CHAPTER 13

ADSORPTION AND CATALYSIS

ADSORPTION

13.1 INTRODUCTION

There are several examples which reveal the fact that the surface of a solid (or liquid) has a tendency to attract and retain the molecules of other immiscible phase with which it is brought into contact. These molecules remain only at the surface and do not go deeper into the bulk. **This tendency of accumulation of molecular species at the surface 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 whose surface the adsorption has taken place is called **adsorbent.**

Adsorption is essentially a **surface phenomenon** and solids, particularly in finely divided state, have large surface area and, therefore, show this property to a much larger extent than liquids. Charcoal, silica gel, alumina gel, clay, Fuller's earth, colloids, metals in finely divided state, etc., act as good **adsorbents.**

The adsorption of gases on metal surfaces is called occlusion.

Examples of Adsorption

(i) If a gas like Cl_2, NH_3 or SO_2 is enclosed in presence of powdered charcoal in a closed vessel, it is observed that the pressure of the gas 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 found that the filtrate obtained after filtration is colourless. The molecules of the dye, thus, concentrate on the surface of charcoal, *i.e.*, solute molecules from solution are adsorbed.

(iii) Water solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by animal charcoal.

(iv) The air becomes dry, *i.e.*, loses moisture in presence of silica gel. Molecules of water concentrate on the surface of gel, *i.e.*, are adsorbed.

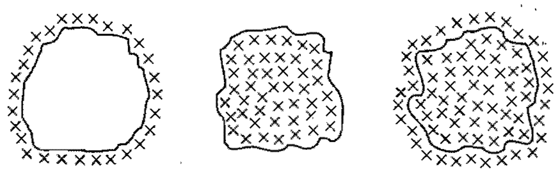
It is clear from the above examples that solid surfaces can hold the gas molecules, liquid molecules and also solid molecules by virtue of adsorption. **The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption.**

13.2 DISTINCTION BETWEEN ADSORPTION AND ABSORPTION

There are two similar sounding terms adsorption and absorption. Both the terms have different meanings. In adsorption, the substance is concentrated only at the surface and does not penetrate through the surface to go deep inside the bulk of the adsorbent, while in absorption, the substance is uniformly distributed throughout the bulk of the solid or liquid. For example, when a chalk stick is dipped in ink, the surface attains 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 that it is white from inside. Water vapours are absorbed by anhydrous calcium chloride while these are 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 take place simultaneously. **Mc Bain** introduced a general term **sorption** to describe both the

Note: Rate of adsorption is high at the beginning and then decreases till equilibrium is attained. On the other hand, rate of absorption remains same throughout the process.



Adsorption Absorption Sorption

Fig. 13.1

processes. However, adsorption is instantaneous, *i.e.*, a fast process while absorption is a slow process, *e.g.*,

(i) If silica gel is placed in a vessel containing water vapours, the latter are adsorbed on the former. On the other hand, if anhydrous $CaCl_2$ is kept in place of silica gel, absorption takes place as the water vapours are uniformly distributed in $CaCl_2$ to form hydrated calcium chloride ($CaCl_2 \cdot 2H_2O$).

(ii) Dyes get adsorbed as well as absorbed in the cotton fibres, *i.e.*, sorption takes place.

13.3 MECHANISM OF ADSORPTION

Adsorption is due to the fact that the surface particles of the adsorbent are in different state than the particles inside the bulk. Inside the adsorbent all the forces acting between the particles are mutually 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. This shows that with increase of surface area, the unbalanced attractive forces of the surface are also increased.

Another important factor regarding adsorption is the **heat of adsorption.** During adsorption, there is always decrease in residual forces of the surface, *i.e.*, there is decrease in surface energy which appears as heat. **Adsorption, therefore, is invariably accompanied by evolution of heat,** *i.e.*, it is an exothermic process. In other words, ΔH of adsorption is always negative. When a gas is adsorbed, the freedom of movement of its molecules becomes 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 instantaneous, the thermodynamic requirement is that ΔG must be negative, *i.e.*, there is decrease in free 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,

ΔS is negative,

ΔH is also sufficiently negative,

and as a combination of these two factors,

ΔG is negative.

ΔH becomes less and less negative as adsorption proceeds further and further. Ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero. This is the state at which equilibrium is attained.

13.4 TYPES OF ADSORPTION (Adsorption of Gases)

There are two main 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 has a rather 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, hydrogen is first adsorbed on nickel by van der Waals' forces. Molecules of hydrogen then dissociate and hydrogen atoms are held on the surface by chemisorption.

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

1. Characteristics of physical adsorption

(i) Lack of specificity: The surface of an adsorbent does not show very strong attraction for a particular gas as the van der Waals' forces are universal.

(ii) Nature of gas: The amount of gas adsorbed by a solid depends on the nature of gas. In general, more easily liquefiable gases (*i.e.*, higher critical temperatures) are readily adsorbed as van der Waals' forces are stronger near the critical temperatures. Thus, 1 g of activated charcoal adsorbs 380 mL of sulphur dioxide (critical temp. 157° C), 16 mL of methane (critical temp. − 83° C) and 4.5 mL of hydrogen (critical temp. −240° C).

Gas	H_2	N_2	CO	CH_4	CO_2	HCl	NH_3	SO_2
Volume adsorbed (c.c.)	4.5	8	9.3	16.2	48	72	181	380
Critical temperature (K)	33	126	134	190	304	324	406	430

(iii) Reversible nature: Physical adsorption of a gas by a solid is generally reversible. The gas adsorbed can be removed by reversing the conditions of temperature and pressure. Thus,

$$\text{Gas} \rightleftharpoons \text{Gas/Solid} + \text{Heat}$$

More of gas is adsorbed when pressure is increased as the volume of the gas decreases (Le-Chatelier's principle) and it 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). As the activation energy in the physical adsorption is more or less zero, the rate of adsorption is not affected even at low temperature.

(iv) Surface area of adsorbent: The extent of adsorption increases with increase of surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface areas are good adsorbents.

(v) Heat of adsorption: No doubt, physical adsorption is an exothermic process but its heat of adsorption is quite low

(20 – 40 kJ mol^{-1} or about 5 kcal mol^{-1}) since the attraction between gas molecules and solid surface is due to weak van der Waals' forces.

2. Characteristics of chemisorption

(i) High specificity: Chemisorption is highly specific and it will only occur if there is some possibility of chemical bonding. For example, oxygen is adsorbed on metals by virtue of oxide formation and hydrogen is adsorbed by transition metals with unpaired *d*-orbitals leading to hydride formation.

(ii) Nature of gas: Chemisorption will occur if there is some possibility of chemical action between the gas and the solid adsorbent.

(iii) Irreversibility: As chemisorption involves compound formation, it is commonly irreversible in nature. Chemisorption is also an exothermic process but the process is very slow at low temperature on account of high energy of activation. Like most chemical changes, it often increases with rise of temperature. A gas adsorbed at low temperature by physical adsorption may change into chemisorption at high temperature.

High pressure is favourable for chemisorption.

(iv) Surface area: Like physical adsorption, chemisorption also increases with increase of surface area of the adsorbent.

(v) Heat of adsorption: Heat of adsorption is high enough (40–400 kJ/mol) as chemisorption involves bond formation.

Comparison of physisorption and chemisorption

	Physical adsorption	Chemical adsorption
1.	It is caused by intermolecular van der Waals' forces.	It is caused by chemical bond formation.
2.	It is not specific.	It is highly specific.
3.	It is reversible.	It is irreversible.
4.	It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It depends on the nature of gas. Gases which form compounds with the adsorbent exhibit chemisorption.
5.	Heat of adsorption is low.	Heat of adsorption is high.
6.	Low temperature is favourable. It decreases with increase of temperature.	High temperature is favourable. It increases with increase of temperature.
7.	No appreciable activation energy is involved.	High activation energy is involved.
8.	High pressure is favourable. Decrease of pressure causes desorption.	High pressure is favourable. Decrease of pressure does not cause desorption.
9.	It depends on the surface area. It increases with increase of surface area.	It also depends on the surface area. It increases with increase of surface area.
10.	It forms multilayers on adsorbent surface under high pressure.	It forms unimolecular layer.

Adsorption of N_2 on the Surface of Iron

Nature of adsorption of nitrogen on the surface of iron depends on the temperature. At 83 K, nitrogen is physisorbed on iron surface as N_2 molecules. The degree of adsorption decreases rapidly as the temperature increases. At room temperature, there is no adsorption of N_2 on iron. When temperature is further increased up to 773 K and above, then nitrogen is chemisorbed on the iron surface as nitrogen atom.

Activation of Adsorption

Adsorbing power of an adsorbent can be increased by a number of ways. Some important methods are described below:

(i) Metallic adsorbents are activated by rubbing the surface.

(ii) Activity of adsorbent can be increased by taking it in powdered state because in the powdered state the surface area is maximum.

(iii) Adsorbing power of adsorbent can be increased by heating with superheated steam. For example, the charcoal is activated by heating between 650 K and 1330 K in vacuum, air or superheated steam.

13.5 ADSORPTION ISOTHERMS

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

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:

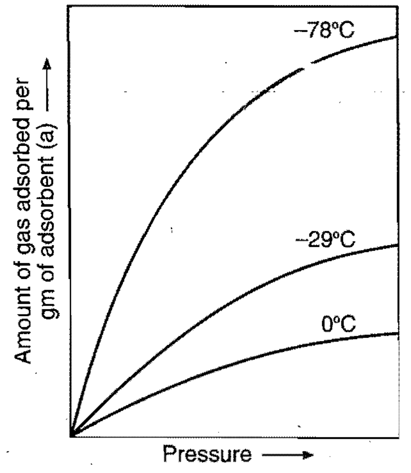


Fig. 13.2 Adsorption isotherm

$$\frac{x}{m} = k \cdot P^{1/n} \qquad \ldots (i)$$

where 'x' is the mass of the gas adsorbed on a mass 'm' of the adsorbent at a 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 when mass of the gas adsorbed per gram of the adsorbent is plotted against the pressure (Fig. 13.2). These curves indicate that at a fixed pressure, there is decrease in physical adsorption with increase in temperature. These curves always seem to approach saturation at high pressure.

Taking logarithm of equation (i),

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P \qquad \ldots \text{(ii)}$$

This is the equation of a straight line. 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. 13.3(a)]. The slope of the straight line gives the value of $1/n$.

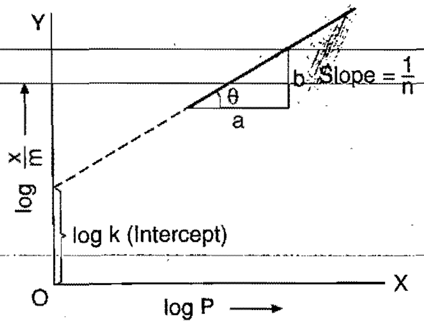


Fig. 13.3 (a) Freundlich isotherm

$$\tan \theta = \frac{b}{a} = \frac{1}{n}$$

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 $1/n$ can have values between 0 and 1 (probable range 0.1 to 0.5). Thus, equation (i) holds good over a limited range of pressure.

When $1/n = 0, x/m =$ constant which shows that adsorption is independent of pressure. When, $1/n = 1$, $x/m = kP$, *i.e.*, $x/m \propto P$. The adsorption varies directly with pressure. See graph in Fig. 13.3(b).

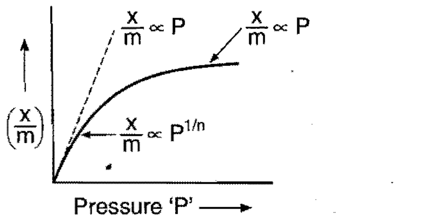


Fig. 13.3(b)

Both the above 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.

Shortcomings of Freundlich adsorption isotherm:

(i) Concept of Freundlich adsorption is purely empirical.

(ii) It does not consider the role of surface area of adsorbent in the process of adsorption.

(iii) It is unable to explain, why the degree of adsorption is constant at higher pressure.

(iv) It is applicable for only physical adsorption because it considers multimolecular layer of adsorption.

The Freundlich adsorption isotherm was modified by Langmuir in 1916.

Langmuir adsorption isotherm: Langmuir (1916) derived a simple adsorption isotherm. He postulated the following theory of adsorption:

(i) Gases form unimolecular layer of adsorption on the surface of adsorbate.

(ii) Gases undergoing adsorption behave ideally.

(iii) Adjacent adsorbed molecules do not interact. In other words, adsorption of a gas molecule at a particular site is independent, whether the neighbouring sites are adsorbed or not.

(iv) Dynamic equilibrium exists on the surface of adsorbent, *i.e.*, two opposite processes take place simultaneously on the surface of adsorbent.

(a) Adsorption or condensation of gas molecules on the surface of solid or adsorbent.

(b) Desorption or evaporation of gas molecules from the surface of adsorbent.

At the stage of adsorption equilibrium, the rate of adsorption becomes equal to the rate of desorption.

Let us derive mathematical relation of adsorption isotherm. Let θ is the fraction of surface area of adsorbent covered by the gas molecules, then $(1-\theta)$ will be the fraction of surface area base which is available for adsorption. Rate of adsorption depends on the fraction of surface area base and the pressure of gas on the surface of adsorbent.

$$\text{Rate of adsorption} = k_1 (1-\theta)P \qquad \ldots \text{(i)}$$

Rate of desorption is directly proportional to the fraction of surface area of adsorbent occupied.

$$\text{Rate of desorption} = k_2\theta \qquad \ldots \text{(ii)}$$

At equilibrium,

$$\text{Rate of adsorption} = \text{Rate of desorption}$$

$$k_1 (1-\theta)P = k_2\theta$$

$$\theta = \frac{k_1 P}{k_2 + k_1 P}$$

$$\theta = \frac{(k_1/k_2)P}{1+\left(\frac{k_1}{k_2}\right)P} = \frac{KP}{1+KP}$$

where, $K = \frac{k_1}{k_2} =$ constant

According to Langmuir, the degree of adsorption is directly proportional to the θ, *i.e.*, fraction of surface area occupied.

$$\frac{x}{m} \propto \theta = \frac{k\,KP}{1+KP} = \frac{K'P}{1+KP} \qquad \ldots \text{(iii)}$$

where, $K' = kK$

Equation (iii) can be rearranged as:

$$\frac{P}{(x/m)} = \frac{1}{K'} + \left(\frac{K}{K'}\right)P$$

It is of the form $y = c + mx$, *i.e.*, equation of straight line but not passing through origin. By plotting $\frac{P}{(x/m)}$ against 'P' we get a straight line.

Slope of the line $AB = \frac{K}{K'} = \tan\theta$

Intercept of the line $= \frac{1}{K'} =$ length OA

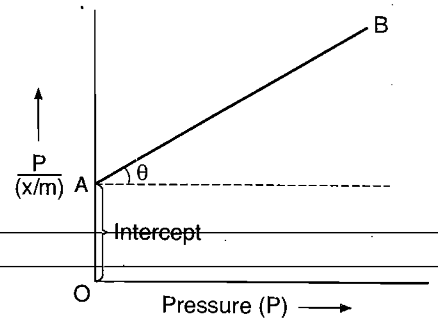


Fig. 13.3(c) Plot of Langmuir adsorption isotherm

Interpretation of Langmuir adsorption isotherm: Let us consider the mathematical relation

$$\frac{x}{m} = \frac{K'P}{1 + KP}$$

Case I. When pressure is very high then $1 + KP \approx KP$

$$\therefore \qquad \frac{x}{m} = \frac{K'P}{KP} = \text{constant}$$

Thus, at high pressure, the degree of adsorption approaches a limiting value.

Case II. When pressure is low then $1 + KP \approx 1$

$$\therefore \qquad \frac{x}{m} = K'P$$

Thus, degree of adsorption is directly proportional to pressure.

Case III. When pressure is moderate then expression is of the form $\frac{x}{m} = KP^{1/n}$; where, $\frac{1}{n}$ lies between 0 and 1.

Alternatively,

If Langmuir adsorption isotherm is expressed as:

$$\frac{x}{m} = \frac{aP}{1 + bP} \qquad \text{...(i)}$$

then, $$\frac{P}{(x/m)} = \frac{1}{a} + \frac{b}{a}P \qquad \text{...(ii)}$$

Thus, a plot of $\frac{P}{(x/m)}$ against will be a straight line with slope $\frac{b}{a}$ and intercept $\frac{1}{a}$.

Equation (i) may also be taken as:

$$\frac{m}{x} = \frac{b}{a} + \frac{1}{a} \times \frac{1}{P}$$

When, $\left(\frac{m}{x}\right)$ is plotted against $\frac{1}{P}$, we get straight line with slope $\left(\frac{1}{a}\right)$ and intercept $\left(\frac{b}{a}\right)$.

13.6 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. The litmus solution when shaken with charcoal becomes colourless. The precipitate of $Mg(OH)_2$ attains blue colour when precipitated in presence of magneson. 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 the increase of temperature.

(ii) The extent of adsorption increases with the 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.

When the concentration of adsorbate is more on the surface of the adsorbent than in the bulk, it is called positive adsorption. If the concentration of the adsorbate is less relative to its concentration in the bulk, it is called negative adsorption.

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

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

(C is the equilibrium concentration, *i.e.*, when adsorption is complete.)

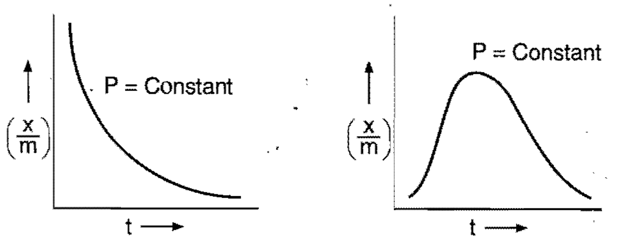
On taking logarithm of the above equation, we have

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

Plotting $\log x/m$ 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 concentration and final concentration gives the value of x. Using the above equation, validity of Freundlich isotherm can be established.

13.7 ADSORPTION ISOBARS AND ISOSTERE

A graph drawn between degree of adsorption (x/m) and temperature 't' at a constant pressure of adsorbate gas is known as adsorption isobar.



(Physisorption isobar) (Chemisorption isobar)

Fig. 13.4

Adsorption isobars of physical and chemical adsorptions show an important difference and this difference is helpful in distinguishing these two types of adsorption.

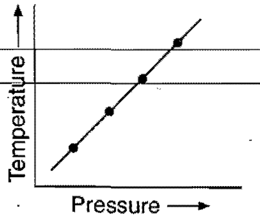


Fig. 13.5

Adsorption Isostere: Degree of adsorption depends on temperature as well as on pressure. When temperature increases, the extent of adsorption decreases. A linear relationship should exist between temperature and pressure with a certain amount of adsorption. *The plot of temperature versus pressure for a given amount of adsorption is called adsorption isostere.*

Preferential Adsorption OR Competing Adsorption

Whenever a mixture is allowed to come in contact with a particular adsorbent under the same conditions, the more strongly adsorbable adsorbate is adsorbed to a greater extent irrespective of its amount present. A preferentially adsorbable adsorbate can displace a weakly adsorbed substance from the surface of the adsorbent.

Determination of Surface Area of Adsorbent

If V litre of a gas is adsorbed at temperature T and pressure 'P' then number of gas molecules adsorbed will be:

$$\text{Number of molecules} = \left(\frac{PV}{RT}\right) \times 6.023 \times 10^{23} \quad \ldots\text{(i)}$$

If monomolecular layer of adsorption is formed then:

Surface area of adsorbent

= Number of molecules × Area of cross-section of a molecule

Area of cross section of molecule is usually determined from the density of the liquefied or solidified adsorbate.

$$\text{Volume of gas molecule} = \frac{M}{\rho \times 6.023 \times 10^{23}}$$

$$\frac{4}{3}\pi r^3 = \frac{M}{\rho N_A}$$

$$r = \left[\frac{3}{4\pi}\frac{M}{\rho N_A}\right]^{1/3}$$

$$\text{Area of cross-section} = \pi r^2 = \pi\left[\frac{3}{4\pi}\frac{M}{\rho N_A}\right]^{2/3}$$

13.8 APPLICATIONS OF ADSORPTION

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

1. **Production of high vacuum:** A bulb of charcoal cooled in liquid air is connected to a vessel which has already been exhausted as far as possible by a vacuum pump. The remaining traces of air are adsorbed by the charcoal. This results in a very high vacuum.

2. **Gas masks:** Gas mask is a device which consists of activated charcoal or a mixture or adsorbents. This apparatus is used to adsorb poisonous gases and thus purify the air for breathing.

3. **Humidity control:** Silica and aluminium gels are used as adsorbents for removing moisture. These gels are used for controlling humidity of rooms. Silica gel is also used in desiccators.

4. **Removal of colouring matter from solution:** Animal charcoal removes colours of solutions by adsorbing coloured impurities. Animal charcoal is used as decolouriser in the manufacture of cane sugar.

5. **Heterogeneous catalysis:** Adsorption of reactants on the solid surface of the catalysts affects the rate of reaction between the reactants. The reaction proceeds more rapidly after adsorption. There are many gaseous reactions of industrial importance involving solid catalysts. Manufacture of ammonia using iron as a catalyst, manufacture of H_2SO_4 by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.

6. **Separation of inert gases:** Due to the difference in degree of adsorption of gases by charcoal, a mixture of inert gases can be separated by adsorption on coconut charcoal at different low temperatures.

7. **Softening of hard water:** The hard water is made to pass through a column packed with zeolite (sodium aluminium silicate). Ca^{2+} and Mg^{2+} ions, which are responsible for hardness, get adsorbed on zeolite, exchanging sodium ions.

$$Na_2Al_2Si_2O_8 + CaCl_2 \longrightarrow CaAl_2Si_2O_8 + 2NaCl$$

The exhausted zeolite is regenerated with 10% of sodium chloride solution.

$$CaAl_2Si_2O_8 + 2NaCl \longrightarrow Na_2Al_2Si_2O_8 + CaCl_2$$

8. **Deionisation of water:** Water can be deionised by removing all dissolved salts with the help of cation and anion-exchanger resin. Cation-exchanger is an organic synthetic resin such as polystyrene containing a macroanion (R—SO_3^-) which has adsorbed H^+ ions. A resin containing a basic group (—N^+R_3) which has adsorbed OH^- ions acts as anion-exchanger. The water containing dissolved salts is first passed through cation-exchanger and then through anion-exchanger. The cation-exchanger removes the cations by exchange with H^+ ions while anion-exchanger removes the anions by exchange with OH^- ions:

$$\underset{\text{Cation-exchanger}}{R^- {-}{-}{-} H^+} + Na^+ \longrightarrow R^- {-}{-}{-} Na^+ + H^+$$

$$\underset{\text{Anion-exchanger}}{R^+ {-}{-}{-} OH^-} + Cl^- \longrightarrow R^+ {-}{-}{-} Cl^- + OH^-$$

The H^+ and OH^- ions thus produced react with each other to form water molecules.

$$H^+ + OH^- \longrightarrow H_2O$$

9. In curing diseases: A number of drugs are adsorbed on the germs and kill them or these are adsorbed on the tissues and heat them.

10. Cleaning agents: Soaps and detergents get adsorbed on the interface and thus reduce the surface tension between dirt and cloth, subsequently the dirt is removed from the cloth.

11. Froth floatation process: A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method. The finely divided ore is added to water containing pine oil and foaming agent. The air is bubbled through the mixture. The foam formed rises to the surface on which mineral particles wetted with oil are adsorbed while earthy matter settles down at the bottom.

12. Adsorption indicators: Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. In the case of precipitation titrations (for example $AgNO_3$ *versus* NaCl) the indicator is adsorbed at the end point producing a characteristic colour on the precipitate.

13. Chromatographic analysis: The phenomenon of adsorption has given an excellent technique of analysis known as chromatographic analysis. The technique finds a number of applications in analytical and industrial fields.

14. Surfactants: Surfactants work as emulsifier in the manufacture of emulsion. The emulsifiers work on the principle of adsorption.

15. Adsorption and kinetics: Many reactions that occur on a metal surface are of zero-order, *e.g.*, decomposition of N_2O on platinum surface. It is because the rate determining step occurs on the surface itself. Once the surface of adsorbent gets covered by the reactant, the rate of reaction becomes independent of concentration of the reactant.

CATALYSIS

13.9 INTRODUCTION

Potassium chlorate when strongly heated decomposes slowly giving oxygen. The decomposition occurs in the temperature range of 380–600°C.

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

However, when a little of manganese dioxide is added, the decomposition takes place at a considerable lower temperature range, *i.e.*, 200–360°C at a much accelerated rate. The manganese dioxide added remains unchanged with regard 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 name **catalyst,** for such substances.

Substances which thus alter the velocity of a reaction, themselves remaining chemically and quantitatively unchanged after the reaction, are known as **catalysts** and the phenomenon is known as **catalysis.** Ostwald (1895), defined a catalyst as: *a substance which changes the reaction rate without affecting the overall energetics of the reaction.*

13.10 HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

Catalytic reactions can be broadly divided into two groups:

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:

(i) Oxidation of sulphur dioxide into sulphur trioxide with oxygen 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 are in gaseous state. The catalyst nitric oxide is also in gaseous state, *i.e.*, all are in the same phase.

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

$$CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(l) + CH_3OH(l)^*$$

Both the reactants and catalyst are in the same phase.

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

$$\underset{\text{Solution}}{C_{12}H_{22}O_{11}(l)} + H_2O(l) \xrightarrow{H_2SO_4(l)} \underbrace{\underset{\text{Glucose}}{C_6H_{12}O_6(l)} + \underset{\text{Fructose}}{C_6H_{12}O_6(l)}}_{\text{Solution}}$$

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

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:

(i) Oxidation of sulphur dioxide into sulphur trioxide in the presence of platinum metal or vanadium pentoxide as catalyst in the contact process for the manufacture of sulphuric acid.

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

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

(ii) Combination between nitrogen and hydrogen to form ammonia in the presence of finely divided iron in Haber process.

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

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

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

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

---

*(l) represents liquid or solution in chemical reactions.

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.

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

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

13.11 TYPES OF CATALYSIS

Catalytic reactions are of the following types:

1. Positive catalysis: When the rate of reaction is accelerated by the foreign substance, it is said to be a **positive catalyst** and the phenomenon as **positive catalysis.**

Examples of positive catalysis:

(i) Decomposition of H_2O_2 in presence of colloidal platinum.

$$2H_2O_2(l) \xrightarrow{Pt} 2H_2O(l) + O_2(g)$$

(ii) Decomposition of $KClO_3$ in presence of manganese dioxide.

$$2KClO_3(s) \xrightarrow[270°C]{MnO_2(s)} 2KCl(s) + 3O_2(g)$$

(iii) Oxidation of ammonia in presence of platinum gauze.

$$4NH_3(g) + 5O_2(g) \xrightarrow[300°C]{Pt(s)} 4NO(g) + 6H_2O(g)$$

(iv) Oxidation of sulphur dioxide in presence of nitric oxide.

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

(v) Oxidation of sulphur dioxide in presence of platinized asbestos or vanadium pentoxide.

$$2SO_2(g) + O_2(g) \xrightarrow[\text{or } Pt(s)]{V_2O_5(s)} 2SO_3(g)$$

(vi) Oxidation of hydrochloric acid into chlorine by Deacon's process in presence of $CuCl_2$.

$$4HCl(g) + O_2(g) \xrightarrow[450°C]{CuCl_2(s)} 2Cl_2(g) + 2H_2O(g)$$

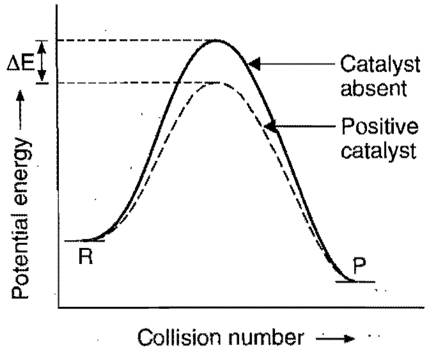


Fig. 13.6

(vii) Hydrogenation of vegetable oil in presence of nickel.

$$\text{Vegetable oil}(l) + H_2(g) \xrightarrow{Ni(s)} \text{Vanaspati ghee}(s)$$

(viii) Synthesis of ammonia by Haber process in presence of a mixture of iron and molybdenum.

$$N_2(g) + 3H_2(g) \xrightarrow[450\text{-}500°C]{Fe(s)} 2NH_3(g)$$

(ix) Manufacture of methyl alcohol in presence of ZnO/Cr_2O_3.

$$CO(g) + 2H_2(g) \xrightarrow[Cr_2O_3(s)]{ZnO(s),\ 250°C} CH_3OH(g)$$

(x) Formation of methane in presence of nickel.

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

Positive catalyst increases the rate by lowering activation energy of reaction. Catalyst changes the mechanism by changing the intermediate, *i.e.*, an intermediate of low energy is formed. It increases the rate by converting some inactive molecules into active ones.

From chemical kinetics:

$$\frac{k_p}{k_a} = e^{\Delta E/RT}$$

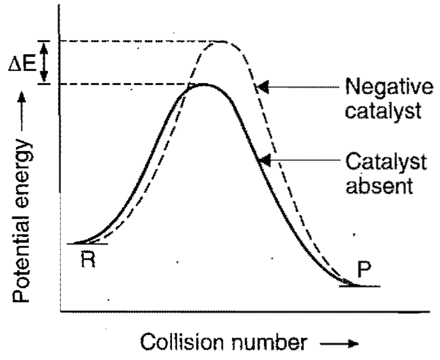
where, k_p = rate constant in presence of catalyst, k_a = rate constant in absence of catalyst.

ΔE = Lowering of activation energy

$$\log_e\left(\frac{k_p}{k_a}\right) = \frac{\Delta E}{RT}$$

$$\frac{k_p}{k_a} = \text{antilog}\left[\frac{\Delta E}{2.303\,RT}\right]$$

2. Negative catalysis: There are certain substances which, when added to the reaction mixture, retard the reaction rate instead of increasing it. These are called **negative catalysts** or **inhibitors** and the phenomenon is known as **negative catalysis.**



ΔE = Increased activation energy

Fig. 13.7

Examples of negative catalysis:

(i) The oxidation of sodium sulphite by air is retarded by alcohol.

$$2Na_2SO_3(s) + O_2(g) \xrightarrow{Alcohol(l)} 2Na_2SO_4(s)$$

Alcohol acts as a negative catalyst.

(ii) The decomposition of hydrogen peroxide decreases in presence of glycerine. Thus, in this reaction glycerine acts as a negative catalyst.

$$2H_2O_2(l) \xrightarrow{\text{Glycerine}(l)} 2H_2O(l) + O_2(g)$$

(iii) The oxidation of chloroform by air is retarded if some alcohol is added to it.

$$2CHCl_3(l) + O_2(g) \xrightarrow{\text{Alcohol}(l)} 2COCl_2(g) + 2HCl(g)$$

(iv) The oxidation of benzaldehyde is retarded if some diphenyl amine is added. It acts as a negative catalyst.

$$2C_6H_5CHO(l) + O_2(g) \xrightarrow{\text{Diphenyl amine}(l)} 2C_6H_5COOH(l)$$

(v) Tetraethyl lead (TEL) acts as an antiknocking agent in the case of petrol. Thus, it decreases knocking of petrol and acts as a negative catalyst.

(vi) Addition of small amount of acetanilide shows slow decomposition of hydrogen peroxide.

Negative catalysts decrease the rate by increasing the activation energy of reaction. Mechanism is altered by altering the intermediate; the new intermediate lies at high energy state.

3. Autocatalysis: In certain reactions, one of the products acts as a catalyst. In the initial stages the reaction is slow but as soon as the products come into existence, the reaction rate increases. This type of phenomenon, in which one of the products itself acts as a catalyst, is known as **autocatalysis.**

Examples of autocatalysis:

(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 autocatalyst.

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

(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 autocatalyst.

(iii) In hydrolysis of ethyl acetate, acetic acid and ethyl alcohol are formed. The reaction is initially very slow but gradually its rate increases. This is due to the formation of acetic acid which acts as an autocatalyst in this reaction.

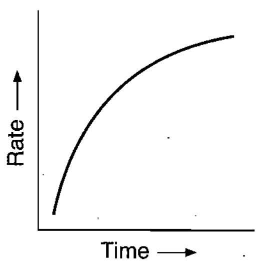


Fig. 13.8

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

In the case of homogeneous autocatalytic reactions, rate increases with passage of time because in such cases rate of reaction is directly proportional to concentration of catalyst, *e.g.*,

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$$

$$\text{Rate} = k\underset{\text{Reactant}}{[CH_3COOC_2H_5]}\underset{\text{Catalyst}}{[CH_3COOH]}$$

4. 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.**

Examples of induced catalysis:

(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.

$$Na_2SO_3 + \frac{1}{2}O_2 \longrightarrow Na_2SO_4$$

$$Na_3AsO_3 + \frac{1}{2}O_2 \longrightarrow Na_3AsO_4$$

(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 mercuric chloride, both are reduced simultaneously. The reduction of potassium permanganate, thus, induces the reduction of mercuric chloride.

13.12 CHARACTERISTICS OF CATALYSIS

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

(i) A catalyst remains unchanged in mass and chemical composition at the end of the reaction: The amount of the catalyst found at the completion of the reaction is the same as taken at the start of the reaction. There is also no change in its composition. However, it is observed that in some cases the physical state may change. For example, manganese dioxide used in the granular form as a catalyst in the decomposition of $KClO_3$ is left as a fine powder at the completion of the reaction.

(ii) A small quantity of the catalyst is generally sufficient to catalyse almost unlimited reaction: For example, in the decomposition of hydrogen peroxide, one gram of colloidal platinum can catalyse 10^8 litre of hydrogen peroxide. One mole of Cu^{2+} in 10^6 litre can catalyse the oxidation of sodium sulphite by atmospheric oxygen.

However, in some reactions the rate of the reaction is proportional to the concentration of the catalyst. For the acid and alkaline hydrolysis of an ester, the rate of reaction is proportional to the concentration of H^+ or OH^- ions.

$$RCOOR'(l) + H_2O(l) \xrightarrow[OH^-]{H^+ \text{ or}} RCOOH(l) + R'OH(l)$$

In Friedel-Crafts reaction, anhydrous aluminium chloride is required in relatively large amount to the extent of 30% of the mass of benzene.

$$C_6H_6(l) + C_2H_5Cl(l) \xrightarrow{AlCl_3(s)} C_6H_5C_2H_5(l) + HCl(l)$$

It is also observed that in certain heterogeneous reactions, the rate of reaction increases with the increase of area of the catalytic surface.

(iii) The catalyst cannot initiate the reaction: The function of a catalyst is to alter the speed of the reaction rather than to start it. The reaction in presence of a positive catalyst adopts some alternative path which requires less amount of activation energy.

However, there are certain instances where it is observed that the reaction cannot be started in absence of a catalyst. For example, there is no reaction between H_2 and O_2 at room temperature but the reaction occurs very readily in presence of platinum black.

$$2H_2(g) + O_2(g) \xrightarrow{\text{Room temp.}} \text{No reaction}$$

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

Similarly, combination of dry chlorine with dry hydrogen is not possible unless water vapours are added. Water vapours which act as a catalyst might be thought to start the reaction.

$$H_2(g) + Cl_2(g) \xrightarrow{\text{Water vapour}} 2HCl(g)$$

The concept is still disputed.

(iv) The catalyst is generally specific in nature: A substance, which acts as a catalyst for a particular reaction, fails to catalyse the other reactions. Different catalysts for the same reactants may form different products. Manganese dioxide which acts as a catalyst for the decomposition of potassium chlorate fails to catalyse the decomposition of potassium perchlorate. Ethanol yields ethene when passed over alumina but in presence of hot copper, acetaldehyde is formed.

$$C_2H_5OH(l) \begin{cases} \xrightarrow{Al_2O_3} C_2H_4(g) + H_2O(g)\ \text{(Dehydration)} \\ \xrightarrow{Cu} CH_3CHO(g) + H_2(g)\ \text{(Dehydrogenation)} \end{cases}$$

Similarly, in the case of formic acid, different products are formed using Cu or Al_2O_3 as catalysts.

$$HCOOH(l) \begin{cases} \xrightarrow{Cu} CO_2(g) + H_2(g)\ \text{(Dehydrogenation)} \\ \xrightarrow{Al_2O_3} CO(g) + H_2O(g)\ \text{(Dehydration)} \end{cases}$$

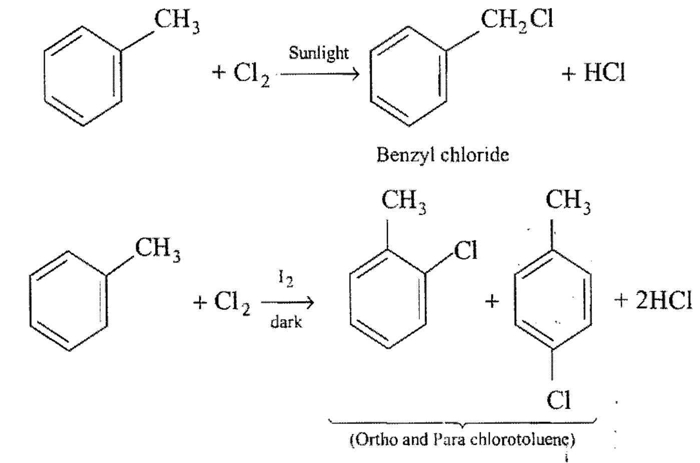
Carbon monoxide and hydrogen combine to form CH_4, CH_3OH, HCHO depending on the nature of the catalyst used.

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

$$CO(g) + 2H_2 \xrightarrow{ZnO + Cr_2O_3} CH_3OH$$

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

Sometimes catalyst may alter the reaction product:



Enzymes have also specific action. However, transition metals like Fe, Co, Ni, Pt, Pd, etc., can catalyse reactions of various types.

(v) The catalyst cannot change the position of equilibrium: In the case of reversible reactions, the concentrations of the products and reactants cannot be affected by the catalyst if the equilibrium has been established. However, the use of a catalyst can help to achieve the equilibrium state in lesser time as forward and backward reactions are influenced to the same extent by the catalyst.

Let us consider a reversible reaction,

$$A + BC \rightleftharpoons AB + C$$

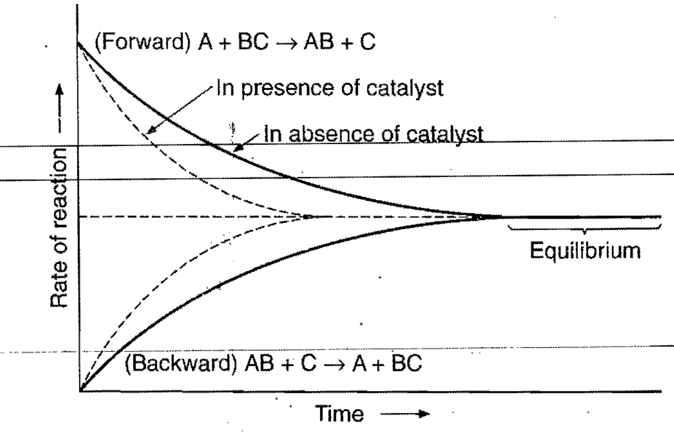


Fig. 13.9 Equilibrium state and catalyst

(vi) 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.** Some examples of the promoters are given below:

(a) In the Haber process for the synthesis of ammonia, traces of molybdenum increase the activity of finely divided iron which acts as a catalyst. Oxides of aluminium and thorium are also used as promoter in this reaction.

(b) 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).

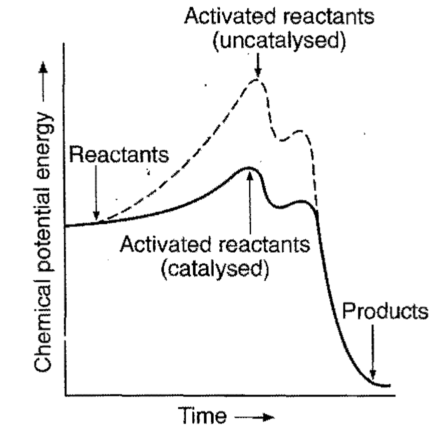


Fig. 13.10

(c) In the hydrogenation of oils, the activity of the catalyst nickel increases on adding small amount of copper and tellurium.

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

(a) 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.

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

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

The poisoning of a catalyst is probably due to the preferential adsorption of poison on the surface of the catalyst, thus reducing the space available for the adsorption of reacting molecules.

(viii) Change of temperature alters the rate of catalytic reaction as it does for the same reaction in absence of a 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.**

However, in the case of colloidal solutions acting as catalysts, the catalytic activity decreases by the rise of temperature as it may cause coagulation of the colloidal solution.

(ix) A positive catalyst lowers the activation energy: According to collision theory, a reaction occurs on account of effective collisions between the reacting molecules. For effective collision, it is necessary that the molecules must possess a minimum amount of energy known as activation energy (E_a). Under this condition, molecules after collision form an activated complex which dissociates to yield the product molecules.

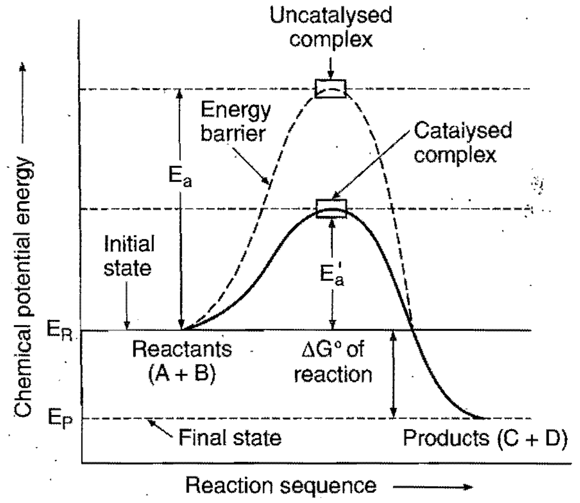


Fig. 13.11 (a)

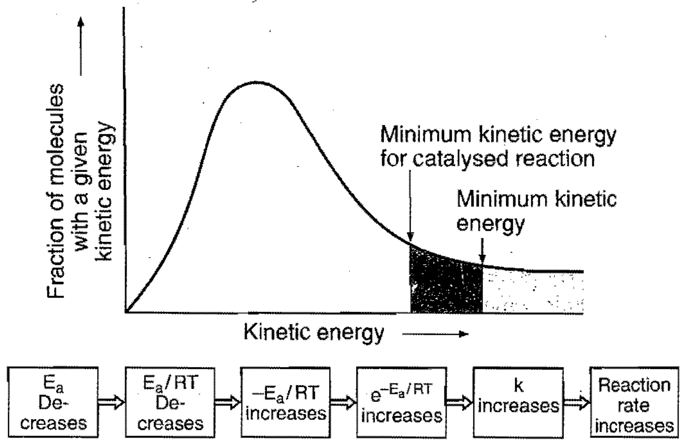


Fig. 13.11 (b) Lowering of energy barrier by the catalyst

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.

Fig. 13.11 (a) shows that activation energy, E_a, in absence of a catalyst is higher than the activation energy, E'_a, in presence of a catalyst. E_R and E_P represent the average energies of reactants and products. The difference gives the value of ΔG, *i.e.*,

$$\Delta G = E_R - E_P$$

13.13 THEORIES OF CATALYSIS

It is not possible to give a uniform explanation of the mechanism of the phenomenon of catalysis as catalytic reactions are of varied nature. However, two broad theories of catalytic action have been proposed. First theory known as **intermediate compound formation theory** explains successfully the homogeneous catalysis while second theory termed as **adsorption theory** explains the heterogeneous catalysis.

1. Intermediate compound formation theory: This theory was proposed by **Clement** and **Desormes** in 1806.

According to this theory, **the catalyst first forms an intermediate compound with one of the reactants. The intermediate compound is formed with less energy consumption than needed for the actual reaction. The intermediate compound being unstable combines with other reactant to form the desired product and the catalyst is regenerated.**

For example, a reaction of the type

$$A + B \overset{K}{=} AB$$

which occurs in presence of a catalyst K, may take place as,

$$\underset{}{A} + \underset{\text{Catalyst}}{K} = \underset{\text{Intermediate compound}}{AK} \qquad \text{(Slow reaction)}$$

$$AK + B = \underset{\text{Product}}{AB} + \underset{\text{Catalyst}}{K} \qquad \text{(Fast reaction)}$$

$$\text{Rate} = K'[A][K \text{ catalyst}]$$

Many catalytic reactions can be explained on the basis of this theory:

(i) The catalytic oxidation of sulphur dioxide to sulphur trioxide in the lead chamber process probably takes place as:

$$\underset{\text{Catalyst}}{2NO} + O_2 \longrightarrow \underset{\text{Intermediate product}}{2NO_2}$$

$$NO_2 + SO_2 \longrightarrow \underset{\text{Product}}{SO_3} + \underset{\text{Catalyst}}{NO}$$

(ii) The catalytic action of manganese dioxide on the decomposition of $KClO_3$ was proposed by McLeod. The reaction probably takes place as follows:

$$2MnO_2 + 2KClO_3 \longrightarrow 2KMnO_4 + Cl_2 + O_2$$

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

$$K_2MnO_4 + Cl_2 \longrightarrow 2KCl + MnO_2 + O_2$$

$$2KClO_3 + [2MnO_2] \longrightarrow 2KCl + 3O_2 + [2MnO_2]$$

The reaction accounts for the fact that oxygen given out is often contaminated with a little of chlorine.

(iii) The formation of methyl benzene (toluene) from benzene and methyl chloride in presence of a catalyst anhydrous aluminium chloride can be explained in the following way:

$$\underset{\text{Catalyst}}{AlCl_3} + CH_3Cl \longrightarrow \underset{\text{Intermediate compound}}{(CH_3)^+(AlCl_4)^-}$$

$$C_6H_6 + (CH_3)^+(AlCl_4)^- \longrightarrow \underbrace{C_6H_5CH_3 + HCl}_{\text{Products}} + \underset{\text{Catalyst}}{AlCl_3}$$

(iv) The formation of diethyl ether from ethyl alcohol using sulphuric acid as a catalyst can be explained as:

$$C_2H_5OH + \underset{\text{Catalyst}}{H_2SO_4} \longrightarrow \underset{\text{Intermediate compound}}{C_2H_5HSO_4}$$

$$C_2H_5HSO_4 + HOC_2H_5 \longrightarrow \underset{\text{Product}}{C_2H_5OC_2H_5} + \underset{\text{Catalyst}}{H_2SO_4}$$

(v) The decomposition of acetaldehyde which occurs as follows,

$$CH_3CHO \xrightarrow{I_2} CH_4 + CO$$

can be explained as shown below:

$$CH_3CHO + \underset{\text{Catalyst}}{I_2} \longrightarrow \underset{\text{Intermediate}}{CH_3I} + HI + CO$$

$$CH_3I + HI \longrightarrow CH_4 + I_2$$

$$CH_3CHO \longrightarrow CH_4 + CO$$

This theory explains why a catalyst remains unchanged in mass and chemical composition at the end of the reaction and is effective even in small quantities. The scope of this theory is, however, limited as the formation of intermediate compound is possible in the case of homogeneous catalysis only. It also fails to explain the action of catalytic promoters, catalytic poisons and action of finely divided catalysts.

(vi) Variable oxidation state of transition metals makes them efficient catalysts. For example, Fe^{3+} catalyses the reaction between iodide and persulphate ions.

$$2I^- + S_2O_8^{2-} \xrightarrow{Fe^{3+}} I_2 + 2SO_4^{2-}$$

The catalytic action can be explained as,

$$2Fe^{3+} + 2I^- \longrightarrow 2Fe^{2+} + I_2$$

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2-}$$

2. Adsorption theory: This theory explains the mechanism of heterogeneous catalysis. The old point of view was that when a catalyst is in solid state and the reactants are in gaseous state or in solutions, the molecules of the reactants are adsorbed on the surface of the catalyst. The increased concentration of the reactants on the surface influences the rate of reaction (law of mass action). Adsorption being an exothermic process, the heat of adsorption is taken up by the surface of the catalyst which is utilised in enhancing the chemical activity of the reacting molecules. The view does not explain the specificity of a catalyst.

Adsorption is broadly of two types: physical and chemical. The chemical adsorption is specific and involves chemical combination on the surface of the catalyst. 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) Some form of association between the catalyst surface and the reactants occurs. This is assumed to be adsorption.

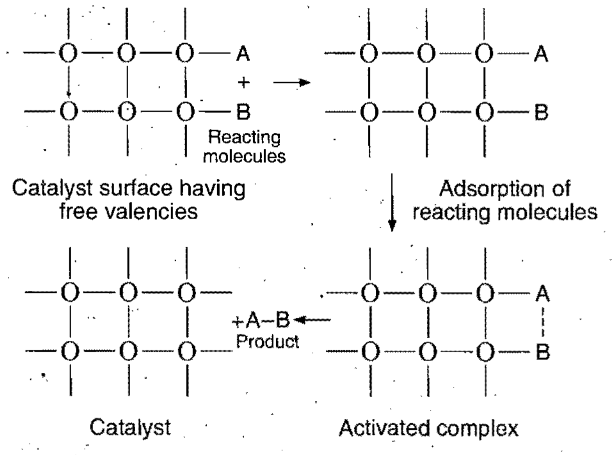


Fig. 13.12 Adsorption of reacting molecules, formation of activated complex and adsorption of products

(iii) Occurrence of chemical reaction on the catalyst surface.

(iv) Desorption of reaction products away from the catalyst surface.

(v) Diffusion of reaction products away from the catalyst surface.

The catalyst surface is a seat of chemical forces of attraction. There are free valencies on the surface of a catalyst. 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 and new molecules so formed may evaporate leaving the way for the fresh reactant molecules (Fig. 13.12).

In case, free valencies are responsible for the catalytic activity, it follows that with the increase of these valencies on the surface of a catalyst, the catalytic activity will be greatly enhanced. The free valencies can be increased in the following two ways:

(a) Sub-division of the catalyst,

(b) Rough surface of the catalyst.

(a) Sub-division of the catalyst: The number of free valencies increases on disintegration. Finely powdered or colloidal catalyst particles having large surface area are very rich in free valencies.

Actually, it is observed that finely divided nickel and colloidal platinum act as efficient catalysts.

(b) Rough surface of the catalyst: There are a number of active spots in the form of edges, corners, cracks and peaks on a rough surface. They give rise to an increase in number of free valencies. These active spots enhance the adsorption and thereby increase the catalytic efficiency of the catalyst.

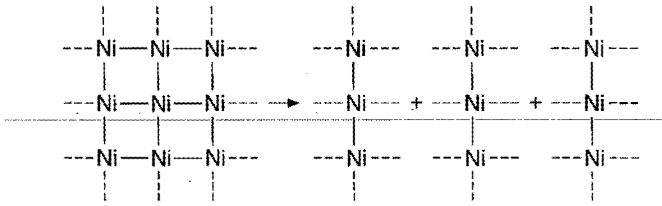


Fig. 13.13 Increase in number of free valencies

The adsorption theory explains the following facts of heterogeneous catalysis:

(i) The surface of the catalyst is used again and again due to alternate adsorption and desorption. **Thus, a small quantity of a catalyst can catalyse large amounts of reactants.**

(ii) Chemical adsorption depends on the nature of the adsorbent and adsorbate. Hence, catalysts are specific in action.

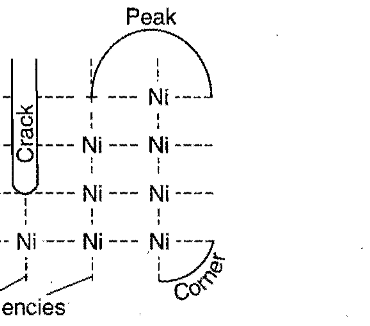


Fig. 13.14

(iii) Desorption leaves the catalytic surface unchanged. Thus, the catalyst at the end of reaction remains same in mass and composition.

(iv) The energy of adsorption compensates the activation energy of the reacting molecules to some extent. Thus, the reactions occur at faster rate.

(v) Greater efficiency of the catalyst in finely divided state and rough surface.

(vi) It adequately explains the poisoning of catalysts. The poisons are preferentially adsorbed at the active centres of the catalyst. This effect reduces the free valencies for the reacting molecules and, thus, the catalytic activity decreases.

(vii) Promoters are responsible for increasing the roughness of the surface of a catalyst. This effect increases the free valencies for the reacting molecules and, thus, the catalytic activity of the catalyst is increased.

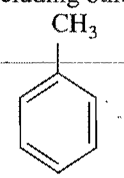
Activity and Selectivity of Heterogeneous Catalysis

Activity is the ability of a catalyst to accelerate chemical reactions. In certain cases the activity can be as high as 10^{10}, *i.e.*, the catalysed reaction is 10^{10} times faster than the uncatalysed reaction.

$$H_2(g) + O_2(g) \longrightarrow \text{No reaction}$$

$$2H_2(g) + O_2(g) \xrightarrow[\Delta]{Pt} 2H_2O(g)$$

Selectivity of a catalyst is its ability to direct the reaction in such a way as to yield particular products excluding others, *e.g.*,

(i) $\underset{n\text{-Heptane}}{CH_3-(CH_2)_5-CH_3} \xrightarrow{Pt(s)}$  $+ H_2(g)$

n-Heptane is catalysed by Pt to toluene.

(ii) Propylene and oxygen selectively give acrolein over bismuth molybdate as catalyst.

$$CH_3-CH=CH_2 + O_2 \xrightarrow[BiMoO_4]{\text{Bismuth molybdate}} \underset{\text{Acrolein}}{CH_2=CH-CHO} + H_2O$$

(iii) Acetylene on hydrogenation in presence of Pt or Ni or Pd catalyst gives ethane.

$$H-C\equiv C-H + 2H_2(g) \xrightarrow{Pt/Pd/Ni} \underset{\text{Ethane}}{CH_3-CH_3}$$

Hydrogenation of acetylene in presence of Lindlar's catalyst gives ethylene.

$$H-C\equiv C-H + H_2 \xrightarrow[\substack{\text{Sulphur or}\\ \text{quinoline}}]{Pd\text{-}BaSO_4} \underset{\text{Ethylene}}{CH_2=CH_2}$$

13.14 ACID-BASE CATALYSIS

Generally, homogeneous catalysis in solution is brought about by acids and bases. On the basis of studies done by Arrhenius and Ostwald in the hydrolysis of esters and nitrites, it was established that in acid-base catalysis, it is the hydrogen ion or hydroxyl ion which acts as catalyst.

Examples of acid-base catalysis:

(i) Hydrolysis of an ester:

$$CH_3COOC_2H_5(l) + H_2O(l) \xrightarrow[OH^-]{H^+ \text{ or}} CH_3COOH(l) + C_2H_5OH(l)$$

(ii) Inversion of cane sugar:

$$C_{12}H_{22}O_{11}(l) + H_2O(l) \xrightarrow{H^+} C_6H_{12}O_6(l) + C_6H_{12}O_6(l)$$

(iii) Conversion of acetone into diacetone alcohol:

$$CH_3COCH_3(l) + CH_3COCH_3(l) \xrightarrow{OH^-} CH_3COCH_2 \cdot C(CH_3)_2OH(l)$$

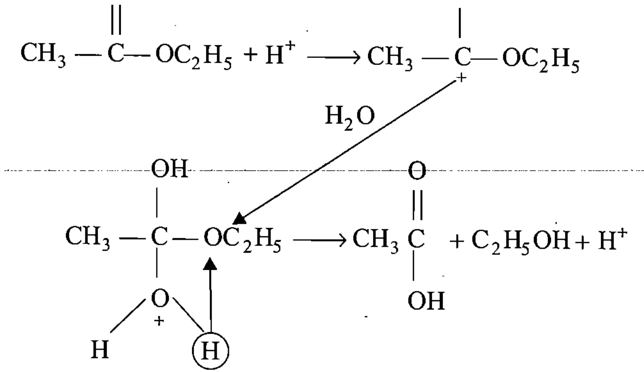
(iv) Decomposition of nitramide:

$$NH_2 \cdot NO_2(l) \xrightarrow{OH^-} N_2O(g) + H_2O(l)$$

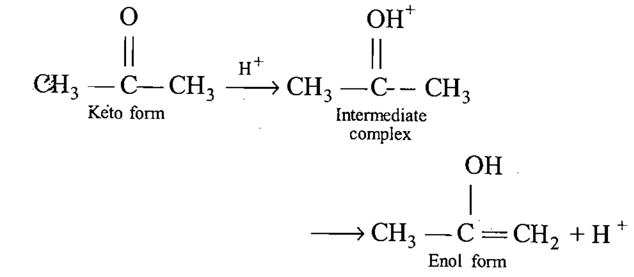
The recent work has shown that all substances which have a tendency to lose or to gain protons can show catalytic activity, *i.e.*, all Bronsted acids and bases act as acid-base catalysts.

Mechanism of Acid-Base Catalysis

(a) In acid catalysis, the proton given by Bronsted acid forms an intermediate complex with the reactant which then reacts to give back the proton (H^+). For example, the hydrolysis of ester occurs in the following manner:



The mechanism of keto-enol tautomerism of acetone is:



(b) In base catalysed hydrolysis, the OH^- ion or any Bronsted base accepts a proton from the reactant to form an intermediate complex which then reacts or decomposes to regenerate the OH^- or Bronsted base. In presence of OH^- ions, the decomposition of nitroamine can be shown as:

$$\begin{array}{l} NH_2NO_2 + OH^- \longrightarrow NHNO_2^- + H_2O \\ \qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\quad N_2O + OH^- \end{array}$$

or in presence of CH_3COO^- ions,

$$\begin{array}{l} NH_2NO_2 + CH_3COO^- \longrightarrow NHNO_2^- + CH_3COOH \\ \qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad N_2O + OH^- \\ OH^- + CH_3COOH \longrightarrow CH_3COO^- + H_2O \end{array}$$

13.15 ENZYME CATALYSIS

Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. Enzymes are actually high molecular mass protein molecules. Enzymes form colloidal solutions in water and are very effective catalysts. They catalyse numerous reactions, especially those connected with natural processes. 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 **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 catalysis:

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

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

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

$$\underset{\text{Glucose}}{C_6H_{12}O_6(l)} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH(l)} + 2CO_2(g)$$

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

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n(l)} + nH_2O(l) \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}(l)}$$

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

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}(l)} + H_2O(l) \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6(l)}$$

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

$$NH_2CONH_2(l) + H_2O(l) \xrightarrow{\text{Urease}} 2NH_3(g) + CO_2(l)$$

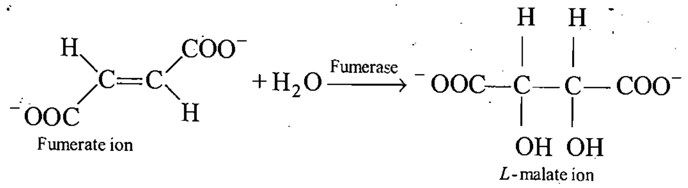
(vi) In stomach, the pepsin enzyme converts proteins into peptides while in intestine, the pancreas trypsin converts proteins into amino acids by hydrolysis.

(vii) Conversion of ethyl alcohol into acetic acid: The *Mycoderma aceti* enzyme converts dilute solutions of alcohol into acetic acid and water.

$$C_2H_5OH(l) + O_2(g) \xrightarrow{\textit{Mycoderma aceti}} CH_3COOH(l) + H_2O(l)$$

(viii) Conversion of milk into curd: It is an enzymatic reaction brought about by *lactic bacilli* enzyme present in curds.

(ix) The enzyme **fumerase** catalyses the hydration process of fumerate ion.



This reaction shows selectivity of enzymes because fumerase enzyme is unable to catalyse '*Cis*' isomer, *i.e.*, malate ion.

(x) In our body, the enzyme **carbonic anhydrase** catalyses the following reaction:

$$CO_2(aq.) + H_2O(l) \rightleftharpoons H^+(aq.) + HCO_3^-(aq.)$$

Forward process takes place when CO_2 goes to tissues from blood, whereas backward process takes place when CO_2 gas is released from the blood to the lungs.

Carbonic anhydrase has very high efficiency, one molecule of it catalyses 10^6 substrate molecules.

(xi) Lysozyme is found in the tear of our eyes. It protects our eyes from bacteria. It breaks down the cell wall of bacteria and then it ruptures due to endo-osmosis.

(xii) Nitrogenase enzyme is found in the bacteria of the root nodules of leguminous plants such as peas and beans. It catalyses the nitrogen fixation, *i.e.*, conversion of N_2 from atmosphere to the NH_3 in the soil.

Table 13.1 gives the summary of some important enzymatic reactions:

Table 13.1 Some enzymatic reactions

	Enzyme	Source	Enzymatic reaction
1.	Invertase	Yeast	Sucrose ⟶ Glucose and fructose
2.	Zymase	Yeast	Glucose ⟶ Ethyl alcohol and carbon dioxide
3.	Diastase	Malt	Starch ⟶ Maltose
4.	Maltase	Yeast	Maltose ⟶ Glucose
5.	Urease	Soyabean	Urea ⟶ Ammonia and carbon dioxide
6.	Pepsin	Stomach	Proteins ⟶ Amino acids
7.	Trypsin	Intestine	Proteins ⟶ Amino acids
8.	Amylase	Saliva	Starch ⟶ Glucose
9.	*Lactic bacilli*	Curd	Fermentation of milk
10.	*Mycoderma aceti*	Vinegar	Ethyl alcohol ⟶ Acetic acid
11.	Lipase	Castor seed	Fat ⟶ Glycerol
12.	Ptylin	Saliva	Starch ⟶ Sugar

Characteristics of Enzyme Catalysis

Enzyme catalysis is intermediate between homogeneous and heterogeneous catalysis. In general, it is similar to inorganic heterogeneous catalysis and sometimes it is called microheterogeneous catalysis. However, it is unique in its efficiency and high degree of specificity. The following characteristics are exhibited by enzyme catalysts:

(i) Most efficient catalysts: The enzyme-catalysed reactions are very fast in comparison to the reactions catalysed by inorganic substances. This is due to the fact that activation energy of a reaction in presence of an enzyme is low. One molecule of an enzyme may transform one million molecules of the reactant per minute.

(ii) High 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 any other amide, not even methyl urea.

(iii) Temperature dependence: The rate of an enzyme reaction depends on the temperature. The enzyme activity rises rapidly with temperature and becomes maximum at a definite temperature, called the **optimum temperature.** Beyond the optimum temperature, the enzyme activity decreases and ultimately becomes zero. The enzyme activity is destroyed at about 70° C. The optimum temperature of enzyme reactions occurring in the human body is 37° C. At higher temperatures (fever), the enzyme activity becomes less. The favourable temperature range for enzymatic activity is 25–37 ° C.

(iv) pH dependence: The rate of an enzyme-catalysed reaction varies with pH of the system. The enzyme activity is maximum at a particular pH called optimum pH. The optimum pH of enzyme reactions occurring in human body is 7.4. The favourable pH range for enzymatic reactions is 5–7.

Activity of enzyme decreases above and below the optimum pH. Effect of pH on enzymatic rate may reflect denaturation.

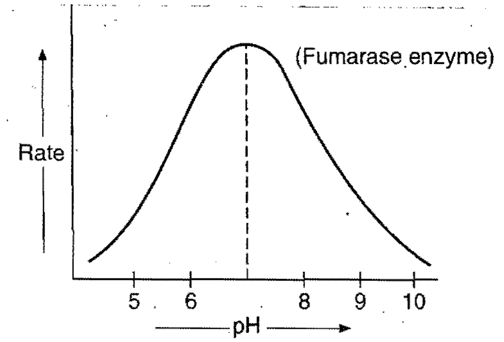


Fig. 13.15

(v) No effect on equilibrium state: Like ordinary catalysts, enzymes cannot disturb the final state of equilibrium of a reversible reaction.

(vi) Colloidal nature: Enzymes form colloidal solutions in water. Their efficiency is retarded in presence of large quantities of electrolytes. Enzymes are destroyed by ultraviolet rays.

(vii) Activators or coenzymes: The enzymatic activity is increased in the presence of certain substances, known as **coenzymes.** It has been observed that when a small non-protein

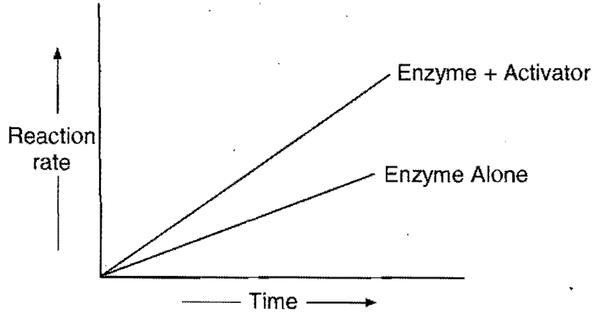


Fig. 13.16 Effect of activators on the rate of enzyme catalysis

(vitamin) is present along with an enzyme, the catalytic activity is enhanced considerably.

Activators are generally metal ions such as Na^+, Mn^{2+}, Co^{2+}, Cu^{2+}, 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.

(viii) 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.

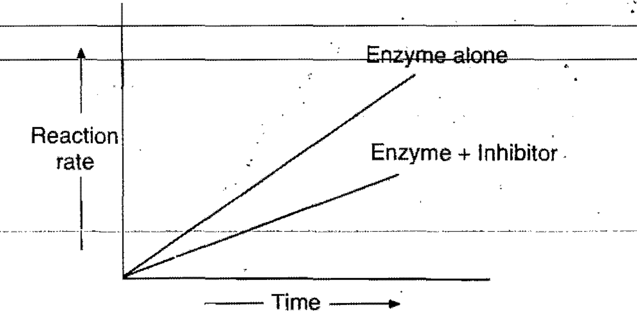


Fig. 13.17 Effect of inhibitor on the rate of enzyme catalysis

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 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.

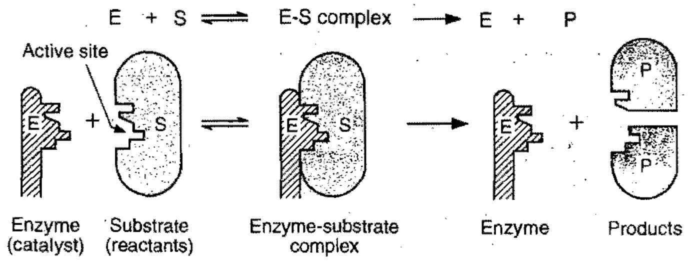


Fig. 13.18

Michaelis and Menten suggested the following mechanism for enzyme catalysis:

Step 1. Binding of enzyme to substrate to form an activated complex,

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

Step 2. Product formation in the activated complex,

$$ES \xrightarrow{k_2} EP$$

Step 3. Decomposition of EP into products and enzyme again, $EP \longrightarrow P + E$

This mechanism accounts for the high specificity of enzymatic reactions.

The rate of enzyme catalysed reaction is given by:

$$\text{rate} = k_2[ES] = \frac{k_2[E][S]}{K_m + [S]} \quad ...\text{(i)} \quad \text{(Michaelis-Menten equation)}$$

K_m = Michaelis-Menten constant

$[S]$ = Concentration of substrate

$[E]$ = Concentration of enzyme

Case I. When, $[S] >>> K_m$, then K_m can be neglected.

$\therefore$ Rate $= k_2[E]$ and the reaction belongs to first order. The rate law may be given as,

$$r_{\max} = k_2[E] \quad ...\text{(ii)}$$

Dividing eq. (i) by (ii)

$$\frac{r}{r_{\max}} = \frac{[S]}{[S] + K_m}$$

when, $K_m = [S], r = \frac{1}{2} r_{\max}$

Case II. When, $[S] <<< K_m$, then reaction will be of second order.

$$\text{Rate} = \frac{k_2}{K_m}[E][S] \quad \text{(Second order rate law)}$$

Enzyme kinetics may be graphically represented as :

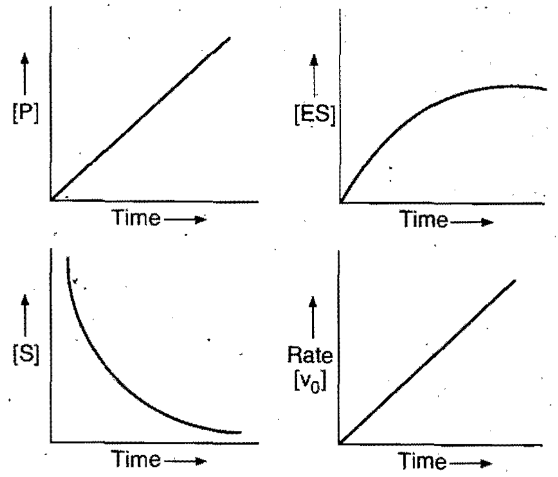


Fig. 13.19 Variation with time in enzyme catalysis

Competitive Enzyme Kinetics

Enzyme X and enzyme Y catalyse the same reaction and exhibit v_0 (rate) versus [S] curves shown ahead :

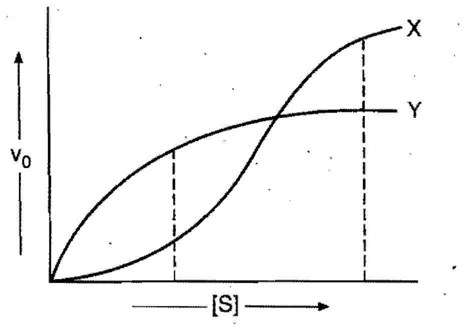


Fig. 13.20

At low substrate concentration, enzyme Y will be more efficient because activation energy will be low, in the presence of enzyme (Y). At high substrate concentration, enzyme X will be more efficient.

13.16 CATALYSTS IN INDUSTRY

Some of the important technical catalytic processes are listed in table 13.2 as to give an idea about the utility of catalysts in industries.

Table 13.2 Some Industrial Catalytic Processes

Process	Catalyst
1. Haber's process for the manufacture of ammonia. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	Finely divided iron. Molybdenum as promoter. Conditions: 200 atmospheric pressure and 450–500°C temperature.
2. Ostwald's process for the manufacture of nitric acid. $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$ $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $4NO_2(g) + 2H_2O(l) + O_2(g) \longrightarrow 4HNO_3(l)$	Platinised asbestos Temperature 300°C.
3. Lead chamber process for the manufacture of sulphuric acid. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$	Nitric oxide.
4. Contact process for the manufacture of sulphuric acid. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $SO_3(g) + H_2SO_4(l) \longrightarrow \underset{\text{Oleum}}{H_2S_2O_7(l)}$ $H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(l)$	Platinised asbestos or vanadium pentoxide (V_2O_5). Temperature 400 – 450°C.
5. Deacon process for the manufacture of chlorine. $4HCl(g) + O_2(g) \longrightarrow 2H_2O(l) + 2Cl_2(g)$	Cupric chloride ($CuCl_2$). Temperature 500°C.
6. Bosch process for the manufacture of hydrogen. $\underbrace{CO + H_2}_{\text{Water gas}} + H_2O(l) \longrightarrow CO_2(g) + 2H_2(g)$	Ferric oxide (Fe_2O_3) + chromic oxide as a promoter. Temperature 400–600°C.
7. Synthesis of methanol. $CO(g) + 2H_2(g) \longrightarrow CH_3OH(l)$	Zinc oxide (ZnO) + chromic oxide as a promoter. Pressure 200 atmospheres and temperature 250°C
8. Hydrogenation of vegetable oils. $Oil(l) + H_2(g) \longrightarrow$ Vanaspati ghee(s)	Nickel (finely divided). Temperature 150 –200°C. High pressure
9. Manufacture of ethyl alcohol by fermentation of molasses (sugar solution). $C_{12}H_{22}O_{11}(l) + H_2O(l) \xrightarrow{\text{Invertase}} C_6H_{12}O_6(l) + C_6H_{12}O_6(l)$ $C_6H_{12}O_6(l) \xrightarrow{\text{Zymase}} 2C_2H_5OH(l) + 2CO_2(g)$	Invertase enzyme and zymase (yeast) enzyme Temperature 25–30°C. Conversion occurs in 2 or 3 days.
10. Manufacture of ethyl alcohol from starch. (a) Starch $\xrightarrow{\text{Diastase}}$ Maltose (b) Maltose $\xrightarrow{\text{Maltase}}$ Glucose $\xrightarrow{\text{Zymase}}$ Alcohol	Germinated barley (diastase enzyme) Temperature 50 – 60°C. Yeast (maltase and zymase enzymes). Temperature 25–30°C.
11. Manufacture of acetic acid from ethyl alcohol. $C_2H_5OH(l) + O_2(g) \longrightarrow CH_3COOH(l) + H_2O(l)$	*Mycoderma aceti.* Temperature 25–30°C.
12. Bergius process for the synthesis of petrol from coal. Coal + $H_2(g) \longrightarrow$ Mix. of hydrocarbons	Ferric oxide (Fe_2O_3) Temperature 475°C. Pressure 200 atmosphere.
13. Polymerisation of ethene to polythene. $\underset{\text{Ethene}}{nCH_2{=}CH_2} \longrightarrow \underset{\text{Polythene}}{\text{[}CH_2-CH_2\text{]}_n}$	$TiCl_4$ and Al R_3 (Ziegler Natta Catalyst)

13.17 ZEOLITES

Zeolites are naturally occurring or synthetic microporous aluminosilicates of general formula:

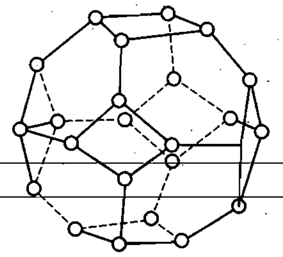
$$M_{x/n}\,[(AlO_2)_x(SiO_2)_y]m\cdot H_2O$$

where, $M = Na^+, K^+$ or Ca^{2+} like metals

n = valency of metal cation

m = molecules of water of crystallization

Zeolite may be considered as open structure of silica in which trivalent aluminium has been substituted in a fraction $x/(x+y)$ of tetravalent sites occupied by silicon atoms. Since a substitution of an atom of silicon by aluminium generates one negative charge on the aluminosilicate frame work, substitution of x atoms generates x negative charge on the aluminosilicate framework. This charge is neutralised by the exchangeable cations M of valency n. The void spaces which can be greater than 50% of the volume are occupied by 'm' molecules of water in the unit cell. Zeolite is derived from the Greek language which means 'boiling stone' because the water trapped in void spaces boils off when the naturally occurring zeolite stone is heated. Building block of zeolite is truncated octahedron (Cubo-octahedron). This structure is called β-cage or sodalite cage.



Truncated octahedron.

Stoichiometric formulae of some well known **zeolites** are:

(i) Faujasite (natural) $Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]250H_2O$

(ii) Gemelinite $Na_2Ca(AlO_2)_2(SiO_2)_4\cdot 6H_2O$

(iii) Zeolite sieve of molecular porosity-5 (ZSM-5)

$$H_x[(AlO_2)_x(SiO_2)_{96-x}].16H_2O$$

(iv) Erionite $Na_2K_2CaMg(AlO_2)_2(SiO_2)_2.6H_2O$

Shape selectivity of zeolite: Zeolite is the most widely studied shape selective catalyst. Shape selectivity of zeolite depends upon pore structure of the catalyst, pore size generally varies between 260 pm to 740 pm. Such catalysts are highly specific, it is because molecules of only a particular size and shape can enter these pores and get adsorbed. Shape selectivity of ZSM-5 in the conversion of alcohols into hydrocarbons are given in following table. The table gives the percentage of different hydrocarbons in the mixtures of hydrocarbons obtained from two different alcohols, *i.e.*, CH_3OH (methyl alcohol) and $nC_7H_{15}OH$ (*n*-heptyl alcohol).

Product	**Starting with CH_3OH (%)**	**Starting with $C_7H_{15}OH$ (%)**
Methane	1.0	0.0
Ethane	0.6	0.3
Isobutane	18.7	19.3
n-butane	5.6	11.0
Iso-pentane	7.8	8.7
Benzene	1.7	3.4
Toluene	10.5	14.3
Xylene	17.2	11.6

Persorption : It is a special type of sorption, introduced by Mc Bain. Persorption is the process in which the molecules like H_2O, CH_3OH, C_2H_5OH are adsorbed in the internal cavity of zeolite or chabazite ($CaAl_2Si_4O_{12}\cdot 6H_2O$).

Phase transfer catalyst: Substrate dissolved in organic layer and an anionic reagent dissolved in the aqueous layer are brought together by a catalyst. The catalyst transports the anion into the organic phase where reaction takes place with the substrate.

Quaternary ammonium and phosphonium salts with their unique ability to dissolve in both aqueous and organic liquids are the most suitable phase transfer catalysts.

13.18 AUTOMOBILE CATALYTIC CONVERTER

Automobile exhaust systems are being designed with built in catalytic converters. This system contains two types of heterogeneous catalyst, powdered noble metals and powdered transition metal oxides. They catalyze the oxidation of unburned hydrocarbon fuel and of partial combustion products such as carbon monoxide.

$$\underset{\text{Iso-octane}}{2C_8H_{18}} + 25O_2(g) \xrightarrow[\text{NiO}]{\text{Pt}} 16CO_2(g) + 18H_2O(g)$$

$$2CO(g) + O_2(g) \xrightarrow[\text{NiO}]{\text{Pt}} 2CO_2(g)$$

The same catalysts also catalyze another reaction, the decomposition of nitrogen oxide NO, into harmless N_2 and O_2.

$$2NO(g) \xrightarrow[\text{NiO}]{\text{Pt}} N_2(g) + O_2(g)$$

SUMMARY AND IMPORTANT POINTS TO REMEMBER

1. Adsorption: It is a tendency of accumulation of molecular species at the surface of a solid or liquid. The molecular species which accumulates is termed **adsorbate** and the material on whose surface adsorption has taken place is called **adsorbent.** The process of removing an adsorbed substance from the surface of the adsorbent is called **desorption.**

2. Distinction between adsorption and absorption: In adsorption, the substance is concentrated only at the surface while in absorption, the substance is uniformly distributed throughout the bulk of the adsorbent. In adsorption, the concentration of the adsorbate increases on the surface only while in absorption, the concentration is uniform throughout the bulk of adsorbent. Both adsorption and absorption take place simultaneously and the process is termed **sorption.** However, adsorption is instantaneous while absorption is a slow process.

3. Physical adsorption or physisorption: If the forces of attraction existing between adsorbate and adsorbent are van der Waals' forces, the adsorption is called **physical adsorption** or **physisorption.** In general, more easily liquefiable gases are readily adsorbed near their critical temperatures. It is generally reversible. It occurs readily at low temperature and decreases with increasing temperature. The extent of adsorption increases with increase of surface area and increase of pressure. Heat of adsorption is quite low (20– 40 kJ mol^{-1} or about 5 kcal mol^{-1}).

4. Chemisorption: If the forces of attraction between adsorbate particles and adsorbent are almost of the same strength as chemical bonds, the adsorption is termed **chemisorption** or **Langmuir adsorption.** This type of adsorption is highly specific and commonly irreversible in nature. It is slow at low temperature but increases with rise of temperature on account of high energy of activation. High pressure is favourable for chemisorption. Heat of adsorption is high (40– 400 kJ mol^{-1} or 10–100 kcal mol^{-1}). It also increases with increase of surface area.

5. Adsorption isotherms: The curve showing the variation of the amount of adsorbate at a particular temperature with pressure or concentration is termed **adsorption isotherm.**

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

$$\frac{x}{m} = k \cdot P^{1/n}$$

where, x is the mass of gas adsorbed, m is the mass of adsorbent, P is the pressure of gas and k, n are constants. Another form of equation is:

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

This is the equation of a straight line. The slope of the straight line gives the value of $\frac{1}{n}$ and the intercept on the y-axis gives the value of $\log k$.

6. Adsorption from solution phase: Solids can adsorb solutes from solutions also. Litmus solution becomes colourless when shaken with charcoal. Similarly, when a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by charcoal. In such cases, the following observations have been made:

(i) The extent of adsorption decreases with the rise of temperature.

(ii) The extent of adsorption increases with the surface area of the adsorbent.

(iii) The extent of adsorption depends upon the concentration of the solute in solution.

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

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

7. Applications of adsorption: Important applications of adsorption are:

(i) Production of high vacuum.

(ii) Gas masks—It is a device which consists of activated charcoal. This is used to adsorb poisonous gases.

(iii) Humidity control—Silica gel and aluminium gel are used for this purpose.

(iv) Removal of colouring matter from solutions—Animal charcoal is used for decolorising cane sugar.

(v) Heterogeneous catalysis (vi) Separation of inert gases by coconut charcoal (vii) Softening of hard water (viii) De-ionising of water (ix) Cleaning agents (x) Froth floatation process (xi) Adsorption indicators (xii) Chromatographic analysis (xiii) In medicines.

8. Catalysis: Substances which alter the velocity of a reaction by mere presence, without undergoing any change in mass and composition, are termed catalysts and the phenomenon is known as catalysis. Catalytic reactions are broadly divided into two groups: (i) Homogeneous catalysis (ii) Heterogeneous catalysis. When the reactants and catalyst are in the same phase, the catalysis is said to be **homogeneous catalysis.**

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

$$CH_3COOCH_3(l) + H_2O(l) \xrightarrow{HCl(l)} CH_3COOH(l) + CH_3OH(l)$$

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

(ii) Those catalytic reactions in which the physical state of reactants is different from the catalysts are termed heterogeneous catalysis.

Examples: $2SO_2(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$

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

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

$$4HCl(g) + O_2(g) \xrightarrow{Cu_2Cl_2(s)} 2H_2O(g) + 2Cl_2(g)$$

9. Types of catalysis:

(i) Positive catalysis: When the rate of reaction is accelerated by a foreign substance, it is said to be a positive catalyst and the phenomenon is positive catalysis.

(ii) Negative catalysis: The substance which when added to the reaction mixture, retards the reaction rate is termed negative catalyst and the phenomenon is known as negative catalysis.

(iii) Autocatalysis: In certain reactions, one of the products acts as a catalyst. In the initial stages the reaction is slow but as soon as the products come into existence, the reaction rate increases.

(iv) Induced catalysis: When one reaction influences the rate of another reaction, which does not occur under ordinary conditions, the phenomenon is known as induced catalysis.

10. Characteristics of catalysis: The following are the characteristics which are common to most of the catalytic reactions:

- (i) A catalyst remains unchanged in mass and chemical composition at the end of the reaction.
- (ii) A small quantity of the catalyst is generally sufficient to catalyse almost an unlimited reaction.
- (iii) A catalyst cannot initiate the reaction.
- (iv) The catalyst is generally specific in nature.
- (v) The catalyst cannot change the position of equilibrium in a reversible reaction. However, it can help to achieve the equilibrium state in lesser time.

(vi) Substances which themselves are not catalysts but when mixed in small quantities with the catalysts enhance their efficiency are called as **promoters** or **activators.**

(vii) Substances which destroy the activity of a catalyst by their presence are known as **catalytic poisons.**

(viii) A catalyst has a particular temperature at which its activity is maximum. This temperature is termed as **optimum temperature.**

(ix) A positive catalyst lowers the activation energy and provides a new pathway involving lower amount of activation energy.

11. Theories of catalysis: Two broad theories of catalytic action have been proposed:

(i) Intermediate compound formation theory: This was proposed by Clement and Desormes in 1806. According to this theory, the catalyst first forms an intermediate with one of the reactants, which being unstable combines with other reactants to form the desired product and the catalyst is regenerated.

$$A + K \text{ (catalyst)} = AK \text{ (intermediate)}$$

$$AK + B = AB + K$$

The scope of this theory is limited as the formation of intermediate is not possible in the case of many reactions.

It also fails to explain the action of promoters and poisons.

(ii) Adsorption theory: The catalytic activity is localised on the surface of a catalyst. The molecules of the reactants are adsorbed on the surface of the catalyst. The increase in concentration of the reactants on the surface increases the rate of reaction (law of mass action). There are free valencies on the surface which are responsible for loose chemical combination of the reactants with the catalyst. If different molecules are adsorbed side by side, they may react readily and new molecules are formed which evaporate leaving the way for the fresh reactant molecules. The free valencies can be increased in two ways:

(a) Sub-division of the catalyst,

(b) Rough surface of the catalyst.

Adsorption theory is a better theory as it can explain a number of characteristics of the catalyst, especially a heterogeneous catalyst.

12. Enzyme catalysis: Enzymes are complex nitrogenous organic compounds of high molecular masses produced by living plants and animals. Enzymes are protein molecules, form colloidal solutions in water and catalyse numerous reactions especially connected with natural processes. The enzymes are also termed as **biochemical catalysts** and the phenomenon is known as biochemical catalysis.

The catalytic activity of enzymes is perhaps the greatest of all the catalysts. Their activity is also due to their capacity to lower the activation energy for a reaction. Each enzyme can catalyse a specific reaction. The enzyme reactions are sensitive to temperature and pH. Generally, the optimum temperature varies between 290–300 K and the favourable pH range is 5–7.

Questions

1. Matrix Matching Problems (For IIT Aspirants):

[A] Match the reactions of Column-I with the catalysts in Column-II:

Column-I (Reaction)	**Column-II (Catalyst)**
(a) $2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)$	(p) Al_2O_3
(b) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$	(q) Pt
(c) $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$	(r) V_2O_5
(d) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$	(s) MnO_2

[B] Match the reaction in List-I with the catalysts in List-II and types of catalysis in List-III:

List-I	**List-II**	**List-III**
(a) Oxidation of SO_2 to SO_3 in lead chamber process	(p) NO	(u) Positive catalyst
(b) Synthesis of methanol from CO and H_2	(q) Pt	(v) Poisoned by CO
(c) Oxidation of CO to CO_2	(r) V_2O_5	(w) Heterogeneous
(d) Oxidation of NH_3 to NO in Ostwald's process	(s) Rh	(x) Homogeneous

[C] Match the Column-I with Column-II:

Column-I	**Column-II**
(a) ZSM-5	(p) $Na_2K_2CaMg(AlO_2)_2(SiO_2)_2 \cdot 6H_2O$
(b) Erionite	(q) Catalyst to convert alcohol to gasoline (petrol)
(c) Gemelinite	(r) $Na_2Ca(AlO_2)_2(SiO_2)_4 \cdot 6H_2O$
(d) Cavity size 550 pm	(s) $H_x[(AlO_2)_x(SiO_2)_{96-x}] \cdot 16H_2O$

[D] Match the List-I with List-II:

List-I	**List-II**
(a) Mo	(p) Promotor
(b) Cu	(q) Negative catalyst
(c) TEL	(r) Decomposition of hydrogen peroxide
(d) Glycerine	(s) Haber process

[E] Match the Column-I with Column-II:

Column-I	**Column-II**
(a) Removal of water by silica gel	(p) Absorption
(b) Removal of water by anhydrous $CaCl_2$	(q) Adsorption
(c) Surface phenomena	(r) Evaporation of liquid
(d) Bulk phenomena	(s) Boiling of liquid

[F] Match the Column-I with Column-II:

Column-I	**Column-II**
(a) $BaSO_4$	(p) Inhibitor for decomposition of H_2O_2
(b) Acetamide	(q) Catalyst
(c) Zeolite	(r) Removes hardness of water
(d) Nickel	(s) Poison for Pd in Lindlar's catalyst

[G] Match the phenomena in Column-I with example in Column-II:

Column-I	**Column-II**
(a) Persorption	(p) H_2 on Ni surface
(b) Sorption	(q) CH_3OH in chabazite
(c) Negative adsorption	(r) NH_3 in H_2O
(d) Occlusion	(s) Dil. NaCl on blood charcoal

Answers

1. [A] (a—s); (b—q, r); (c—q); (d—p).
[B] (a—p—x, u); (b—q, s—v, u); (c—p—x, u); (d—q—u, v, w).
[C] (a—q, s); (b—p); (c—r); (d—s).
[D] (a—p, s); (b—p); (c—q); (d—r).
[E] (a—q); (b—p); (c—q, r); (d—p, s).
[F] (a—s); (b—p); (c—q, r); (d—q).
[G] (a—q); (b—r); (c—s); (d—p).

• PRACTICE PROBLEMS •

1. Show that the maximum enzyme catalysed reaction rate will occur for

$$[H^+]_{opt} = \sqrt{k_1k_2}$$

The general pH control enzyme catalysed reaction is

$$EH_2^{2+} \rightleftharpoons EH^+ \rightleftharpoons E$$

Only EH^+ is capable for binding substrate and catalysing the desired reaction;

$$k_1 = \frac{[EH^+][H^+]}{[EH_2^{2+}]};\ k_2 = \frac{[E][H^+]}{[EH^+]}$$

[**Hint:** $k_1k_2 = \frac{[E][H^+]^2}{[EH_2^{2+}]}$

In pH control it may be considered that $[E] \approx [EH_2^{2+}]$, *i.e.*, enzyme combines almost completely with H^+ ions.

Thus, $k_1k_2 \approx [H^+]^2; [H^+] = \sqrt{k_1k_2}$]

2. The rate of decomposition of acetaldehyde into methane and CO in the presence of I_2 at 800 K follows the rate law

$$\text{Rate} = k[CH_3CHO][I_2]$$

The decomposition is believed to go by a two steps mechanism:

$$CH_3CHO + I_2 \longrightarrow CH_3I + HI + CO$$

$$CH_3I + HI \longrightarrow CH_4 + I_2$$

What is the catalyst for the reaction? Which of the two steps is a slower one?

[**Ans.** I_2 is catalyst; first step is slow.]

3. A solution of palmitic acid ($M = 256$) in benzene contains 4.24 g acid per litre. When this solution is dropped on the water surface, benzene evaporates and palmitic acid forms monomolecular film of the solid type. If we wish to cover an area of 500 cm^2 with a monolayer, what volume of solution should be used? The area occupied by one palmitic acid molecule may be taken to be 2.1×10^{-20} m^2.

[**Ans.** 0.0239 cm^3]

[**Hint:** V litre volume of solution taken.

$$W = (4.24 \times V)\ g$$

$$\text{Number of atoms} = \frac{W}{\text{Atomic mass}} \times \text{Avogadro's number}$$

$$= \frac{4.24V}{256} \times 6.023 \times 10^{23}$$

$$\text{Area} = 500 \times 10^{-4}\ m^2 = \left[\frac{4.24V}{256} \times 6.023 \times 10^{23}\right] \times 21 \times 10^{-20}$$

$V = 0.0000239$ litre $= 0.0239\ cm^3$]

4. Give the mechanism of the following reactions:
   (a) In lead chamber process, NO(g) is used as catalyst in the oxidation of SO_2 to SO_3.
   (b) NO(g) catalyses the decomposition ozone to oxyg
   (c) Ozone layer depletion by Freon or Teflon.

[**Hint:** (a) $2NO(g) + O_2(g) \longrightarrow \underset{\text{Intermediate}}{2NO_2}$

$$2NO_2(g) + 2SO_2(g) \longrightarrow 2SO_3(g) + 2NO(g)$$

OR

$$SO_2(g) + H_2O + NO_2(g) \longrightarrow \underset{\text{Intermediate}}{H_2SNO_5}$$

$$H_2SNO_5 \longrightarrow H_2SO_4 + NO(g)$$

(b) $NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$

$$O_3(g) \longrightarrow O_2(g) + O(g)$$

$$NO_2(g) + O(g) \longrightarrow NO(g) + O_2(g)$$

$$2O_3(g) \longrightarrow 3O_2(g) \quad \text{(Overall reaction)}$$

(c) Chlorine atoms furnished by freon and teflon act as a catalyst in the decomposition of ozone in the ozone layer.

$$O_3 \xrightarrow{\text{Sunlight}} O_2 + [O]$$

$$O_3 + Cl \longrightarrow O_2 + OCl$$

$$OCl + O \longrightarrow Cl + O_2$$]

5. One gram of charcoal adsorbs 100 mL of 0.5 M CH_3COOH to form a mono-layer and thereby the molarity of acetic acid is reduced to 0.49 M. Calculate the surface area of the charcoal adsorbed by each molecule of acetic acid. Surface area of charcoal = 3.01×10^2 m^2/gm. **(IIT 2003)**

[**Hint:** Number of moles of acetic acid initially present

$$= \frac{MV}{1000} = \frac{0.5 \times 100}{1000} = 0.05$$

Number of moles of acetic acid left

$$= \frac{MV}{1000} = \frac{0.49 \times 100}{1000} = 0.049$$

Number of moles of acetic acid adsorbed

$$= 0.05 - 0.049 = 0.001 \text{ mol}$$

Number of molecules of acid adsorbed

$$= 0.001 \times 6.023 \times 10^{23} = 6.023 \times 10^{20}$$

Area occupied by single molecule of acetic acid

$$= \frac{\text{Total area}}{\text{Number of molecules adsorbed}}$$

$$= \frac{3.01 \times 10^2}{6.023 \times 10^{20}}$$

$= 5 \times 10^{-19}\ m^2$]

OBJECTIVE QUESTIONS

: Questions with single correct answer

1. Adsorption is the phenomenon in which a substance:
   (a) accumulates on the surface of the other substance
   (b) goes into the body of the other substance
   (c) remains close to the other substance
   (d) oxidises or reduces the other substance
2. Physical adsorption is appreciable at:
   (a) higher temperature (b) lower temperature
   (c) room temperature (d) 100° C
3. The rate of chemisorption:
   (a) decreases with increase of pressure
   (b) is independent of pressure
   (c) is maximum at one atmospheric pressure
   (d) increases with increase of pressure
4. A poisonous gas is adsorbed at activated charcoal. The activated charcoal is:
   (a) absorber (b) adsorbate
   (c) adsorbent (d) absorbate
5. Chromatography is a technique based on:
   (a) solubilities of solute
   (b) adsorption of solute
   (c) chemical adsorption followed by dispersion
   (d) differential adsorption of different constituents of a mixture
6. Which of the following is not a characteristic of chemisorption?
   (a) Adsorption is irreversible
   (b) ΔH is of the order of 400 kJ
   (c) Adsorption is specific
   (d) Adsorption increases with increase of surface area
7. In the Freundlich adsorption isotherm equation :
   $\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log P$, the value of '$n$' is: **[CET (J&K) 2009]**
   (a) any value from 0 to 1
   (b) a negative integer
   (c) a positive integer
   (d) a positive or negative fractional number
8. Which of the following is not the application of adsorption?
   (a) De-ionisation of water
   (b) Gas masks
   (c) Hygroscopic nature of $CaCl_2$
   (d) Heterogeneous catalysis
9. Which one of the following is not a correct statement?
   (a) Physical adsorption is reversible in nature
   (b) Physical adsorption involves van der Waals' forces
   (c) Rate of physical adsorption increases with increase of pressure on the adsorbate
   (d) High activation energy is involved
10. Which one of the following is the correct statement?
    (a) Chemisorption is reversible in nature
    (b) Chemisorption is high at low temperature
    (c) Chemisorption depends on the nature of gas
    (d) Chemisorption does not involve activation energy
11. A catalyst is a substance which:
    (a) increases the equilibrium concentration of the product
    (b) changes the equilibrium constant of the reaction
    (c) shortens the time to reach equilibrium
    (d) supplies energy to the reaction
12. A catalyst:
    (a) increases the free energy change in the reaction
    (b) decreases the free energy change in the reaction
    (c) does not increase or decrease the free energy change in the reaction
    (d) can either decrease or increase the free energy change depending on what catalyst we use
13. Which of the following statements is more correct?
    (a) A catalyst only accelerates the rate of a chemical reaction
    (b) A catalyst can retard the rate of a chemical reaction
    (c) A catalyst can control the speed of a reaction
    (d) A catalyst alters the speed of a reaction
14. A catalyst is a substance which: **[JEE (WB) 2008]**
    (a) increases the equilibrium constant of the reaction
    (b) increases the equilibrium concentration of products
    (c) does not alter the reaction mechanism
    (d) changes the activation energy of the reaction
15. Which of the following reactions is an example for homogeneous catalysis? **[CET (J&K) 2006]**
    (a) $2H_2O_2(l) \xrightarrow{MnO_2(s)} 2H_2O(l) + O_2(g)$
    (b) $2SO_2(g) + O_2(g) \xrightarrow{V_2O_5(s)} 2SO_3(g)$
    (c) $2CO(g) + O_2(g) \xrightarrow{NO(g)} 2CO_2(g)$
    (d) $H_2(g) + C_2H_4(g) \xrightarrow{Ni(s)} C_2H_6(g)$
16. The substance which decreases the rate of a chemical reaction is called:
    (a) inhibitor (b) poison (c) moderator (d) promoter
17. The decomposition of hydrogen peroxide can be slowed down by the addition of a small amount of acetamide. The latter acts as:
    (a) inhibitor (b) promoter (c) moderator (d) poison
18. The temperature at which the catalytic activity of the catalyst is maximum, is called:
    (a) critical temperature (b) room temperature
    (c) absolute temperature (d) optimum temperature
19. Efficiency of the catalyst depends on its:
    (a) molecular weight (b) number of free valencies
    (c) physical state (d) amount used
20. Which of the following types of metals make the most efficient catalysts?

(a) Transition metals (b) Alkali metals
(c) Alkaline earth metals (d) Radioactive metals

21. Enzymes are made up of: **[CG (PET & PMT) 2007]**
(a) edible proteins
(b) proteins with specific structure
(c) nitrogen containing carbohydrate
(d) carbohydrates

22. In lead chamber process, which one of the following oxides is used as a catalyst?
(a) NO (b) NO_2 (c) N_2O_3 (d) N_2O_5

23. Enzymes are:
(a) substances made by chemists to activate washing powders
(b) catalysts found in organisms
(c) synthetic catalysts
(d) very active vegetative catalysts

24. Alcoholic fermentation is brought about by the action of:
(a) yeast (b) CO_2 (c) O_2 (d) CO

25. Glucose or fructose is converted into C_2H_5OH in the presence of:
(a) invertase (b) diastase (c) maltase (d) zymase

26. The name catalysis was given by:
(a) Rutherford (b) Langmuir
(c) Graham (d) Berzelius

27. In the reaction, $KMnO_4 + H_2SO_4 + H_2C_2O_4 \longrightarrow$ Products, Mn^{2+} ions act as:
(a) positive catalyst (b) negative catalyst
(c) autocatalyst (d) enzyme catalyst

28. In the Haber process of synthesis of NH_3:
(a) Mo acts as a catalyst and Fe as a promoter
(b) Fe acts as a catalyst and Mo as a promoter
(c) Fe acts as inhibitor and Mo as a catalyst
(d) Fe acts as promoter and Mo as autocatalyst

29. TEL minimises the knocking effect when mixed with petrol. It acts as:
(a) positive catalyst (b) negative catalyst
(c) autocatalyst (d) induced catalyst

30. Edges and peaks are more effective in a catalyst because:
(a) they have more free valencies
(b) they have limited number of atoms
(c) they have limited number of molecules
(d) none of the above

31. Hydrolysis of starch involves the use of the enzyme:
(a) maltase (b) zymase
(c) invertase (d) diastase

32. Which of the following statements is incorrect?
(a) Enzymes exist in colloidal state
(b) Enzymes are catalysts
(c) Enzymes can catalyse any reaction
(d) Urease is an enzyme

33. Which of the following catalysts is used in Friedel-Crafts reaction for preparation of toluene from benzene?
(a) Anhydrous aluminium chloride
(b) Nickel
(c) Platinum (d) Palladium

34. Platinised asbestos is used as a catalyst in the manufacture of H_2SO_4. It is an example of:
(a) homogeneous catalyst (b) heterogeneous catalyst
(c) autocatalyst (d) induced catalyst

35. The catalyst used in the manufacture of sulphuric acid by contact process is:
(a) Al_2O_3 (b) Cr_2O_3 (c) V_2O_5 (d) MnO_2

36. The formation of diethyl ether from ethanol is catalysed by:
(a) H_2SO_4 (b) Al_2O_3 (c) Cu (d) Ni

37. Which of the following catalysts is sensitive to temperature changes?
(a) Fe (b) Pt (c) Ni (d) Enzyme

38. The catalyst used in the Deacon's process for the manufacture of chlorine is:
(a) Pt (b) $CuCl_2$ (c) V_2O_5 (d) Fe

39. A catalytic poison renders the catalyst ineffective because: **(IIT 1991)**
(a) it is preferentially adsorbed on the catalyst
(b) it adsorbs the molecules of the reactants
(c) it combines chemically with the catalyst
(d) it combines with one of the reactants

40. A finely divided state of the catalyst is more efficient because in this state:
(a) more surface area is available
(b) more energy is stored in the catalyst
(c) positive charge is acquired
(d) negative charge is acquired

41. The catalyst used in the hydrogenation of oils is:
(a) V_2O_5 (b) Fe (c) Ni (d) Pt

42. Which of the following statements is not true? **(MLNR 1993)**
(a) The action of a catalyst is specific
(b) The catalyst does not alter the equilibrium
(c) A small amount of catalyst is sufficient to catalyse large amounts of reactants
(d) The catalyst initiates the reaction

43. The catalyst used in the manufacture of hydrogen by Bosch's process is:
(a) Fe_2O_3 (b) Cr_2O_3
(c) $Fe_2O_3 + Cr_2O_3$ (d) Cu

44. The catalyst used for olefin polymerisation is: **[JEE (WB) 2009]**
(a) Ziegler-Natta catalyst (b) Wilkinson catalyst
(c) Raney nickel catalyst (d) Merifield resin

45. The modern theory of catalysis is based on:
(a) active masses (b) atomic or molecular weights
(c) size of the particles (d) number of free valencies

46. According to adsorption theory of catalysis, the reaction rate increases, because:
(a) adsorption produces heat which increases the rate of reaction
(b) in the process of adsorption, the kinetic energy of the molecules increases
(c) the concentration of reactants at the active centres becomes high due to adsorption
(d) the activation energy of the reaction becomes high due to adsorption

47. Which one of the following statements is false?
    (a) Enzymes are highly specific
    (b) Enzymes increase activation energy
    (c) Enzymes require optimum temperature
    (d) Enzymes require optimum pH
48. An example of an autocatalytic reaction is:
    (a) hydrogenation of oils
    (b) decomposition of nitroglycerine
    (c) oxidation of Na_3AsO_3 in presence of Na_2SO_3
    (d) thermal decomposition of $KClO_3$ in presence of MnO_2
49. Enzyme catalysis is an example of:
    (a) autocatalysis (b) heterogeneous catalysis
    (c) homogeneous catalysis (d) induced catalysis
50. The biocatalysts are:
    (a) enzymes (b) minerals
    (c) plants (d) all proteins
51. Which one of the following statements is incorrect in the case of heterogeneous catalyst? **(CPMT 1990)**
    (a) The catalyst lowers the energy of activation
    (b) The catalyst actually forms a compound with the reactant
    (c) The surface of the catalyst plays a very important role
    (d) There is no change in the energy of activation
52. Regarding criteria of catalysis which one of the following statements is not true? **(CPMT 1990)**
    (a) The catalyst is unchanged chemically during the reaction
    (b) A small quantity of catalyst is often sufficient to bring about a considerable amount of the reaction
    (c) In reversible reaction, the catalyst alters the equilibrium position
    (d) The catalyst accelerates the rate of reaction
53. In which of the following processes, a catalyst is not used?
    (a) Haber's process (b) Deacon's process
    (c) Solvay process (d) Lead chamber process
54. The effect of a catalyst in a chemical reaction is to change the:
    (a) activation energy (b) equilibrium concentration
    (c) heat of reaction (d) final products
55. Protons accelerate the hydrolysis of esters. This is an example of:
    (a) a promoter (b) a heterogeneous catalyst
    (c) an acid-base catalyst (d) an autocatalyst
56. In the Ostwald's process for the manufacture of HNO_3, the catalyst used is:
    (a) Fe (b) Pt
    (c) V_2O_5 (d) Mo
57. The efficiency of an enzyme in catalysing a reaction is due to its capacity:
    (a) to form a strong enzyme substrate complex
    (b) to decrease the bond energies in the substrate molecule
    (c) to change the shape of the substrate molecule
    (d) to lower the activation energy of the reaction
58. The enzymes are killed:
    (a) at a very high temperature
    (b) during the chemical reaction
    (c) at low temperature
    (d) under atmospheric pressure
59. The enzyme ptyalin used for digestion of food is present in:
    (a) saliva (b) blood
    (c) intestine (d) adrenal glands
60. Which of the following acts as a negative catalyst?
    (a) Lead tetraethyl as antiknock compound
    (b) Glycerol in decomposition of H_2O_2
    (c) Ethanol in the oxidation of chloroform
    (d) All of the above
61. Which of the following types of materials act as effective catalysts?
    (a) Alkali metals (b) Transition metals
    (c) Alkaline earth metals (d) Radioactive metals
62. In which of the following reactions is a catalyst required?
    (a) $S + O_2 \longrightarrow SO_2$ (b) $C + O_2 \longrightarrow CO_2$
    (c) $2SO_2 + O_2 \longrightarrow 2SO_3$ (d) All of these
63. Which is not the characteristic of a catalyst? **(AFMC 1992)**
    (a) It changes the equilibrium point
    (b) It initiates the reaction
    (c) It alters the rate of reaction
    (d) It increases the average KE of molecules
64. In chemical reaction, the catalyst: **(AFMC 1993)**
    (a) alters the amount of products
    (b) lowers the activation energy
    (c) decreases ΔH of forward reaction
    (d) increases ΔH of forward reaction
65. Which statement is not correct? **[PMT (MP) 1993]**
    (a) Physical adsorption is due to van der Waals' forces
    (b) Physical adsorption decreases at high temperature and low pressure
    (c) Physical adsorption is reversible
    (d) Adsorption energy for chemical adsorption is generally lesser than that for physical adsorption
66. In the adsorption of oxalic acid by activated charcoal, the activated charcoal is known as:
    (a) adsorbent (b) adsorbate
    (c) absorber (d) none of these
67. Which can adsorb larger volume of hydrogen gas?
    (a) Colloidal solution of palladium
    (b) Finely divided nickel
    (c) Finely divided platinum
    (d) Colloidal $Fe(OH)_3$
68. Platinum is used as a catalyst in:
    (a) oxidation of ammonia to form nitric acid
    (b) hardening of oils
    (c) production of synthetic rubber
    (d) synthesis of methanol
69. Hydrolysis of cane sugar is catalysed by:
    (a) H^+ (b) mineral acids
    (c) enzymes (d) all of these
70. $KClO_3$ on heating decomposes into KCl and O_2. If some MnO_2 is added the reaction goes much faster because:
    (a) MnO_2 decomposes to give oxygen
    (b) MnO_2 provides heat by reacting
    (c) better contact is provided by MnO_2
    (d) MnO_2 acts as catalyst

71. Which acts as poison for Pd-charcoal in Lindlar's catalyst?
(a) $BaSO_4$ (b) Quinoline
(c) Both (a) and (b) (d) None of these

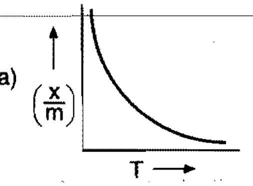
72. The inhibitors:
(a) retard the rate of a chemical reaction
(b) stop a chemical reaction immediately
(c) are reducing agents
(d) do not allow the reaction to proceed

73. The catalyst used in the manufacture of nitric acid by Ostwald's process is:
(a) Mo (b) Pt (c) V_2O_5 (d) Fe

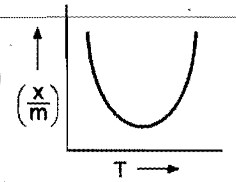
74. Which is an example of autocatalysis?
(a) Hydrolysis of methyl acetate
(b) Decomposition of TNG
(c) Oxidation of oxalic acid by $KMnO_4$
(d) All of the above

75. Which plot is the adsorption isobar for chemisorption?

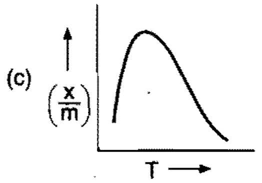
(a)



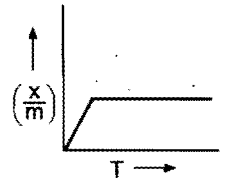
(b)



(c)



(d)



76. In the titration between oxalic acid and acidified potassium permanganate, the manganous salt formed during the reaction catalyses the reaction. The manganous salt acts as:
(a) promoter (b) positive catalyst
(c) autocatalyst (d) none of these

77. Adsorption is accompanied by:
(a) decrease in entropy of the system
(b) decrease in enthalpy of the system
(c) $T\Delta S$ for the process is negative
(d) all of the above

78. Consider the following statements:
1. Zeolites are aluminosilicates.
2. Aluminium can occupy two adjacent sites in zeolites.
Which of the following statements is correct? **(SCRA 2009)**
(a) 1 only (b) 2 only
(c) both 1 and 2 (d) neither 1 nor 2

79. Zeolites are used as catalyst in:
(a) petrochemical industries during cracking
(b) the preparation of H_2SO_4
(c) the hydrolysis of ester
(d) all of the above

80. Choose the correct statement for chemical adsorption: **[CET (Gujarat) 2006]**
(a) Value of adsorption enthalpy is above -20 kJ mol^{-1}
(b) van der Waals' forces exist between adsorbent and adsorbate
(c) Usually monomolecular layer is formed on adsorbent
(d) Multimolecular layer may be formed on adsorbent

81. The function of zymase is to: **(AIIMS 1992)**
(a) change starch into sugar
(b) ferment glucose to alcohol and carbon dioxide
(c) change malt sugar into glucose
(d) change starch into malt sugar and dextrin

82. Which of the following relations is/are correct? **(AIIMS 1995)**
(i) x/m = constant (at high pressure)
(ii) x/m = constant × $P^{1/n}$ (at intermediate pressure)
(iii) x/m = constant × P^n (at low pressure)
(a) All are correct (b) All are wrong
(c) (i) and (ii) are correct (d) (iii) is correct

83. The principle(s) involved in chromatographic operation is/are: **(AIIMS 1996)**
(a) adsorption (b) absorption
(c) partition (d) none of these

84. The function of enzymes in the living system is to: **(CBSE 1997)**
(a) transport oxygen
(b) provide immunity
(c) catalyse biochemical reaction
(d) provide energy

85. Which one of the following is a shape selective catalyst?
(a) V_2O_5 (b) Cr_2O_3
(c) Hydrated zeolites (d) ZSM-5

86. The process which is catalysed by one of the products is called: **(DPMT 1999)**
(a) acid-based catalyst (b) autocatalyst
(c) negative catalyst (d) positive catalyst

87. The heats of adsorption in physisorption lie in the range (kJ/mol):
(a) 40–400 (b) 40–100 (c) 10–400 (d) 1–10

88. In physical adsorption, the forces associated are: **[CET (Haryana) 2000]**
(a) ionic (b) covalent
(c) van der Waals' (d) H-bonding

89. In Ziegler-Natta polymerisation of ethylene, the active species are:
(a) $AlCl_3$ (b) EtA
(c) CH_2CH_2 (d) Ti^{3+}
(e) $TiCl_4$

90. ZSM-5 converts:
(a) alcohol to petrol (b) benzene to toluene
(c) toluene to benzene (d) heptane to toluene

91. A catalyst increases the rate of reaction by: **(CPMT 1999)**
(a) decreasing enthalpy
(b) decreasing internal energy

(c) decreasing activation energy
(d) increasing activation energy

92. The role of a catalyst in a reversible reaction is to: **(EAMCET 1999)**
(a) increase the rate of forward reaction
(b) decrease the rate of backward reaction
(c) alter the equilibrium constant of a reaction
(d) allow the equilibrium to be achieved quickly

93. A catalyst in finely divided state is more efficient because in this state:
(a) it has got large activation energy
(b) it can react with one reactant more effectively
(c) it has large surface area
(d) all of the above

94. In case of autocatalysis: **(KCET 2002)**
(a) reactant catalyses
(b) heat produced in the reaction catalyses
(c) product catalyses
(d) solvent catalyses

95. Which of the following statements is false? **(KCET 2002)**
(a) Increase of pressure increases the amount of adsorption
(b) Increase of temperature may decrease the amount of adsorption
(c) The adsorption may be monolayered or multilayered
(d) Particle size of the adsorbent will not affect the amount of adsorption

96. Rate of physi-sorption increases with: **(IIT 2003)**
(a) decrease in temperature (b) increase in temperature
(c) decrease in pressure (d) decrease in surface area

97. Which of the following characteristics is not correct for physical adsorption? **(AIEEE 2003)**
(a) Adsorption increases with increase in temperature
(b) Adsorption is spontaneous
(c) Both enthalpy and entropy of adsorption are negative
(d) Adsorption on solid is reversible

98. According to adsorption theory of catalysis, the speed of reaction increases because: **(CBSE 2003)**
(a) the concentration of the reactant molecules at the active centres of catalyst becomes high due to adsorption
(b) in the process of adsorption, the activation energy of the molecules becomes large
(c) adsorption produces heat which increases the speed of the reaction
(d) adsorption lowers the activation energy of the reaction

99. The chemical equilibrium of a reversible reaction is not influenced by: **(KCET 2004)**
(a) catalyst (b) pressure
(c) temperature (d) concentration

100. Identify the gas which is readily adsorbed by activated charcoal: **(KCET 2004)**
(a) N_2 (b) H_2 (c) O_2 (d) SO_2

101. Pick out the one which does not belong to the family of enzymes: **(KCET 2004)**
(a) lipase (b) pepsin (c) ptylin (d) cellulose

102. Which one of the following statements about zeolite is false? **[CBSE (PMT) 2004]**
(a) They are used as cation exchanger
(b) They have open structure which enables them to take up small molecules
(c) Zeolites are aluminosilicates having a three dimensional network
(d) Some of the SiO_4^{4-} units are replaced by AlO_4^{5-} and AlO_6^{9-} ions in zeolites

103. Adsorption of gases on solid surface is generally exothermic because: **[IIT (S) 2004]**
(a) enthalpy is positive (b) entropy decreases
(c) entropy increases (d) free energy increases

104. Identify the correct statement regarding enzymes. **(AIEEE 2004)**
(a) Enzymes are specific biological catalysts that can normally function at very high temperature ($T \approx 1000$ K)
(b) Enzymes are normally heterogeneous catalysts that are very specific in action
(c) Enzymes are specific biological catalysts that cannot be poisoned
(d) Enzymes are specific biological catalysts that possess well defined active site

105. The extent of adsorption of a gas on a solid depends on: **(KCET 2005)**
(a) nature of the gas (b) pressure of the gas
(c) temperature of the gas (d) all are correct

106. The conversion of maltose to glucose is possible by the enzyme: **(AFMC 2005)**
(a) zymase (b) lactase
(c) maltase (d) diastase

107. Which of the following is true in respect of adsorption? **[PET (Kerala) 2006]**
(a) $\Delta G < 0; \Delta S > 0; \Delta H < 0$ (b) $\Delta G < 0; \Delta S < 0; \Delta H < 0$
(c) $\Delta G > 0; \Delta S > 0; \Delta H < 0$ (d) $\Delta G < 0; \Delta S < 0; \Delta H > 0$
(e) $\Delta G > 0; \Delta S > 0; \Delta H > 0$

108. If x/m is the mass of adsorbate adsorbed per unit mass of adsorbent, P is the pressure of the adsorbate gas, a and b are constants, which of the following represents **"Langmuir adsorption isotherm"?** **[PET (Kerala) 2006]**
(a) $\log\left(\frac{x}{m}\right) = \log\left(\frac{a}{b}\right) + \frac{1}{a}\log P$
(b) $\frac{x}{m} = \frac{b}{a} + \frac{1}{aP}$ (c) $\frac{x}{m} = \frac{1+bP}{aP}$
(d) $\frac{1}{(x/m)} = \frac{a}{b} + \frac{P}{a}$ (e) $\frac{1}{(x/m)} = \frac{b}{a} + \frac{1}{aP}$

109. The efficiency of an enzyme to catalyse a reaction is due to its capacity to: **[PMT (Kerala) 2006]**
(a) reduce the activation energy of the reaction
(b) form strong enzyme-substrate complex
(c) decrease the bond energy of all substrate molecules
(d) increase the free energy of the catalyst-substrate reaction
(e) alter the substrate geometry to fit into the shape of the enzyme molecule

110. Although, nitrogen does not adsorb on a surface at room temperature, it adsorbs on the surface at 83 K. Which one of the following statements is correct? **[PMT (HP) 2006]**
(a) At 83 K, there is formation of monomolecular layer
(b) At 83 K, there is formation of multimolecular layers
(c) At 83 K, nitrogen molecules are held by chemical bonds
(d) At 83 K, nitrogen is adsorbed as atoms

111. What is the equation form of Langmuir adsorption isotherm under high pressure? **[CET (Gujarat) 2006]**
(a) $\frac{x}{m}=\frac{a}{b}$ (b) $\frac{x}{m}=aP$ (c) $\frac{x}{m}=\frac{1}{aP}$ (d) $\frac{x}{m}=\frac{b}{a}$

[**Hint:** Langmuir adsorption isotherm may be given as:

$$\frac{x}{m}=\frac{aP}{a+bP}$$

~~At high pressure, $a+bP\approx bP$~~

$$\therefore \quad \frac{x}{m}=\frac{aP}{bP}$$

$$\frac{x}{m}=\frac{a}{b}\ ]$$

112. Freundlich adsorption isotherm is: **[MHT-CET 2007; DCE 2009]**
(a) $\frac{x}{m}=KP^{1/n}$ (b) $x=mKP^{1/n}$
(c) $\frac{x}{m}=KP^{-n}$ (d) all of these

113. Which of the following statements is incorrect regarding physisorption? **(AIEEE 2009)**
(a) It occurs because of van der Waals' forces
(b) More easily liquefiable gases are adsorbed readily
(c) Under high pressure it results into multimolecular layer on adsorbent surface
(d) Enthalpy of adsorption ($\Delta H_{\text{adsorption}}$) is low and positive

114. Active charcoal is a good catalyst because: **[Jamia Millia Islamia (Engg.) 2006]**
(a) it is made of carbon atoms
(b) it is very reactive
(c) it has more adsorption power
(d) it has inert nature towards reagent

115. According to the adsorption theory of catalysis, the speed of reaction increases because: **(AIIMS 2007)**
(a) adsorption produces heat which increases the speed of the reaction
(b) adsorption lowers the activation energy of the reaction
(c) the concentration of reactant molecules at the active centres of the catalyst becomes high due to adsorption
(d) in the process of adsorption, the activation energy of the molecules becomes large

116. The Langmuir adsorption isotherm is deduced using the assumption: **[CBSE (Med.) 2007]**
(a) the adsorption sites are equivalent in their ability to adsorb the particles
~~(b) the heat of adsorption varies with coverage~~
~~(c) the adsorbed molecules interact with each other~~
(d) the adsorption takes place in multilayers

117. The efficiency of enzyme catalysis is due to its capacity to: **[PET (Kerala) 2007]**
(a) form a strong enzyme-substrate complex
(b) change the shape of the substrate
~~(c) lower the activation energy of the reaction~~
(d) form a colloidal solution in water
(e) decrease the bond energies in substrate molecules

118. Which type of phenomenon is used when coloured dye is removed from solution of sugar by charcoal ? **[CET (Gujarat) 2008]**
(a) Absorption
(b) Adsorption
(c) Absorption and adsorption both
(d) None of the above

119. Shape selective catalysis is a reaction catalysed by : **[PMT (Kerala) 2008]**
(a) zeolites (b) enzymes
(c) platinum (d) Ziegler-Natta catalyst
(e) acids or bases

Assertion-Reason TYPE QUESTIONS

The questions given below consist of two statements each printed as '**Assertion**' **(A)** and '**Reason**' **(R).** While answering these questions you are required to choose any one of the following four responses:

(a) If both (A) and (R) are true and (R) is the correct explanation of (A).
(b) If both (A) and (R) are true but (R) is not the correct explanation of (A).
(c) If (A) is correct but (R) is incorrect.
(d) If (A) and (R) are both incorrect.

1. (A) A catalyst does not alter the equilibrium constant of the reaction.
(R) The catalyst forms a complex with the reactants and provides an alternate path with the lower energy of activation for the reaction; the forward and backward reactions are affected to the same extent. **(AIIMS 2010)**

2. (A) Hydrolysis of ethyl acetate in presence of acid is a reaction of first order whereas in presence of alkali, it is a reaction of second order.
(R) Acid only acts as a catalyst whereas alkali acts as one of the reactants.

3. (A) In chemisorption, adsorption keeps on increasing with temperature.
(R) Heat keeps on providing more and more activation energy.

4. (A) A reaction cannot become fast by itself unless a catalyst is added.
(R) A catalyst always increases the speed of a reaction.

5. (A) A catalyst speeds up a reaction but doesn't participate in its mechanism.
(R) A catalyst provides an alternative path of lower activation energy to the reactants.

6. (A) Fruit formation process shows increase in rate with passage of time.
   (R) Hydrolysis of ester is a homogeneous autocatalytic reaction.
7. (A) A catalyst speeds up the process without participating in its mechanism.
   (R) A catalyst provides an alternative path of lower activation energy to the reactants.
8. (A) Catalysts are always transition metals.
   (R) Transition metals have a variable oxidation state.
9. (A) The mass of nickel catalyst recovered after being used in the hydrogenation of an oil is less than the mass of nickel added to the reaction.
   (R) Catalyst take part in the reaction but are recovered in the end.
10. (A) All enzymes are proteins, but all proteins are not enzymes.
    (R) Enzymes are biocatalysts and posses a stable configuration having active sites.
11. (A) The reaction of oxalic acid with acidified $KMnO_4$ is first slow and then proceeds with faster speed.
    (R) Acidified $KMnO_4$ is a strong oxidising agent.
12. (A) For adsorption ΔG, ΔS and ΔH all have negative values.
    (R) Adsorption is a spontaneous process accompanied by decrease in randomness.
13. (A) A gas with higher critical temperature is adsorbed more than a gas with lower critical temperature.
    (R) Higher critical temperature implies that the gas is more easily liquefiable.
14. (A) Physical adsorption of molecules on the surface requires activation energy.
    (R) Because the bonds of adsorbed molecules are broken. **(AIIMS 1994)**
15. (A) Activity of an enzyme is pH dependent.
    (R) Changes in pH affect the solubility of the enzyme in water. **(AIIMS 2003)**
16. (A) Alcohols are dehydrated to hydrocarbons in presence of acidic zeolite.
    (R) Zeolites are porous catalyst. **(AIIMS 2004)**
17. (A) ZSM-5 is used as a catalyst in petrochemical industries.
    (R) Zeolites are three-dimensional network silicates in which some silicon atoms are replaced by aluminium atoms.
18. (A) A catalyst increases the rate of a reaction.
    (R) In presence of a catalyst, the activation energy of the reaction increases. **[EAMCET (Engg.) 2007]**

    [**Hint:** A negative catalyst may increase the activation energy of reaction.]
19. (A) NO is used as a homogeneous catalyst for oxidation of CO.

$$2CO + O_2 \longrightarrow 2CO_2$$

    (R) NO increases the rate of oxidation.

Answers : OBJECTIVE QUESTIONS

1. (a)	2. (b)	3. (d)	4. (c)	5. (d)	6. (b)	7. (a)	8. (c)
9. (d)	10. (c)	11. (c)	12. (c)	13. (d)	14. (d)	15. (c)	16. (a)
17. (a)	18. (d)	19. (b)	20. (a)	21. (b)	22. (a)	23. (b)	24. (a)
25. (d)	26. (d)	27. (c)	28. (b)	29. (b)	30. (a)	31. (d)	32. (c)
33. (a)	34. (b)	35. (c)	36. (a)	37. (d)	38. (b)	39. (a)	40. (a)
41. (c)	42. (d)	43. (c)	44. (a)	45. (d)	46. (c)	47. (b)	48. (b)
49. (b)	50. (a)	51. (d)	52. (c)	53. (c)	54. (a)	55. (c)	56. (b)
57. (d)	58. (a)	59. (a)	60. (d)	61. (b)	62. (c)	63. (b)	64. (b)
65. (d)	66. (a)	67. (a)	68. (a)	69. (d)	70. (d)	71. (c)	72. (a)
73. (b)	74. (d)	75. (c)	76. (c)	77. (d)	78. (a)	79. (a)	80. (c)
81. (b)	82. (c)	83. (a)	84. (c)	85. (d)	86. (b)	87. (c)	88. (c)
89. (d)	90. (a)	91. (c)	92. (d)	93. (c)	94. (c)	95. (d)	96. (a)
97. (a)	98. (a)	99. (a)	100. (d)	101. (d)	102. (d)	103. (b)	104. (b)
105. (d)	106. (c)	107. (b)	108. (c)	109. (a)	110. (b)	111. (a)	112. (d)
113. (d)	114. (c)	115. (b)	116. (a)	117. (c)	118. (b)	119. (a)	

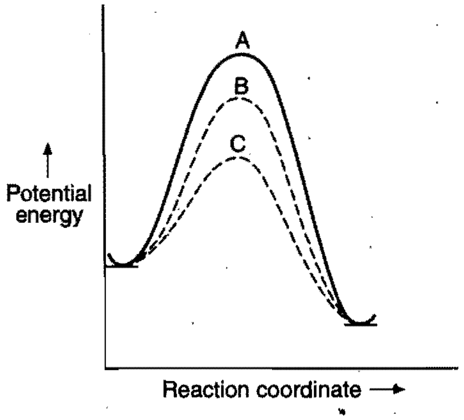
Answers : ASSERTION-REASON TYPE QUESTIONS

1. (a)	2. (a)	3. (d)	4. (d)	5. (d)	6. (a)	7. (d)	8. (b)
9. (b)	10. (b)	11. (b)	12. (a)	13. (b)	14. (d)	15. (b)	16. (b)
17. (b)	18. (b)	19. (b)					

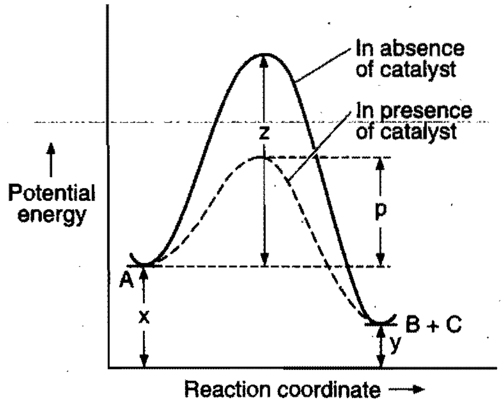
BRAIN STORMING PROBLEMS

OBJECTIVE QUESTIONS *for* IIT ASPIRANTS

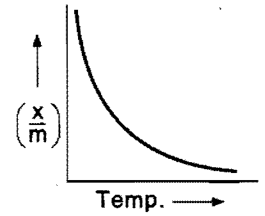
1. In presence of a catalyst, the activation energy is lowered by 3 kcal at 27°C. Hence, the rate of reaction will increase by:
   (a) 32 times (b) 243 times (c) 2 times (d) 148 times
   [**Hint:** $\frac{\text{Rate in presence of catalyst}}{\text{Rate in absence of catalyst}} = \text{Antilog}\left[\frac{\Delta E}{2.303RT}\right]$
   $= \text{Antilog}\left[\frac{3000}{2.303 \times 2 \times 300}\right]$]
2. According to the adsorption theory of catalysis, the rate of reaction increases because:
   (a) adsorption lowers the activation energy of the reaction
   (b) concentration of reactant molecules at the active centres of the catalyst becomes high due to adsorption
   (c) adsorption produces heat which increases the rate of reaction
   (d) adsorption increases the activation energy of the reaction
3. Which of the following characteristics is not correct for physical adsorption?
   (a) Adsorption is spontaneous
   (b) ΔH and ΔS are negative
   (c) It is reversible in nature
   (d) Degree of adsorption increases with temperature
4. Freundlich adsorption isotherm gives a straight line on plotting:
   (a) $\frac{x}{m}$ vs. P (b) $\log\left(\frac{x}{m}\right)$ vs. P
   (c) $\log\left(\frac{x}{m}\right)$ vs. $\log P$ (d) $\frac{x}{m}$ vs. $\frac{1}{P}$
5. Adsorption is an exothermic process. The amount of substance adsorbed should: **(DPMT 2009)**
   (a) increase with decrease in temperature
   (b) increase with increase in temperature
   (c) decrease with decrease in temperature
   (d) decrease with increase in temperature
6. In homogeneous catalytic reactions, there are three alternative paths A, B and C (shown in the figure). Which one of the following indicates the relative ease with which the reaction can take place?



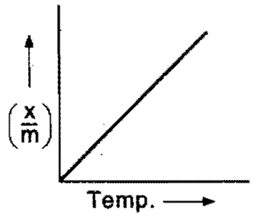
   (a) $A > B > C$ (b) $C > B > A$ (c) $B > C > A$ (d) $A = B = C$
   [**Hint:** Activation energy in the different paths lies in the following sequence: $C < B < A$.
   Lesser is the activation energy, greater is the ease with which the reaction can take place.
   $\therefore C > B > A$ (Decreasing ease with which the reaction can take place.)]
7. For the reaction ($A \longrightarrow B + C$); the energy profile diagram is given in the figure.



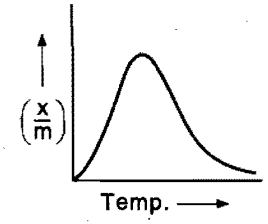
   The decrease in energy of activation in presence of catalyst is:
   (a) z (b) $z - p$ (c) $y - z$ (d) $z - x$
8. Which of the following represents physical adsorption?



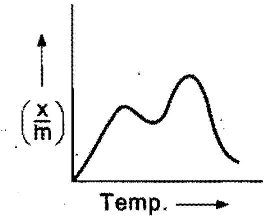
(a)



(b)



(c)



(d)

9. The colloidal system consisting of a liquid adsorbate in a solid adsorbent is termed as:
   (a) aerosol (b) foam
   (c) emulsion (d) gel

10. Which can adsorb a larger volume of hydrogen gas?
(a) Colloidal solution of palladium
(b) Finely divided nickel
(c) Finely divided platinum
(d) Colloidal $Fe(OH)_3$

11. Which is false for a catalyst?
(a) A catalyst can initiate a reaction
(b) It does not alter the position of equilibrium in a reversible reaction
(c) A catalyst remains unchanged in quality and composition at the end of reaction
(d) Catalysts are sometimes very specific in reaction

12. The curve showing the variation of pressure with temperature for a given amount of adsorption is called:
(a) adsorption isobar (b) adsorption isotherm
(c) adsorption isostere (d) adsorption isochore

13. Which of the following statements is incorrect?
(a) Adsorption always leads to a decrease in enthalpy and entropy of the system
(b) Adsorption arises due to unsaturation of valence forces of atoms or molecules on the surface
(c) Adsorption increases with rise in temperature
(d) Adsorption decreases the surface energy

14. Which of the following gas molecules have maximum value of enthalpy of physisorption?
(a) C_2H_6 (b) Ne (c) H_2O (d) H_2
[**Hint:** Since, H_2O can be liquefied easily, hence it will have the maximum enthalpy of physisorption.]

15. Which of the following gases is adsorbed most by activated charcoal? **[AMU (Med.) 2010]**
(a) CO_2 (b) N_2 (c) CH_4 (d) H_2
[**Hint:** CO_2 is an easily liquefiable gas, hence it is adsorbed most by charcoal.]

16. Which of the following factors are responsible for the increase in the rate of a surface catalysed reaction? **[PMT (Kerala) 2006]**
I. A catalyst provides proper orientation for the reactant molecules to react
II. Heat of adsorption of reactants on a catalyst helps reactant molecules to overcome activation energy
III. The catalyst increases the activation energy of the reaction
IV. Adsorption increases the local concentration of reactant molecules on the surface of the catalyst
Select the correct answer using the codes given below:
(a) I and II (b) I and III (c) II and IV (d) I, II and III
(e) I, II and IV

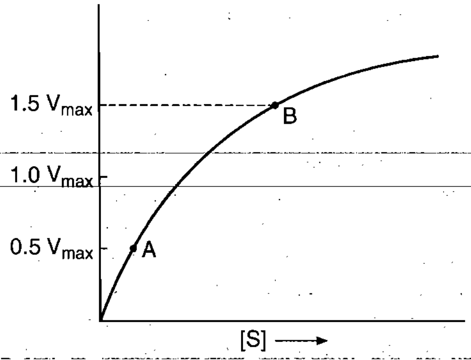
17. In Langmuir's model of adsorption of a gas on a solid surface: **(AIEEE 2006)**
(a) the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered
(b) the adsorption at a single site on the surface may involve multiple molecules at the same time
(c) the mass of gas striking a given area of surface is proportional to the pressure of the gas
(d) the mass of gas striking a given area of surface is independent of the pressure of the gas

18. An enzyme $[E]$ is combined with the substrate $[S]$ as follows:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} P + E$$

The overall reaction rate is given by:
$\text{Rate} = \frac{V_{\max}[S]}{K_m + [S]}$ and the rate of reaction varies with substrate concentration as:



The order of reaction at point A is:
(a) one (b) two (c) three (d) zero

19. Which type of graph gives straight line in Langmuir adsorption isotherm ? **[CET (Gujarat) 2008]**
(a) $\frac{x}{m} \rightarrow \frac{1}{P}$ (b) $\frac{m}{x} \rightarrow \frac{1}{P}$
(c) $\log\left(\frac{x}{m}\right) \rightarrow \frac{1}{P}$ (d) $\log\left(\frac{x}{m}\right) \rightarrow P$

20. Plot of $\log\left(\frac{x}{m}\right)$ against $\log P$ is a straight line inclined at an angle of 45°. When the pressure is 0.5 atm and Freundlich parameter, k is 10, the amount of solute adsorbed per gram of adsorbent will be : ($\log 5 = 0.6990$) **[PET (Kerala) 2008]**
(a) 1 g (b) 2 g (c) 3 g (d) 5 g
(e) 2.5 g
[**Hint :** According to Freundlich Adsorption Isotherm :

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log P$$

When $\log\left(\frac{x}{m}\right)$ is plotted against $\log P$, we get straight line of slope $(1/n)$ and intercept $(\log k)$.

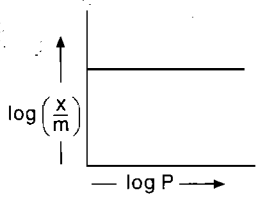
$$\frac{1}{n} = \tan 45° = 1$$

$$\log k = \log 10 = 1$$

$$\frac{x}{m} = k\,(P)^{1/n} = 10\,(0.5)^1 = 5$$

When $m = 1\,g$, $x = 5\,g$]

21. Following graphs will be true when :
(a) $P = 0$ (b) $P = 1$
(c) $\frac{1}{n} = 0$ (d) $\frac{1}{n} = \infty$



Answers

1. (d)	**2.** (b)	**3.** (d)	**4.** (c)	**5.** (d)	**6.** (b)	**7.** (b)	**8.** (a)
9. (d)	**10.** (a)	**11.** (a)	**12.** (c)	**13.** (c)	**14.** (c)	**15.** (a)	**16.** (e)
17. (c)	**18.** (a)	**19.** (b)	**20.** (d)	**21.** (c)			

LINKED COMPREHENSION TYPE QUESTIONS

Passage 1

Only the surface atoms in an adsorbent, play an active role in adsorption. These atoms possess some residual forces like van der Waals' forces and chemical forces.

In the process of adsorption, weak adsorbate is substituted by strong adsorbate. Activated charcoal used in gas mask is already exposed to the atmospheric air, so the gases and water vapours in air are adsorbed on its surface. When the mask is exposed to chlorine atmosphere, the gases are displaced by chlorine. Porous and finely powdered solids, e.g., charcoal and Fuller's earth adsorb more as compared to the hard non-porous material. It is due to this property that the powdered charcoal is used in gas masks. In general, easily liquefiable gases like CO_2, NH_3, Cl_2 *and* SO_2, *etc., are adsorbed to a greater extent than the elemental gases, e.g.,* H_2, N_2, O_2, *He, etc.*

Answer the following questions:

1. Gas masks work on the principle of:
   (a) physical adsorption
   (b) chemical adsorption
   (c) both physical and chemical adsorptions
   (d) absorption
2. Which of the following gases will be most easily adsorbed by the charcoal in the gas mask?
   (a) H_2 (b) O_2 (c) N_2 (d) SO_2
3. Gas mask contains:
   (a) charcoal granules (b) powdered charcoal
   (c) calcium carbonate (d) Fuller's earth
4. Which of the following gas molecules has maximum value of enthalpy of physisorption in a gas mask?
   (a) C_2H_6 (b) Ne (c) H_2O (d) H_2
5. Which of the following gases will substitute O_2 from adsorbed charcoal?
   (a) H_2 (b) N_2 (c) Ar (d) Cl_2

Passage 2

Freundlich adsorption isotherm is obeyed by the adsorptions where the adsorbate forms a multimolecular layer on the surface of adsorbent. In such cases, the degree of adsorption varies linearly with pressure but at high pressure, it becomes independent of pressure.

The relation of Freundlich adsorption isotherm is:

$$\frac{x}{m} = kP^{1/n}$$

where, k and n are constants.

Langmuir adsorption isotherm is obeyed by the adsorption where the adsorbate forms only a unimolecular adsorbed layer. The mathematical relation of Langmuir adsorption isotherm is:

$$\frac{x}{m} = \frac{aP}{1 + bP}$$

Select whether the following statements are true or false:

1. When $\log\left(\frac{x}{m}\right)$ is plotted against $\log P$, we get a straight line with slope $(1/n)$.
   (a) True (b) False
2. The degree of adsorption (x/m) at low pressure will be:
   $$\frac{x}{m} = a$$
   (a) True (b) False
3. When $\left(\frac{m}{x}\right)$ is plotted against $\frac{1}{P}$, we get a straight line with slope $(1/a)$ and intercept (b/a).
   (a) True (b) False
4. In the mathematical relation of Freundlich adsorption isotherm, the value of $(1/n)$ is $0 \le \frac{1}{n} \le 1$.
   (a) True (b) False
5. Freundlich adsorption isotherm is valid for chemisorption.
   (a) True (b) False

Answers

Passage 1.	**1.** (c)	**2.** (d)	**3.** (b)	**4.** (c)	**5.** (d)
Passage 2.	**1.** (a)	**2.** (b)	**3.** (a)	**4.** (a)	**5.** (b)

SELF ASSESSMENT

ASSIGNMENT NO. 13

SECTION-I

Straight Objective Type Questions

This section contains 8 multiple choice questions. Each question has 4 choices (a), (b), (c) and (d), out of which only one is correct.

1. At high pressure, Langmuir adsorption isotherm takes the form:

(a) $\frac{x}{m} = \frac{aP}{1+bP}$ (b) $\frac{x}{m} = \frac{a}{b}$

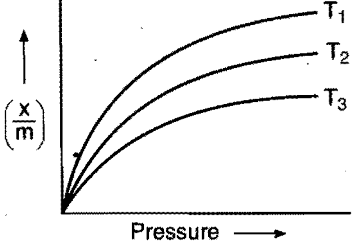
(c) $\frac{x}{m} = aP$ (d) $\frac{m}{x} = \frac{b}{a} + \frac{1}{aP}$

2. Which of the following is used to adsorb water?

(a) Silica gel (b) Anhydrous $CaCl_2$

(c) Coal (d) Coke

3. Select the correct option for the following graph:



(a) $T_1 > T_2 > T_3$ (b) $T_1 = T_2 = T_3$

(c) $T_1 < T_2 < T_3$ (d) $T_1 > T_2 < T_3$

4. Which of the following substances adsorbs H_2 gas most strongly?

(a) Platinum black (b) Nickel powder

(c) Activated charcoal (d) Silica gel

5. The order of volume of gases NH_3, CO_2 and CH_4 adsorbed by one gram of charcoal at 298 K is:

(a) $CH_4 > CO_2 > NH_3$ (b) $NH_3 > CH_4 > CO_2$

(c) $NH_3 > CO_2 > CH_4$ (d) $CO_2 > NH_3 > CH_4$

6. Activated charcoal is prepared by:

(a) adding $Ba_3(PO_4)_2$ to charcoal

(b) treatment with conc. HNO_3

(c) heating charcoal with steam to make it more porous

(d) adding silica to charcoal

7. In the manufacture of H_2SO_4 by contact process the presence of AS_2O_3 acts as:

(a) catalytic promoter (b) induced catalyst

(c) catalytic poison (d) autocatalyst

8. In Rosenmund reactions, presence of $BaSO_4$ acts as .... for Pd.

(a) promoter (b) moderator

(c) inhibitor (d) poison

SECTION-II

Multiple Answers Type Objective Questions

9. Which of the following are correct about a catalyst?

(a) It participates in the reaction but is recovered at last

(b) It does not affect ΔG

(c) It does not affect ΔH

(d) It alters the mechanism of reaction

10. Which of the following statements are correct?

(a) Physical adsorption is of multimolecular layer

(b) Degree of chemical adsorption increases with increase in temperature

(c) Adsorption increases the surface energy

(d) Sometimes solvent is adsorbed in preference to solute

11. Which of the following are zeolites?

(a) Granite (b) Faujasite

(c) Natrolite (d) Thomisite

12. Which of the following act as negative catalysts?

(a) Ethanol in oxidation of chloroform

(b) Tetra ethyl lead used as antiknocking agent

(c) Glycerol in the decomposition of H_2O_2

(d) Fe in the formation of ammonia by Haber's process

13. Select the correct statements about enzymes:

(a) Enzymes are biological catalysts found in organisms

(b) All enzymes are proteins

(c) Enzymes can catalyse any reaction

(d) Enzymes' activity is optimum at 27° C

SECTION-III

Matrix-Matching Type Questions

This section contains 3 questions. Each question contains statement given in two columns which have to be matched. Statements (a, b, c and d) in Column-I have to be matched with statements (p, q, r and s) in Column-II. The answers to these questions have to be appropriately bubbled as illustrated in the following examples:

If the correct matches are (a-p,s) (b-q,r), (c-p,q) and (d-s), then the correctly bubbled 4 × 4 matrix should be as follows:

	p	q	r	s
a	●	○	○	●
b	○	●	●	○
c	●	●	○	○
d	○	○	○	●

14. Match the Column-I with Column-II:

Column-I **(Process)**	**Column-II** **(Catalyst)**
(a) Cracking of hydrocarbons	(p) Ni
(b) Ostwald's process	(q) NO
(c) Sulphuric acid manufacture	(r) Pt
(d) Catalytic converter	(s) NiO

15. Match the Column-I with Column-II:

Column-I **(Catalyst)**	**Column-II** **(Process)**
(a) Ni	(p) Cracking of hydrocarbons
(b) $AlCl_3$	(q) Fischer-Tropsch process
(c) Co/Al_2O_3	(r) Hydrogenation of oil
(d) Zeolite	(s) Friedel-Crafts reaction

16. Match the Column-I with Column-II:

Column-I	**Column-II**
(a) Chemisorption	(p) Exothermic
(b) Physisorption	(q) Endothermic
(c) Desorption	(r) Removal of adsorbed substance
(d) Activation of adsorbent	(s) Specific

Answers

1. (b) **2.** (a) **3.** (c) **4.** (a) **5.** (c) **6.** (c) **7.** (c) **8.** (d)
9. (a, b, c, d) **10.** (a, b, d) **11.** (b, c, d) **12.** (a, b, c) **13.** (a, b, d) **14.** (a-r) (b-r) (c-q, r) (d-p, s)
15. (a-r) (b-s) (c-q) (d-p) **16.** (a-p, s) (b-p), (c-q, r) (d-q)