

Chemical Dynamics



Notes

- Silica gel packed in small cloth bags is used for adsorbing moisture in bottles of medicine and in small electronic instruments.
- Animal charcoal is used for decolourizing many compounds during their manufacture.
- In chromatography, the selective adsorption of different solutes on the surface of solid adsorbent helps in their separation.
- Mordants are used during dyeing process with certain dyes. In such cases, the mordants fix the dye on the fabric by adsorption.



Intext Questions 17.1

- Indicate which of the following statements are true or false. (T/F)
 - More easily liquifiable gases are adsorbed more strongly.
 - Non-porous adsorbents would adsorb more quantity of a gas than porous adsorbents under similar conditions.
 - The extent of adsorption increases with rise in temperature.
 - Chemisorption is highly specific in nature.
 - Adsorption can occur from solutions also.

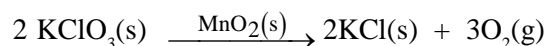
17.2 Catalysis

When hydrogen and oxygen gases are kept in contact with each other, no observable reaction occurs. If we add a small piece of platinum gauge in the mixture of these gases, the reaction occurs readily. Here platinum gauge speeds up the reaction and is called a **catalyst**.

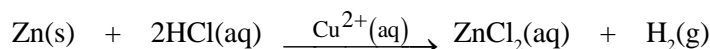
A catalyst is a substance which changes the rate of a reaction but remains chemically unchanged at the end of the reaction.

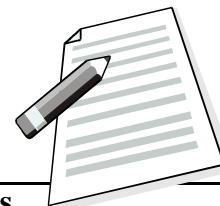
The phenomenon of change of reaction rate by addition of a substance which itself remains unchanged chemically is called **catalysis**. The following are some more examples of catalysis:

- Decomposition of potassium chlorate occurs at high temperature. If a small amount of the manganese dioxide is added, the decomposition occurs at much lower temperature. Here, manganese dioxide acts as catalyst.



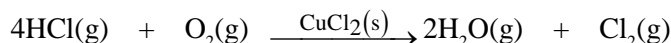
- The evolution of hydrogen by the reaction between zinc and hydrochloric acid is catalysed by $\text{Cu}^{2+}(\text{aq})$ ions.





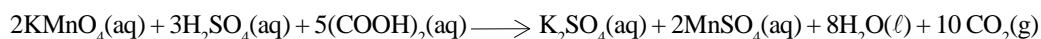
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- (iii) The oxidation of hydrogen chloride gas by oxygen occurs more quickly if the gases are passed over cupric chloride.



Auto-catalysis

In certain reactions, one of the products of the reaction acts as the catalyst. For example, the oxidation of oxalic acid by acidified potassium permanganate occurs as



At room temperature, the reaction is quite slow in the beginning. Gradually it becomes fast due to the catalytic action of Mn^{2+} ions which are one of the products as MnSO_4 in the reaction.

The phenomenon in which one of the products of a reaction acts as a catalyst is known as auto-catalysis.

Negative Catalysis

Some catalysts retard a reaction rather than speed it up. They are known as negative catalysts. For example :

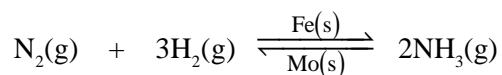
- (i) Glycerol retards the decomposition of hydrogen peroxide.
- (ii) Phenol retards the oxidation of sulphurous acid.

Promoters and Poisons

Certain substances increase or decrease the activity of the catalyst, although, by themselves they do not show any catalytic activity.

*The substances which increase the activity of a catalyst are called **promoters** and those which decrease the activity of a catalyst are called **poisons**.* For example :

- (i) In Haber's process for the manufacture of ammonia, the catalytic activity of iron is enhanced by molybdenum which acts as promoter.



- (ii) Copper promotes the catalytic activity of nickel during hydrogenation of oils.
- (iii) In Haber's process the catalyst iron is poisoned by hydrogen sulphide H_2S .
- (iv) In contact process for the manufacture of sulphuric acid, the catalyst platinum is poisoned by even the traces of arsenious oxide As_2O_3 .

17.2.1 General Characteristics of a Catalyst

The following are the general characteristics of a catalyst :

- (i) A catalyst remains unchanged at the end of the reaction.

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The amount and the chemical composition of a catalyst remain unchanged in a catalytic reaction. However, the catalyst may undergo a physical change. For example, manganese dioxide, which is used as a catalyst in thermal decomposition of potassium chlorate becomes powder during the course of the reaction.

(ii) A small quantity of the catalyst is generally enough.

In most of the reactions, only a minute amount of catalyst is required. Only one gram of Cu^{2+} ions is sufficient to catalyse the oxidation of 10^9 litres of sodium sulphite solution. In some cases, the rate of reaction is directly proportional to the concentration of catalyst present. Catalysis by acids or bases is usually of this type.

(iii) A catalyst does not alter the position of equilibrium state of a reversible reaction.

A catalyst allows the equilibrium to be reached faster. However, it does not alter the equilibrium composition of the reaction mixture. It is because, a catalyst increases the rates of forward and backward reaction equally.

(iv) Catalysts are generally specific in their action.

Generally, one catalyst will change the rate of only one reaction. For example, manganese dioxide catalyses the decomposition of potassium chlorate but not of potassium perchlorate.

(v) A catalyst cannot initiate a reaction.

A catalyst can change the rate of a reaction which occurs even in the absence of catalyst. It cannot start a reaction.

(vi) The activity of a catalyst can be increased by the presence of promoters and decreased by the presence of poisons.

Presence of a promoter increases the activity of a catalyst, while the presence of a poison decreases it.

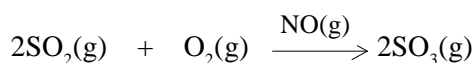
17.2.2 Homogeneous and Heterogeneous Catalysis

The phenomenon of catalysis can be divided into two main types – homogeneous and heterogeneous catalysis, on the bases of the number of phases present in the reaction mixture (A phase is a homogeneous part of a system).

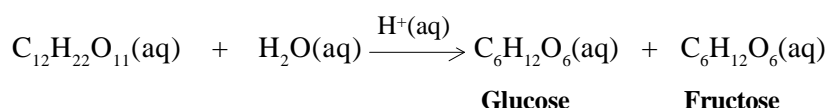
(a) Homogeneous Catalysis

When the catalyst is present in the same phase as the reactants, the phenomenon is called homogeneous catalysis. For example :

(i) Nitric oxide catalyses the oxidation of sulphur dioxide to sulphur trioxide in the lead chamber process.



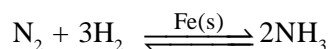
(ii) Hydrogen ions catalyse the inversion of cane sugar



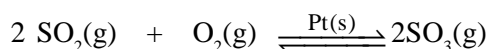
**(b) Heterogeneous Catalysis**

When the catalyst is present in a phase other than that of reactants the phenomenon is called **heterogeneous catalysis**. For example :

(i) Iron (s) catalyses the formation of NH_3 gas.



(ii) In contact process for the manufacture of sulphuric acid, platinized asbestos is used as the catalyst

**17.2.3 Catalysis and Activation Energy**

We have seen that a catalyst increases the rate of a reaction. We explain it by considering the Fig 17.8.

In this figure E_a is the activation energy of uncatalysed reaction and E'_a is the activation energy of the catalysed reaction. A catalyst lowers the activation energy as you can see in the figure ($E'_a < E_a$). The reduction in activation energy is achieved by providing an alternative pathway of lower energy for the reaction.

You can also see in this figure that the relative energies of reactants and products are not changed. The enthalpy change is the same for the catalysed and uncatalysed reactions.

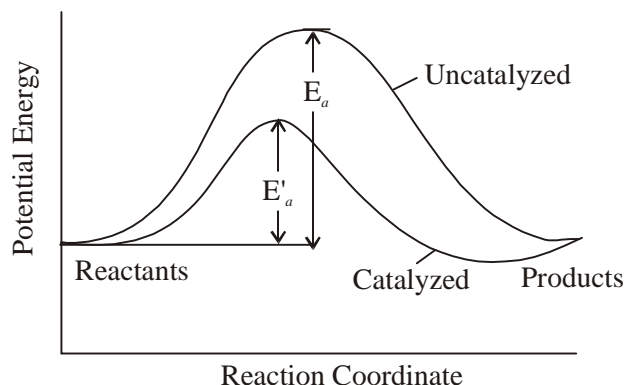


Fig. 17.8 : Graphical representation of the effect of catalyst on a reaction.

**Intext Questions 17.2**

1. List any two characteristics of a catalyst.

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2. A small amount of alcohol when added to a solution of sodium sulphite slows down its oxidation to sodium sulphate. What type of catalyst is alcohol?
.....
3. How would the activation energy be affected in the above reaction (given in Q.No.2) on adding the alcohol?
.....
4. Addition of molybdenum enhances the catalytic activity of iron in the Haber's process for the manufacture of ammonia. What are the substances like molybdenum called?
.....



What You Have Learnt

- The phenomenon of attracting and retaining the molecules of a gas or of a dissolved substance on the surface of a solid is called adsorption.
- The substance which gets adsorbed is called the adsorbate and the solid substance which adsorbs is called the adsorbent.
- The substances that are porous in nature and have rough surfaces are better adsorbent.
- Easily liquifiable gases are more readily adsorbed.
- Extent of adsorption decreases with rise in temperature and increases with the increase in pressure of the gas.
- Physical adsorption is due to van der Waal forces and chemisorption is due to forces similar to chemical bonds.
- Pressure dependence of adsorption of a gas at a constant temperature is given by Freundlich Adsorption Isotherm

$$\frac{x}{m} = k p^{\frac{1}{n}}$$
- A catalyst is the substance which changes the rate of a reaction, but itself remains chemically unchanged during the reaction.
- The catalysts which increase the rate of a reaction are called the positive catalysts while those which decrease the rate are called the negative catalysts.
- Auto catalysed reactions are those in which one of the products acts as the catalyst.
- A promoter enhances the activity of a catalyst while a poison hampers it.
- A catalyst can't initiate a reaction, nor can it alter the position of equilibrium state of a reversible reaction.
- When the catalyst is present in the same phase as the reactants it is called a homogeneous catalyst.



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- When the catalyst is present in a phase other than that of reactants it is called a heterogeneous catalyst.
- A catalyst changes the rate of a reaction by changing its path and the activation energy.



Terminal Exercise

1. What is the difference between adsorption and absorption?
2. Distinguish between physical and chemical adsorption.
3. List the factors that affect adsorption.
4. What type of solids make better adsorbents?
5. Easily liquifiable gases are adsorbed more readily. Explain.
6. What is 'extent of adsorption'?
7. How does extent of adsorption vary with temperature in case of (i) physical adsorption and (ii) chemisorption? Depict graphically.
8. What is enthalpy of adsorption?
9. Explain the effect of temperature on extent of physical adsorption with the help of Le Chatelier's Principle.
10. What is an adsorption isotherm?
11. State mathematically Freundlich Adsorption Isotherm and depict it graphically. Under what conditions is it applicable.
12. Give the mathematical equation of Freundlich Isotherm for adsorption of solutes from solutions.
13. Give any three applications of adsorption.
14. What is a (i) catalyst and (ii) negative catalyst?
15. What are promoters and poisons? Give one example of each.
16. What is auto catalysis. Give one example.
17. Give any five characteristics of catalysis.
18. Distinguish between homogeneous and heterogeneous catalysis.
19. Give two examples each of homogeneous and heterogeneous catalysis.
20. How does a catalyst change the rate of reaction. Explain with the help of appropriate example.

Chemical Dynamics**Notes****Answers to the Intext Questions****17.1**

(i) T, (ii) F, (iii) F, (iv) T, (v) T

17.2

1. See text section 17.2.1
2. Negative catalyst
3. Increase
4. Promoters