PHYSICAL CHEMISTRY

CATALYSIS

B.Sc – II [HONS]

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CATALYSIS

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Catalyst:- A catalyst is a substance that increases the rate of the reaction without being consumed in the reaction.

Definition of catalysis:- The phenomenon of increase in the rate of the reaction with the help of a catalyst is catalysis.

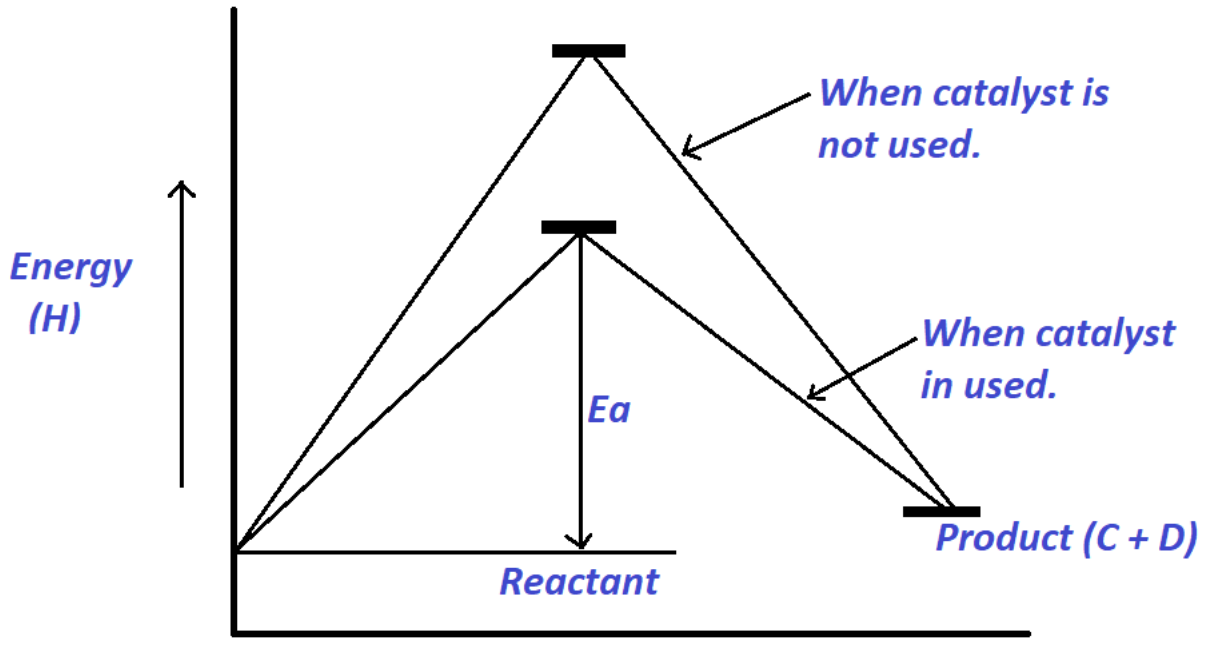
Catalyst is used generally in very small quantity.

Enzymes:- Enzymes are biological catalysts which are used by organisms to speed up their cellular reactions.

Theory:- Each catalyst has its own specific way of functioning but in general a catalyst functions by lowering the energy of activation which in turn makes the rate constant larger and hence rate of the reaction higher.

Following graph can be plotted for the functioning of catalyst.

$$A + B + Q = C + D$$



From the above graph two things are visible.

1. When catalyst is used in a particular chemical reaction the value of activation energy decreases.
2. The rate of a chemical reaction increases when a catalyst is used. i,e the value of K increases.

Promoters:- Promoters are substances that enhance the activity of a catalyst.

Here, Fe is a catalyst and Mo is a promoter.

Ex:- $N_2(g)+3H_2(g) \xrightarrow[Mo(s)]{Fe(s)} 2NH_3(g)$

Inhibitors or Poisons:- Decrease the activity of a catalyst.

Ex:- Oxides of As (AS_2O_3 or AS_2O_5) poison the catalytic power of Pt in contact process in making SO_3 from SO_2.

Types of catalysis:-

According to phase of reactants and catalysts there are two types of catalysis.

1. Homogeneous catalysis.
2. Heterogeneous catalysis.

(1). Homogeneous (Homo = Same, Geneous = Phase):-

When the phase of catalyst and reactants is the same it is called as homogeneous catalysis.

It is believed that have catalyst combines with reactants to give an intermediate and, than this intermediate gives rise to product by generating the catalyst.

Reactants + Catalyst ⟶ Intermediate ⟶ Product + Catalyst.

Example:-

(1). $R - COOR + H_2O \xrightarrow[(Catalyst)]{H^+Cl(l)} R - COOH + R - OH$

(2). $O_3 + O \xrightarrow[(Catalyst)]{Cl(l)} 2\,O_2$

(3). $2CO(g) + O_2(g) \xrightarrow[(Catalyst)]{NO(g)} 2CO_2$

(4). $2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$

(5). $C_{12}H_{22}O_{11(aq)} + H_2O(i) \xrightarrow{H_2SO_4\ (i)} C_6H_{12}O_6 + C_6H_{12}O_6$

(2). Heterogeneous catalysis (Hetro = Different):-

That catalysis is called as heterogeneous catalyst in which reactants and catalyst are in different phases.

- Generally, here catalyst is found in solid state and reactants are in gaseous state.
- It is also called as surface catalyst because the reaction is taking place at the surface of the solid catalyst.
- These catalysts have enormous surface are as between 1 + 500m^2/g for contact.
- Generally, here the reactions taking place are of zero order because despite of an enormous surface area once the reactant gas covers the surface, increasing the reactant concentration can't increase the rate.

Ex:- (1). $2HI(g) \xrightarrow[(Catalyst)]{\text{Gold, } \Delta} H_2 + I_2$

(2). $2N_2O(g) \xrightarrow[Pt(cat)]{\Delta} 2N_2 + O_2$

(3). $C_2H_4(g) + H_2(g) \xrightarrow[\Delta\ or\ Pd\ or\ Pt]{\text{Ni,(cat)}} C_2H_6$

(4). $SO_2(g) + O_2(g) \xrightarrow{Pt\ (s)} 2SO_3(g)$

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

(6). $4NH_3(g) + 5O_2(g) \xrightarrow{Pt\ (s)} 4NO + 6H_2O$

(7). Vegetable oils (l) + $H_2(g) \xrightarrow{Ni\ (s)}$ Vegetable ghee

The addition of H_2 or C_2H_4 takes place in the following steps.

- Chemical adsorption of reactant (C_2H_4, H_2) on to the surface of metal.
- H_2 splits in to H – atoms which get chemically bound to the solid catalyst.

$H - H + 2m(s) \xleftrightarrow{catalyst} 2m - H$

- The H – atoms migrate over the surface of the metal and eventually collide with an adsorbed C_2H_4 molecule and the reaction takes place.

$$C_2H_4(g) + 2m - H \longleftrightarrow C_2H_6(g) + 2m(s)$$

- Manufacture of NH_3 by Haber process.

$$N_2(g) + 3H_2(g) \xrightleftharpoons{Fe\ (catalyst)} 2NH_3(g)$$

- $CO + 2H_2(g) \xrightarrow{Cu,\ ZnO - Cr_2O_3} CH_3OH(l)$

Nature of solid catalyst:-

- Solid catalyst may be metals, metal oxide, metal sulphide, clays etc.
- These metals may be used in pure form or in mixture.
- They may be crystalline, micro crystalline or amorphous.

Important features of solid catalyst:-

(1). Activity:-

- The activity of a catalyst depends upon the strength of chemisorption to a large extent.
- The reactant must adsorb reasonably strongly for the catalyst to be active but must not adsorb so strongly that they are immobilized and other reactant are left with no space on the catalyst surface for adsorption.
- It has been found that for Hydrogenation the catalytic activity increases as we from group 5 – metals to group11.
- The maximum activity is shown by group 7 to group 10.

Ex:- $2H_2(g) + O_2(g) \xrightarrow{Pt} 2H_2O(l)$

(2).Selectivity:-

- A particular catalyst is very selective for a particular reaction.
- For example, starting with H_2 and CO, using different catalyst we get different products.

Ex:- 1. $CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$

2. $CO(g) + 2H_2(g) \xrightarrow{Cu/ZnO - Cr_2O_3} CH_3COH(g)$

3. $CO(g) + H_2(g) \xrightarrow{Cu} HCHO(g)$

Shape – Selective catalyst – Zeolites:-

- The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape – selective catalysis.

Ex:- Zeolites are shape – selective catalysis zeolites are being very widely used as catalysts in petrochemical industry for cracking of hydrocarbons and isomerization. An important zeolite catalyst used in the petroleum industry is Zsm – 5. It converts alcohol directly in to gasoline (petrol) by dehydrating them so, that a mixture of Hydrocarbons is – formed.

Enzyme catalysis:-

- General thousands of reactions are going on in organisms at ordinary temperature. So, enzyme catalyst is required for organisms.
- Enzymes are proteins with high molar mass ranging from 15,000 to 1,000,000 gm/mol.
- They increase rates by 10^8 to 10^{20} times.
- **Ex:-** $H_2NCONH_{2(Urea)} + H_2O \xrightarrow{\text{urease enzyme}} 2NH_3 + 2CO_2$
- Enzymes have active sites on their surface where substrates bind through intermolecular force H- bonds, dipole force and other weak attractions.
- Two models of enzyme action have been proposed.
  (a). Lock – and key model.
  (b). Induced – fit – model.

  (a). Lock – and key model:- In this model the key (substrate) fits the lock (active site) and then the chemical change begins.

  (b). Induced – fit – model:- In these model the enzyme change shape when the substrate landed at the active site. Here, the substrate inducing the active site to adopt a perfect fit.

Kinetics of Enzyme catalysis:-

(a). $E + S \longleftrightarrow ES$ (Fast, Reversible)

(b). $ES \longrightarrow E + P$ (Slow rate determined)

- The rate of enzyme catalyst reaction changes from first order to zero order as the concentration of substrate is increased.