Catalysis

Important Facts

A catalyst is a substance that changes the rate of a reaction but is recovered chemically unchanged at the end of reaction. This phenomenon is called catalysis.

If a catalyst increases the rate of a reaction it is called **positive catalyst.**

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

The substances which increase the efficiency of catalyst are known as **promoters or activators.** In other words promoters are the catalyst for the catalyst.
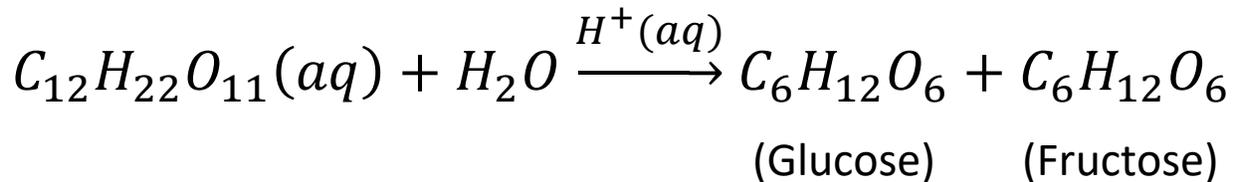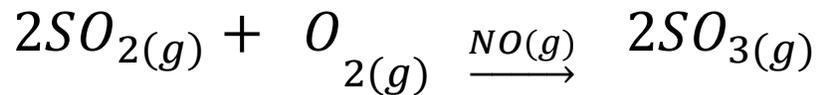
Presence of small quantities of impurities in the reacting system substances makes the catalyst inactive. These are called catalytic **inhibitors or poisons.** Arsenious oxide hydrogen cyanide is two more powerful catalytic poisons.

A catalyst does not affect the state of equilibrium in a reversible reaction.

A catalyst is specific in nature.

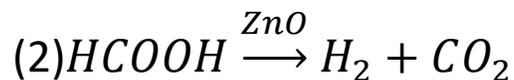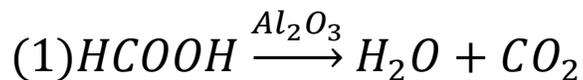A catalyst has an optimum temperature at which its efficiency is maximum.

If in a reaction, the phase of a catalyst & reactants are same. It is called **homogeneous catalysis**.e.g,

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO(g)} 2SO_{3(g)}$$

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

<div align="center">(Glucose)   (Fructose)</div>

If in a reaction, the state of catalyst is different from that of reactants, this type of catalysis is known as **heterogeneous** catalysis.

$$N_2(g) + 3H_2(g) \xrightarrow{Finely\ divided\ iron} 2NH_3(g)$$
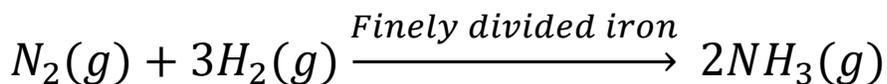
Heterogeneous catalysts are also specific in nature

$$(1) HCOOH \xrightarrow{Al_2O_3} H_2O + CO_2$$

$$(2) HCOOH \xrightarrow{ZnO} H_2 + CO_2$$

If the tube in which above reaction is taking place is filled with aluminium oxide the reaction (1) takes place. If tube is filled with ZnO the reaction (2) occurs.

Heterogeneous catalysis is a surface catalysis. It can be illustrated by taking an example of bromination of ethylene.

$$CH_2 = CH_2(g) + Br_2(g) \rightarrow BrCH_2 - BrCH_2(g)$$
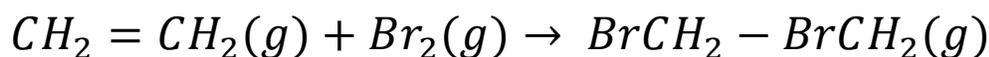
The above reaction readily takes place in a glass container at 470 K. First it was assumed to be an ordinary catalytic reaction.

However it was found that reaction rate was higher in a smaller vessel or in a vessel packed with glass beads. The rate of reaction is, however, reduced in a container coated internally with paraffin wax. This shows that reaction is not occurring in gas phase but taking place on the glass surface which acts as a catalyst.

Enzymes are protein molecules present in the living system having molecular weight ranging from 10^4 to 10^6 g mol^{-1}.They are highly efficient biological catalysts which catalyse reactions occurring in the living cells.

The reaction in enzyme catalysis occurs at specific site on the protein molecule. So this site is known as **active site** .The reactant in enzyme catalysis is referred to as **substrate**

$$\text{Cane sugar} \xrightarrow[+H_2O]{invertase} Invert\ Sugar \xrightarrow[Glucose+Fructose]{zymase} Alcohol + CO_2$$

Enzymes are highly efficient and specific in nature. They are also highly sensitive to temperature and acidity and basicity of the solution.

The mechanism of enzyme reaction was proposed by Michaelis and Menten.

Let E represents Enzyme and S represents the substrate with which enzyme reacts. The first stage is the formation of intermediate complex represented by X or ES:

$$E + S \xrightarrow{k1} \underset{intrmediate\ complex}{X} \text{-----------------------(1)}$$

The complex may either dissociate back into E and S or may give rise to the final product P i.e.

$$X \xrightarrow{k_2} E + S \qquad \qquad \text{...(2)}$$

$$X \xrightarrow{k_3} P \qquad \qquad \text{...(3)}$$

Or

$$E + S \underset{k2}{\overset{k1}{\rightleftharpoons}} \underset{Activated\ Complex}{ES\ or\ X} \xrightarrow{k_3} E + \underset{product}{P}$$

The rate of formation of complex X or ES is given by

$$\frac{dX}{dt} = k_1[E][S] - k_2[X] - k_3[X]$$

$$\frac{dX}{dt} = k_1[E][S] - (k_1 + k_3)[X] \qquad \qquad \text{...(4)}$$

The rate of formation of product from Eq. 3 is given by

$$\frac{d(P)}{dt} = k_3[X] \qquad \qquad \text{...(5)}$$

$$[E]_0 = \underset{molar\ concentration\ of\ unreacted\ enzyme}{[E]} + [X]$$

$$[X] = coc^n\ of\ enzyme\ gone\ into\ complex\ formation$$

Putting the value of [E] from above equation in Eq. 4 i.e.

$$[E] = [E]_0 - [X]$$

$$\frac{dx}{dt} = k_1\{[E]_0 - [X]\}[S] - (k_1 + k_2)[X]$$

$$\frac{dx}{dt} = k_1[E]_0[S] - k_1[X][S] - (k_1 + k_2)[X] \qquad \text{...(6)}$$

As the reaction proceeds the intermediate complex decomposes and stage comes when $\frac{dx}{dt} = 0$ known as stationary state.

$$0 = k_1[E]_0[S] - k_1[X][S] - (k_1 + k_2)[X]$$

Eq. 6 can be written as

$$0 = k_1[S][E]_0 - [X]\{k_1 + (k_1 + k_2)\}$$

$$k_1[S][E]_0 = [X]\{k_1[S] + (k_1 + k_2)\}$$

$$[X] = \frac{k_1[S][E]_0}{\{k_1[S] + (k_1 + k_2)\}}$$

$$[X] = \frac{E_0}{1 + \dfrac{k_1 + k_2}{k_1[S]}}$$

Substituting this value of [X] in Eq. 5,

$$\frac{dP}{dt} = k_3 \frac{E_0}{1 + \dfrac{k_1 + k_2}{k_1[S]}}$$

The above equation is known as **Michaelis Menten equation**

The quantity $\dfrac{k_1 + k_2}{k_1}$ is known as **Michaelis constant**

denoted by **Km.** If quantity $\dfrac{dP}{dt} = k_3 \dfrac{E_0}{2}$,

Then

$$k_3 \frac{E_0}{2} = k_3 \ \frac{E_0}{1+\frac{k_1+k_2}{k_1[S]}}$$

$$\frac{1}{2} = \frac{1}{1+\frac{k_1+k_2}{k_1[S]}}$$

$$2 = 1 + \frac{k_1+k_2}{k_1[S]}$$

$$1 = \frac{k_1+k_2}{k_1[S]}$$

$$[S] = \frac{k_1+k_2}{k_1}$$ =Km i.e.Michaelis constant is

equal to concentration of substrate at which the rate of formation of product is half the maximum rate obtained at a high concentration of S.

(1)If[S] is very small as compared to Km, the factor $\frac{K_m}{[S]}$ will be large as compared to unity. Hence rate of formation of product will be directly proportional [S] i.e. reaction will be first order with respect to S

(2) If[S] is very large as compared to Km, the factor $\frac{K_m}{[S]}$ will be small as compared to unity. Hence rate of formation of product will be independent of [S] i.e. reaction will be zero order with respect to S.

(3)In both the cases reaction remains first order with respect to total concentration $[E_0]$ of the enzyme.

When one of the products of a reaction acts as a catalyst the phenomenon is known as auto catalysis

$$2KMnO_4 + 5H_2C_2O_4 + H_2SO_4$$
$$\rightarrow \quad \underset{autocatalyst}{2MnSO_4} + K_2SO_4 + 8H_2O + 10\ CO_2$$
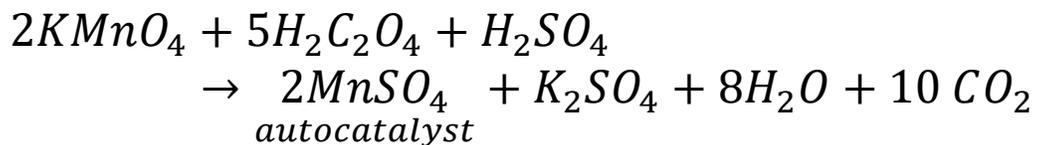
Catalysts in a fine powdered state are more effective than in lump form. This is because free valencies which are responsible

For catalytic activity increase as the particle size decreases.