5.1 Adsorption

There are several examples, which reveal that the surface of a solid has the tendency to attract and retain the molecules of the phase with which it comes into contact. These molecules remain only at the surface and do not go deeper into the bulk. **The accumulation of molecular species at the surface rather than in the bulk of a solid or liquid is termed adsorption**. The molecular species or substance, which concentrates or accumulates at the surface is termed **adsorbate** and the material on the surface of which the adsorption takes place is called **adsorbent**.

Adsorption is essentially a surface phenomenon. Solids, particularly in finely divided state, have large surface area and therefore, charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state, etc. act as good adsorbents.

Adsorption in action

- (i) If a gas like O₂, H₂, CO, Cl₂, NH₃ or SO₂ is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface.
- (ii) In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate turns colourless. The molecules of the dye, thus, accumulate on the surface of charcoal, i.e., are adsorbed.
- (iii) Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.
- (iv) The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

It is clear from the above examples that solid surfaces can hold the gas or liquid molecules by virtue of adsorption. The process of removing an adsorbed substance from a surface on which it is adsorbed is called **desorption**.

5.1.1 Distinction between Adsorption and Absorption

In adsorption, the substance is concentrated only at the surface and does not penetrate through the surface to the bulk of the adsorbent, while in absorption, the substance is uniformly distributed throughout the bulk of the solid. For example, when a chalk stick is dipped in ink, the surface retains the colour of the ink due to adsorption of coloured molecules while the solvent of the ink goes deeper into the stick due to absorption. On breaking the chalk stick, it is found to be white from inside. A distinction can be made between absorption and adsorption by taking an example of water vapour. Water vapours are absorbed by anhydrous calcium chloride but adsorbed by silica gel. In other words, in adsorption the concentration of the adsorbate increases only at the surface of the adsorbent, while in absorption the concentration is uniform throughout the bulk of the solid.

Both adsorption and absorption can take place simultaneously also. The term sorption is used to describe both the processes.

5.1.2 Mechanism of Adsorption

Adsorption arises due to the fact that the surface particles of the adsorbent are not in the same environment as the particles inside the bulk. Inside the adsorbent all the forces acting between the particles are mutually

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balanced but on the surface the particles are not surrounded by atoms or molecules of their kind on all sides, and hence they possess unbalanced or residual attractive forces. These forces of the adsorbent are responsible for attracting the adsorbate particles on its surface. The extent of adsorption increases with the increase of surface area per unit mass of the adsorbent at a given temperature and pressure.

Another important factor featuring adsorption is the heat of adsorption. During adsorption, there is always a decrease in residual forces of the surface, i.e., there is decrease in surface energy which appears as heat. Adsorption, therefore, is invariably an exothermic process. In other words, ΔH of adsorption is always negative. When a gas is adsorbed, the freedom of movement of its molecules become restricted. This amounts to decrease in the entropy of the gas after adsorption, i.e., ΔS is negative. Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a process to be spontaneous, the thermodynamic requirement is that, at constant temperature and pressure, ΔG must be negative, i.e., there is a decrease in Gibbs energy. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH has sufficiently high negative value as – $T\Delta S$ is positive. Thus, in an adsorption process, which is spontaneous, a combination of these two factors makes ΔG negative. As the adsorption proceeds, ΔH becomes less and less negative ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero. At this state equilibrium is attained.

5.1.3 Types of Adsorption

There are mainly two types of adsorption of gases on solids. If accumulation of gas on the surface of a solid occurs on account of weak van der Waals' forces, the adsorption is termed as **physical adsorption or physisorption**. When the gas molecules or atoms are held to the solid surface by chemical bonds, the adsorption is termed **chemical adsorption or chemisorption**. The chemical bonds may be covalent or ionic in nature. Chemisorption involves a high energy of activation and is, therefore, often referred to as activated adsorption. Sometimes these two processes occur simultaneously and it is not easy to ascertain the type of adsorption. A physical adsorption at low temperature may pass into chemisorption as the temperature is increased. For example, dihydrogen is first adsorbed on nickel by van der Waals' forces. Molecules of hydrogen then dissociate to form hydrogen atoms which are held on the surface by chemisorption.

Some of the important characteristics of both types of adsorption are described below:

Characteristics of physisorption

- (i) Lack of specificity: A given surface of an adsorbent does not show any preference for a particular gas as the van der Waals' forces are universal.
- (ii) *Nature of adsorbate:* The amount of gas adsorbed by a solid depends on the nature of gas. In general, easily liquefiable gases (i.e., with higher critical temperatures) are readily adsorbed as van der Waals' forces are stronger near the critical temperatures. Thus, 1g of activated charcoal adsorbs more sulphur dioxide (critical temperature 630K), than methane (critical temperature 190K) which is still more than 4.5 mL of dihydrogen (critical temperature 33K).

(iii) *Reversible nature:* Physical adsorption of a gas by a solid is generally reversible. Thus,

Solid + Gas ≠ Gas/Solid + Heat

More of gas is adsorbed when pressure is increased as the volume of the gas decreases (Le–Chateliers's principle) and the gas can be removed by decreasing pressure. Since the adsorption process is exothermic, the physical adsorption occurs readily at low temperature and decreases with increasing temperature (Le-Chatelier's principle).

- (iv) Surface area of adsorbent: The extent of adsorption increases with the increase of surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface areas are good adsorbents.
- (v) Enthalpy of adsorption: No doubt, physical adsorption is an exothermic process but its enthalpy of adsorption is quite low (20–40 kJ mol⁻¹). This is because the attraction between gas molecules and solid surface is only due to weak van der Waals' forces.

Characteristics of chemisorption

- (i) *High specificity:* Chemisorption is highly specific and it will only occur if there is some possibility of chemical bonding between adsorbent and adsorbate. For example, oxygen is adsorbed on metals by virtue of oxide formation and hydrogen is adsorbed by transition metals due to hydride formation.
- (ii) *Irreversibility:* As chemisorption involves compound formation, it is usually irreversible in nature. Chemisorption is also an exothermic process but the process is very slow at low temperatures on account of high energy of activation. Like most chemical changes, adsorption often increases with rise of temperature. Physisorption of a gas adsorbed at low temperature may change into chemisorption at a high temperature. Usually high pressure is also favourable for chemisorption.
- (iii) *Surface area:* Like physical adsorption, chemisorption also increases with increase of surface area of the adsorbent.
- (iv) *Enthalpy of adsorption:* Enthalpy of chemisorption is high (80-240 kJ mol⁻¹) as it involves chemical bond formation.

Table 5.1: Comparison of Physisorption and Chemisorption

Physisorption

- 1. It arises because of van der Waals' forces.
- **2.** It is not specific in nature.
- **3.** It is reversible in nature.
- **4.** It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.
- **5.** Enthalpy of adsorption is low (20-40 kJ mol⁻¹) in this case.

Chemisorption

- 1. It is caused by chemical bond formation.
- 2. It is highly specific in nature.
- **3**. It is irreversible.
- 4. It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
- **5.** Enthalpy of adsorption is high (80-240 kJ mol⁻¹) in this case.

- **6.** Low temperature is favourable for adsorption. It decreases with increase of temperature.
- 7. No appreciable activation energy is needed.
- **8.** It depends on the surface area. It increases with an increase of surface area.
- 9. It results into multimolecular layers on adsorbent surface under high pressure.
- **6.** High temperature is favourable for adsorption. It increases with the increase of temperature.
- **7.** High activation energy is sometimes needed.
- **8.** It also depends on the surface area. It too increases with an increase of surface area.
- **9.** It results into unimolecular layer.

5.1.4 Adsorption Isotherms

The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as **adsorption isotherm**.

Freundlich adsorption isotherm: Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature. The relationship can be expressed by the following equation:

$$\frac{x}{m} = k.p^{1/n} \ (n > 1)$$
 ... (5.1)

where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure P, k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature. The relationship is generally represented in the form of a curve where mass of the gas adsorbed per gram of the adsorbent is plotted against pressure (Fig. 5.1). These curves indicate that at a fixed pressure, there is a decrease in physical adsorption with increase in temperature. These curves always seem to approach saturation at high pressure.

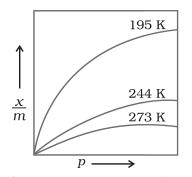


Fig. 5.1: Adsorption isotherm

Taking logarithm of eq. (5.1)

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \qquad \dots (5.2)$$

The validity of Freundlich isotherm can be verified by plotting $\log \frac{x}{m}$ on y-axis (ordinate) and $\log p$ on x-axis (abscissa). If it comes to be a straight line, the Freundlich isotherm is valid, otherwise not (Fig. 5.2). The slope of the straight line gives the value of $\frac{1}{n}$. The intercept on the y-axis gives the value of $\log k$.

Freundlich isotherm explains the behaviour of adsorption in an approximate manner. The factor $\frac{1}{n}$ can have values between 0 and 1 (probable range 0.1 to 0.5). Thus, equation (5.2) holds good over a limited range of pressure.

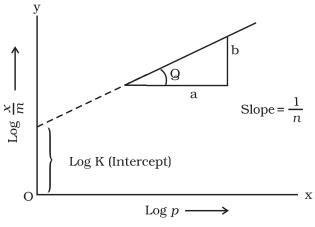


Fig. 5.2: Freundlich isotherm

When $\frac{1}{n} = 0$, $\frac{x}{m} = \text{constant}$, the adsorption is independent of pressure.

When $\frac{1}{n} = 1$, $\frac{x}{m} = k p$, i.e. $\frac{x}{m} \propto p$, the adsorption varies directly with pressure.

Both the conditions are supported by experimental results. The experimental isotherms always seem to approach saturation at high pressure. This cannot be explained by Freundlich isotherm. Thus, it fails at high pressure.

5.1.5 Adsorption from Solution Phase

Solids can adsorb solutes from solutions also. When a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by the charcoal and the concentration of the acid decreases in the solution. Similarly, the litmus solution when shaken with charcoal becomes colourless. The precipitate of $Mg(OH)_2$ attains blue colour when precipitated in presence of magneson reagent. The colour is due to adsorption of magneson. The following observations have been made in the case of adsorption from solution phase:

- (i) The extent of adsorption decreases with an increase in temperature.
- (ii) The extent of adsorption increases with an increase of surface area of the adsorbent.
- (iii) The extent of adsorption depends on the concentration of the solute in solution.
- (iv) The extent of adsorption depends on the nature of the adsorbent and the adsorbate.

The precise mechanism of adsorption from solution is not known. Freundlich's equation approximately describes the behaviour of adsorption from solution with a difference that instead of pressure, concentration of the solution is taken into account, i.e.,

$$\frac{x}{m} = kC^{1/n} \tag{5.3}$$

(*C* is the equilibrium concentration, i.e., when adsorption is complete). On taking logarithm of the above equation, we have

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C \qquad \dots (5.4)$$

Plotting $\log \frac{x}{m}$ against $\log C$ a straight line is obtained which shows the validity of Freundlich isotherm. This can be tested experimentally by taking solutions of different concentrations of acetic acid. Equal volumes of solutions are added to equal amounts of charcoal in different flasks. The final concentration is determined in each flask after adsorption. The difference in the initial and final concentrations give the value of x. Using the above equation, validity of Freundlich isotherm can be established.

5.1.6 Applications of Adsorption

The phenomenon of adsorption finds a number of applications. Important ones are listed here:

(i) *Production of high vacuum*: The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum.

- (ii) Gas masks: Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.
- (iii) Control of humidity: Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.
- (iv) Removal of colouring matter from solutions: Animal charcoal removes colours of solutions by adsorbing coloured impurities.
- (v) Heterogeneous catalysis: Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of $\rm H_2SO_4$ by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.
- (vi) Separation of inert gases: Due to the difference in degree of adsorption of gases by charcoal, a mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.
- (vii) *In curing diseases*: A number of drugs are used to kill germs by getting adsorbed on them.
- (viii) Froth floatation process: A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil and frothing agent (see Unit 6).
- (ix) Adsorption indicators: Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic colour at the end point.
- (x) Chromatographic analysis: Chromatographic analysis based on the phenomenon of adsorption finds a number of applications in analytical and industrial fields.

Intext Questions

- **5.1** Write any two characteristics of Chemisorption.
- **5.2** Why does physisorption decrease with the increase of temperature?
- **5.3** Why are powdered substances more effective adsorbents than their crystalline forms?

5.2 Catalysis

Potassium chlorate, when heated strongly decomposes slowly giving dioxygen. The decomposition occurs in the temperature range of 653-873K.

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

However, when a little of manganese dioxide is added, the decomposition takes place at a considerably lower temperature range, i.e., 473-633K and also at a much accelerated rate. The added manganese dioxide remains unchanged with respect to its mass and composition. In a similar manner, the rates of a number of chemical reactions can be altered by the mere presence of a foreign substance.

The systematic study of the effect of various foreign substances on the rates of chemical reactions was first made by Berzelius, in 1835. He suggested the term **catalyst** for such substances.

Substances, which accelerate the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as catalysts, and the phenomenon is known as catalysis. You have already studied about catalysts and its functioning in Section 4.5.

Promoters and poisons

Promoters are substances that enhance the activity of a catalyst while poisons decrease the activity of a catalyst. For example, in Haber's process for manufacture of ammonia, molybdenum acts as a promoter for iron which is used as a catalyst.

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

5.2.1

Homogeneous and Heterogeneous Catalysis

Catalysis can be broadly divided into two groups:

(a) Homogeneous catalysis

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

(i) Oxidation of sulphur dioxide into sulphur trioxide with dioxygen in the presence of oxides of nitrogen as the catalyst in the lead chamber process.

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

The reactants, sulphur dioxide and oxygen, and the catalyst, nitric oxide, are all in the same phase.

(ii) Hydrolysis of methyl acetate is catalysed by H⁺ ions furnished by hydrochloric acid.

$$CH_3COOCH_3(I) + H_2O(I) \xrightarrow{HCI(I)} CH_3COOH(aq) + CH_3OH(aq)$$

Both the reactants and the catalyst are in the same phase.

(iii) Hydrolysis of sugar is catalysed by H^+ ions furnished by sulphuric acid.

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{H_2SO_4(l)} C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$$
Solution
Solution
Solution

Both the reactants and the catalyst are in the same phase.

(b) 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:

(i) Oxidation of sulphur dioxide into sulphur trioxide in the presence of Pt.

$$2SO_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$$

The reactant is in gaseous state while the catalyst is in the solid state.

(ii) Combination between dinitrogen and dihydrogen to form ammonia in the presence of finely divided iron in **Haber's process**.

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

The reactants are in gaseous state while the catalyst is in the solid state.

(iii) Oxidation of ammonia into nitric oxide in the presence of platinum gauze in **Ostwald's process**.

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

The reactants are in gaseous state while the catalyst is in the solid state.

(iv) Hydrogenation of vegetable oils in the presence of finely divided nickel as catalyst.

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

One of the reactants is in liquid state and the other in gaseous state while the catalyst is in the solid state.

5.2.2 Adsorption Theory of Heterogeneous Catalysis

This theory explains the mechanism of heterogeneous catalysis. The old theory, known as adsorption theory of catalysis, was that the reactants in gaseous state or in solutions, are adsorbed on the surface of the solid catalyst. The increase in concentration reactants on the surface increases the rate of reaction. Adsorption

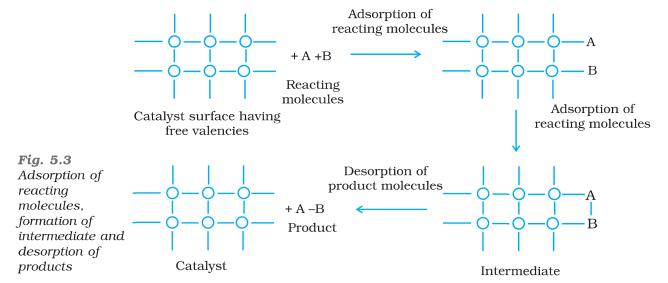
of the reactants on the surface increases the rate of reaction. Adsorption being an exothermic process, the heat of adsorption is utilised in enhancing the rate of the reaction.

The catalytic action can be explained in terms of the intermediate compound formation, the theory of which you have already studied in Section 4.5.1

The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory. The catalytic activity is localised on the surface of the catalyst. The mechanism involves five steps:

- (i) Diffusion of reactants to the surface of the catalyst.
- (ii) Adsorption of reactant molecules on the surface of the catalyst.
- (iii) Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate (Fig. 5.3).
- (iv) Desorption of reaction products from the catalyst surface, and thereby, making the surface available again for more reaction to occur.
- (v) Diffusion of reaction products away from the catalyst's surface. The surface of the catalyst unlike the inner part of the bulk, has free valencies which provide the seat for chemical forces of attraction. When a gas comes in contact with such a surface, its molecules are held up there due to loose chemical combination. If different molecules are adsorbed side by side, they may react with each other resulting in the formation of new molecules. Thus, formed molecules may evaporate leaving the surface for the fresh reactant molecules.

This theory explains why the catalyst remains unchanged in mass and chemical composition at the end of the reaction and is effective



even in small quantities. It however, does not explain the action of catalytic promoters and catalytic poisons.

Important features of solid catalysts

(a) Activity

The activity of a catalyst depends upon the strength of chemisorption to a large extent. The reactants must get adsorbed reasonably strongly on to the catalyst to become active. However, they must not get adsorbed so strongly that they are immobilised and other reactants are left with no space on the catalyst's surface for adsorption. It has been found that for hydrogenation reaction, the catalytic activity increases from Group 5 to Group 11 metals with maximum activity being shown by groups 7-9 elements of the periodic table (Class XI, Unit 3).

$$2H_2(g) + O_2(g) \xrightarrow{Pt} 2H_2O(1)$$

(b) Selectivity

The selectivity of a catalyst is its ability to direct a reaction to yield a particular product selectively, when under the same reaction conditions many products are possible. Selectivity of different catalysts for same reactants is different. For example, starting with H_2 and CO, and using different catalysts, we get different products.

(i)
$$CO(g) + 3H_2(g) \xrightarrow{Ni} CH_4(g) + H_2O(g)$$

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

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

Thus, it can be inferred that the action of a catalyst is highly selective in nature. As a result a substance which acts as a catalyst in one reaction may fail to catalyse another reaction.

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**. Zeolites are good shape-selective catalysts because of their honeycomb-like structures. They are microporous

5.2.3 Shape-Selective Catalysis by Zeolites

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aluminosilicates with three dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms giving Al–O–Si framework. The reactions taking place in zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of the zeolites. They are found in nature as well as synthesised for catalytic selectivity.

Zeolites are being very widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. An important zeolite catalyst used in the petroleum industry is ZSM-5. It converts alcohols directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons.

5.2.4 Enzyme Catalysis

Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. They are actually protein molecules of high molecular mass and form colloidal solutions in water. They are very effective catalysts; catalyse numerous reactions, especially those connected with natural processes. Numerous reactions that occur in the bodies of animals and plants to maintain the life process are catalysed by enzymes. The enzymes are, thus, termed as **biochemical catalysts** and the phenomenon is known as **biochemical catalysis**.

Many enzymes have been obtained in pure crystalline state from living cells. However, the first enzyme was synthesised in the laboratory in 1969. The following are some of the examples of enzyme-catalysed reactions:

(i) *Inversion of cane sugar*: The invertase enzyme converts cane sugar into glucose and fructose.

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{Invertase} C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$$
Cane sugar

Glucose

Fructose

(ii) Conversion of glucose into ethyl alcohol: The zymase enzyme converts glucose into ethyl alcohol and carbon dioxide.

$$\begin{array}{c} {\rm C_6H_{12}O_6(aq)} \xrightarrow{{\rm Zymase}} {\rm 2C_2H_5OH(aq)} + {\rm 2CO_2(g)} \\ {\rm Glucose} & {\rm Ethyl~alcohol} \end{array}$$

(iii) Conversion of starch into maltose: The diastase enzyme converts starch into maltose.

$$2(C_{\scriptscriptstyle 6}H_{\scriptscriptstyle 10}O_{\scriptscriptstyle 5})_{\scriptscriptstyle n}(aq) + nH_{\scriptscriptstyle 2}O(l) \xrightarrow{Diastase} nC_{\scriptscriptstyle 12}H_{\scriptscriptstyle 22}O_{\scriptscriptstyle 11}(aq)$$
 Starch Maltose

(iv) *Conversion of maltose into glucose*: The maltase enzyme converts maltose into glucose.

$$\begin{array}{c} C_{12}H_{22}O_{11}(aq) \,+\, H_2O(l) \xrightarrow{\quad Maltase \quad} 2C_6H_{12}O_6(aq) \\ \text{Maltose} & \text{Glucose} \end{array}$$

(v) Decomposition of urea into ammonia and carbon dioxide: The enzyme urease catalyses this decomposition.

$$NH_2CONH_2(aq) + H_2O(1) \xrightarrow{Urease} 2NH_3(g) + CO_2(g)$$

- (vi) In stomach, the pepsin enzyme converts proteins into peptides while in intestine, the pancreatic trypsin converts proteins into amino acids by hydrolysis.
- (vii) Conversion of milk into curd: It is an enzymatic reaction brought about by lacto bacilli enzyme present in curd.

Table 5.2 gives the summary of some important enzymatic reactions.

Table 5.2: Some Enzymatic Reactions

Enzyme	Source	Enzymatic reaction
Invertase	Yeast	Sucrose → Glucose and fructose
Zymase	Yeast	Glucose \rightarrow Ethyl alcohol and carbon dioxide
Diastase	Malt	Starch → Maltose
Maltase	Yeast	Maltose → Glucose
Urease	Soyabean	Urea → Ammonia and carbon dioxide
Pepsin	Stomach	Proteins \rightarrow Amino acids

Characteristics of enzyme catalysis

Enzyme catalysis is unique in its efficiency and high degree of specificity. The following characteristics are exhibited by enzyme catalysts:

- (i) Most highly efficient: One molecule of an enzyme may transform one million molecules of the reactant per minute.
- (ii) Highly specific nature: Each enzyme is specific for a given reaction, i.e., one catalyst cannot catalyse more than one reaction. For example, the enzyme urease catalyses the hydrolysis of urea only. It does not catalyse hydrolysis of any other amide.
- (iii) Highly active under optimum temperature: The rate of an enzyme reaction becomes maximum at a definite temperature, called the optimum temperature. On either side of the optimum temperature, the enzyme activity decreases. The optimum temperature range for enzymatic activity is 298-310K. Human body temperature being 310 K is suited for enzyme-catalysed reactions.
- (iv) *Highly active under optimum pH*: The rate of an enzyme-catalysed reaction is maximum at a particular pH called optimum pH, which is between pH values 5-7.
- (v) Increasing activity in presence of activators and co-enzymes: The enzymatic activity is increased in the presence of certain substances, known as co-enzymes. It has been observed that when a small non-protein (vitamin) is present along with an enzyme, the catalytic activity is enhanced considerably.
 - **Activators** are generally metal ions such as Na⁺, Mn²⁺, Co²⁺, Cu²⁺, etc. These metal ions, when weakly bonded to enzyme molecules, increase their catalytic activity. Amylase in presence of sodium chloride i.e., Na⁺ ions are catalytically very active.
- (vi) Influence of inhibitors and poisons: Like ordinary catalysts, enzymes are also inhibited or poisoned by the presence of certain substances. The inhibitors or poisons interact with the active functional groups on the enzyme surface and often reduce or completely destroy the catalytic activity of the enzymes. The use of many drugs is related to their action as enzyme inhibitors in the body.

Mechanism of enzyme catalysis

There are a number of cavities present on the surface of colloidal particles of enzymes. These cavities are of characteristic shape and possess active groups such as $-NH_2$, -COOH, -SH, -OH, etc. These are actually the active

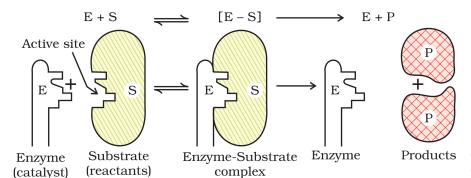


Fig. 5.4: Mechanism of enzyme catalysed reaction

centres on the surface of enzyme particles. The molecules of the reactant (substrate), which have complementary shape, fit into these cavities just like a key fits into a lock. On account of the presence of active groups, an activated complex is formed which then decomposes to yield the products.

Thus, the enzyme-catalysed reactions may be considered to proceed in two steps.

Step 1: Binding of enzyme to substrate to form an activated complex. $E + S \rightarrow ES^{\neq}$

Step 2: Decomposition of the activated complex to form product. $ES^{\neq} \rightarrow E + P$

5.2.5 Catalysts in Industry

Some of the important technical catalytic processes are listed in Table 5.3 to give an idea about the utility of catalysts in industries.

Table 5.3: Some Industrial Catalytic Processes

	Process	Catalyst
1.	Haber's process for the manufacture of ammonia $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	Finely divided iron, molybdenum as promoter; conditions: 200 bar pressure and 723-773K temperature. Now-a-days, a mixture of iron oxide, potassium oxide and alumina is used.
2.	Ostwald's process for the manufacture of nitric acid. $4\mathrm{NH_3}(g) + 5\mathrm{O_2}(g) \rightarrow 4\mathrm{NO}(g) + 6\mathrm{H_2O}(g)$ $2\mathrm{NO}(g) + \mathrm{O_2}(g) \rightarrow 2\mathrm{NO_2}(g)$ $4\mathrm{NO_2}(g) + 2\mathrm{H_2O}(l) + \mathrm{O_2}(g) \rightarrow 4\mathrm{HNO_3}(aq)$	Platinised asbestos; temperature 573K.
3.	Contact process for the manufacture of sulphuric acid. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $SO_3(g) + H_2SO_4(aq) \rightarrow H_2S_2O_7(l)$ oleum $H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(aq)$	Platinised asbestos or vanadium pentoxide (V_2O_5); temperature 673-723K.

Intext Questions

- **5.4** In Haber's process, hydrogen is obtained by reacting methane with steam in presence of NiO as catalyst. The process is known as steam reforming. Why is it necessary to remove CO when ammonia is obtained by Haber's process?
- **5.5** Why is the ester hydrolysis slow in the beginning and becomes faster after sometime?
- **5.6** What is the role of desorption in the process of catalysis.