

B. Sc. II-Sem

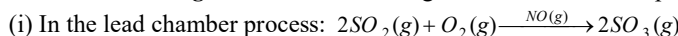
Catalysis

“Catalyst is a substance which speeds up and speeds down a chemical reaction without itself being used up.” **Berzelius** (1836) introduced the term *catalysis* and *catalyst*. **Ostwald** (1895) redefined a catalyst as, “A substance which changes the reaction rate without affecting the overall energetics of the reaction is termed as a catalyst and the phenomenon is known as *catalysis*.”

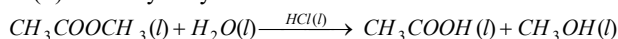
Types of catalysis

Catalytic reactions can be broadly divided into the following types,

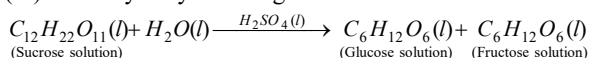
(1) **Homogeneous catalysis:** When the reactants and the catalyst are in the same phase (*i.e.* solid, liquid or gas). The catalysis is said to be *homogeneous*. The following are some of the examples of homogeneous catalysis.



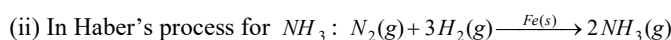
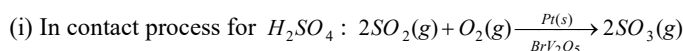
(ii) In the hydrolysis of ester



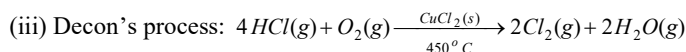
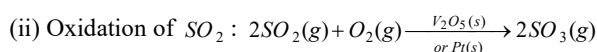
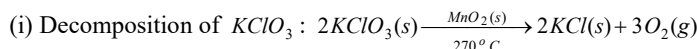
(iii) In the hydrolysis of sugar



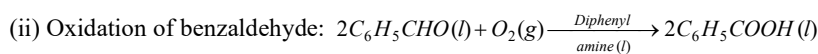
(2) **Heterogeneous catalysis:** The catalytic process in which the reactants and the catalyst are in different phases is known as *heterogeneous catalysis*. Some of the examples of heterogeneous catalysis are given below.



(3) **Positive catalysis:** When the rate of the reaction is accelerated by the foreign substance, it is said to be a *positive catalyst* and phenomenon as *positive catalysis*. Some examples of positive catalysis are given below.



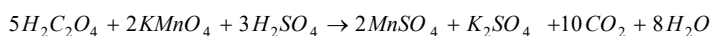
(4) **Negative catalysis:** There are certain substance which, when added to the reaction mixture, retard the reaction rate instead of increasing it. These are called *negative catalyst* or *inhibitors* and the phenomenon is known as *negative catalysis*. Some examples are as follows.



(iii) Tetra ethyl lead (TEL) is added to petrol to retard the ignition of petrol vapours on compression in an internal combustion engine and thus minimise the *knocking effect*.

(5) **Auto-catalysis:** In certain reactions, one of the product acts as a catalyst. In the initial stages the reaction is slow but as soon as the products come into existences the reaction rate increases. This type of phenomenon is known as *auto-catalysis*. Some examples are as follows,

(i) The rate of oxidation of oxalic acid by acidified potassium permanganate increases as the reaction progresses. This acceleration is due to the presence of Mn^{2+} ions which are formed during reaction. Thus Mn^{2+} ions act as auto-catalyst.



(ii) When nitric acid is poured on copper, the reaction is very slow in the beginning, gradually the reaction becomes faster due to the formation of nitrous acid during the reaction which acts as an auto-catalyst.

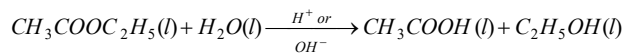
(6) **Induced catalysis:** When one reaction influences the rate of other reaction, which does not occur under ordinary conditions, the phenomenon is known as *induced catalysis*. Some examples are as follows,

(i) Sodium arsenite solution is not oxidised by air. If, however, air is passed through a mixture of the solution of sodium arsenite and sodium sulphite, both of them undergo simultaneous oxidation. The oxidation of sodium sulphite, thus, induces the oxidation of sodium arsenite.

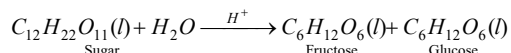
(ii) The reduction of mercuric chloride ($HgCl_2$) with oxalic acid is very slow, but potassium permanganate is reduced readily with oxalic acid. If, however, oxalic acid is added to a mixture of potassium permanganate and $HgCl_2$ both are reduced simultaneously. The reduction of potassium permanganate, thus, induces the reduction of mercuric chloride.

(7) **Acid-base catalysis:** According to the *Arrhenius* and *Ostwald* H^+ or H^- ion act as a catalyst.

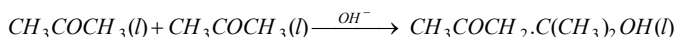
(i) For example, Hydrolysis of an ester,



(ii) Inversion of cane sugar,



(iii) Conversion of acetone into diacetone alcohol,



Characteristics of catalysis

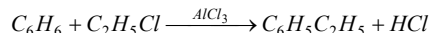
The following are the characteristics which are common to most of catalytic reactions.

(1) A catalyst remains unchanged in mass and chemical composition at the end of the reaction.

(2) **A small quantity of the catalyst is generally sufficient to catalyse almost unlimited reactions**

(i) For example, in the decomposition of hydrogen peroxide, one gram of colloidal platinum can catalyse 10^8 litres of hydrogen peroxide.

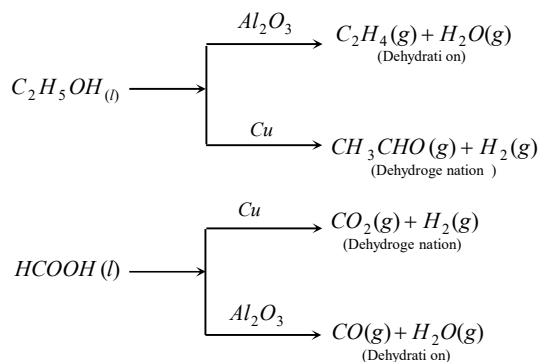
(ii) In Friedel craft's reaction, anhydrous aluminium chloride is required in relatively large amount to the extent of 30% of the mass of benzene,



(3) **The catalyst can not initiate the reaction:** The function of the catalyst is to alter the speed of the reaction rather than to start it.

(4) **The catalyst is generally specific in nature:** A substance, which acts as a catalyst for a particular reaction, fails to catalyse the other reaction, different catalysts for the same reactant may give different products.

Examples :



(5) **The catalyst can not change the position of equilibrium :** The catalyst catalyses both forward and backward reactions to the same extent in a reversible reaction and thus has no effect on the equilibrium constant.

(6) **Catalytic promoters :** Substances which themselves are not catalysts, but when mixed in small quantities with the catalysts increase their efficiency are called as *promoters* or *activators*.

(i) For example, in Haber's process for the synthesis of ammonia, traces of molybdenum increase the activity of finely divided iron which acts as a catalyst.

(ii) In the manufacture of methyl alcohol from water gas ($CO + H_2$), chromic oxide (Cr_2O_3) is used as a promoter with the catalyst zinc oxide (ZnO).

(7) **Catalytic poisons** : Substances which destroy the activity of the catalyst by their presence are known as **catalytic poisons**.

(i) For example, the presence of traces of arsenious oxide (As_2O_3) in the reacting gases reduces the activity of platinized asbestos which is used as catalyst in contact process for the manufacture of sulphuric acid.

(ii) The activity of iron catalyst is destroyed by the presence of H_2S or CO in the synthesis of ammonia by Haber's process.

(iii) The platinum catalyst used in the oxidation of hydrogen is poisoned by CO .

(8) **Change of temperature alters the rate of catalytic reaction as it does for the same reaction in absence of catalyst** : By increasing the temperature, there is an increase in the catalytic power of a catalyst but after a certain temperature its power begins to decrease. A catalyst has thus, a particular temperature at which its catalytic activity is maximum. This temperature is termed as **optimum temperature**.

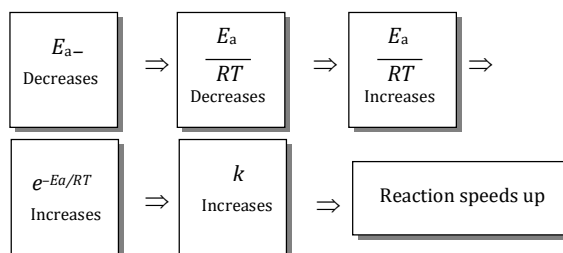
(9) **A positive catalyst lowers the activation energy**

(i) According to the collision theory, a reaction occurs on account of effective collisions between the reacting molecules.

(ii) For effective collision, it is necessary that the molecules must possess a minimum amount of energy known as activation energy (E_a).

(iii) After the collision molecules form an activated complex which dissociate to yield the product molecules.

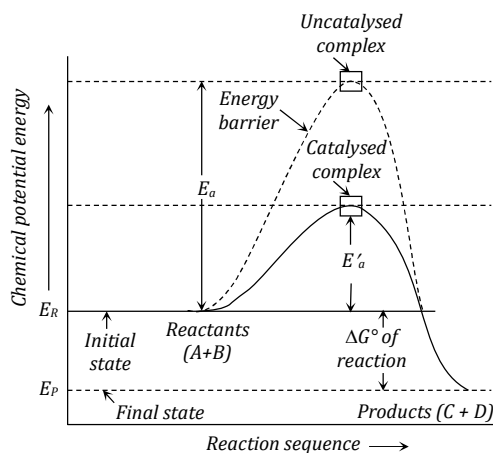
(iv) The catalyst provides a new pathway involving lower amount of activation energy. Thus,



larger number of effective collisions occur in the presence of a catalyst in comparison to effective collisions at the same temperature in absence of a catalyst. Hence the presence of a catalyst makes the reaction to go faster.

(v) Figure shows that activation energy E_a , in absence of a catalyst is higher than the activation energy E'_a , in presence of a catalyst.

(vi) E_R and E_P represent the average energies of reactants and products. The difference gives the value of ΔG , i.e., $\Delta G = E_R - E_P$



Theories of catalysis

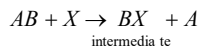
There are two theories of catalysis which is described as follows.

(1) Intermediate compound theory

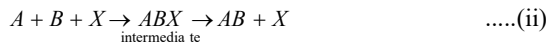
(i) This theory was proposed by **Clement and Desormes** in 1806. According to this theory, the desired reaction is brought about by a path involving the formation of an unstable intermediate compound, followed by its decomposition into the desired end products with the regeneration of the catalyst.

(ii) The intermediate compound may be formed in either of two ways

(a) When the intermediate compound is reactive and reacts with the other reactants.



(b) When the intermediate is unstable and decomposes to give the final product.



Where, A , B and C are the reactant molecules and X is the molecule of the catalyst. The first type of reaction sums up to, $AB + C \rightarrow CB + A$

While the second to, $A + B \rightarrow AB$ in many cases, the intermediate compounds postulated to be formed are known compounds and often their presence is detected.

(2) Adsorption theory

(i) This theory is applicable to reactions between gases in the presence of a solid catalyst. Some typical examples are as follows.

(ii) The contact process for the oxidation of SO_2 to SO_3 with atmospheric oxygen in the presence of platinum as the catalyst.

(iii) The Haber's process for the synthesis of ammonia with iron as the catalyst.

(iv) Adsorption results in the loosening of the chemical bonds in the reactant molecules, so that their rupture becomes easier. This is confirmed by the observed lower activation energies for heterogeneous catalytic reactions in the presence of the catalysts as compared to that for the same reaction in the absence of the catalyst.

Enzyme catalysis

(1) Enzymes are complex nitrogenous substances these are actually protein molecules of higher molecular mass.

(2) Enzymes catalyse numerous reactions, especially those connected with natural processes.

(3) Numerous reactions occur in the bodies of animals and plants to maintain the life process. These reactions are catalysed by enzymes. The enzymes are thus, termed as **bio-chemical catalysts** and the phenomenon is known as **bio-chemical catalysis**.

(4) **Nitrogenase** an enzyme present in bacteria on the root nodules of leguminous plants such as peas and beans, catalyses the conversion of atmospheric N_2 to NH_3 .

(5) In the human body, the enzyme carbonic anhydrase catalyses the reaction of CO_2 with H_2O ,



The forward reaction occurs when the blood takes up CO_2 in the tissues, and the reverse reaction occurs when the blood releases CO_2 in lungs.

(6) In manufacturing of ethyl alcohol

