# <u>CATALYSIS</u>

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. Catalyst may increase or decrease the rate of reaction.

***TYPE OF CATALYST**:*

Type of catalyst: There are two main types of catalyst:

a) Positive catalysis

b) Negative catalysis

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

eg: Combination of nitrogen and hydrogen to form ammonia in the presence of finely divided iron (Haber process for ammonia)

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

**b) Negative catalyst**: A catalyst which retards the (or decreases) the rate of reaction is called negative catalyst and the process is called negative catalysis.

eg : 1) Decomposition of hydrogen peroxide

$2H_2O_2 \rightarrow 2H_2O + O_2$ is retarded by the presence of dil. acid or glycerol.

***CATALYSIS***

Type of catalysis: There are two main types of catalysis:

a) Homogeneous catalysis

b) Heterogeneous catalysis

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

eg: 1) Decomposition of acetaldehyde ($CH_3CHO$) with iodine ($I_2$) as catalyst.

$$\underset{\text{vapour}}{CH_3CHO} \; + \; \underset{\text{vapour}}{\xrightarrow{(I_2)}} \; \underset{\text{gas}}{CH_4} + \underset{\text{gas}}{CO}$$

2) Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst

$$\underset{\text{liq}}{C_{12}H_{22}O_{11}} + \underset{\text{liq}}{H_2O} \; \underset{\text{liq}}{\xrightarrow{H_2SO_4}} \; \underset{\text{liq}}{C_6H_{12}O_6} + \underset{\text{liq}}{C_6H_{12}O_6}$$

b) **Heterogeneous catalysis**: The catalysis in which the catalyst is in a different physical phase from the reactants is termed heterogeneous catalysis.

eg:

1) Combination of sulphur dioxide ($SO_2$) and oxygen in the presence of finely divided platinum

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

2) Combination of nitrogen and hydrogen to form ammonia in the presence of finely divided iron (Haber process for ammonia)

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

***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.

eg:

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

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$

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

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

***CHARACTERISTICS OF CATALYTIC REACTION***:

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

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

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

3) A catalyst is specific in its action.

4) A catalyst cannot initiate a reaction.

***PROMOTERS*:**

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

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

eg: Molybdenum (Mo) or aluminium oxide ($Al_2O_3$) promotes the activity of iron catalyst in the Haber synthesis for the manufacture of ammonia

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

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 absorbed 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 molecule and hence the rate of reaction.

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

***CATALYTIC POISONING:***

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

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

$$SO_2 + O_2 \xrightarrow[As_2O_3]{Pt} 2SO_3$$

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

$$N_2 + 3H_2 \xrightarrow[H_2S]{Fe} 2NH_3$$

Explanation of catalytic poisoning:

1) The poison is adsorbed on the catalyst surface to the reactants.

2) The catalyst may combine chemically with the impurity.

$$Fe + H_2S \rightarrow FeS + H_2$$

***ACID-BASE CATALYSIS:***

A number of homogeneous catalytic reactions are known which are catalyzed 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.

eg: 1) Inversion of cane suger :

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

2) Hydrolysis of ester:

$$CH_3COOC_2H_5 \xrightarrow{H^+/OH^-} CH_3COOH + C_2H_5OH$$

ethyl acetate

Mechanism of acid-base catalysis :

a) In acid catalysis, the $H^+$ (or a proton donated by Bronsted acid) forms an intermediate complex with the reactant which then reacts to give back the proton.

eg: Mechanism of keto-enol tautomerism of acetone

b) In base catalysis, the $OH^-$ ion (or any Bronsted base) accepts a proton from the reactant to form an intermediate complex which then reacts or decomposes to regenerate the $OH^-$ (or Bronsted base).

eg: Decomposition of nitramide by $OH^-$ ions and $CH_3COO^-$ ions may be explained as follows

i) By $OH^-$ ions

$$NH_2NO_2 + OH^- \rightarrow H_2O + \underset{\text{Intermediate Complex}}{NHNO_2^-} \rightarrow N_2O + OH^-$$

ii) By $CH_3COO^-$ ions :

$$NH_2NO_2 + CH_3COO^- \rightarrow CH_3COOH + NHNO_2^-$$

$$NHNO_2^{--} \rightarrow N_2O + OH^-$$

$$OH^- + CH_3COOH \rightarrow H_2O + CH_3COO\text{-}$$

## ***ENZYME CATALYSIS:***

Enzymes are protein molecules which acts as catalyst to speed up organic reactions in living cells. The catalysis brought about by enzymes is known as enzyme catalysis.

eg; 1) Inversion of cane sugar by invertase.

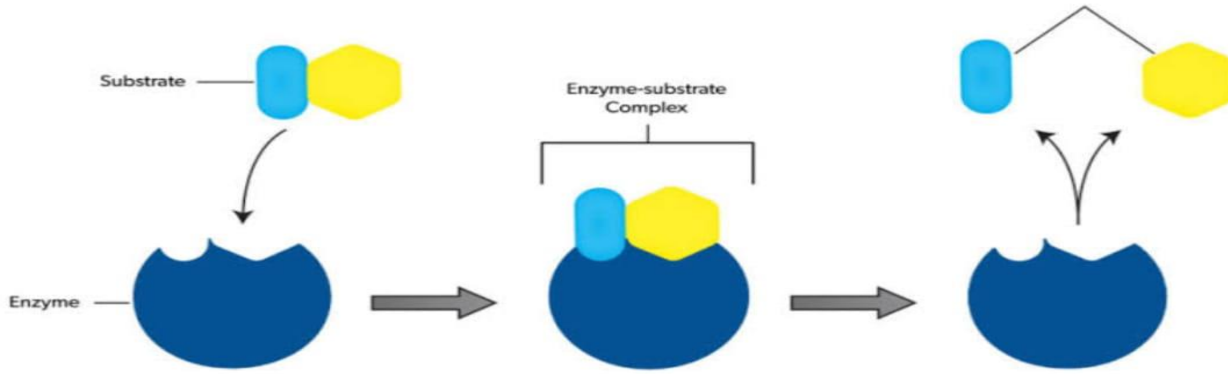
$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

2) Conversion of glucose into ethanol by zymase.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{zymase}} \underset{\text{ethanol}}{2C_2H_5OH} + 2CO_2$$

**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 ($NH_2$, COOH, SH, OH) are termed active centers. 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 act once decomposes to yield the products. Thus, the substrate molecules enter the cavities, forms complex and reacts, and at once the products get out of the cavities.




Michaelie and Menten proposed the following mechanism for enzyme catalysis

$$E + S \rightleftarrows ES \rightarrow P + E$$

Where E= enzyme, S= substrate(reactant), ES= activated complex, P= product

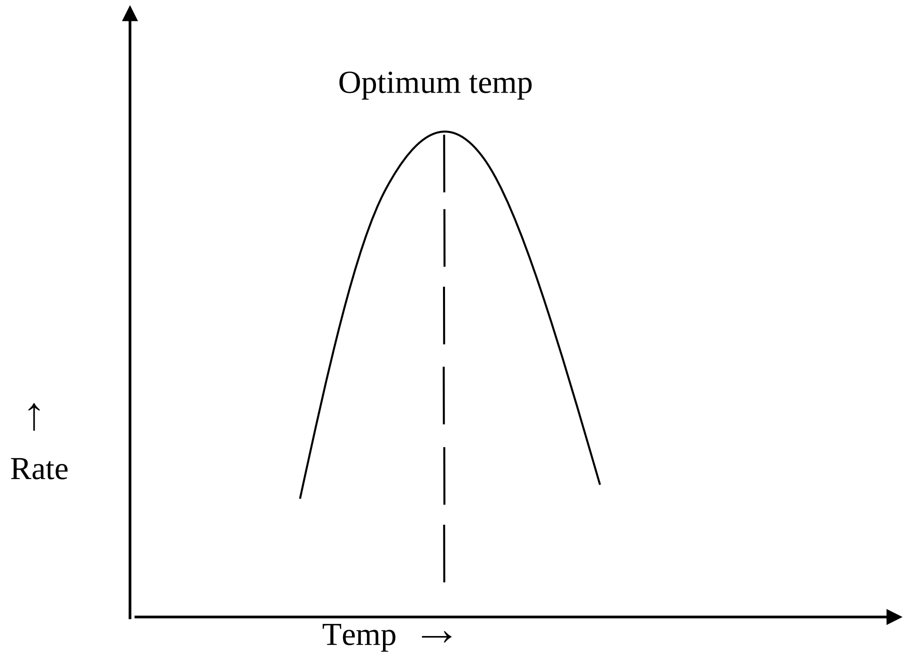
***CHARACTERISTICS OF ENZYME CATALYSIS*:**

1) Enzymes are the most efficient catalyst known.

2) Enzyme catalysis is marked by absolute specificity.

3) The rate of enzyme catalyzed reaction is maximum at the optimum temperature.

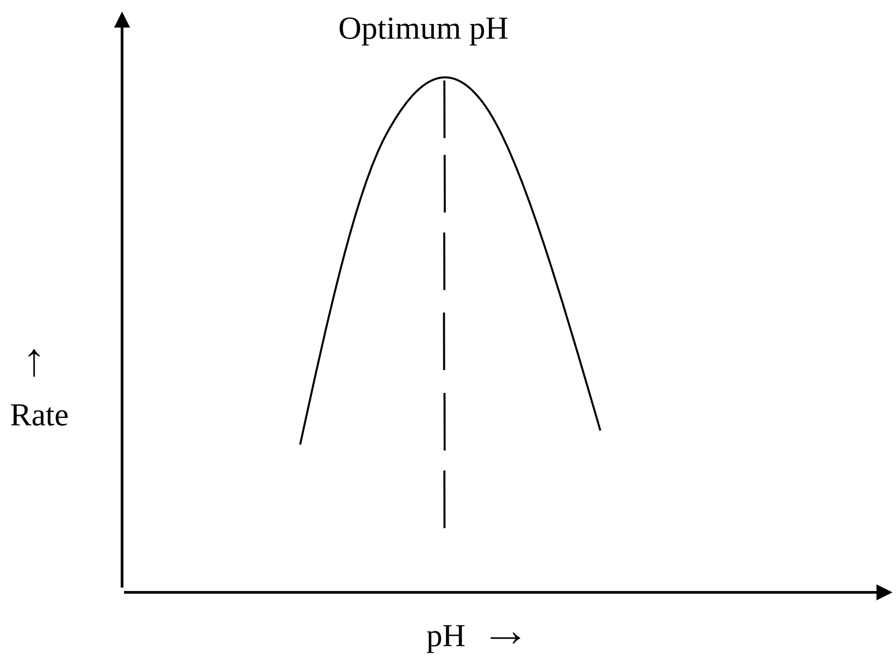
The rate of an enzyme catalyzed reaction is increased with the rise of temperature but up to a certain point. Thereafter the enzyme is denatured as its protein structure is gradually destroyed. Thus the temperature at which the reaction rate is maximum is called the optimum temperature.




eg: 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.

4) Rate of enzyme catalyzed reactions is maximum at the optimum pH :

The rate of an enzyme catalysed reaction varies with PH but up to a certain value. The rate passes through a maximum at a particular pH, known as the optimum pH.



Thus many enzymes of the body function best at PH of about 7.4, the PH of the blood and body fluids.

*APPLICATION OF CATALYST IN INDUSTRIES*: Catalyst speed up a chemical reaction by lowering the amount of energy so catalysis is the backbone of many industrial processes, which use chemical reactions to turn raw material into useful product.

- Hydrogen industry
- Natural gas processing
- Petroleum refining
- Petrochemicals
- Fine chemicals