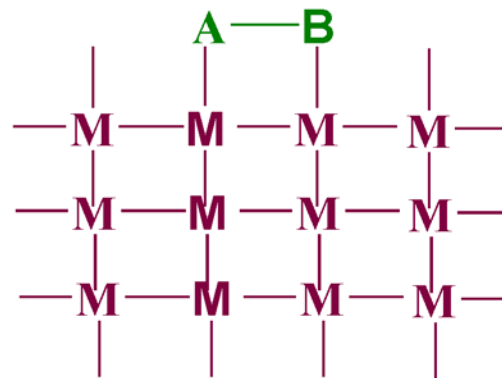


b) Adsorption of reactant molecules adjacent to one another

A—B
+



d) desorption of the product AB; leaving the surface for further action



c) reaction of the reactants on the surface of the catalyst

Advantages of adsorption theory

- a) **The catalyst is more efficient in finely divided state:** Increases in disintegration increases surface area thereby increasing the number of free valencies or active centres, which are responsible for the adsorption of reactant molecules and consequently, the activity of the catalyst is also enhanced
- b) **Enhanced activity of a rough surfaced catalyst:** Rough surface possesses cracks, peaks, corners, etc. and consequently, have larger number of active spots, which in turn must be catalytically more active
- c) **Action of promoters** is explained by assuming that a loose compound is formed between the catalyst and the promoter, which possesses an increased adsorption capacity than the pure catalyst only
- d) **Action of catalytic poisons:** The catalytic poison preferentially adsorb on the active sites of the catalyst, thereby reducing the number of active sites available for the promotion of the molecules of reactants

e.g In contact process for the manufacture of sulphuric acid, catalytic poison As_2S_3 adsorb on the active site of Pt forming platinum sulphide on the surface of Pt, thereby reducing the catalytic activity

Assignment

- ▶ What are enzymes? Give two examples of enzyme catalyzed reactions.
- 1. Explain the terms: Prosthetic group, cofactor, coenzyme in connection with enzyme catalysis
- 2. Explain homogeneous catalysis and its mechanism. What are the limitations of this theory?

Enzymes: The Catalysts of Life

Enzymes are highly complicated non-living nitrogenous organic substances produced by living organisms. They are proteins with high relative molar mass of the order of 10,000 or even more units. They possess incredible capacity in bringing about many complex chemical reactions like hydrolysis, oxidation, reduction etc.

Enzyme Catalysis: Catalytic activity brought about by enzymes

Brought inside the body

e.,g digestion of food

Brought outside the body

e.,g manufacture of ethyl alcohol from molasses

Examples



Characteristics of enzymes

1. Enzymes are proteins that can act as effective catalyst and speed up the reaction by high factor upto 10^{20}

Carbonic
anhydrase



Under ideal conditions even a single molecule of catalysts is capable of catalysing as many as 36 million molecules of carbonic acid in just one minute

2. Enzymes are highly specific and their specificity is of three types
 - a. Reaction type-specific
 - b. Substrate specific
 - c. Stereochemistry specific (stereospecific)

The enzyme invertase can break up sucrose in to glucose and fructose but fails to break up very similar disaccharide maltose which require another enzyme maltase

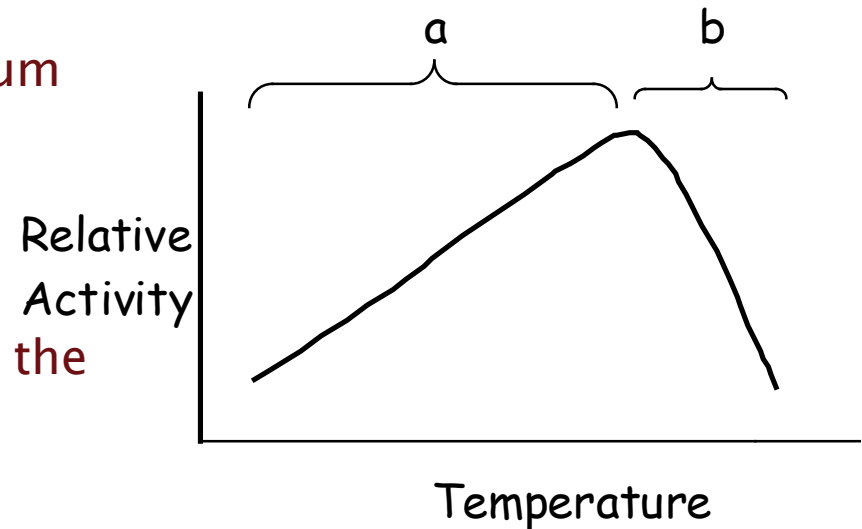
3. *Effect of Temperature*

All enzymatic reactions exhibit maximum efficiency at optimum temperature

Above this temperature enzyme gets denatured. Thereby losing its activity.

Below optimum temperature the rate of the reaction is slow due to the temperature effect

For most enzymes the reaction rate increase up to 45° C and above 45° C thermal denaturation takes place. Above 55° C rapid thermal denaturation destroy completely the catalytic activity of enzyme protein



4. Enzyme catalysed reactions are much more sensitive to catalytic poisons such as HCN, H₂S, CS₂ etc. The inhibitors interact with the active functional groups present on the enzyme surface and often reduce or completely destroy the catalytic activity of the enzymes

5. The activity of certain enzymes depend upon certain non-protein substances called Co-enzymes. For each enzyme, there is only one co-enzyme

6. Enzymes lose their activity when exposed to ultraviolet radiations or in presence of electrolytes

7. Even a small amounts of an enzyme can be highly efficient in bringing about a particular biological reaction, because a typical enzyme molecule may be regenerated million times in a minute

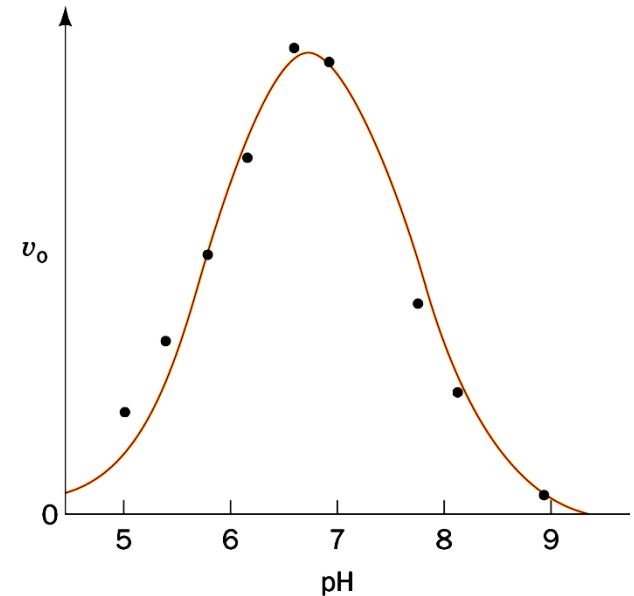
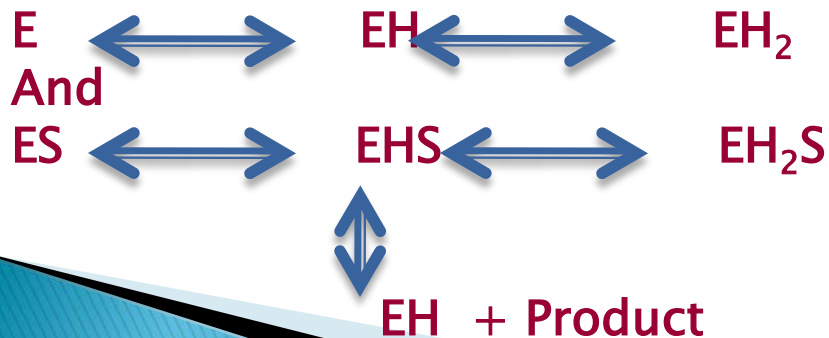
8. Like ordinary catalysts, enzymes cannot disturb the final state of equilibrium of a reversible reaction

9. Effect of pH

Effect of pH on the rate of enzyme catalysed reaction is of complex nature but the favourable pH range for most of the reactions is 5–7

- Binding of substrate to enzyme
- Ionization state of “catalytic” amino acid residue side chains
- Ionization of substrate
- Variation in protein structure

Multistage equilibria exists in these reactions



Prosthetic group: Enzymes are associated with non-protein components called prosthetic groups

Co-factor: The prosthetic groups could be metal ions such as Zn^{2+} , Mg^{2+} , Co^{2+} , K^+ , Na^+ etc. called as co-factor

Co-enzyme: If the prosthetic group is a small organic molecule, it is referred to as a co-enzyme

Apo-enzyme: Many of the coenzymes for biological processes are derived from vitamins like thiamine, riboflavin, niacin, etc. In such enzymes the protein part of the enzyme is called apoenzyme

Neither apoenzyme nor coenzyme is able to catalyse the reaction alone. The two must combine together before acting as a catalyst

Mechanism of enzyme action

The substrate is bound to a particular active site in the enzyme, where the necessary functional groups are gathered

These functional groups are poised in just the right position for the attack on the substrate

The enzymes can increase the rate of biochemical reactions by factors ranging from 10^6 to 10^{12}

The high turnover number suggest that the substrate molecule cannot be very tightly bound to the enzymes; if they were, they might block the active sites.

Reaction would then be slow, because the active site is not quickly cleared out

There is an equilibrium between the substrate (S) and the active site of enzyme (E)



The second step is the rate determining step

The rate of enzyme catalysed reaction increases because enzyme catalyst decreases the activation energy of a reaction to a sufficient amount

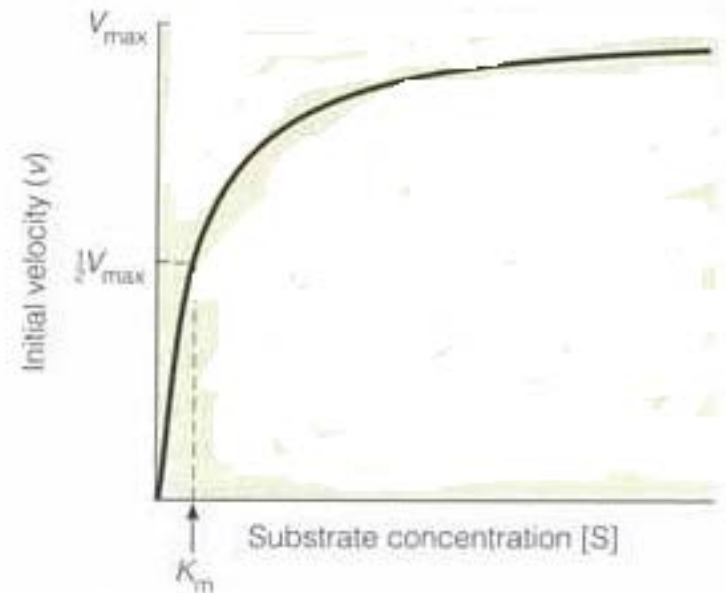
The reaction rate of an enzyme-catalysed reaction changes from first order to zero order as the concentration of substrate, [S] is increased

Each molecule has 1 or more active sites at which the substrate must be bound in order that the catalytic action may occur

At low [S], most of these active sites remain unoccupied at any time.

As the [S] increased, the number of active sites which are occupied increases and hence the reaction rate also increases

At very high [S], all the active sites are occupied at any time so that further increase in substrate concentration cannot further increase the formation of enzyme-substrate complex, because all available sites are in use



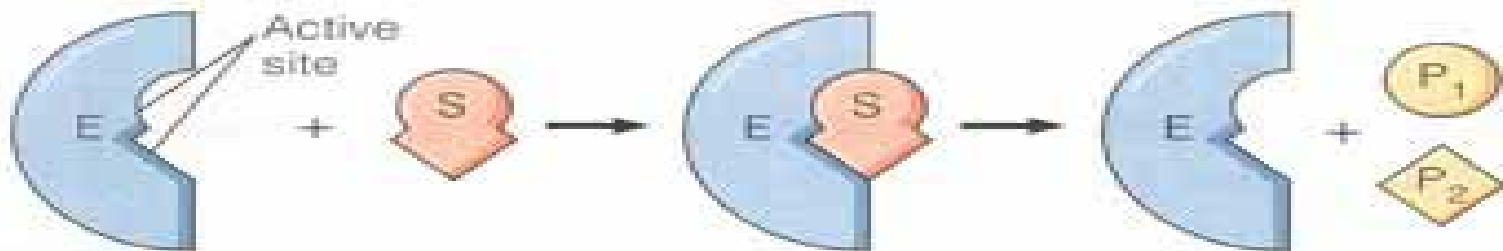
Lock and key model

Developed by Fischer (1894) to explain the specificity of enzymes

An enzyme is ordinarily a very large protein molecule that contains one or more active sites, where the reactions with the substrate takes place; the rest of the molecule maintains the three-dimensional integrity of the network

The active site has a rigid structure, similar to a lock. A substrate molecule has a complementary structure that causes it to fit and function like a key

Geometry of an active site only fit one type of substrate in most cases. That's why enzymes are highly specific in action

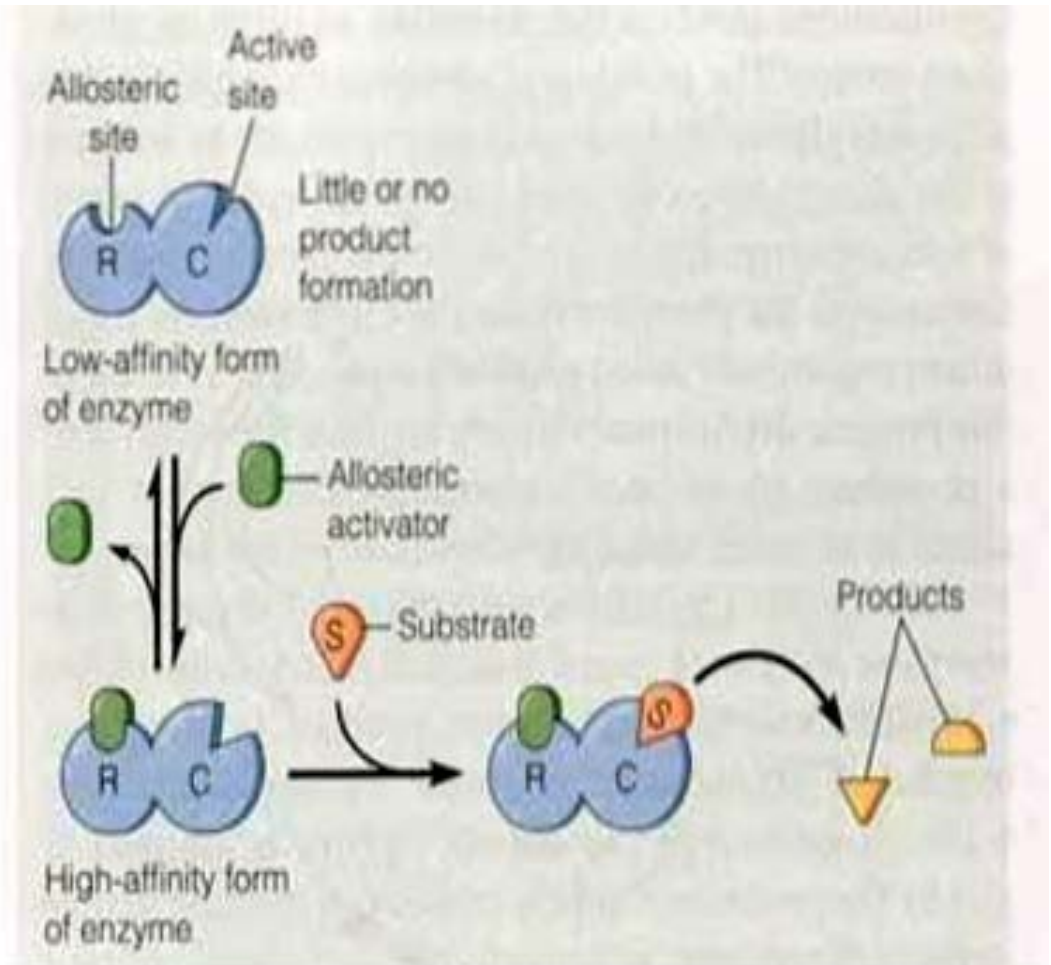


(a) Lock-and-key model

Role of a promoter

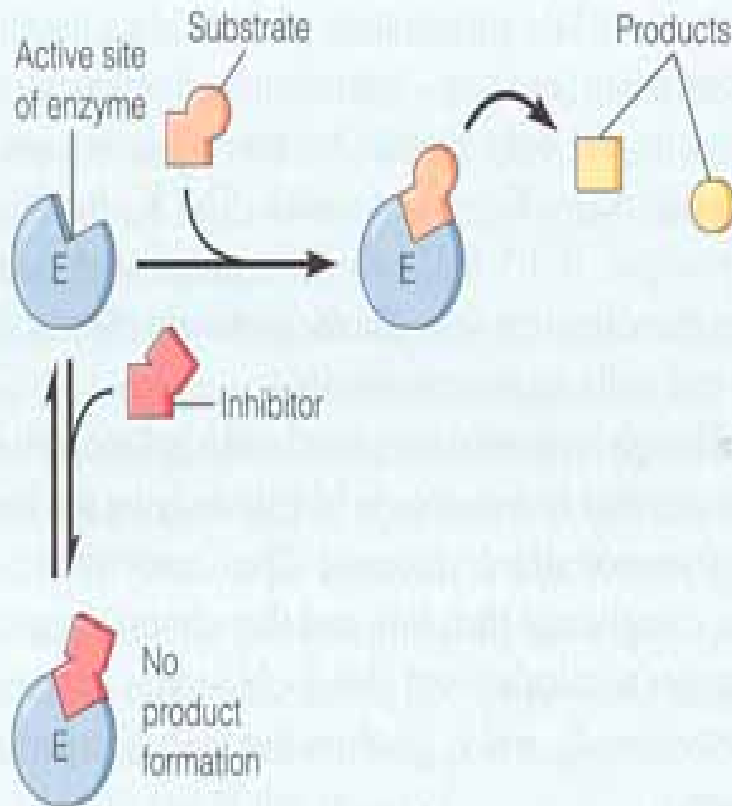
Promoter first attaches itself on the appropriate binding site on the surface of enzyme, thereby changing the shape of active sites

Now substrates can easily fit in leading to the formation of enzyme substrate complex . Subsequently one or more products will form and separate from the enzyme



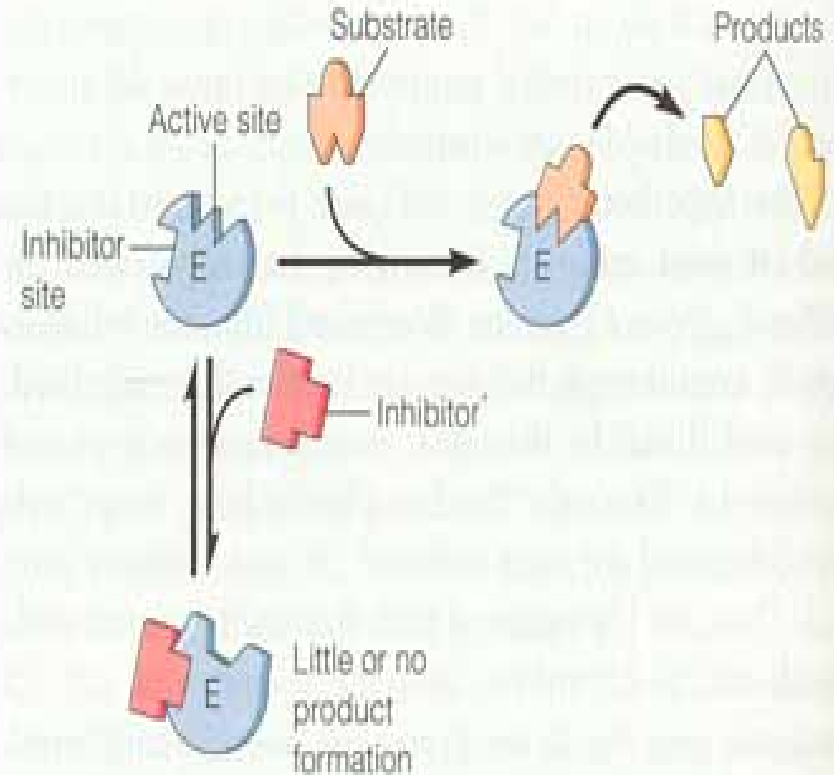
Role of a poison

Competitive inhibitors



(a) **Competitive inhibition.** Inhibitor and substrate both bind to the active site of the enzyme. Binding of an inhibitor prevents substrate binding, thereby inhibiting enzyme activity.

Noncompetitive inhibitors



(b) **Noncompetitive inhibition.** Inhibitor and substrate bind to different sites. Binding of an inhibitor distorts the enzyme, thereby decreasing the likelihood of substrate binding.

Figure 6-15 Modes of Action of Competitive and Noncompetitive Inhibitors. Both (a) competitive and (b) noncompetitive inhibitors (red) bind reversibly to the enzyme (E), thereby inhibiting its activity. The two kinds of inhibitors differ in the site on the enzyme to which they bind, however.