Catalysis

A substance which alters the speed of a chemical reaction without itself undergoing any chemical change is called a catalyst. The reaction which occurs with the help of a catalyst is termed catalyzed or catalytic reaction. The phenomenon is called catalysis.
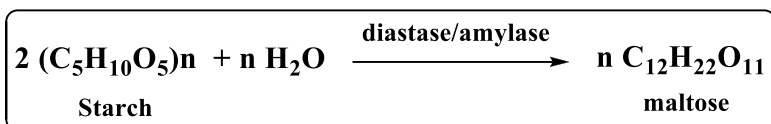
Types of catalysis

1. Enzyme catalysis
2. Acid-base catalysis
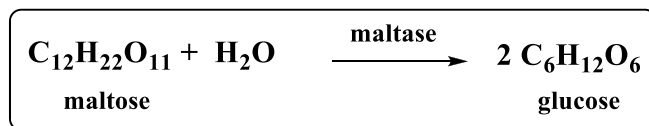3. Auto catalysis

1. Enzyme catalysis

Enzymes are proteins which act as catalysts for many chemical reactions occurring in plants and animals. They are, therefore called biocatalyst and the enzyme catalyzed reactions are known as enzyme catalysis.
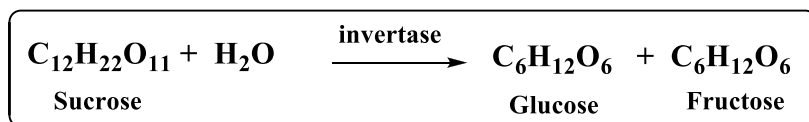
Examples

i) Starch is hydrolyzed into maltose by the enzyme diastase/amylase.

$$2 \ (C_5H_{10}O_5)n \ + n \ H_2O \ \xrightarrow{\text{diastase/amylase}} \ n \ C_{12}H_{22}O_{11}$$
$$\text{Starch} \qquad\qquad\qquad\qquad\qquad\qquad \text{maltose}$$

ii) Maltose is hydrolyzed to give glucose with the help of the enzyme maltase.

$$C_{12}H_{22}O_{11} + \ H_2O \ \xrightarrow{\text{maltase}} \ 2 \ C_6H_{12}O_6$$
$$\text{maltose} \qquad\qquad\qquad\qquad\qquad \text{glucose}$$

iii) Hydrolysis of sucrose is catalyzed by the enzyme invertase.

$$C_{12}H_{22}O_{11} + \ H_2O \ \xrightarrow{\text{invertase}} \ C_6H_{12}O_6 \ + \ C_6H_{12}O_6$$
$$\text{Sucrose} \qquad\qquad\qquad\qquad \text{Glucose} \qquad \text{Fructose}$$

iv) Fermentation of glucose takes place in the presence of the enzyme zymase.

$$C_6H_{12}O_6 \ \xrightarrow{\text{zymase}} \ 2 \ C_2H_5OH \ + \ 2 \ CO_2$$
$$\text{Glucose}$$
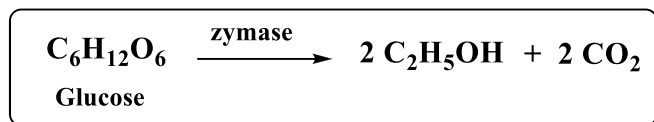
2. Acid-base catalysis

Many reactions in solution are catalyzed either by acids (H^+ ions) or by bases (OH^-) or by both. In such reactions the acid or base is present in the same liquid phase of the reactants. This type of homogeneous catalysis is called acid-base catalysis.

Examples

i) Acid catalyzed reactions

a) Ethyl acetate is hydrolyzed by water extremely slowly. However the ester hydrolysis is catalyzed by dil. mineral acids.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Ethyl acetate   Acetic acid   Ethyl alcohol

b) Sucrose is hydrolyzed by dil. mineral acids to give glucose and fructose.

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

Sucrose   Glucose   Fructose

ii) Base catalyzed reactions

a) Hydrolysis of ethyl acetate by NaOH yields sodium acetate and ethyl alcohol.

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$$

b) The decomposition of nitramide into N_2O and H_2O is catalyzed by alkali.

$$H_2N_2O_2 \xrightarrow{OH^-} N_2O + H_2O$$

Nitramide

c) Aldol condensation of aldehyde and ketone is catalyzed by a base.

$$CH_3CHO + CH_3CHO \xrightarrow{OH^-} CH_3CHOHCH_2CHO$$

Acetaldehyde   Acetaldehyde   Aldol

3. Auto catalysis

Catalysts are generally foreign substances added to the reaction mixture. However, in some reactions one of the product formed acts as catalyst. Such reactions are called auto catalyzed reactions and the phenomenon is known as auto catalysis.

Examples

a) Decolourisation of acidified potassium permanganate by hot oxalic acid is catalyzed by the Mn^{2+} ion, which is one of the products of the reaction.

$$2\ MnO^-_4 + 16\ H^+ + 5\ C_2H_4^{2-} \xrightarrow{Mn^{2+}} 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$$

b) In a similar manner, the acid hydrolysis of ethyl acetate is catalyzed by acetic acid which is also a product of the reaction.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Ethyl acetate   Acetic acid   Ethyl alcohol

Surface catalyzed reactions

♦ Reactions which proceed through adsorption of liquid or gaseous reactants on the surface of the catalyst are known as surface catalyzed reactions.

♦ Here the catalyst is present in a different phase from the reactants. (Heterogeneous catalysis)

Examples

   i) Oxidation of SO_2 to SO_3 by atm. oxygen in the presence of Pt or V_2O_5 as catalyst.

$$2\ SO_2 + O_2 \xrightarrow{\text{Pt/V}_2\text{O}_5} 2\ SO_3$$
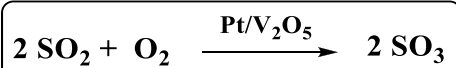
   ii) Combination of N_2 and H_2 to give ammonia is catalyzed by iron. (Haber process)

$$N_2 + 3\ H_2 \xrightarrow{\text{Fe}} 2\ NH_3$$
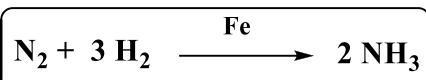
   iii) Oxidation of ammonia to nitric oxide in the presence of Pt. (Ostwald process)

$$4\ NH_3 + 5\ O_2 \xrightarrow{\text{Pt}} 4\ NO + 6\ H_2O$$
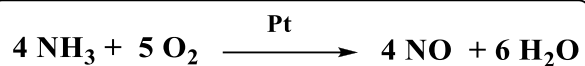
   iv) Dehydration of alcohol by alumina.

$$C_2H_5OH \xrightarrow{\text{Al}_2\text{O}_3} C_2H_4 + H_2O$$
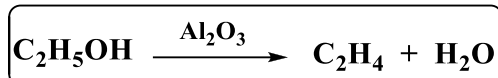
   v) Dehydrogenation of alcohol by copper.

$$C_2H_5OH \xrightarrow{\text{Cu}} CH_3CHO + H_2$$
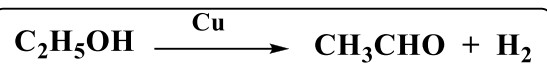
Catalytic poisons

   The presence of certain substance even in traces reduces or sometimes completely destroys the activity of the catalyst. Such substances are called catalytic poisons.

Examples

   ♦ The presence of traces of arsenic oxide in SO_2 poisons the Pt catalyst in the manufacture of sulphuric acid by contact process.
   ♦ Carbon monoxide acts as a poison to finely divided iron in Haber`s process for the manufacture of NH_3.
   ♦ HCN poisons colloidal Pt catalyzing the decomposition of H_2O_2.
   ♦ Traces of bromine vapours acts as poisons to finely divided Ni in the hydrogenation of vegetable oil.

Promoters

   There are some substances which themselves are not catalyst by promote the activity of a catalyst. Such substances are known as promoters.

 Examples

   ♦ The presence of a small quantity of molybdenum promotes the catalytic activity of iron in the Haber`s process.
   ♦ Addition of Cu, Fe or tellurium enhances the activity of Ni in the hydrogenation of vegetable oil.
   ♦ Metallic Cu acts as a promoter to the, iron catalyst in the manufacture of hydrogen from water gas. (Bosch`s process)

Mechanism and kinetics of enzyme catalyzed reactions

      The mechanism of enzyme catalyzed reactions was proposed by *Michaelis and Menten*. It involves the formation of an intermediate between the enzyme (E) and the substrate (S) followed by its decomposition into the product.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [ES] \xrightarrow{k_2} Products$$
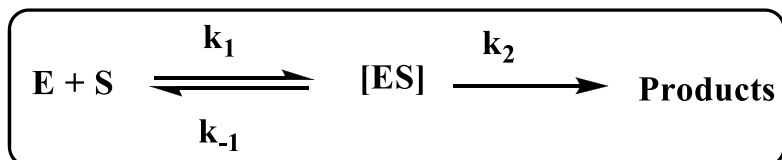
The rate of formation of the product is given by

$$\frac{d[P]}{dt} = k_2 \ [ES] \longrightarrow \quad (1)$$

Assuming a steady-state condition to the concentration of the intermediate

$$k_1 \ [E] \ [S] = k_{-1} \ [ES] + k_2$$

$$= [ES] \ [k_{-1} + k_2]$$

$$or \ [ES] = \frac{k_1 \ [E] \ [S]}{[k_{-1} + k_2]}$$

$$= \frac{[E] \ [S]}{\dfrac{[k_{-1} + k_2]}{k_1}}$$

$$or \ [ES] = \frac{[E] \ [S]}{k_m} \longrightarrow \quad (2)$$

$$where, \ k_m = \frac{k_{-1} + k_2}{k_1}$$

This is called Michaelis constant.

If $[E]_0$ is the initial concentration of the enzyme, then at any instant

$$[E]_0 = [E] + [ES]$$

$$[E] = [E]_0 - [ES]$$

Substituting the value of $[E]$ in eqn - (2)

$$[ES] = \frac{\{[E]_0 - [ES]\}\ [S]}{k_m}$$

$$= \frac{[E]_0\ [S] - [ES]\ [S]}{k_m}$$

$$\text{or } [E]_0\ [S] = [ES]\ [\,k_m + [S]\,]$$

$$\therefore [ES] = \frac{[E]_0\ [S]}{k_m + [S]}$$

Substituting the value of $[ES]$ in eqn - (1)

$$\boxed{\text{Rate of reaction} = \frac{k_2\ [E]_0\ [S]}{k_m + [S]}} \longrightarrow (3)$$

This relation is called Michaelis-Menten equation.

Eqn (3) is valid at all concentrations of the substrate

Case: 1 (zero order)

at sufficiently high substrate concentration, $[S] \gg k_m$

$$\text{Rate of reaction} = k_2\ [E]_0$$

Case: 2 (first order)

If $[S] \ll k_m$

$$\boxed{\text{Rate of reaction} = \frac{k_2\ [E]_0\ [S]}{k_m}}$$

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