

## ① Catalyst:

It has been observed that the rate of a chemical reaction is altered by the presence of a foreign substance called catalyst. A catalyst accelerates or retards a chemical reaction and is regenerated, unchanged in mass and chemical composition, at the end of the reaction. The phenomenon of acceleration or retardation of the rate due to the presence of a catalyst is known as catalysis.

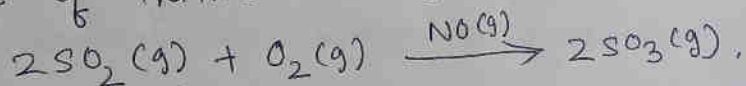
When the rate of a reaction increases due to the presence of a catalyst, it is called positive catalysis, e.g. finely divided iron (catalyst) in the synthesis of ammonia. When the rate of a reaction decreases in the presence of catalyst, it is called negative catalysis, e.g. phosphoric acid in the decomposition of hydrogen peroxide.

### Types of catalytic reactions:-

Catalytic reactions are divided into two classes:-

- Homogeneous catalytic reaction (Homogeneous catalysis)
- Heterogeneous catalytic reaction (Heterogeneous catalysis).

Homogeneous Catalysis:- In such reactions the catalyst is in the same phase as the ~~reacting substances~~ reactants and the reacting system is homogeneous throughout. e.g. ① In the lead chamber process  $\text{SO}_2$  is oxidised to  $\text{SO}_3$  in presence of nitric oxide gas.



② Hydrolysis of sucrose is catalysed with the help of  $\text{HCl}$ .

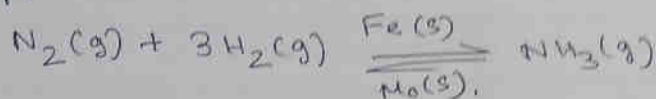
$$\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s}) + \text{H}_2\text{O}(\text{l}) \xrightarrow{\text{H}^+(\text{aq})} \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + \text{C}_6\text{H}_{12}\text{O}_6(\text{l})$$

Sucrose, glucose fructose

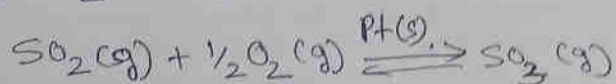
(2)

Heterogeneous catalysis - In heterogeneous catalysis, the catalyst is in different phase than the reactants. These are very helpful in industries. e.g.,

(i) Haber process in the manufacture of ammonia.



(ii) Contact process for the manufacture of sulphuric acid involves the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in the presence of platinum catalyst.



Acid base catalysis (Homogeneous type catalysis).

When a chemical reaction is catalysed by acids or bases or by both, then this type of reaction is called acid catalysed or base catalysed or acid-base catalysed reactions.

- A reaction which is catalysed by  $\text{H}^+$  or  $\text{H}_3\text{O}^+$  ion, and not by any other Brønsted acid, is called specifically proton catalysed reaction. e.g. keto-enol tautomerism, inversion of sugar etc.

- A reaction which is catalysed by any Brønsted ~~react~~ <sup>acid</sup> is called general acid catalysed reaction.

- A reaction catalysed by  $\text{OH}^-$  ions, is said to be specific base catalysed reaction.

- A reaction which is catalysed by any Brønsted base is known as general base catalysed reaction.

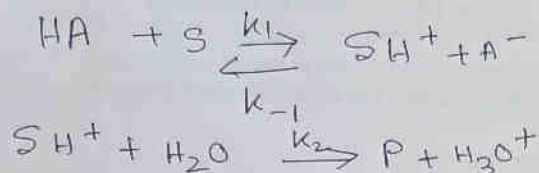
- A reaction which requires the presence of both proton donor and proton acceptor is an example of acid-base catalysis. e.g. mutarotation of glucose [Here ~~water~~  $\text{H}_2\text{O}$  used can behave as both a Brønsted acid and Brønsted base]

(3)

### Kinetics of acid base reactions.

#### (A) Acid catalyzed reaction

Let S be the substrate (reactant), HA is any acid, and P is the product.



Applying Steady state Approximation [SSA].

$$\frac{d[\text{SH}^+]}{dt} = k_1 [\text{S}] [\text{AH}] - k_{-1} [\text{SH}^+] [\text{A}^-] - k_2 [\text{SH}^+] [\text{H}_2\text{O}] = 0$$

We will ~~not~~ neglect the  $[\text{H}_2\text{O}]$  term, since the volume of  $\text{H}_2\text{O}$  is taken in large excess, and its concentration change is supposed to be negligible.

$$\text{So } \frac{d[\text{SH}^+]}{dt} = k_1 [\text{S}] [\text{AH}] - k_{-1} [\text{SH}^+] [\text{A}^-] - k_2 [\text{SH}^+] = 0$$

$$\text{Or } [\text{SH}^+] = \frac{k_1 [\text{S}] [\text{AH}]}{k_{-1} [\text{A}^-] + k_2} \rightarrow (1)$$

The rate of the reaction

$$\frac{d[\text{P}]}{dt} = k_2 [\text{SH}^+] = \frac{k_2 k_1 [\text{S}] [\text{AH}]}{k_{-1} [\text{A}^-] + k_2} \rightarrow (2) \quad \left[ \begin{array}{l} \text{putting the} \\ \text{value of } [\text{SH}^+] \\ \text{from eqn } (1) \end{array} \right]$$

Here two cases may arise.

$$(1) \quad k_2 \gg k_{-1} [\text{A}^-]$$

$$\frac{d[\text{P}]}{dt} = \frac{k_2 k_1 [\text{S}] [\text{AH}]}{k_2}$$

[neglecting  $k_{-1} [\text{A}^-]$  in the denominator]

$$\frac{d[\text{P}]}{dt} = k_1 [\text{S}] [\text{AH}] \rightarrow (3)$$

Here the rate of the reaction depends on the acid concentration  $[\text{AH}]$ , It is called generalised acid catalyzed reaction.

$$(2) \quad \text{when } k_2 \ll k_{-1} [\text{A}^-]$$

$$\frac{d[\text{P}]}{dt} = \frac{k_1 k_2 [\text{S}] [\text{AH}]}{k_{-1} [\text{A}^-]}, \rightarrow (4)$$

Now if we consider the dissociation of acids



$$\text{then the equilibrium constant } K = \frac{[\text{H}^+] [\text{A}^-]}{[\text{HA}]} \text{ or } \frac{[\text{HA}]}{[\text{A}^-]} = \frac{[\text{H}^+]}{K}$$

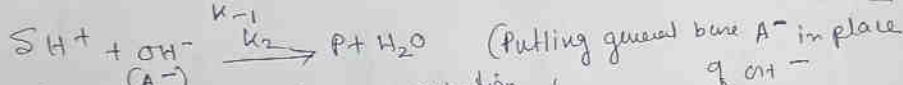
(4)

Putting this value in eqn<sup>n</sup> (4)

$$\frac{d[P]}{dt} = \frac{k_1 k_2 [S][H^+]}{k_{-1} K}$$

Here rate of the reaction depends upon the concentration of  $[H^+]$ . This type of reaction is called specific acid catalyzed reaction.

(B) ~~S + AH~~ <sup>Acid</sup> catalyzed reaction [When the intermediate reacts with  $OH^-$  rather than  $H_2O$ ]



Applying steady state approximation

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

$$[SH^+] = \frac{k_1 [S][AH]}{k_{-1} [A^-] + k_2 [A^-]}$$

Now the rate:

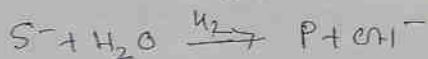
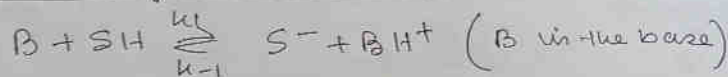
$$\frac{dP}{dt} = [SH^+][A^-] \quad \frac{dP}{dt} = k_2 [SH^+][A^-]$$

Putting the value of  $[SH^+]$

$$\frac{dP}{dt} = \frac{k_2 k_1 [S][AH][A^-]}{[A^-](k_{-1} + k_2)} = \frac{k_2 k_1 [S][AH]}{k_{-1} + k_2}$$

So the rate depends upon the concentration of the acid  $[AH]$ .  
So it is a general acid catalyzed reaction.

(c) Base catalyzed reaction



$$d[S^-] = k_1 [B][SH] - k_{-1} [S^-][BH^+] - k_2 [S^-][H_2O] = 0$$

$$\text{or } k_1 [B][SH] - k_{-1} [S^-][BH^+] - k_2 [S^-] = 0$$

$$\text{on } [S^-] = \frac{k_1 [B][SH]}{k_{-1} [BH^+] + k_2} \rightarrow (1)$$

(5)

~~Here two cases may arise.~~

~~Case I - When  $k_2 \gg k_{-1} [BH^+]$ .~~

$$[S^-] =$$

Now the rate of the reaction  $\frac{d[P]}{dt} = k_2 [S^-] [H_2O]$

Putting the value of  $[S^-]$  from eqn (1).

$$\frac{d[P]}{dt} = \frac{k_2 k_1 [B] [SH]}{k_{-1} [BH^+] + k_2}$$

When  $k_2 \gg k_{-1} [BH^+]$

$$\frac{d[P]}{dt} = \frac{1/2 k_1 [B] [SH]}{k_2}$$

$$\frac{d[P]}{dt} = k_1 [B] [SH]$$

The rate will depend upon the concn<sup>n</sup> of the Reactant  $[B]$

### Adsorption theory of heterogeneous catalyst.

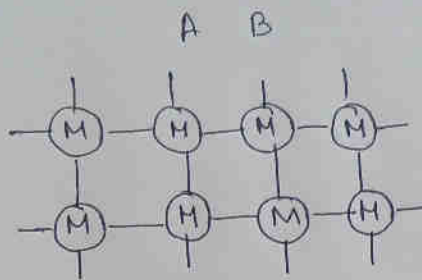
Inside the adsorbent (let be a metal) every atom is linked to the surrounding atoms and all valencies are satisfied. On the other hand, an atom situated in the surface of the catalyst possesses a free ~~energy~~ valency turned outward. When a gas comes in contact with such a surface its molecules are held up there due to adsorption.

~~This theory~~ For the process, it involves five steps.

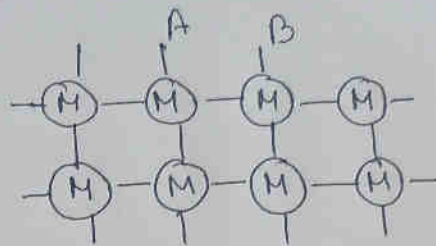
- (1) Diffusion of reactant to the surface of the catalyst.
- (2) Adsorption of the reactant molecules at the surface of the catalyst.
- (3) Occurrence of chemical reaction at the surface of the catalyst through the formation of the intermediates.
- (4) Desorption of product molecules from the surface of the catalyst.
- (5) Diffusion of the product molecules away from the surface of the catalyst.

⑥

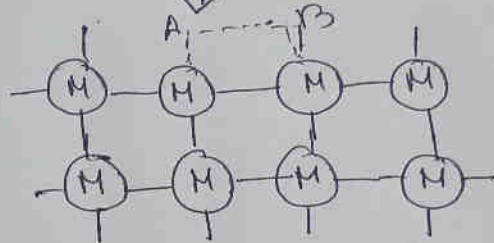
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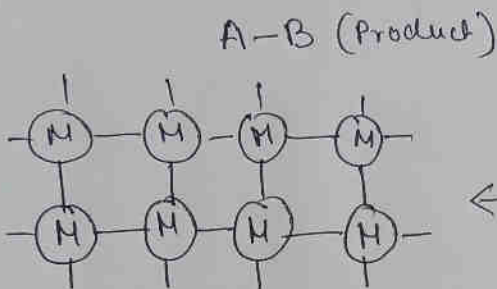
Diffusion of the reactant molecules.



Adsorption of the reactant molecule.

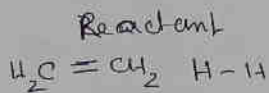


formation of the intermediate.

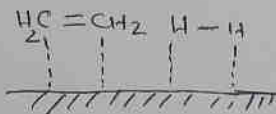


Desorption of the product.

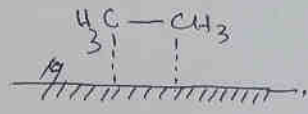
② Catalytic hydrogenation of ethene.



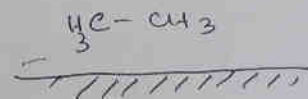
Adsorbent.



Adsorption



Reaction



Desorption

