Chapter 5

Kinetics of catalyzed reactions

A catalyst may be defined as the substance which when present in a chemical reaction accelerates its speed and is recovered unchanged in amount & chemical characteristics when the reaction is over. The process involving the use of catalyst in a chemical reaction is known as catalysis.

Characteristics of Catalyst:

- A catalyst can't initiate a chemical reaction. It can increase or accelerate the speed of a reaction already in progress. Thus a catalyst can catalyse a spontaneous reactions with negative ΔG .
- Catalyst are required only in small amount.
- A catalyst remains unchanged in amount as well as in chemical characteristics at the end of the reaction only state & colour may be changed.
- A catalyst is of specific nature. i.e. different catalysts are needed for different reaction.
- A catalyst does not influence the equilibrium constant of an equilibrium reaction. However, it can only influence the extent of attainment of equilibrium.

Types of catalysis:

(1) Positive catalysis/Promoters: The phenomenon in which a catalyst increases the speed of a reaction.

e.g: (i) Pt in contact process for H_2SO_4 preparation.
(ii) Pt in ostwald process for HNO_3 preparation.

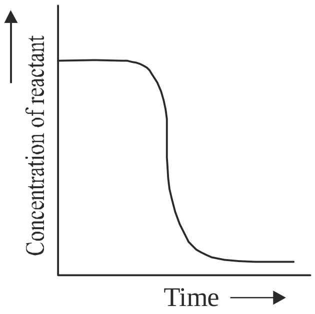
(2) Negative catalysis/Inhibitiors: The phenomenon in which a catalyst decreases the speed of reaction.

e.g: (i) Decomposition of H_2O_2 is retarded in presence of Glycerol or H_3PO_4.
(ii) Ethyl alcohol retards oxidation of chloroform to phosgene.
(iii) Ethylene glycol decreases the rusting of iron.

(3)Autocatalysis: The process in which one of the product of reaction catalyse the reaction.

e.g. : In the hydrolysis of ethyl acetate, $H^{\oplus}$ ions of acetic acid auto - catalyse the reaction.

$$CH_3COOC_2H_5 + H_2O \xrightarrow[(H^+)]{} CH_3COOH + C_2H_5OH$$



(4) Induced catalysis: The process in which a substance induces a similar reaction which is not otherwise possible.

e.g. In presence of sodium sulphite oxidation of sodium arsenite becomes feasible.

$$Na_2SO_3 + Na_3AsO_3 \xrightarrow[\text{Air}]{[O]} Na_2SO_4 + Na_3AsO_4$$

Homogenous catalysis: The process in which reactant and catalyst both have same physical state.

e.g. (i) $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

(ii) $\underset{\text{Sugar}}{C_{12}H_{22}O_{11}}(aq) + H_2O(\ell) \xrightarrow{H^+(aq)} \underset{\text{Glu cose}}{C_6H_{12}O_6}(aq) + \underset{\text{fractose}}{C_6H_{12}O_6}(aq)$

(iii) $CH_3CHO(g) \xrightarrow{I_2(g)} CH_4(g) + CO(g)$

Theory of Homogeneous catalysis:

The catalysis can be explained with the help of intermediate compound formation theory. According to this theory catalyst first combines with one of the reactant to form intermediate compound, which again react with other reactant to give product of the reaction and regeneration of the catalyst.

$$A + B \xrightarrow{P} AB$$

(i) $A + P \longrightarrow [AP]^*$ (Intermediate compound)

(ii) $[AP]^* + B \longrightarrow \underset{\text{Product}}{AB} + \underset{\text{catalyst}}{P}$

e.g. $2C_2H_5OH \xrightarrow[\text{(catalyst)}]{H_2SO_4} \underset{\text{ether}}{C_2H_5OC_2H_5} + H_2O$

(i) $C_2H_5OH + H_2SO_4 \longrightarrow \underset{\text{(Intermediate compound)}}{C_2H_5HSO_4} + H_2O$

(ii) $C_2H_5HSO_4 + C_2H_5OH \longrightarrow \underset{\text{product}}{C_2H_5OC_2H_5} + \underset{\text{catalyst}}{H_2SO_4}$

Acid and Bases Catalysis: The mechanism of acid catalyzed reactions involves an equilibrium reaction in which there occurs a transfer of proton from an acid to a substrate S. The protonated substrate then reacts with water to form the product P.

$$S + HA \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^- \; ; \; SH^+ + H_2O \xrightarrow{k_2} P + H_3O^+$$

The rate of appearance of product is given by

$$\frac{d[P]}{dt} = k_2\left[SH^+\right] \quad \text{... (1)}$$

(**Note:** That the cocentration of H_2O is not included in the above rate expression as its concentration does not change appreciably.)

The concentration of SH^+ can be obtained by applying the steady-state approximatino to SH^+. Thus, we have

$$\frac{d\left[SH^+\right]}{dt} = 0 = k_1[S][HA] - k_{-1}\left[SH^+\right]\left[A^-\right] - k_2\left[SH^+\right]$$

Hence, $$\left[SH^+\right] = \frac{k_1[S][HA]}{k_{-1}\left[A^-\right] + k_2} \quad \text{... (2)}$$

Substituting equation (2) in equation (1), we get

$$\frac{d[P]}{dt} = \frac{k_2k_1[S][HA]}{k_{-1}\left[A^-\right] + k_2} \quad \text{... (3)}$$

Two Specific Cases: Two cases may be distinguished.

Case-I: $k_2 >> k_{-1}\left[A^-\right]$. In this case, equation (3) may be written as

$$\frac{d[P]}{dt} = k_1[S][HA] \qquad \text{... (4)}$$

that is, the reaction rate is first-order with respect to each of the substrate and acid molecules. The reaction for which the rate depends on the concentration of HA is said to be subject to **general acid catalysis.**

Case-II: $k_2 << k_{-1}\left[A^-\right]$. In this case, equation (3) may be written as

$$\frac{d[P]}{dt} = k_2\frac{k_1}{k_{-1}}[S]\frac{[HA]}{\left[A^-\right]}$$

Invoking the equilibrium constant expression $K_a = \frac{\left[H^+\right]\left[A^-\right]}{[HA]}$

for $[HA]$ in equation (3), we get

$$\frac{d[P]}{dt} = k_2\frac{k_1}{k_{-1}}\frac{1}{K_a}[S]\left[H^+\right] \qquad \text{... (5)}$$

Thus, the reaction rate depends on the hydrogen-ion concentration although the proton is initially transferred from HA. In this case, the reaction is said to be subject to **specific hydrogen-ion catalysis.**
Since H^+ acts as a catalyst, its concentration remains constant and thus equation (5) may be written as

$$\frac{d[P]}{dt} = k'[S] \qquad \text{... (6)}$$

where $$k' = k_2\frac{k_1}{k_{-1}}\frac{1}{K_a}\left[H^+\right] = k_{H^+}\left[H^+\right] \qquad \text{... (7)}$$

The constant k_{H^+} is known as the catalytic coefficient of hydrogen ion. Writing equation (7) in the logarithm form, we have

$$\log\left(k'/s^{-1}\right) = \log\left(k_{H^+}/\text{mol}^{-1}\text{dm}^3\text{s}^{-1}\right) - pH$$

Thus, if a plot is made between $\log\left(k'/s^{-1}\right)$ and pH, it would yield a straight line of slope = -1.

Generalization of Rate Constant: The base catalyzed reactions involve the transfer of a proton from the substrate molecule to the base. If the rate of the reaction depends on the concentration of the base, the reaction is said to be subject to general base catalysis. For a reaction catalyzed by OH^-, the rate constant is given by

$$k = k_{OH^-}\left[OH^-\right]$$

that is, it varies linearly with the hydroxy-ion concentration.
In general, if a reaction which follows the rate law

$$\frac{d[S]}{dt} = k[S]$$

and is catalyzed by all the catalytic species H^+, OH^-, HA and A^-, then the first-order rate constant k in a buffer solution containing HA and A^- may be written as

$$k = k_0 + k_{H^+}\left[H^+\right] + k_{OH^-}\left[OH^-\right] + k_{HA}[HA] + k_{A^-}\left[A^-\right] \qquad \text{... (8)}$$

where the constants k_{H^+}, k_{OH^-}, k_{HA} and k_{A^-} are the various catalytic coefficeints and k_0 is the rate constant at low concentration of all of the catalytic species.

It may happen that the constant k_{H^+} is much larger than other constants and thus equation (8) reduces to

$$k = k_0 + k_{H^+}\left[H^+\right]$$

and the reaction to which this belongs to is an example of specific hydrogen-ion catalyst reaction.

Similarly, if constant k_{OH^-} is much larger than other constants and thus equation (8) reduces to

$$k = k_0 + k_{OH^-}\left[OH^-\right]$$

and the reaction to which this belongs to is an example of specific hydroxyl ion catalyst reaction.

Heterogenous catalysis: The process in which reactant and catalyst are in different physical state.

e.g. (i) $N_2(g) + 3H_2(g) \xrightarrow{Fe(s)} 2NH_3\ (g)$

(ii) Vegetable oil$(\ell) + H_2\ (g) \xrightarrow{Ni\ (s)}$ solid fat (s)

Theory of Heterogeneous catalysis:

This can be explained by adsorption theory. It takes in following steps.

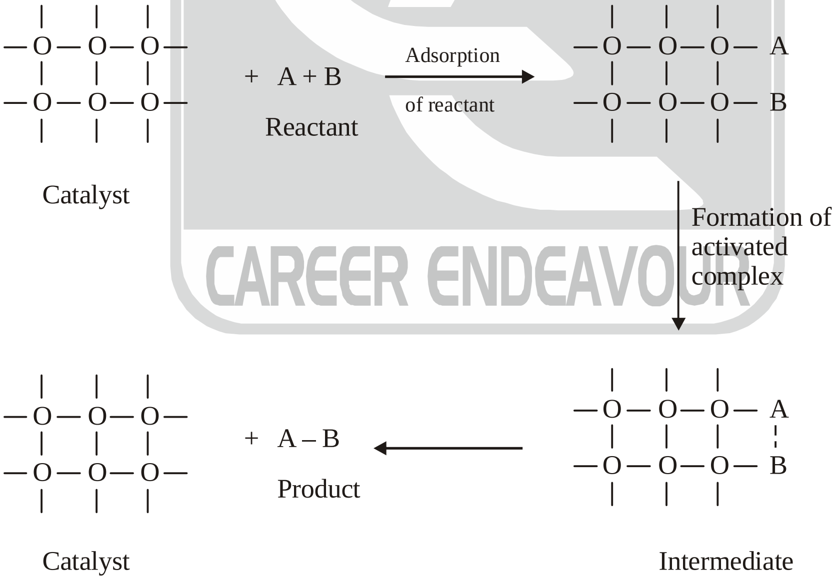
(i) Diffusion of the reactant towards catalyst surface.

(ii) Some association between the catalyst surface and the reactants i.e. adsorption.

(iii) Occurence of the chemical reactants on the catalyst surface.

(iv) Dissociation of the reaction products from the catalyst surface i.e. desorption.

(v) Diffusion of the products from the catalyst surface.



SOLVED PROBLEMS

1. The reversible reaction $S \longleftrightarrow P$ is catalyzed by a catalyst. The equilibrium constant $K_{eq} = [P]/[S]$ is 2×10^3. The forward rate constant was found to be 5×10^4 sec^{-1} and 4×10^{-6} sec^{-1} in the presence and in the absence of the catalyst respectively. What is the expected rate constant for the reverse reaction in the absence of the catalyst?
(a) 5×10^8 sec^{-1} (b) 2×10^{-9} sec^{-1} (c) 0.8×10^{-10} sec^{-1} (d) 5×10^{-9} sec^{-1}

Soln. For uncatalyzed reaction: $K_{eq} = \frac{k_f}{k_b}$

$$2\times10^3 = \frac{4\times10^{-6}}{k_b}$$ [Value of K_{eq} remains constant for a particular temperature]

$$k_b = 2\times10^{-9}\ \text{sec}^{-1}$$

Correct option is (b)

2. Which of the following is NOT a property of a catalyst ?
(a) It lowers the activation energy for both the forward and reverse processes.
(b) It increases the rate of both the forward and reverse processes.
(c) It may be recovered unchanged at the end of the reaction.
(d) It increases the equilibrium constant.

Soln. **Correct option is (d)**

KINETICS OF ENZYME CATALYSIS

The Michaelis-Menton mechanism: Enzymes are homogeneous biological catalysis. Experimental studies of enzyme kinetics are typically conducted by monitoring the initial rate of product formation in a solution in which enzyme is present at very low concentration.

Let $[S]_0$ and $[E]_0$ be the initial concentrations of substrate and Enzyme respectively. The main features of enzyme catalysed reactions are as follows.
(i) The initial rate of product formation is proportional to the total concentration of enzyme $[E]_0$ for a given initial conc. of substrate $[S]_0$.
(ii) For a given $[E]_0$ and high value of $[S]_0$ the rate of product formation become independent of $[S]_0$ reaching a maximum value known as the maximum velocity v_{max}.
The Michaelis-Menton mechanism,

Step-I: $E + S \underset{k_2}{\overset{k_1}{\rightleftharpoons}} ES \qquad (\text{fast})$

Step-II: $ES \xrightarrow{k_3} P + E \qquad (\text{slow})$

Rate of reaction is given by

$$r = -\frac{d[S]}{dt} = +\frac{d[P]}{dt} = k_3[ES] \qquad \text{... (1)}$$

Using steady state approximation for ES, we have

$$k_1[E][S] = k_2[ES] + k_3[ES]$$

Or, $$[ES] = \frac{k_1[E][S]}{k_2 + k_3} \qquad \text{... (2)}$$