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313en15

ADSORPTION AND CATALYSIS

Surface of solids plays a crucial role in many physical and chemical phenomena. There are two main reasons for this special role. Firstly, the surface of a substance interacts first with its surroundings. Secondly, the surface molecules are in a different state as compared to the molecules in the interior of the solid. The surface molecules interact more readily with other substances which come close by and are responsible for many special properties. In this lesson we shall study about two such properties – adsorption and catalysis.



OBJECTIVES

After reading this lesson you will be able to :

- define adsorption;
- distinguish between physical adsorption and chemisorption;
- list and explain the various factors that affect adsorption;
- state Freundlich adsorption isotherm mathematically and explain it;
- explain Langmuir isotherm;
- define catalysis;
- distinguish between homogeneous and heterogeneous catalysis, and
- explain the role of activation energy in catalysis.

15.1 ADSORPTION

The surface of a solid attracts and retains molecules of a gas or a dissolved substance which comes in its contact. These molecules remain only at the surface and do not go deeper into the bulk Fig. 15.2(a).



Notes

The phenomenon of attracting and retaining the molecules of a gas or a dissolved substance by the surface of a solid, resulting in their higher concentration on the surface is called adsorption.

The substance which gets adsorbed is called the **adsorbate** and the solid substance which adsorbs is called the **adsorbent**.

A molecule in the interior of a solid is surrounded by other molecules in all directions (Fig. 15.1). However, a molecule at the surface is surrounded by other molecules within the solid phase but not from the outside. Therefore, these surface molecules have some unbalanced or residual forces.

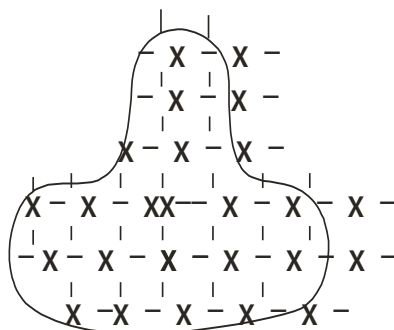


Fig. 15.1 : Molecules in the interior and at the surface of a solid

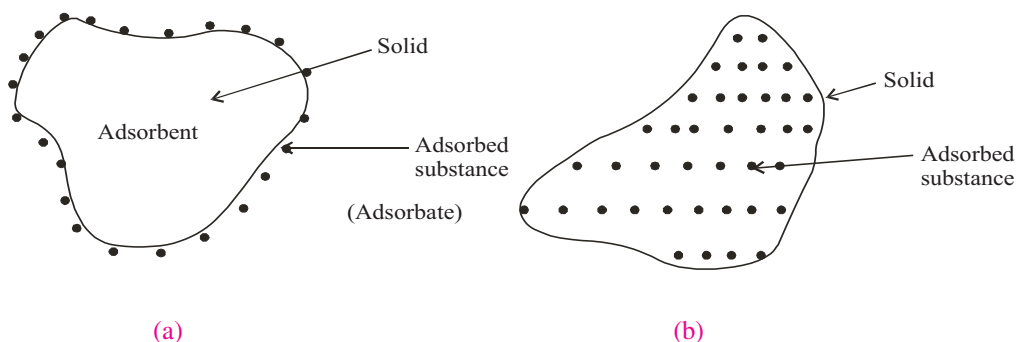


Fig. 15.2 : (a) Adsorption (b) Absorption

15.1.1 Adsorption and Absorption

The phenomenon of *adsorption* is different from that of *absorption*. The latter term implies that a substance is uniformly distributed throughout the body of a solid, Fig. 15.2(b). If we leave a small lump of calcium chloride in open, it absorbs water vapour (moisture) from air and after some time even starts dissolving in it. On the other hand if we keep a sample of silica gel in open, it adsorbs water vapour on its surface as shown in Fig. 15.2 (a).

15.1.2 Factors Affecting Adsorption

Adsorption occurs on the surface of almost all solids. However, the extent of adsorption of a gas on the surface of a solid depends upon the following factors:

- (i) Nature and surface area of the adsorbent
- (ii) Nature of the adsorbed gas
- (iii) Temperature
- (iv) Pressure of the gas

Let us now discuss these factors briefly.

(i) Nature and Surface Area of the Adsorbent

Different solids would adsorb different amounts of the same gas even under similar conditions. Substances like charcoal and silica gel are excellent adsorbents. The substances that are porous in nature and have rough surfaces are better adsorbents.

The extent of adsorption also depends upon the surface area of the solid. Greater the surface area, more is the surface available for adsorption and greater is the adsorption. The surface area depends upon the particle size of the substance. A cube of each side equal to 1 cm has six faces. Each of them is a square with surface area of 1 cm^2 . Thus, the total surface area of this cube is 6 cm^2 Fig. 15.3 (a). If its each side is divided into two equal halves, $\frac{1}{2}\text{ cm}$ long, and the cube is divided into two equal halves, $\frac{1}{2}\text{ cm}$ long, and the cube is cut along the lines indicated in the Fig (b), the cube would be divided into 8 smaller cubes with each side 0.5 cm long [Fig. 15.3 (b)]. Surface area of each small cube would be $(6 \times 0.5 \times 0.5) = 1.5\text{ cm}^2$ and the total surface area of all the 8 smaller cubes would be 12 cm^2 which is double the surface area of the original cube. If it is subdivided into smaller cubes, each of side equal to $1 \times 10^{-6}\text{ cm}$ the surface area will increase to $6 \times 10^6\text{ cm}^2$ or 600 m^2 . The increase in surface area would result in greater adsorption.

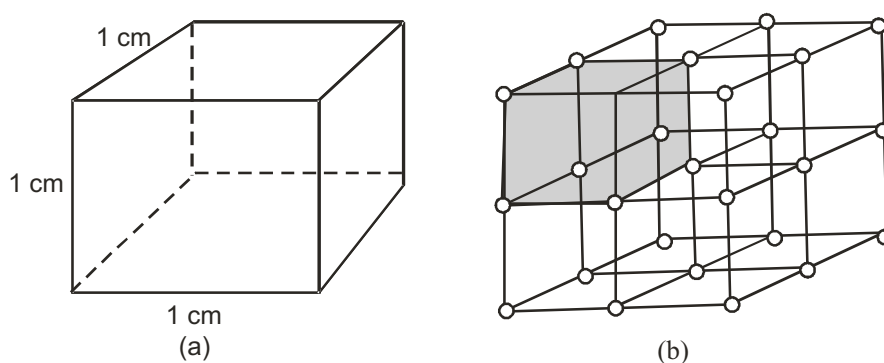


Fig. 15.3 : Subdivision of a cube



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Now we can explain why the solids that are porous in nature and have rough surfaces are better adsorbents. It is so because each of these features increases the surface area.

(ii) The Nature of the Adsorbed Gas

The extent of adsorption also depends upon the nature of the gas. The gases which are more easily liquifiable or are more soluble in water are more readily adsorbed than others. For example, under similar conditions, the amount of SO₂ or NH₃ adsorbed by charcoal is much more than that of H₂ or O₂ gases. It is because the intermolecular forces are stronger in more easily liquifiable gases, therefore, they get adsorbed more strongly.

(iii) Temperature

The extent of adsorption decreases with rise in temperature. For example, under one atmosphere pressure, one gram of charcoal adsorbs about 10 cm³ of N₂ gas at 272 K, 20 cm³ at 248 K and 45 cm³ at 195 K.

*Adsorption is an exothermic process. The change in enthalpy when one mole of a substance is adsorbed, is called **enthalpy of adsorption**. The adsorption process is similar to the condensation process. The reverse process is called **desorption** and is *endothermic* in nature. It is similar to the evaporation process. When a gas is kept in contact with a solid adsorbent in a closed container, a dynamic equilibrium is established in due course of time.*



Since the forward process (adsorption) is exothermic in nature, according to the Le Chatelier's principle, it would be favoured at low temperature. Therefore, the extent of adsorption would increase on decreasing the temperature and would decrease on increasing the temperature.

(iv) Pressure of the gas

At a constant temperature the extent of adsorption increases with increase in the pressure of the gas (adsorbate). We shall study the relation between the two in detail a little later.

15.1.3 Physical and Chemical Adsorption

Adsorption can be divided into two main categories – physical and chemical adsorption.

(i) Physical Adsorption

It is the common type of adsorption. The basic feature of **physical adsorption** is that the adsorbate molecules are held at the surface of the adsorbent by weak van

der Waals forces. These are the forces that exist between particles of all matter. Because of their universal nature, these forces would operate between any adsorbent and adsorbate pair. Therefore, the physical adsorption is observed on surface of any solid. Only, the extent of adsorption varies according to the nature of the adsorbent and adsorbate as discussed earlier.

Physical adsorption is characterized by low *enthalpy of adsorption*, that is about $10 - 40 \text{ kJ mol}^{-1}$.

Another feature of the physical adsorption of a gas by a solid is that it is *reversible* in nature and an equilibrium is established between the adsorbent and the adsorbate as discussed earlier. Increase of pressure increases the adsorption and the release of pressure desorbs the gas. When temperature is increased, the physical adsorption decreases and when it is lowered, the adsorption increases. In physical adsorption, several layers of adsorbate are adsorbed one over the other.

(ii) Chemisorption or Chemical Adsorption

We have seen earlier that some unsaturated valencies exist on the surface of a solid. Whenever a chemical combination takes place between the adsorbent and the adsorbate the adsorption becomes very strong. This type of adsorption caused by forces similar to chemical bonds between the adsorbent and the adsorbate is called **chemisorption** or **chemical adsorption**.

The enthalpy of chemisorption is as high as that of chemical bonds (bond enthalpies) and is in the range of $40 - 400 \text{ kJ mol}^{-1}$. Chemisorption is highly specific and is possible between a specific adsorbent – adsorbate pair. Like most of the chemical changes it is irreversible. Attempts to release the adsorbed gas gives the gas and some amount of a definite compound. For example, oxygen gas is chemisorbed on tungsten. It is released from the surface of tungsten as a mixture of oxygen and tungsten oxide. Unlike physical adsorption, chemisorption first increases and then decreases with rise in temperature [Fig. 15.4 (b)]. This shows that chemisorption has an energy of activation*. During chemisorption, only one layer of adsorbate molecules is adsorbed. The main distinctions between physical adsorption and chemisorption are summarized in Table 15.1.

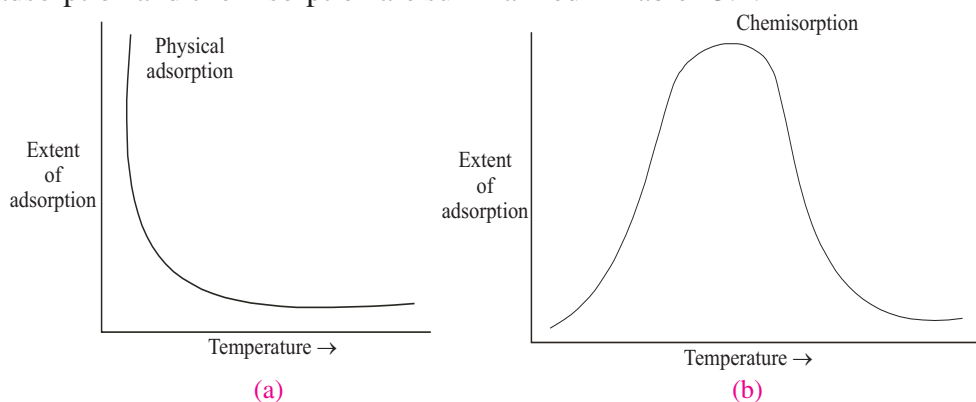


Fig. 15.4 : Effect of temperature on (a) physical adsorption and (b) chemisorption.

* You will learn more about energy of activation later in this lesson.



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Table 15.1 : Physical Adsorption and Chemisorption

Physical Adsorption	Chemisorption
1. The forces operating between adsorbate and adsorbent are the weak van der Waals forces.	1. The forces operating between adsorbate and adsorbent are strong and similar to chemical bonds.
2. The enthalpy of adsorption is low and ranges from 10 to 40 kJ mol ⁻¹ .	2. The enthalpy of adsorption is high and ranges from 40 to 400 kJ mol ⁻¹ .
3. No activation energy is involved.	3. Significant activation energy is involved.
4. Adsorption occurs more readily at low temperature and high pressure.	4. Chemisorption occurs at relatively high temperature and high pressure.
5. It is not specific in nature. All gases are adsorbed on all solids and no compounds are formed.	5. It is highly specific in nature and occurs between those adsorbents and adsorbates which have a possibility of compound formation between them.
6. It is reversible in nature. The gas is desorbed on increasing the temperature or decreasing the pressure.	6. It is irreversible in nature. Desorption also separates some amount of the compound formed.
7. Multilayer formation is common.	7. Monolayer formation occurs.



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15.1.4 Adsorption Isotherms

The extent of adsorption is measured in terms of the quantity $\frac{x}{m}$ where, x is the mass of the gas (adsorbate) adsorbed at equilibrium on mass m of the adsorbent. $\frac{x}{m}$ is the mass of the adsorbate adsorbed per unit mass of the adsorbent. The graph showing variation in $\frac{x}{m}$ with pressure (p) at a constant temperature is called **adsorption isotherm**. Let us see the variation in extent of adsorption in case of gases and of solutes from their solutions.

(i) Adsorption of Gases

The adsorption isotherm of a gas which is adsorbed on a solid is shown in Fig. 15.5. It shows that the extent of adsorption of a gas on a solid increases with the increase in the pressure of the gas, p at three different constant temperatures. The curves also show that the extent of adsorption, decreases at a fixed pressure as the temperature is increased (see the dotted line).

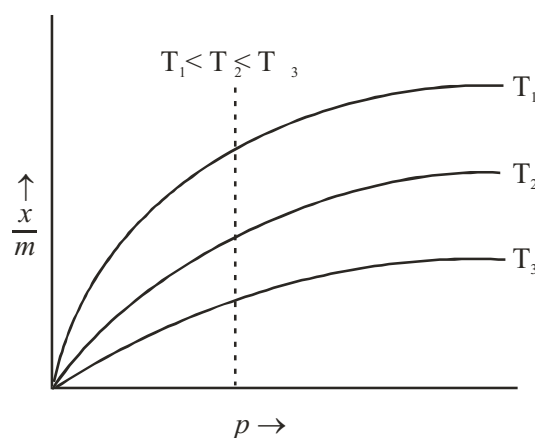


Fig. 17.5 : Adsorption isotherm of a gas

Freundlich Adsorption Isotherm

Freundlich gave an empirical mathematical relationship between the extent of adsorption $\left(\frac{x}{m}\right)$ and the equilibrium pressure (p) of the gas as :

$$\frac{x}{m} = k p^{\frac{1}{n}} \quad \text{where } n > 1$$

In this relation k is a constant at a given temperature and depends upon the nature of the adsorbate and adsorbent. The value of n changes with pressure. It is 1 at low pressures and increases with pressure. The relationship is valid at a constant temperature. Therefore, it is called **Freundlich Adsorption Isotherm**. On taking logarithm of the above equation, we get

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

This is an equation of a straight line and a plot of $\log \frac{x}{m}$ against $\log p$ should be a straight line with slope $\frac{1}{n}$ as depicted in Fig. 15.6. In actual practice, a straight line is obtained provided the data at very low and very high pressures is neglected.

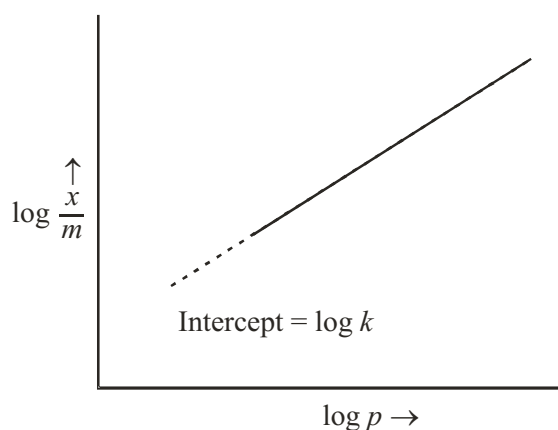


Fig. 15.6 : Plot of $\log \frac{x}{m}$ against $\log p$.

15.1.5 Langmuir Adsorption Isotherm

Adsorption Isotherm : One of the drawbacks of the Freundlich adsorption isotherm is that it fails at high pressure of the gas. Langmuir derived an adsorption isotherm on theoretical considerations based on kinetic theory of gases. This is



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named as the Langmuir adsorption isotherm. This isotherm is based on the assumption that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not nearby sites are occupied. In his derivation, Langmuir considered adsorption to consist of the following two opposing processes :

Adsorption of the gas molecules on the surface of the solid.

Desorption of the adsorbed molecules from the surface of the solid.

Langmuir believed that eventually a dynamic equilibrium is established between the above two opposing processes. He also assumed that the layer of the adsorbed gas is only one molecule thick i.e., unimolecular. Since such type of adsorption is obtained in the case of **chemisorption**. Langmuir adsorption isotherm works particularly well for chemisorption.

The Langmuir adsorption isotherm is represented by the relation.

$$\frac{x}{m} = \frac{a p}{1 + b p} \quad \dots(15.1)$$

where a and b are two Langmuir parameters. At very high pressure, the above isotherm acquires the limiting form.

$$\frac{x}{m} = \frac{a}{b} \quad (\text{at very high pressure}) \quad \dots(15.2)$$

At very low pressure, Eq. (15.1) is reduced to $x/m = ap$ (at very low pressure) $\dots(15.3)$

In order to determine the parameters a and b , Eq. (15.1) may be written in its inverse form:

$$\frac{m}{x} = \frac{1 + b p}{a p} = \frac{b}{a} + \frac{1}{a p} \quad \dots(15.4)$$

A plot of m/x against $1/p$ gives a straight line the slope and intercept equal to $1/a$ and b/a , respectively. Thus, both parameters can be determined.

The Langmuir isotherm, in the form of Eq. (15.1) is generally more successful in interpreting the data than the Freundlich isotherm when a monolayer is formed. A plot of x/m versus p is shown in (Fig15.7). At low pressures, according to Eq. (15.3), pressure x/m increases linearly with p . At high pressure according to Eq. (15.2), x/m becomes constant i.e. the surface is fully covered and change in pressure has no effect and no further adsorption takes place, as is evident from Fig. 15.7.

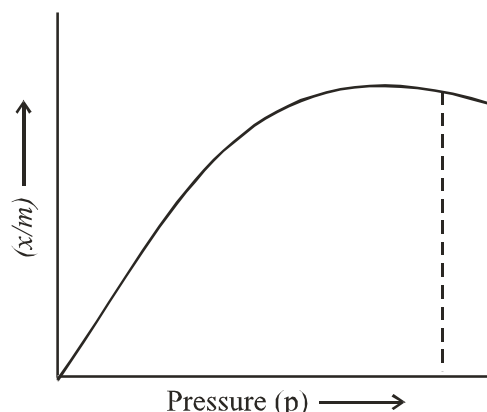


Fig. 15.7 : Langmuir Adsorption isotherm.

(ii) Adsorption from Solutions.

Adsorption occurs from solutions also. The solute gets adsorbed on the surface of a solid adsorbent. Charcoal, a good adsorbent, is often used to adsorb acetic acid, oxalic acid and organic dyestuffs from their aqueous solutions.

The extent of adsorption, $\frac{x}{m}$ depends upon the concentration c of the solute.

Freundlich isotherm is applicable to adsorption from solutions when concentration is used in place of pressure as shown below.

$$\frac{x}{m} = k c^{\frac{1}{n}}$$

and in the logarithmic form as

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log c$$

The plot of $\log \frac{x}{m}$ against c is also a straight line, provided very low and very high concentrations are avoided.

15.1.6 Applications of Adsorption

The phenomenon of adsorption finds many applications, some of which are given below:

1. Activated charcoal is used in gas masks in which toxic gases are adsorbed and air passes through it.
2. Silica gel packed in small cloth bags is used for adsorbing moisture in bottles of medicine and in small electronic instruments.
3. Animal charcoal is used for decolourizing many compounds during their manufacture.



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- 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 15.1

- 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.

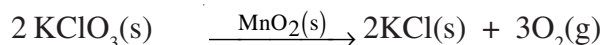
15.2 CATALYSIS

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**.

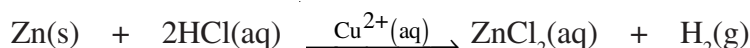
A catalyst is a substance which changes the rate of a reaction but remains chemically unchanged at the end of the reaction.

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:

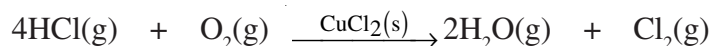
- Decomposition of potassium chlorate occurs at high temperature. If a small amount of the manganese dioxide is added, the decomposition occurs at much lower temperature. Here, manganese dioxide acts as catalyst.



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

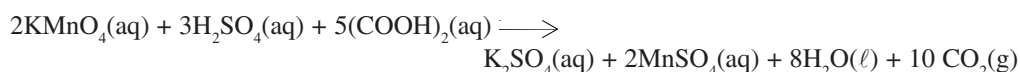


- The oxidation of hydrogen chloride gas by oxygen occurs more quickly if the gases are passed over cupric chloride.



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 :

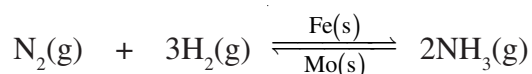
- (i) Glycerol retards the decomposition of hydrogen peroxide.
- (ii) Phenol retards the oxidation of sulphurous acid.

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 .

15.2.1 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.

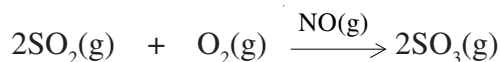
15.2.2 Homogeneous and Heterogeneous Catalysis

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).

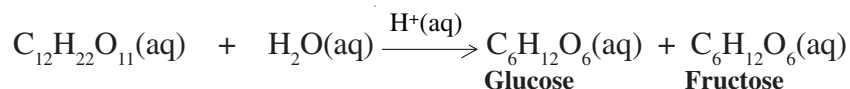
(a) *Homogeneous Catalysis*

*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.



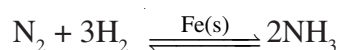
(ii) Hydrogen ions catalyse the *inversion of cane sugar*



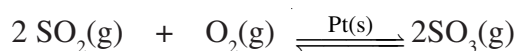
(b) Heterogeneous Catalysis

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



15.2.3 Catalysis and Activation Energy

We have seen that a catalyst increases the rate of a reaction. We explain it by considering the Fig 15.8.

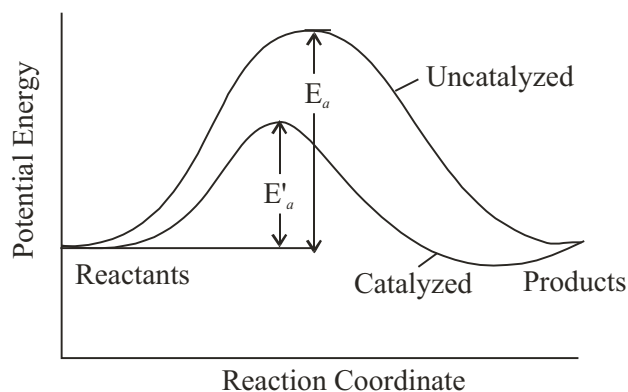


Fig. 15.8 : Graphical representation of the effect of catalyst on a reaction.

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.



Notes



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INTEXT QUESTIONS 15.2

1. List any two characteristics of a catalyst.
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

$$\frac{x}{m} = k p^n$$
- 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.
- 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.



Notes



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.

MODULE - 5

Chemical Dynamics



Notes

Adsorption and Catalysis

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.



ANSWERS TO THE INTEXT QUESTIONS

15.1

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

15.2

1. See text section 15.2.1
2. Negative catalyst
3. Increase
4. Promoters