(27) According to transition state theory, the reaction can be shown passing through which of the following steps ?

(A) Reactants → Products → Activated complex

(B) Reactants → Products

(C) Reactants → Activated complex → Products

(D) Reactants → Activated complex products → Activated complex → Products

(28) For elementary reaction, which of the following is correct ?

(A) Order of reaction > molecularity (B) Order of reaction ≠ molecularity

(C) Order of reaction = molecularity (D) Order of reaction < molecularity.

(29) According to molecular collision theory, the reaction is subjected to .....

(A) Number of molecular collisions of reactant

(B) Number of collisions between reactants and activated complex

(C) The collision rate between reactants and product molecules

(D) Number of effective molecular collisions of reactants

(30) Which scientist explained the effect of temperature on the reaction rate constant ?

(A) Faraday (B) Waag and Guldberg

(C) Le-Chatelier (D) Arrhenius

2. Answer the following questions in brief :

(1) Mention limitation of thermodynamics.

(2) Why does the rate of reaction increase with increase in temperature ?

(3) The charcoal powder burns faster than the piece of charcoal. Why ?

(4) What is called chemical reaction rate ?

(5) Mention the mathematical form of instantaneous rate for the reaction R → P.

(6) What is called specific rate constant ?

(7) Write definition of order of reaction.

(8) The reaction becomes fast by the use of suitable catalyst. Why ?

(9) Write unit of rate constant for zero order reaction.

(10) Write equation of rate constant for first order reaction.

(11) What is called molecularity ?

(12) Write Arrhenius equation.

(13) Mention the value of slope in the graph of log K versus $\frac{1}{T}$.

(14) What is meant by collision theory ? Explain.

(15) Explain half reaction time : Mention its relation with K for the first order reaction.

(16) Write definition of energy of activation.

(17) What is meant by threshold energy ? Why is it required ?

(18) How many times the reaction rate constant increases when temperature of reaction is increased by 10^0 ?

(19) Give examples of very slow and very fast reactions.

(20) For the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$. write the equation for reaction rate.

3. Answer the following questions in detail :

(1) Mention the factors affecting rate of chemical reaction.

(2) A second order reaction is in respect to some reactant. If the concentration of reactant is (1) doubled and (2) halved, then how will the rate constant be changed ?

(3) Explain the effect of temperature, on the rate of chemical reaction.

(4) Mention Arrhenius equation. Explain the terms involved in it.

(5) Write important points of collision theory.

(6) Give definitions : (i) Reaction order (ii) Molecularity.

(7) Derive the equation of rate constant for the first order reaction.

(8) Explain graphical method to determine the order of reaction.

(9) Give information about energy barrier of chemical reaction and explain its importance.

(10) Describe Ostwald's isolation method for determination of order of reaction.

(11) Explain the terms : Half reaction time and energy of activation.

(12) Explain the effect of concentration of reactant on the rate of reaction.

(13) Explain the effect of catalyst on rate of reaction.

(14) Describe the method to determine instantaneous rate.

(15) What is meant by steady state and intermediate compound ?

4. Calculate the following examples :

(1) The initial concentration of N_2O_5 in the first order reaction $N_2O_5(g) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$ is 1.24×10^{-2} mol lit^{-1} at 318 K temperature. The concentration of N_2O_5 decreases to 0.20×10^{-2} mol lit^{-1} after 1 hour. Calculate the rate constant of this reaction at this temperature.

(2) The rate constant of a first order reaction is 1.20×10^{-3} s^{-1}. What time it will take to have reactant 3 gram from 5 gram ?

(3) During decomposition of SO_2Cl_2, its concentration becomes half of its initial concentration in 60 minutes. What will be the rate constant of this reaction ?

(4) The following results are obtained in one pseudo first order reaction :

Time (second)	0	30	60	90
Concentration of reactant mol lit^{-1}	0.551	0.312	0.173	0.085

(i) Calculate average rate of reaction between 30 and 60 seconds (ii) Calculate the rate constant of this first order reaction.

(5) Prove for the first order reaction that the time required for completion of 99% reaction is double than the time required for completion of 90% reaction.

(6) Sucrose is converted to glucose and fructose in presence of acidic solution which is first order reaction. The half reaction time of this reaction is $t_{1/2} = 3.0$ hours. How many times the initial concentration becomes less after 9 hours ?

(7) The decomposition of NH_3 on the platinum surface is zero order reaction. If $K = 2.5 \times 10^{-4}$ Ms^{-1}, what will be the rate of introduction of N_2 and H_2 ?

(8) If the rate of reaction is doubled by increasing the temperature from 298 K to 308 K, then calculate the energy of activation of the reaction.

(9) The half life period of ^{14}C is 5370 years. In a sample of dead tree, the proportion of ^{14}C is found to be 60% in comparison to living tree. Calculate the age of the sample.

(10) The radioactive ^{90}Sr that is formed due to nuclear explosion has half life period of 28.1 years. In the body of a child born at this time ^{90}Sr is found to be 1µg (10^{-6} gram), then what will be ^{90}Sr left in the body of the child when (a) the age of the child will be 20 years and (b) when the age of child will be 70 years. (^{90}Sr is not lost in any other way).

(11) The rate constant of a reaction is 2×10^{-3} min^{-1} at 300 K temperature. By increase in temperature by 20 K, its value becomes three time; then calculate the energy of activation of the reaction. What will be its rate constant at 310 K temperature ?

(12) In a reaction $R \rightarrow P$ the concentration [M] obtained at different times (t) are shown in the following table, calculate the average rate r_{av} of the reaction.

Time (t) (second)	0	5	10	20	30
Concentration [M]	160×10^{-3}	80×10^{-3}	40×10^{-3}	10×10^{-3}	3.5×10^{-3}

(13) The rate constant of a reaction of first order is 70 sec^{-1}. What time will be taken to have the concentration $\frac{1}{18}$ part of the initial concentration ?

(14) The decomposition rate constant of hydrocarbon is 2.428×10^{-5} sec^{-1} at 550 K and activation energy is 197.7 k joule mol^{-1}, then calculate Arrhenius constant.

(15) In the reaction of decomposition of reactant A into product, the rate constant is 4.5×10^{3} sec^{-1} at 283 K temperature and energy of activation is 60 k joule mol^{-1}. At which temperature, the value of rate constant K will be 3×10^{4} sec^{-1} ?

Unit

2

Surface Chemistry

2.1 Introduction

The study of the boundary separating two bulk states or phases is called surface chemistry. This boundary is also known as surface or interface. It is shown by hyphen or slash viz. solid-liquid or solid /liquid. The meaning of this is that the solid and the liquid are two separate states or phases and the interface is between them. As gases mix completely there is no possibility of interface because both of this will be included in one phase. The bulk phase may be pure solid or solution. Interface is a layer of bulk phase consisting of thickness of several molecules. It depends upon the size of the molecules in the bulk phase. In short, surface phenomenon is the phenomenon that keeps the solid and liquid or solid and gas phases in contact even though they are being separate. Such type of phenomena are dissolution, crystallisation, reactions on the electrode, heterogeneous catalysis, corrosion of metals etc. The study of surface phenomenon is useful in industry, analytical chemistry and everyday life.

The surface should be pure and clean. For this $10^{-8} - 10^{-9}$ pascal high vacuum is created and the surfaces of metals can be used. So as to keep them free from the effect of the air they are kept in vacuum. In this unit we shall study the aspects related with surface chemistry such as adsorption, catalysis, colloids, enzymes etc.

2.2 Adsorption

In the solid or liquid state, the molecules experience attraction from all sides but the molecules on the surface experience attraction from below and the sides. Because of this the force on the molecules drawing down is more. Hence, the energy of the molecules on the surface is more. Thus a strain is produced in the surface of the solid or liquid due to the imbalanced or residual forces. If such a surface is brought in contact with any gas or liquid, then it tries to keep it nearer to it by attraction.

For example, suppose in a solution of dye-colour, powder of activated charcoal is added, then in a short time there will be a decrease in the intensity of the colour. The reason for this is that the molecules of the dye colour are attracted towards the solid surface of charcoal. Suppose, such molecules remain on the surface of the solid and do not enter into the solid, then the concentration of the solution on the surface will be more than the concentration of the solution in the inner bulk. Thus change in concentration on the surface is observed. **This phenomenon in which the molecules are maintained on the solid or liquid surface and the concentration of molecules on the surface becomes more than the concentration of the molecules in the bulk, is called adsorption.**

The surface energy decreases due to adsorption. **The solid substance on which adsorption takes place is called adsorbent and the substance which is adsorbed is called adsorbate.** The whole phenomenon is called adsorption. In the earlier example, charcoal is the adsorbent and the molecules or particles of the dye are adsorbate; the whole phenomenon showing adsorption is the surface phenomenon.

Suppose, the adsorbed molecules, for some reason (by decreasing pressure or increasing heat) release from the surface or mix in the gas then it is called desorption. It is reverse or opposite phenomenon. Charcoal, silica gel, chalk, alumina, clay etc. are good adsorbents because they are more porous. Hence, their contact surface is more. If a piece of coal is taken and also powdered coal is taken then as the surface of contact is more in powder; adsorption will be more on powder. Thus, the use of powder state consisting of small particles is more effective in adsorption phenomenon. In many chemical reactions, the catalyst is used in fine powder form. Colloids, which we will study later on in this unit, have very small particles and so the contact surface available is more and so colloids are good adsorbents.

Another phenomenon is called absorption; in which the molecules of the substance are spread in the whole part of the solid or liquid. Hence, it possesses homogeneous (single phase) form. As we have seen, in adsorption, there is heterogeneous (more than one phase) form. Suppose, the light yellow coloured sugar is dissolved in water, we get light yellow coloured sugar solution. As the yellow colour is uniform throughout the solution, the concentration of sugar at all the places will be same. Now, if we add charcoal to this solution, then the yellow colour of solution will decrease and the concentration of solution will be more on the surface of the charcoal than that in the solution. The phenomenon before addition of charcoal is absorption and the phenomenon after addition of charcoal is adsorption. Sometimes, both these phenomena occur simultaneously. It is called sorption. e.g. water is absorbed on the anhydrous calcium chloride while water is adsorbed on silica gel. The dihydrogen gas is first adsorbed on the palladium metal and then it is absorbed. Hence, it experiences phenomenon of sorption.

In the following examples, the phenomenon of adsorption is involved :

(1) If gases like O_2, H_2, CO, Cl_2, NH_3 or SO_2 are filled in closed vessels containing charcoal then their pressures decrease because of the adsorption of gas on the surface of charcoal.

(2) The intensity of the colour of the solution of methylene blue decreases by addition of charcoal because of adsorption of methylene blue on charcoal.

(3) To make yellow sugar colourless, its solution is passed through the layer of charcoal so that the yellow colour is adsorbed on the charcoal and the sugar becomes colourless due to adsorption of yellow colour.

(4) To make the air dry by removing the moisture, it is kept in a closed vessel containing silica gel, so that the moisture (water) is adsorbed on the gel and the air becomes dry.

2.2.1 Mechanism of Adsorption :

The reason for the adsorption is that the molecules on the surface and the molecules in the bulk are not in the same condition. There is attraction force from all the sides on the particles in the bulk and remains balanced but the molecules on the surface do not have attraction from all the sides and so they are not balanced or there are residual forces. These residual forces are responsible for the attraction of the adsorbent on their surface. At the given temperature and pressure the adsorption depends on the area of the surface. More the area of the surface more will be the attraction and more will be the adsorption but if the area of the surface is less then attraction will be less and so adsorption will be less. The second factor in the adsorption mechanism is the heat of adsorption. Adsorption is an exothermic phenomenon or the value of ΔH is negative. The entropy of the molecules decreases due to adsorption. Hence, ΔS also becomes negative. Thus the adsorption phenomenon is associated with the decrease in both ΔH and ΔS. According to second law of the thermodynamics, for any spontaneous reaction, the value of ΔG must be negative. Hence, in equation $\Delta G = \Delta H - T\Delta S$ as the value of ΔS is decreasing the value of $- T\Delta S$ will be positive. Hence, the value of ΔH should be more negative and high. As the phenomenon of adsorption proceeds, the value of ΔH becomes less and less negative; so that the value of ΔH becomes almost that of $T\Delta S$ and the value of ΔG becomes zero. In this situation, the equilibrium is attained.

2.2.2 Types of Adsorption :

There are two types of adsorption (i) Physical adsorption or physisorption and (ii) Chemical adsorption or chemisorption

In physical adsorption, the molecules are adsorbed through van der Waals' forces, while in chemical adsorption, the attraction forces are of chemical bond type. Physical adsorption is a physical process while chemical adsorption is a chemical process. Adsorption is generally an exothermic process. The value of enthalpy of adsorption for chemical adsorption is comparatively more negative than the enthalpy value of physical adsorption.

The comparison of physical and chemical adsorption is given in the following table 2.1.

Table 2.1 Comparison of physical adsorption and chemical adsorption

Physical adsorption	Chemical adsorption
(1) There are van der Waals' forces between adsorbent and adsorbate	(1) There are chemical bond type forces between adsorbent and adsorbate
(2) The value of adsorption enthalpy is about 20 to 40 k $Jmol^{-1}$ i.e. less and negative	(2) The value of adsorption enthalpy is about 80 to 240 k $Jmol^{-1}$ i.e. more and negative
(3) Generally results at low temperature and adsorption decreases with increase in temperature	(3) Generally results at high temperature. There is no special effect of change in temperature
(4) It is not specific i.e. all the gases are adsorbed in a more or less proportion on all solid adsorbents	(4) It is specific. It results if there is possibility of chemical bond formation between adsorbent and adsorbate.
(5) It is instantaneous	(5) It can be slow or fast
(6) Multimolecular layers can be formed on the adsorbent	(6) Generally unimolecular layer is formed on the adsorbent

(7) It is reversible	(7) It is irreversible
(8) Less energy of activation is required	(8) More energy of activation is required
(9) It depends on the nature of the gas. Gases which can be easily liquefied are adsorbed rapidly	(9) It depends on the nature of the gas. The gases which react with adsorbent show more adsorption.

In this unit; we shall study only the adsorption phenomenon of an adsorbate on the solid adsorbent. Some of the illustrations of this are as follows :

(1) Suppose we enter into the atmosphere of chlorine gas by putting on gas mask containing active charcoal, the charcoal will adsorb chlorine and we will be saved from the poisonous effect of chlorine.

(2) To remove moisture from the moist air, silica gel is used as adsorbent. To keep some of the electronic instruments free from moisture, so they may not be damaged by the moisture.

(3) The harmful effect of gaseous pollution in the air can be avoided from their harmful effect by use of charcoal as adsorbent.

(4) Sugar can be made colourless by removing colour (like yellow) from it.

2.2.3 Factors Affecting Adsorption :

The adsorption of gases on the adsorbate depends on the following factors :

(1) Nature of adsorbate (2) Nature of adsorbent (3) The specific area of the adsorbent (4) The pressure on the gas that is adsorbed (5) The temperature (6) Activation of the adsorbent. We shall study some of these factors :

(1) Nature of adsorbate : As studied earlier, physical adsorption being not specific, every gas can be adsorbed on any solid in a more or less proportion. At the given temperature and pressure, the gases like NH_3, HCl, CO_2 etc. which can be easily liquefied are adsorbed in more proportion; while the permanent gases like H_2, O_2, N_2 etc. which cannot be easily liquefied are adsorbed in less proportion. The liquefaction of gas has relation with critical temperature (T_C). Hence, the gases with higher critical temperature are adsorbed more; chemical adsorption being of specific type, if combination is possible, only then adsorption will take place. You have earlier studied about liquefaction of gases, critical temperature, critical pressure and critical volume.

(2) Nature of adsorbent : Generally adsorbents are substances like carbon, animal charcoal, metal oxides, silica gel, alumina and clay. All these adsorbents have their characteristic adsorption properties on the basis of their components and their structure.

(3) Specific area of adsorbent : Specific area means the surface area available for 1 gram adsorbent. More the surface area, more will be the adsorption. More the porosity of the adsorbent more will be the specific area. Hence, in the reactions, porous or powder form of adsorbent adsorbs more gas than blocks of the substance because the available area is more. The iron powder adsorbs more than the iron block. The pores of adsorbent must be big enough so that the adsorbed gas can enter into them.

(4) Adsorption isotherm : Generally the magnitude or the proportion of adsorption of adsorbate gas is expressed as $\frac{x}{\mathrm{m}}$ where m is the weight of the adsorbent and x is the concentration or number of moles of adsorbate when dynamic equilibrium is established between free gas and the adsorbed gas. Experimentally $\frac{x}{\mathrm{m}}$ is determined and at definite temperature, if we plot a graph of $\frac{x}{\mathrm{m}}$ versus p then a curve (isotherm) as shown in fig. 2.1 is obtained. This curve is known as adsorption isotherm curve.

As shown in fig. 2.1 different curves are obtained at different temperatures. In addition, the graphs of isotherms are of different shapes. They are of five different types. We shall study the general isotherm without going into the details of different isotherms. Scientists Freundlich and Langmuir had studied such isotherms and the adsorption isotherm obtained is as shown in fig. 2.1.

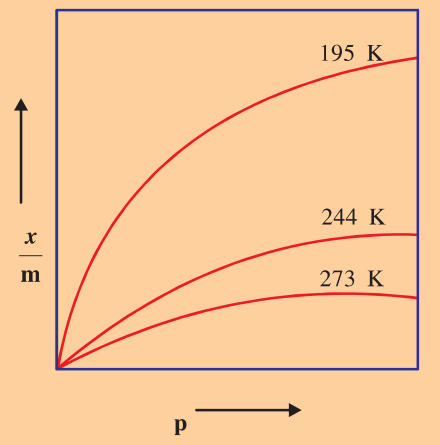


Fig. 2.1 Absorption isotherm

(5) Temperature : There is an effect of increase in temperature on adsorption isotherm. As studied earlier, adsorption is an exothermic reaction, and so according to Le-Chatelier's principle, an increase in temperature will show a decrease in quantity of gas adsorbed. Hence, as shown in fig. 2.1 a decrease in temperature results in an increase in quantity of gas adsorbed.

2.3 Freundlich Adsorption Isotherm

The adsorption of gaseous adsorbate on solid adsorbent at definite temperature is proportional to the pressure of the adsorbed gas. This relation can be shown as below :

$$\frac{x}{\mathrm{m}} \alpha \ \mathrm{p}^{\frac{1}{\mathrm{n}}} \quad \text{OR} \quad \frac{x}{\mathrm{m}} = \mathrm{Kp}^{\frac{1}{\mathrm{n}}} \qquad \text{..... (2.1)}$$

where $\frac{x}{\mathrm{m}}$ is the adsorption per gram of absorbent in which m is the weight of adsorbent and x is the pressure (P) of the adsorbed gas. K and n are constants which depend on nature of gas and the temperature. This is called Freundlich adsorption isotherm. The graph shown in fig. 2.2 shows Freundlich adsorption isotherm. The value of specific adsorption $\frac{x}{\mathrm{m}}$ increases with increase in pressure; but as n > 1 the value of $\frac{x}{\mathrm{m}}$ does not increase so suddenly with increase of p. After certain pressure, the value of adsorption remains almost constant. This isotherm curve is called Freundlich adsorption isotherm. Taking logarithm of equation 2.1

$$\log \frac{x}{\mathrm{m}} = \log \mathrm{K} + \frac{1}{\mathrm{n}} \log \mathrm{p} \qquad \text{..... (2.2)}$$

As this equation is of the type Y = C + mX if the graph of log $\frac{x}{\mathrm{m}}$ versus log p is plotted a straight line will be obtained which is shown in fig. 2.2.

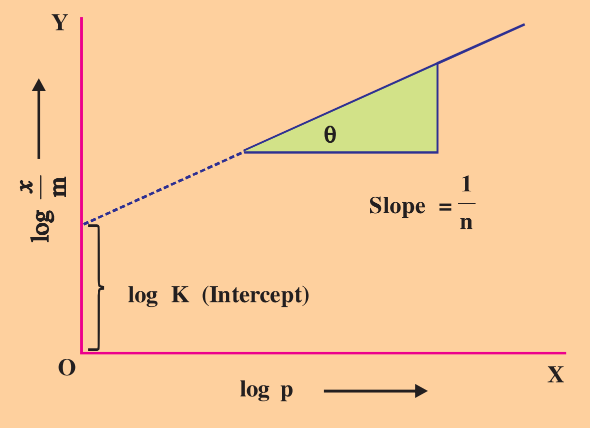


Fig. 2.2 Freundlich isotherm

The value of the slope of the graph will be $\frac{1}{n}$ and the value of intercept will be log K. From this, the values of the constants K and n can be obtained. In addition, whether any adsorption process follows Freundlich equation or not can also be verifed. For this process, if the graph of log $\frac{x}{m}$ versus log p obtained is a straight line, then it satisfies or obeys Freundlich equation.

If you will observe the results carefully in the demonstration experiment on adsorption of methylene blue on charcoal, the explanation will be clear and can be verified.

Limitations of Freundlich adsorption isotherm : In the Freundlich adsorption isotherm, the following deviations and limitations are seen :

(1) This isotherm is applicable in certain limits of pressure but it shows deviation at high pressure so that the curve of the isotherm is changed.

(2) K and n are constants but for the same adsorbent and adsorbate, they change with temperature.

(3) Freundlich adsorption isotherm is empirical; there is no theoretical proof of it.

(4) If the value of $\frac{1}{n}$ is 1 then $\frac{x}{m} = Kp$ so the adsorption will be directly proportional to pressure but if the value of $\frac{1}{n}$ becomes 0, then $\frac{x}{m}$ = constant; so the adsorption will be independent of pressure. Thus, by increasing pressure, the adsorption attains saturation which cannot be explained by Freundlich isotherm i.e. at high pressures it shows deviation.

2.4 Langmuir Adsorption Isotherm

Freundlich adsorption isotherm is empirical. There is no theoretical basis. Langmuir derived a new isotherm on basis of kinetic theory of gases which is called Langmuir adsorption isotherm. It is assumed that all adsorption sites are equal and it is independent of the neighbor sites. He has considered two processes opposite to each other in the isotherm derived by him.

(1) There is adsorption of gas molecules on the surface of solid substance. It is known as condensation.

(2) There is desorption of adsorbed gas molecules from the surface of solid substance. It is called evaporation.

Langmuir assumed that there is dynamic equilibrium established between the above two processes. In addition, he also assumed that adsorbed gas possesses thickness of one molecule or monomolecular layer is formed. Such an aspect is in chemical adsorption. The Langmuir adsorption isotherm can be derived and can be shown in short by the following formula. Langmuir adsorption isotherm can be derived, but it is not in our syllabus. So, it can be written in short as follows :

$$\frac{x}{m} = \frac{ap}{1 + bp} \qquad \text{..... (2.3)}$$

where x/m is the adsorption of gas per gram of adsorbent as seen in Freundlich adsorption isotherm and p is the pressure of the gas; a and b are constants. The above equation can be written in two situations : (1) At low pressure and (2) At high pressure.

(1) **At low pressure :** In the equation $\frac{x}{m} = \frac{ap}{1 + bp}$ if the value p is taken to be low, then the value of bp can be neglected in comparison to 1. Hence $\frac{x}{m} = ap$ i.e. at low pressure, the adsorption of gas is directly proportional to the pressure.

(2) **At high pressure :** In the equation $\frac{x}{m} = \frac{ap}{1 + bp}$, if the value of p is taken high then, 1 can be neglected in comparison to the value of bp. Hence, $\frac{x}{m} = \frac{a}{b} =$ constant. Thus, at high pressure adsorption will be almost constant which is clear from figure 2.1. To determine the constants a and b the equation $\frac{x}{m} = \frac{ap}{1 + bp}$ can be written by inverting it, i.e. it will be $\frac{m}{x} = \frac{1 + bp}{ap}$

$$\text{Now } \frac{m}{x} = \frac{1 + bp}{ap} = \frac{1}{ap} + \frac{bp}{ap} = \frac{1}{ap} + \frac{b}{a} \qquad \text{..... (2.4)}$$

This equation is also the equation for straight line and so if a graph of $\frac{m}{x}$ versus $\frac{1}{p}$ is plotted, then the value of the slope will be equal to $\frac{1}{a}$ and the value of intercept will be equal to $\frac{b}{a}$. From this, the values of constants a and b can be obtained.

Freundlich adsorption isotherm shown in figure 2.1, shows that in the beginning the values of adsorption $\frac{x}{m}$ increases with increase in pressure of gas but when the value of pressure increases, the isotherm tends to become constant, that is the adsorption attains saturation and more adsorption will not take place which supports the above two situations.

2.5 Adsorption From Solution

Freundlich adsorption isotherm can be applied to liquid system like that of gaseous system. The adsorption of substance dissolved in solution can be adsorbed on the solid adsorbent. In the practical book, the experiment of adsorption of methylene blue on charcoal is given for demonstration experiment. You should understand this experiment thoroughly by observation and make this study more simple and intensive. Similar to this, other experiments can be carried out. The adsorption of acetic acid from solution of acetic acid on activated charcoal can be carried out. For this, solutions of acetic acid having different concentration can be taken and definite weight of adsorbent - activated charcoal can be added and the concentration of acetic acid not absorbed can be determined. From the difference of concentrations before adsorption and after adsorption the concentration difference of acetic acid can be determined which will be x • m is known because it is taken by weighing adsorbent. Hence, the graph of $\frac{x}{\text{m}}$ versus concentration of acetic acid before adsorption is plotted and Freundlich adsorption isotherm curve will be obtained. By plotting graph of $\log \frac{x}{\text{m}}$ versus log C a straight line will be obtained which is the proof of Freundlich equation. From this, the following can be written for Freundlich and Langmuir adsorption isotherm for physical and chemical adsorption.

Freundlich adsorption isotherm	**Langmuir adsorption isotherm**
(1) Physical adsorption : $\frac{x}{\text{m}} = \text{Kp}^{\frac{1}{\text{n}}}$ OR $\log \frac{x}{\text{m}} = \log \text{K} + \frac{1}{\text{n}} \log \text{p}$	$\frac{x}{\text{m}} = \frac{\text{ap}}{1 + \text{bp}}$ OR $\frac{\text{m}}{x} = \frac{1}{\text{ap}} + \frac{\text{b}}{\text{a}}$
(2) Chemical adsorption : $\frac{x}{\text{m}} = \text{KC}^{\frac{1}{\text{n}}}$ OR $\log \frac{x}{\text{m}} = \log \text{K} + \frac{1}{\text{n}} \log \text{C}$	$\frac{x}{\text{m}} = \frac{\text{aC}}{1 + \text{bC}}$ OR $\frac{\text{m}}{x} = \frac{\text{b}}{\text{a}} + \frac{1}{\text{C}}$

Applications or uses of adsorption : There are many applications of adsorption phenomenon. Some of them are as follows :

(1) Charcoal adsorbent is used to produce high vacuum, in adsorption of small proportion of gases.

(2) While working in the atmosphere of poisonous gas like chlorine, the gas mask that are used contains active charcoal as adsorbent which adsorbs poisonous gas and provides protection.

(3) Silica gel is used as adsorbent for keeping electronic instruments etc. free from moisture.

(4) Activated charcoal is used for removal of impurity of colour from sugar and other substances.

(5) Vanadium pentoxide used as heterogeneous catalyst in production of sulphuric acid and the iron powder used as heterogeneous catalyst in production of ammonia are useful as solid adsorbents.

(6) In separation of inert gases by Dewar's method activated charcoal is used as adsorbent.

(7) Substances used for treatment of certain diseases act as adsorbent and adsorb the microorganism.

(8) In froth floatation method, in concentration of sulphide minerals, turpentine oil or pine oil are used as adsorbents.

(9) In certain titrations eosin or fluorescin is used as an indicator e.g. In the titration of halide with silver nitrate adsorbate like fluorescin is adsorbed on the precipitates of silver halide. Such indicators are called adsorption indicators.

(10) In chromatographic separation, solid substance can be used as adsorbent and separation of inorganic anions, mixture of amino acid, analysis of dyes in the ink can be carried out by adsorption chromatography. In your book of practicals, demonstration experiment of separation of Pb^{2+} and Cd^{2+} by adsorption chromatography is included. In addition, separation of dyes in the ink by adsorption on adsorbent like filter paper is also included in demonstration experiments.

2.6 Catalysis

In the earlier standards you have studied that oxygen gas is obtained by heating potassium chlorate but this reaction is slow. So, if manganese dioxide is added to it, the decomposition of potassium chlorate becomes fast and manganese dioxide remains in the original form. This means that the decomposition rate of potassium chlorate is slow in absence of manganese dioxide but it becomes faster in its presence. Thus, manganese dioxide as a specific substance, without taking part in the reaction affects the reaction rate. Hence, the following can be deduced.

The substance which is not used in the chemical reaction, is obtained back in its original form and increases the rate of reaction or decreases the time required for going towards the product, is called catalyst and thus the phenomenon of increasing rate of reaction with the help of catalyst if called catalysis. As catalyst does not take part in the reaction, its small amount is essential. Many catalysts are used in industry. In the study of adsorption vanadium pentoxide and iron powder are mentioned as catalysts. Nature is also a unique designer of the use of catalysts. The enzymes associated with many biochemical reactions in living beings makes cell reactions fast and sustains the life viz. invertase enzyme forms glucose and fructose from sucrose; urease enzyme transforms urea to ammonia and carbon dioxide as well as pepsin enzyme transforms proteins into amino acids. In obtaining ammonia from dinitrogen and dihydrogen by Haber's process, iron powder is used as catalyst and vanadium pentoxide works as catalyst in obtaining sulphuric acid by contact process.

Even though every catalyst is specific; it normally decreases the activation energy of a reaction. You have studied about activation energy in the unit on chemical kinetics. The decrease in activation energy with the help of catalyst is shown in fig. 1.9 in unit 1.

(1) Catalyst increases equally both the rates of forward and reverse reactions but does not make any effect on equilibrium constant, i.e., is more proportion of product is not obtained.

(2) Catalyst decreases activation energy, i.e., is it lowers the potential energy barrier. Hence, that reaction results in less time.

Types of catalysis : There are two types of catalysis (1) Homogeneous catalysis and (2) Heterogeneous catalysis.

(1) Homogeneous Catalysis : If the catalyst is in the same phase as the reactants are, it is called homogeneous catalyst and this phenomenon is called homogeneous catalysis. It is believed that in this catalysis the catalyst reacts with reactant by undergoing chemical reaction and forms an intermediate compound. This later on decomposes because it is unstable. This is discussed in chemical kinetics and this unstable compound reacts with other reactant and gives the product and the catalyst is obtained back or is recovered. The examples of homogeneous catalysis are as follows :

(1) $O_3(g) + O(g) \xrightarrow{[Cl(g)]} 2O_2(g)$: Decomposition of ozone.

(2) $2CO(g) + O_2(g) \xrightarrow{[NO(g)]} 2CO_2(g)$: Oxidation of carbon monoxide.

(3) $C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{[H^+(aq)]} \underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}$:

This reaction is called inversion of sucrose.

(4) $SO_2(g) + \frac{1}{2}O_2(g) \xrightarrow{[NO(g)]} 2SO_3(g)$: Method of preparation of sulphuric acid by Lead Chamber process

(5) $CH_3COOCH_3(l) + H_2O(l) \xrightarrow{[H^+(aq)]} CH_3COOH(l) + CH_3OH(l)$: Hydrolysis of ester

(2) Heterogeneous Catalysis : When the catalyst is in different phase from the phase of the reactant the catalyst is called heterogeneous catalyst and this phenomenon is called heterogeneous catalysis. As studied in adsorption, this phenomenon is also known as surface catalysis. Generally, the catalyst is in solid form and reactants are in liquid or gaseous forms. The reaction occurs on the surface of the solid catalyst because it is a surface phenomenon. We have studied this in detail in adsorption. Some examples of heterogeneous catalysis are as follows :

(1) $2HI(g) \xrightarrow{[Au]} H_2(g) + I_2(g)$: Decomposition of gaseous HI on the surface of gold.

(2) $SO_2(g) + \frac{1}{2}O_2(g) \xrightarrow{[V_2O_5(s)]} SO_3(g)$: In oxidation reaction of $SO_2(g)$ use of Vanadium pentoxide (V_2O_5) to obtain sulphuric acid by contact process.

(3) $N_2(g) + 3H_2(g) \xrightarrow{[Fe(s)]} 2NH_3(g)$: To obtain ammonia gas in presence of iron powder by Haber's Process.

(4) $CO(g) + 2H_2(g) \xrightarrow{[Cu / ZnO\text{-}Cr_2O_3]} CH_3OH(l)$: Method of obtaining methanol from carbon monoxide.

(5) By using nickel metal (Raney nickel) in preparing vegetable ghee from vegetable oil (groundnut oil, etc.) saturated fatty acid is obtained by hydrogenation from unsaturated fatty acids. In industry there are many such reactions called catalytic hydrogenation, which depends on such heterogeneous catalysis. Some modern industrial processes based on catalysis are shown in table 2.2.

Table 2.2 Industries based on catalysis

Reactants	Catalyst	Product
Homogeneous :		
(1) Propylene, Oxygen	Mo (VI) complex	Propylene oxide
(2) Methanol, CO	$[Rh(CO)_2I_2]^-$	Acetic acid
(3) Butadiene HCN	Ni, Pd complex compound	Adiponitrile
(4) α-Olefine CO, H_2	Rh/Pd Rhodium palladium complex compound	Aldehyde

Heterogeneous :		
(1) Ethylene O_2	Silver, Cesium chloride on aluminium	Ethylene oxide
(2) Propylene, NH_3, O_2	Bismuth molyblate	Acrylonitrile
(3) Ethylene	Organo chromium and titanium	High density (HDP) polyethylene

2.7 Nature of Solid Catalyst

Solid catalyst can be metals, metal oxides, metal sulphides, clay etc. They can be used in pure form or in mixture form. It is used in crystalline, amorphous or fine particle forms. Their certain characteristics are as follows :

(1) Activity : The basis of activity of catalyst is on the strength of chemical adsorption. The reactant should be adsorbed in proper proportion but not so strongly, that it may not give site to other molecules of the reactant. It is noted that the catalytic activity increases as we move towards metals from group five to group eleven

e.g. $2H_2(g) + O_2(g) \xrightarrow{Pt} 2H_2O(l)$

(2) Selectivity : The selectivity of the catalyst means the reaction should be pushed in such a direction so that the required product can be obtained e.g. In the reaction between $H_2(g)$ and $CO(g)$ different products are obtained in presence of different catalysts viz.

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

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

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

It is apparent from the above reactions that the selection or selectivity of the catalyst is determined for the reaction which we obtain. The effect of catalyst is specific or selective. Hence, any catalyst can be useful for a certain reaction but it may prove to be useless for other reaction. Thus, the catalyst is selective for certain reactions viz. Pepsin enzyme only will be able to convert amino acid from protein in the deodenum.

2.8 Shape-Selective Catalysis by Zeolite

The catalytic-reaction depends on the pore-structure of catalyst, size of reactant and molecules of product. It is called shape-selective catalysis. Zeolites are good shape-selective catalysts. Their structure is like honey comb. Zeolite are chemically three dimensional network silicates in which silicon atoms are replaced by aluminium atoms. They are naturally available as well as can be prepared artificially. Before using zeolites as catalyst, they are heated in the vacuum so that water of hydration is removed. Hence, zeolite becomes porous. The size of their pores is 260 pm to 740 pm. Hence, the molecules whose size is less than this are adsorbed and can be desorbed. Reactions of zeolite catalyst depend on the size and shape of product and reactant. Hence, they are called shape-selective catalysts.

They are mainly used in petrochemical industries for isomerisation and cracking of hydrocarbons. One important zeolite is ZSM-5 which is used in petrochemicals. It converts alcohol directly to gasoline (petrol) by its dehydration. Hence, mixture of hydrocarbons is formed.

Adsorption theory of Heterogeneous Catalysis : This theory explains the heterogeneous equilibrium. The old theory which is the adsorption theory of catalysis mentions that the reactants which are in gaseous or liquid state are absorbed on the surface of solid catalyst. As the concentration of molecules increase on solid surface, the rate of reaction increases. As adsorption is exothermic, the heat that is released is used in increasing the reaction rate.

The catalytic reaction can be explained on the basis of the formation of intermediate compound. This has been studied in chemical kinetics.

According to modern adsorption theory, there is combination and according to the modern theory, intermediate compound formation, the catalytic activity of the catalyst gets localized on the solid surface of catalyst. Five steps are included in the mechanism.

(1) Diffusion of reactant on the surface of the catalyst.

(2) Adsorption of molecules of reactants on the surface of catalyst.

(3) Occurrence of reaction on the surface of the catalyst by formation of intermediate compound.

(4) Desorption of molecules of product from the surface of the catalyst and to provide surface for more reaction to occur.

(5) The diffusion of product away from the surface of the catalyst.

On the surface of catalyst there are more molecules having free valence than in the inner bulk, which become the sites for chemical attraction forces. When gas comes in contact with such surface, the molecules because of weak chemical combination get filled in the sites. They react with each other and form a new molecule. This new molecule leaves the surface by evaporation and new second molecule of reactant comes on the surface. Thus, this theory explained that the catalyst remains as it was at the end of the completion of reaction and so it is required in less proportion. This theory does not give any explanation for the promoter and catalytic poisoning. Promoter means such substance which helps the catalyst in catalytic action and makes the reaction faster e.g. In the production of ammonia by Haber's process alongwith iron powder as catalyst, molybdenum is used as promoter. In production of sulphuric acid, in the presence of platinum catalyst, the impurity of copper decreases the efficiency of the catalyst. It is called catalytic poison.

2.9 Enzyme Catalysis

In dilute solutions, at normal temperature and pressure, many reactions can be carried out by living microorganisms e.g. They collect small molecules and form complex biopolymer like protein and DNA. They get decomposed and extract necessary energy required for continuing many reactions.

Such reactions are catalysed by biochemical catalyst and such biochemical catalysts are called enzymes. Enzymes are proteins and their molecular masses are in the range of 15,000 to 1,00,000 grammole^{-1}. They increase the rate of reaction by 10^8 to 10^{20} times. They are very effective catalysts and they are very specific-any reaction results with any specific enzyme. As seen earlier, the enzyme named urease hydrolyses urea; but other enzyme present in the body does not work for this reaction

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

The enzyme named zymase converts glucose into ethanol and carbon dioxide. The enzyme named pepsin converts proteins into amino acids. In the animals like cows and buffalos the enzyme called cellulase is present and so they are able to get necessary energy for their body by eating the paper, cloth etc. which are cellulose containing compounds. The notable specificity of enzymes is due to the specific active sites on their surface. The reactant molecule which is called substrate of the reaction binds at that active site and the chemical change starts. In most of the cases, the substrate is combined with intermolecular forces - hydrogen bond, dipole forces and other weak attraction bonds.

2.9.1 Mechanism of enzyme catalysis :

According to lock and key model, the key (enzyme) fits with substrate the lock (active site) so that the lock opens and chemical change starts. Modern X-ray crystal study and spectroscopic methods show that in many cases, when substrate reaches to active site, the enzyme changes its shape. This induced fit model of enzyme shows that the substrate induces the active site and makes it completely fit and not rigid shape like key and lock as per the earlier model. This can be thought as we put our hand in hand gloves, then until the hand glove (active site) attains the functional shape of hand (substrate), the shape of the glove will not be clear.

$$\mathbf{E + S \rightleftharpoons [ES] \longrightarrow E + P}$$

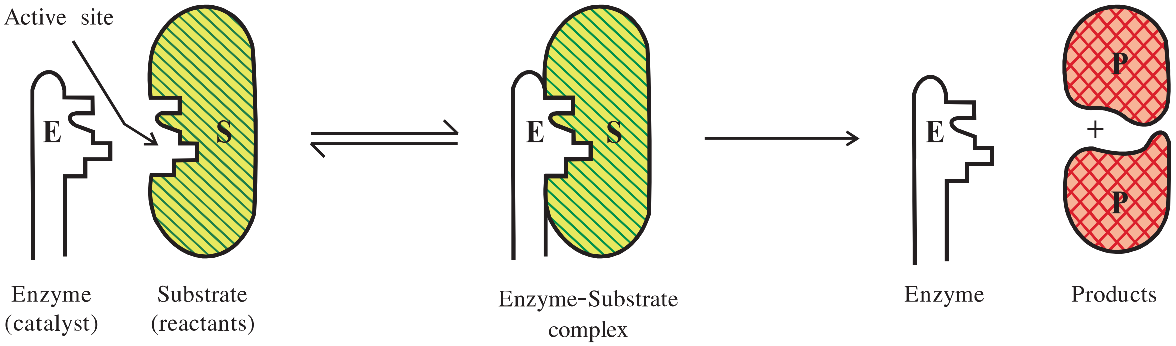


Fig. 2.3 Mechanism of enzyme catalysed reaction

The kinetics of enzyme catalysis is in good agreement with general catalysis. In enzyme catalysed reaction the substrate (S) and the enzyme (E) combine and form intermediate enzyme-substrate complex (ES) whose concentration determines the rate of product (P). In almost all the enzyme reactions, common reactions are as below :

(1) $E + S \rightleftharpoons ES$ (Fast and reversible)

(2) $ES \rightarrow E + P$ (Slow and rate determining)

The rate of enzyme catalysed reactions increases as the concentration of substrate is increased; the change is from first order to zero order. At higher temperature, enzymes cannot survive and so they exhibit failure in the results of the reaction at higher temperature.

2.9.2 Characteristics of Enzyme Catalysis :

Enzyme catalysis possesses unique and high order specificity in its efficiency. The following characteristics are seen in enzymatic production :

(1) One molecule of enzyme can convert ten lacs of reactant molecules to product in one minute.

(2) As the enzyme is specific for every reaction, use of other enzyme is fruitless.

(3) The temperature range of 298-310 K is considered best for the enzyme catalysis. At very high temperature, the enzyme gets destroyed. As the temperature of human body is near 310 K, favourable temperature is available for enzyme catalysed reactions. It is necessary to note that when there is fever the temperature of the body becomes higher than 310 K; there is effect on the enzyme catalyst reactions and there is disturbance in biochemical reactions in human body.

(4) Generally in enzyme catalysed reactions, the rate of reaction is higher in the pH range 5 to 7.

(5) The coenzymes like activators which are with enzymes makes the catalytic reaction of enzyme fast viz. presence of trace amounts of vitamins work as coenzyme for protein in them. Hence, trace amounts of vitamins are essential in body.

(6) Like general catalysis, the inhibition of catalysis or poisoning decreases its activity. Similarly presence of some substances supplies the inhibition or poisoning effect and decreases the activity of the enzyme. Because of certain medicines such effect is produced on enzyme catalyst.

2.9.3 Catalysis in Industries :

The catalysts used in industries and the processes are shown in table 2.3

Table 2.3

Process	Catalyst
(1) Production of ammonia by Haber's process $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	Finely powdered form iron, catalyst, molybdenum promoter, 200-atmosphere pressure and 723-773 K temperature
(2) Ostwald's process of production of nitric acid $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$ $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $4NO_2(g) + 2H_2O(l) + O_2(g) \rightarrow 4HNO_3(aq)$	Platinised asbestos, Temperature 573 K
(3) Production of sulphuric acid by Contact process $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $SO_3(g) + H_2SO_4(aq) \rightarrow H_2S_2O_7(l)$ and $H_2S_2O_7(l) + 2H_2O(l) \rightarrow 2H_2SO_4(aq)$	Platinised asbestos or vanadium pentoxide (V_2O_5), Temperature 673-723 K.

2.10 Colloids

As studied in earlier standards the true solutions are homogeneous systems viz. solution of common salt or solution of sugar. If we mix sand and water and keep aside for sometime after shaking it, then the sand will settle down. In the earlier homogeneous solution common salt or sugar does not settle down. Thus, the settling down of sand is called suspension. There is a large group of systems in between these two states which is called colloidal dispersion. For simplicity we call them as colloidal solution or colloid or sol. The definition of colloid can be given as below :

"Colloid is a heterogeneous system in which one phase is called the dispering phase and has very fine particles suspended in dispersion medium". The difference between solution and colloid is the size of the particles in them. In solutions particles are ions or small molecules. The dispersion system possesses some macromolecules. Such macromolecules are the protein, synthetic polymer, or aggregate as many atoms, ions or molecules. Colloid molecules are bigger than normal molecules but their sizes are not such that they may get separated but are small and remain suspended in solution. The size of the colloid particles is 1 to 1000 nm. The colloidal particles because of their small size have a large proportion of surface area per gram. Suppose we take a cube of 1 cm length then the total surface of its six sides will be 6 cm^2. If we divide this cube into uniform 10^{12} cubes, then it will be of the size of colloid particle and the total surface area will be 60,000 cm^2 or 6 m^2. Because of this surface area colloid possesses specific property viz. it can act as adsorbent.

Type of colloids : The types of colloids are classified on the basis of the following points :

(a) Physical state of dispersion phase and dispersing medium.

(b) The nature of attraction between dispersing phase and dispersion medium.

(c) Types of particles of dispersed phase

(a) Classification on the basis of the physical states of dispersing phase or dispersion medium : This classification is made on the basis of the dispersing phase and dispersion medium to be solid, liquid or gas. Eight types of colloid systems are included in this classification. This classification is shown in table 2.4.

Table 2.4 Classification of colloid systems

Dispersing phase	Dispersion medium	Type of colloid	Example
(1) Solid	solid	solid sol	Some coloured glass and gemstone
(2) Solid	liquid	sol	Cell fluid
(3) Solid	gas	aerosol	Smoke, dust
(4) Liquid	solid	gel	Cheese, butter jelly,
(5) Liquid	liquid	emulsion	Milk, Hair cream
(6) Liquid	gas	aerosol	Mist, cloud pesticides spray
(7) Gas	solid	solid sol	Pumice stone, Foam rubber
(8) Gas	liquid	foam	Froth, foam

Many natural and artificial things used in everyday life are colloids. Many biological fluids are aqueous sols. Proteins, nucleic acid etc. are aqueous solutions of colloid particles, ions and small molecules. From the systems mentioned in table 2.4 the most common is 'sol' i.e., dispersion of solid in liquid, and emulsion, which means dispersion of liquid in liquid. In this unit we will study dissolution and emulsion. If dispersion medium in colloid is water, then it is called aqua sol or hydrosol and if the dispersion medium is alcohol then it is called alcosol.

(b) Classification on the basis of nature of interaction between dispersing phase and dispersion medium : There are two types of such colloids (a) Lyophilic and (b) Lyophobic. In lyophilic type, the colloid particle attracts solvent and in lyophobic type, repels solvent. If dispersion medium is water then lyophilic is called hydrophilic and the lyophobic is called hydrophobic colloid.

(1) Lyophilic colloid : Lyophilic colloids are liquid-attracting. Their colloid solutions can be directly obtained viz. lyophilic colloid is obtained by mixing gum, gelatin, starch, rubber etc. with suitable liquid (dispersion medium). If the dispersion medium is removed from this type of colloid then dispersing system is obtained back and if the dispersion medium is added again the lyophilic colloid is obtained again. Thus, these colloid solutions are possessing reversible property and so are called reversible sols. They are comparatively very stable and so their coagulation does not occur on its own and so, they are called stable colloids. Coagulation means precipitation of colloid solution. We shall study in detail about this later on.

(2) Lyophobic colloids : Lyophobic colloids are liquid-repelling. If metals, their sulphides are mixed with dispersion medium colloidal sol is not obtained. Special methods are to be used for their preparation which we shall study later on. In such sols, if an electrolyte is added in small proportion and heated or stirred well, precipitates are obtained or get coagulated. Hence, they are not stable. If dispersion medium is separated and then again mixed with dispersion medium then those precipitates do not give sol again. Hence, they are called irreversible sols. Some substances are added to give stability. They are called stabilizers.

(c) Classification on the basis of types of dispersing phases : Colloids can be classified on the basis of types of dispersing phase. For example (1) multimolecular (2) macromolecular and (3) associated colloids. The information about them is as follows :

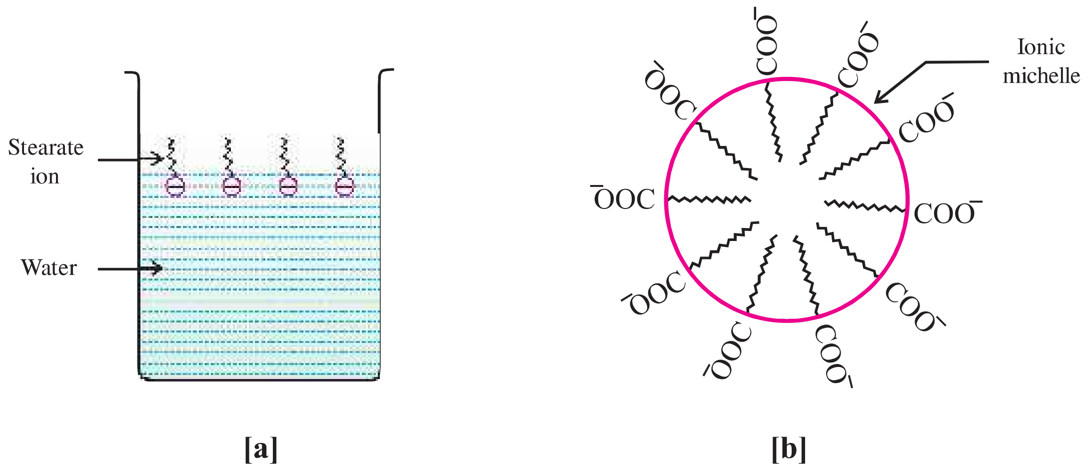
(1) Multimolecular Colloid : When dissolution is carried out, atoms of substances of small particles in very large amount associate with each other and prepare a species whose diameter is more than 1 nm; that is in the range of diameter of colloid particle. Such a species that is formed is called multimolecular colloid e.g. Gold dissolution possesses particles of different sizes having atoms. Similarly dissolution of sulphur possesses thousands or more molecules of sulphur.

(2) Macromolecular Colloid : The molecular masses of macromolecular colloid are very high. When such molecules are dissolved in proper solvent a solution that is obtained in which the small size of macromolecular substance changes into the size of colloidal particles. Such a system is called macromolecular colloid. These colloids are very stable and in many aspects appear like true solutions e.g. starch, cellulose, protein and enzymes. In manmade macromolecular substances like, nylon, polyethylene, polystyrene, artificial rubber etc. are also included.

(3) Associated Colloid : Some substances at lower concentrations show general behaviour but at higher concentration associated particles are formed, which is called micelle. The formation of micelle takes place at temperature higher than certain temperature called Kraft temperature (T_K). At concentration higher than certain value, micelle is formed and this is called critical micelle concentration (CMC). On dilution these colloids change into their original ions. Surface active substances - like soap, artificial detergent are included in this. Such colloids possess both types of lyophilic and lyophobic parts; 100 or more molecules are present in micelle.

Mechanism of micelle formation : We take example of soap solution. Soaps are considered to be salts of fatty acids viz. sodium stearate $CH_3(CH_2)_{16}$ $COO^- Na^+$ or $R\,COO^-Na^+$ where $R = CH_3(CH_2)_{16}$ chain. It is main component in most of the soaps. When they are dissolved in water, they dissociate into $R\,COO^-$ and Na^+. There are two parts in the ion $R\,COO^-$. One hydrocarbon chain R is known as nonpolar tail and it is hydrophobic and the polar group COO^- is known as polar ionic head. Head is hydrophilic. Hence, $R\,COO^-$ ions are present on the surface and their COO^- part remains in water and hydrocarbon part R remains away from it on the surface. At high concentration they are dragged in the bulk of solution and they associate in spherical form and attract towards the centre of their hydrocarbon chain. At this time COO^- part remains outside on the surface. This type of formation of association on ions is called micelle. Such micelle contains about 100 such ions.

Similarly, in detergent, e.g. sodium lauryl sulphate- $CH_3(CH_2)_{11}$ $SO_4^-Na^+$, its polar group- SO_4^- is with long hydrocarbon chain. So, micelle formation in this is similar to that in the soap. The cleansing action is shown in fig. 2.4.



[a] [b]

Fig. 2.4 Micelle

2.11 Methods of preparing colloid-Sol

The methods to prepare lyophilic and lyophobic sols are as follows :

2.11.1 Preparation of lyophobic sol :

Lyophobic sol can be prepared by the following two methods : (A) Condensation methods (B) Dispersion methods.

(A) Condensation methods : In condensation methods the particles of atomic or molecular sizes are induced to combine, so that the associate having dimensions of colloid, are formed. For this (i) Chemical as well as (ii) Physical methods are taken into use.

(i) Chemical methods : Colloidal solution-Sol can be prepared by process like double decomposition, oxidation-reduction or hydrolysis e.g.

$$As_2O_3 + 3H_2S \xrightarrow{\text{Double decomposition}} \underset{\text{(sol)}}{As_2S_3} + 3H_2O$$

$$SO_2 + 2H_2S \xrightarrow{\text{Oxidation}} \underset{\text{(sol)}}{3S} + 2H_2O$$

$$2AuCl_3 + 3HCHO + 3H_2O \xrightarrow{\text{Reduction}} \underset{\text{(sol)}}{2Au} + 3HCOOH + 6HCl$$

$$FeCl_3 + 3H_2O \xrightarrow{\text{Hydrolysis}} \underset{\text{(sol)}}{Fe(OH)_3} + 3HCl$$

(ii) Physical methods :

(a) By exchange of solvent : When any true solution is mixed with other solvent in excess in which the dissolved solute is insoluble and the solvent is soluble, a colloid solution is obtained e.g. colloid of sulphur is obtained when excess of water is added to a solution of sulphur prepared in alcohol.

(b) Excessive cooling : To obtain colloid solution of ice in organic solvent like chloroform or ether the solution in water is cooled. The molecules of water which cannot remain separate, associate and form particles of the size of colloid particles and sol is obtained.

(B) Dispersion methods : In dispersion methods, big particles of the substance are broken in the presence of dispersion medium and changed to smaller particles. Some suitable stabilising agent is added to make them stable. Some known methods among the dispersion methods are as follows :

(i) Mechanical dispersion : In mechanical dispersion method the original suspension of the substance are made smaller in dispersion medium by grinding with colloid mill and brought to colloidal state. Such mills are ball mill, ultrasonic disperser and colloid mill used for grinding. Colloid mill is shown in Fig. 2.5.

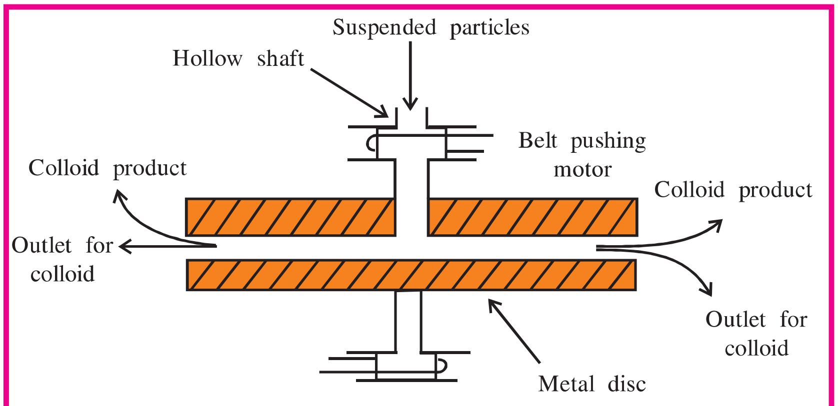


Fig. 2.5 Colloid mill

As shown in the fig. 2.5 there are two layers in the colloid mill. At very high velocity about 7000 revolutions per minute, the two layers are rotated in direction opposite to each other. The suspended particles get grinded and change to small colloidal size and the sol is obtained.

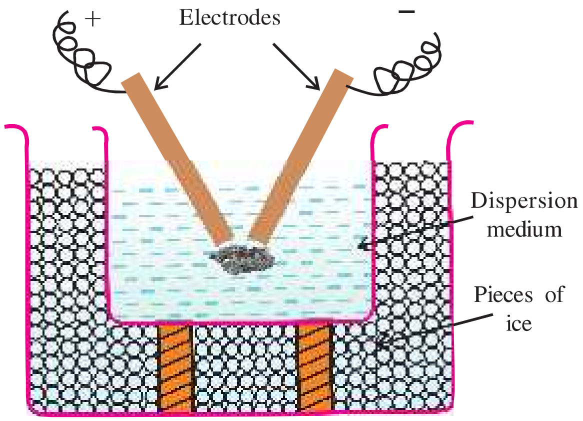


Fig. 2.6 Bredig's Arc Method

(ii) Electric dispersion or Bredig's Arc method : In Bredig's Arc method, dispersion and condensation both are involved. Colloidal solutions of metals like gold, silver, platinum etc. are obtained by this method. As shown in figure 2.6 electric spark is applied between the electrodes of the metal kept in dispersion medium. High degree of heat is produced due to the spark which evaporates the metal. Hence, particles of the size of the colloids of the metals are obtained in the medium. Ice is filled in the outer vessel to cool this system.

(iii) Peptization : Suitable precipitates of electrolyte are obtained. The precipitates are stirred in the dispersion medium in presence of electrolyte, taken in small proportion and the precipitates are converted to colloidal particles and sol is obtained. This transformation method is called peptization. The cations and the anions used in this reaction; any one of them is present in the solution are common. Because of this, positive or negative electric charge is produced on the precipitates. As a result of this it breaks into small pieces and the size of the particles is in the range of colloid particles e.g. Freshly prepared ferric hydroxide ($Fe(OH)_3$) precipitates are mixed with aqueous ferric chloride ($FeCl_3$) solution which is called peptizing agent and is stirred. Hence, Fe^{3+} ions are adsorbed on the surface of the precipitates. As a result particles are changed to the size of colloid particles and sol is obtained.

2.11.2 Preparation of Lyophilic Sols :

As lyophilic sols are very stable, they can be prepared by mixing lyophilic substance with dispersion medium and stirring it e.g. the sols of gelatin, gum, starch, egg albumin etc. can be obtained by adding water and then stirring. Some sols being reversible, if the solvent has evaporated, they can be again prepared by adding solvent. You are familiar regarding this with colloid of gum.

2.12 Purification of Colloidal Solution-sol

There are impurities in the sols prepared by different methods. This is because of the presence of electrolytes, other soluble substances which are also present as impurity. These impurities can make the sol unstable. Hence their purification is necessary.

In the very important method of purification, semipermeable membrane is used and the soluble impurities from the sol are removed. This is called dialysis.

(1) Dialysis : Across the semipermeable membranes like parchment paper, butter paper, cellophane membranes, the particles of the true solutions can pass through but the particles of colloid which are larger in size are not able to pass through. You have studied earlier about this in osmosis. A bag of such semipermeable membrane is prepared and sol is filled in. As shown in fig. 2.7 it is dipped in a vessel filled with distilled water. The particles of the electrolyte can come out but the colloid particles are not able to come out. Fresh distilled water should be added to the vessel and a siphon system can be arranged so that continuous purification can be carried out by dialysis. In the above method, if two electrodes are kept outside the bag and electric current is passed, the cation and the anion of the electrolyte will be attracted rapidly to the electrodes of opposite charge and the impurity will be removed very fast. Hence, this method is faster than general dialysis. This method is called electrodialysis. By this method better purification can be carried out.

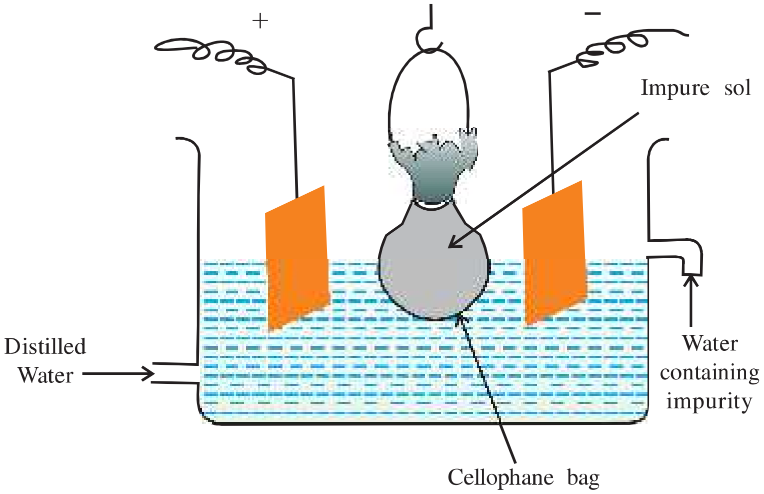


Fig. 2.7 Electrodialysis

When the kidney of a person is not functioning properly and becomes incapable of throwing out unnecessary waste, then an artificial machine is used for the function of kidney. This is called kidney dialysis in common practice. It is used in hospitals and is based on such a principle.

(2) Ultrafiltration : In ultrafiltration method, colloidal solution, special type of filter paper which is known ultrafilters is used for filtration. Such filter papers allow only the electrolyte to pass through. Such filter papers are prepared by impregnation of colloidal particles on ordinary filter paper. To make the filtration fast, external pressure is increased and it is sucked so that the rate of filtration becomes faster.

(3) Ultracentrifugation : In ultracentrifugation method, colloidal solution is taken into a hard glass tube and is placed in the ultracentrifuge machine. When ultracentrifuge is started the inner tube performs rotational motion with very high speed. As a result the colloidal particles are collected at the bottom of the glass tube because of centrifugal force. Impurities remain dissolved in the upper solution. It is called centrifugate. The colloidal particles which have settled down in the tube are mixed with suitable dispersing medium so that sol is regenerated and the upper impure solution is thrown away.

2.13 Important Properties of Colloidal Solution-sol

The important properties of colloidal sol are of four types : (1) Colligative properties (2) Optical properties (3) Mechanical properties and (4) Electrical properties.

(1) Colligative properties : The colligative properties are proportional to the concentration of substance or the concentration of the particles inside it. Colloidal solution-sol shows colligative properties like decrease in vapour pressure, elevation in boiling point, depression in freezing point, osmotic pressure. As the average molecular mass of colloidal particles is very high, the mole fraction of dispersed phase is very low. Hence, notable change is not observed in the results of colligative properties. Only osmotic pressure method is used to determine the molecular masses of polymer molecules like colloid.

Fig 2.8

(Three beams of white light passing through a colloid of sulphur particles in water change from orange to pink and bluish green. The colours produced depend on the size of the particles and also on the position of viewers. The smaller the particles, the shorter (blue) the wavelength.)

(2) Optical properties : Scientist Tyndall mentioned in 1869, that if a ray of light is passed through colloidal solution placed in the dark, then its path is illuminated. This phenomenon is called Tyndall effect. It is due to scattering of rays of light by colloid particles. The illuminated path is called Tyndall cone. You must have observed a similar phenomenon. If there is hole in the ceiling of a closed room, and if sunlight enters into the room through the hole, then the dust particles (like colloid particles) scatter this light and you will see an illuminating path. When the head lights of vehicles are on at night, you will find an illuminated path on the road at night. True solutions do not show Tyndall effect because the particles are very small so that they are not able to scatter the rays of light.

If three rays of light are passed through colloidal sulphur, they are changed from orange to pink, and from bluish to green colour. These colours depend on the size of the colloid particles and the position of the observer. If the size of the particles is small then wavelength is less (bluish).

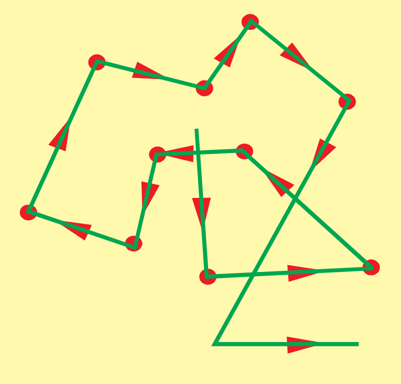


Fig. 2.9 Brownian movement

(3) Mechanical properties : Brownian movement : Botanist Robert Brown suggested in 1827 that if the pollen grains of the flower are placed in water, then they do not remain stationary but continuously and randomly move. Phenomenon similar to this was noted later on for the colloidal particles when the colloidal particles were observed under the instrument like ultramicroscope, they were moving continuously in zigzag directions as shown in fig. 2.9.

If there is an increase in the size of the particles, then the effect (collision) becomes average and the Brownian movement becomes slow. At last if the dispersed particles become so big that their dimensions are such that the medium particles of smaller dimension of the particles are not able to move them by pushing- that is, Brownian movement cannot be observed. Two important results are obtained from this property.

(1) According to kinetic theory, on the basis of this hypothesis, the molecules are in continuous motion, and straight way are demonstrated by this observation.

(2) Brownian movement attacks against the gravitation force existing on the particles and as a result they do not allow colloidal particles to settle down at the bottom and does not make the colloid unstable. Hence, the colloidal solution-sol attains stability.

(4) Electrical properties : Electrophoresis : A colloidal particle possesses positive or negative electric charge. The polarity of the sol not only depends on the dispersing phase but also on dispersion medium which has equal but of opposite positive or negative charge. Hence, colloidal system is neutral. Colloidal particles possess similar electric charge and so experience repulsion. Hence, they are not able to form big molecule by combination. So, the sol remains stable and the particles do not settle down. Arsenious sulphide, gold, silver and platinum possess negative electric charge in their colloidal solutions;

while the colloids of ferric hydroxide, aluminum hydroxide, zirconium hydroxide possess positive electric charge. The existence of positive or negative electric charge of the colloid can be determined by the phenomenon like electrophoresis. In this the colloid particles according to their electric charge are attracted towards positive or negative electrode under the effect of electric field. The electrophoresis instrument is shown in fig. 2.10.

Colloidal solution is filled in U-shaped tube. Platinum electrodes are fixed on the two ends of the tube. On passing electric current the colloidal particles are moving towards the electrode of opposite charge. Suppose we take arsenious sulphide sol then the colloidal particles will move towards anode because arsenious sulphide colloid possesses negative electric charge. Iron hydroxide colloid possesses positive charge and so will get attracted towards negative electrode.

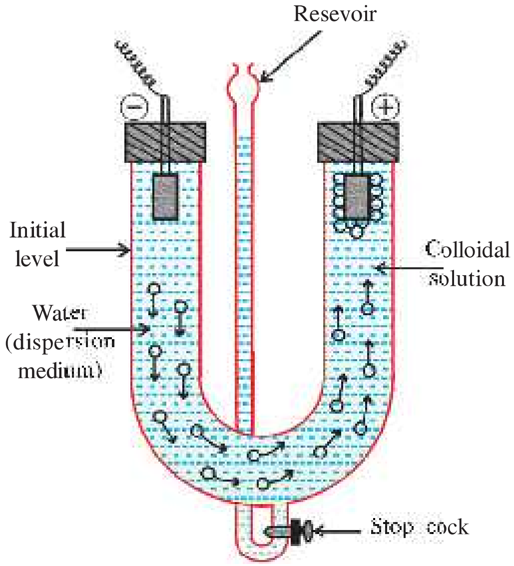


Fig. 2.10 Electrophoresis

2.14 Coagulation of Colloids

For the stability of the colloids presence of electrolyte in small proportion is essential but if the concentration of electrolyte is increased then the colloid particles in the solution attract the ions of opposite electric charge and become neutral. Neutral particles combine with each other and start forming associated and become larger in size. As a result they get precipitated and separate from colloidal solution. **The formation of association of colloid particles by addition of electrolyte to form an insoluble precipitate is called coagulation. If concentration of electrolyte is less, then association of particles occurs but they do not get precipitated and can go back to the form of colloid. This phenomenon is known as flocculation.** If concentration of electrolyte gets increased, they result in coagulation. When the water of a river containing colloidal clay enters the water of the sea, it gets induced for coagulation because of the salts present in sea water and the layers of the clay are formed. It is necessary to note that the coagulation of colloidal solution does not occur until certain amount of electrolyte is not available to coagulate by the electrolyte. The minimum amount (in milli-moles) of the electrolyte required for complete coagulation of colloidal solution or sol is called the coagulation or precipitation value of the electrolyte.

The coagulation values of different electrolytes are different. Scientists Hardy and Schulze studied the behaviour of different electrolytes. The two laws that they have noted are as follows :

(1) The effective ion for the coagulation of sol is that which possesses opposite electric charge compared to electric charge of colloidal particles.

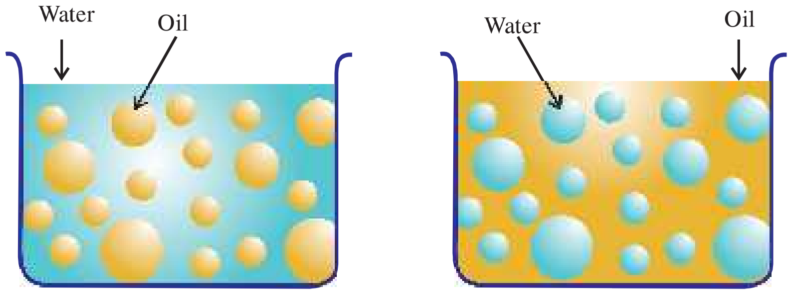
(2) The coagulating power of the electrolyte is in the fourth power of the valency of the coagulating ions.

It can be said from the above rules that for negatively charged sol like As_2S_3, positive ions (cations) can have coagulation and if the positively charged sol like $Fe(OH)_3$, negative ions (anions) can have coagulation. The order of different coagulating ion for negatively charged As_2S_3 is monovalent ion (Na^+) < divalent ion (Ba^{2+}) < trivalent ion (Fe^{3+}) i.e. $Fe^{3+} > Ba^{2+} > Na^+$. Similarly, for sol like $Fe(OH)_3$ having positive charge trivalent $PO_4^{3-} > SO_4^{2-} > Cl^-$. From this it can be said that the concentration of ions necessary for coagulation will be concentration of trivalent ion < concentration of divalent ion < concentration of monovalent ion. Both the above observations are known as Schulze-Hardy rules.

These observations show that necessary precaution should be taken for keeping the colloidal solution having small proportion of electrolyte, separated from the atmosphere; otherwise coagulation will result and the colloid solution will become useless.

2.15 Emulsion

Emulsions are colloids but the dispersion medium and dispersed phase both are in liquid form. There are two main types of emulsion (1) Oil in water (oil / water) emulsion and (2) Water in oil (water /oil) emulsion.



Oil in water

Water in oil

Fig. 2.11 Types of emulsions

(1) Oil /water emulsion : In this type of emulsion, oil (organic solvent) acts as dispersed phase and water acts as dispersion medium. The examples of this type of emulsions are milk, vanishing cream etc.

(2) Water /oil emulsion : In this type of emulsion, water is dispersed phase and oil (organic solvent) acts as dispersion medium. Cold-cream, butter, cod-liver oil etc are this type of emulsions.

2.15.1 Test of Emulsion :

The methods to test both the types of emulsion as described above are as follows :

(i) Dye test : Certain dyes soluble in oil are added to emulsion and if the background becomes coloured then emulsion is water in oil. If coloured droplets or small particles are formed then it can be said that the emulsion is oil in water.

(ii) Dilution test : If dilution of emulsion with water is possible then it can be said that dispersion medium is water and so the emulsion is oil in water type. If the added water makes a separate layer then it can be said that the emulsion is of water in oil type.

2.15.2 Preparation of Emulsions :

(1) Emulsification : The method of preparation of emulsion is called emulsification. Emulsion can be obtained by forcibly mixing the two liquids. Hence, unstable emulsion will be obtained. Dispersed drops will immediately come nearer and will form a separate layer. For stabilization of emulsion, some third substance is added in small proportion which is called emulsifier. it is always required; Soap and detergents are mostly used as emulsifiers. They form a layer on the drops and stop them from coming near to each other. Hence, emulsion becomes stable. Other stabilizing substances are protein, gum, agar etc.

The type of emulsion depends on the relative proportion of both the liquids. If water is more, then oil in water type and if oil is more, then water in oil type emulsion is formed. This type of emulsion depends on the nature of emulsifying substance. For example, in presence of soluble salt (alkali metal atom containing soap) like emulsifier, the oil in water type emulsion is favoured; while in insoluble soap (soap containing non-alkali metal) water in oil type emulsion is favoured.

2.15.3 Demulsification :

Separation of two components of emulsion is called demulsification. The techniques used for demulsification are freezing, boiling, centrifugation, electrostatic precipitator or chemical methods to destroy emulsifier.

2.16 Uses of Colloids

Colloids and emulsions have many uses in our everyday life and industries. Some of them are as follows :

(1) Rubber plating : The negatively charged particles of rubber colloid are deposited on the handles of vessels and other wares. Rubber gloves are prepared by depositing colloids like this on suitable thing.

(2) Sewage disposal : Electrically charged colloidal particles of dirt are there in the sewage water which do not settle easily. They are removed by making them electrically discharged near the electrodes. Dirty water is passed from one tunnel in which metal electrodes are fixed.

Because of high electric potential (30,000 volt or more) the colloidal particles are attracted towards the electrode of charge opposite to their own and the electric charge is neutralized so that coagulation takes place. The displaced matter can be used as fertilizer and the water can be used for irrigation purpose.

(3) Cottrell Smoke Precipitator : Smoke is the dispersion of negatively charged colloidal particles of carbon in air. It is passed through Cottrell precipitator at high voltage. Hence, carbon separates from the particles.

Such precipitators are set in the chimney of industrial plant. There are two plates of metal which are electrically charged by high electric voltage. The carbon particles become chargeless and get precipitated, while gases go out through the chimney.

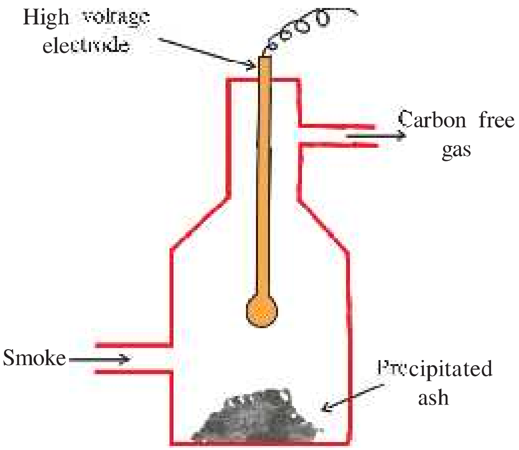


Fig. 2.12 Cottrell Smoke Precipitator

(4) In preparation of nano products : By using reversible micelle as catalyst such substances are prepared.

(5) In medicines : Most of the medicinal and pharmaceutical preparations are emulsions. It is believed that medicines in this form are more effective, and mixes or gets absorbed easily.

(6) Germicides : Germicides like Dettol, Lysol when mixed with water oil in water type emulsions are obtained.

(7) In metallurgy : Emulsions play an important role in industries. The concentration of ore containing sulphide is carried out by froth floatation method. Finely grinded ore is concentrated by emulsion formed between pine oil and water

(8) Construction of roads : An emulsion is pepared of alsphalt (without melting it) in water and used for construction of roads.

SUMMARY

- The study of chemistry regarding the boundary separating two bulk states or phases is called surface chemistry. This boundary surface is known as interface. It is expressed as hyphen (–) or slash (/). Dissolution, crystallization, catalysis, metallic corrosion are surface phenomena.
- The surface should be completely pure which can be obtained by vacuum generating method and can be stored also.
- In this unit, surface phenomena like adsorption, catalysis, colloid and emulsion are studied.
- In adsorption, the substance which is in solid form and on which other gas or liquid is adsorbed is called adsorbent. The substance that is adsorbed is called adsorbate and the whole phenomenon is called adsorption. The phenomenon opposite to adsorption is called desorption.
- Absorption is such a phenomenon in which there is homogeneous system viz. any coloured solution but if solid adsorbent like charcoal is added to it then there is decrease in intensity of the colour which is adsorption. The combined phenomenon of adsorption and absorption is called sorption. In adsorption the concentration of adsorbate is more than that in the bulk. More porous the adsorbent more will be adsorption. Adsorption is an exothermic phenomenon.
- In adsorption, the residual particles on the surface are responsible for the adsorption that is due to difference in forces of attraction.
- Adsorption is of two types– Physical and Chemical. The points of difference between them are given in the unit.
- Adsorption is used in many fields as well as in everyday life viz. To wear gas mask in which there is adsorbent to save from the poisonous gas like chlorine. Silica gel is used as adsorbent for keeping the electronic instruments moisture free. In the removal of yellow colour from sugar, the phenomenon of adsorption is used.
- The factors affecting adsorption are (1) nature of adsorbate (2) nature of adsorbent (3) specific area of adsorbent surface (4) pressure of adsorbed gas (5) temperature. The detailed discussion about each one is included in the unit.
- At constant temperature the graph of pressure of gas adsorbed or concentration is called adsorption isotherm. There are five different types of isotherms. The study of adsorption isotherm was done by scientist Freundlich and gave the equation $\frac{x}{m} = Kp^{\frac{1}{n}}$ or $\log \frac{x}{m} = \log K + \frac{1}{n} \log p$ (for pressure (p)) and $\frac{x}{m} = KC^{\frac{1}{n}}$ or $1\log \frac{x}{m} = \log K + \frac{1}{n} \log C$ (for concentration (C)) where K and n are constants. This was an empirical isotherm and had no scientific base.
- Langmuir on the basis of kinetic theory of gases gave isotherm equation.

  $\frac{x}{m} = \frac{ap}{1 + bp}$, $\frac{x}{m} = \frac{aC}{1 + bC}$ (where a and b are constants)

- The study of Freundlich isotherm can be understood by the study of demonstration experiment in practicals book. There are many uses of adsorption which are described in the unit.
- Catalysis is also a surface phenomenon. Some chemical reactions are slow. To increase their rates, the substance used in small proportion is called catalyst. This phenomenon is called catalysis. The catalyst is obtained back in original form at the end of the reaction.
- There are two types of catalysis (1) Homogeneous and (2) Heterogeneous. In homogeneous catalysis, catalyst and the reactant are in one phase e.g. hydrolysis of methyl acetate in presence of H^+ (2) In heterogeneous catalysis the catalyst and the reactants are in different phases e.g. Production of sulphuric acid in presence of V_2O_5 by contact process. There are many uses of homogeneous and heterogeneous catalysis as shown in the unit.
- The characteristics of catalysis are activity, selectivity that is specific reaction; selection of specific catalyst e.g. zeolite. The zeolite named ZSM-5 is used to obtain gasoline from alcohol. Catalyst increases the rate of reaction but does not affect the equilibrium because it affects equally both the forward and the reverse reaction. Hence, more product is not obtained.
- Enzymes are proteins and are necessary for biochemical reaction. For every reaction separate and specific enzyme works viz. invertase can transform sugar into glucose and fructose. Urease can decompose urea into ammonia and carbon dioxide.
- For enzyme catalysis the lock and key model or induced fit model are proposed. As the lock can be opened by suitable key, similarly for a particular reaction suitable enzyme will be required. The enzymes work at the temperature of the body i.e. 298-310 K temperature is considered the best.
- Colloid chemistry is also a surface phenomenon. The colloidal solution is called sol. There are two components called dispersing phase and dispersion medium in it. The particles are of some particular size so this is a heterogeneous system. Colloids are of two types-Lyophilic and Lyophobic. The colloid which has attraction for solvent (dispersion medium) is used called lyophilic colloid e.g. gum. The colloid which has repulsion towards the solvent (dispersion medium is called lyophobic colloid. If water is as a medium then they are respectively called hydrophilic and hydrophobic. Colloids are of eight types which depend on the dispersing phase and dispersion medium. This is shown in the unit. Multimolecular, macromolecular and associated colloids are also known. In associated colloids molecules come nearer and form an association which is called micelle.
- The certain temperature, at which the micelle is formed is called Kraft's temperature (T_K). Below the critical micelle concentration (CMC), it remains in colloidal state and at higher than that concentration it is changed to solid in the form of precipitates. The formation micelle is obtained in the cleansing action of soap. Molecules like soap are shown as RCOONa, and their ionization form will be $RCOO^-Na^+$. From this $RCOO^-$, R part combines with organic impurity and drags inside. It is called tail. The upper charged part COO^- attracts dust etc. and removes the dirt. It is called head.
- The methods of preparation of colloids are as follows :
- **Condensation method :** In these methods, oxidation, reduction, decomposition etc. types of reactions are associated. In physical methods, excessive cooling is used, and in dispersion

methods-mechanical dispersion (use of colloid mill), electrical dispersion (Bredig arc method) and peptization are used.

- For purification of prepared colloidal solution, a method like dialysis and better method like electrodialysis can be used. On addition of certain electrolytes to colloid solutions, precipitation occurs which is called coagulation. The order of concentration for coagulation for iron sol having positive charge is trivalent > divalent > monovalent for negative ions (anions). Similarly for arsenious sulphide colloid having negative charge, the order of coagulation remains the same but positive ions (cations) are used. Amongst the other methods used for purification of colloids are ultrafiltration and ultracentrifugation.
- The properties of colloidal solutions-sol are as follows : (1) Colligative properties (2) Optical properties (3) Mechanical and (4) Electrical properties.
- In colligative properties determination of molecular masses is by osmosis method. In optical properties- Tyndall effect and in mechanical properties Brownian movement and in electrical properties, instrument called electrophoresis is used for determination of electrical charge of colloid. There are two laws given by Hardy and Schulze for the study of coagulation of colloids. The electrolytes having electric charge opposite to that on the colloid are required for coagulation of colloid. For colloid having positive or negative electric charge negative or positive ions of the electrolyte respectively are useful. In concentration, highest concentration of monovalent and less than that concentration of divalent ion and the least concentration of trivalent produces coagulation.
- Emulsions are also colloids, in which both the dispersion medium and the dispersed phase are in liquid form. They are of two types- Oil / water and water/oil. The examples of water/oil emulsion are cold cream, butter etc; while in oil/water emulsion the examples are milk, vanishing cream etc. There are two methods for the test of emulsions (1) Dye test and (2) Dilution test. Demulsification is the opposite phenomenon of emulisification.
- There are many uses of colloids. Its specific uses are rubber plating, sewage disposal, Cottrell smoke precipitator, preparation of nano-substances, medicines, as germicides in metallurgy, construction of roads etc. which are described in detail in the unit.

EXERCISE

1. Select the proper choice from the given multiple choices :

(1) What is called the boundary that separates the phases in two bulks ?

(A) Line (B) Point (C) Slash (D) Interface.

(2) On which does the interface depend ?

(A) on the volume of molecules in the bulk-phase

(B) on the weight of molecules in the bulk phase

(C) on the number of molecules in the bulk phase

(D) on the physical state of molecules in the bulk phase

(3) Which of the following is not an example of surface phenomenon ?

(A) Dissolution (B) Corrosion

(C) Electrode reaction (D) Homogeneous catalysis

(4) How many Pascal high vacuum is required for obtaining completely pure surface of metals ?

(A) 10^{-8} to 10^{-9} (B) 10^{-8} to 10^{-10} (C) 10^{-6} to 10^{-9} (D) 10^{-8} to 10^{-7}

(5) What is the phenomenon called when the molecules adsorbed on the surface are released by any reason ?

(A) Sorption (B) Desorption (C) Adsorption (D) Precipitation

(6) Because of adsorption............

(A) Surface energy decreases

(B) Surface energy increases

(C) The value of surface energy becomes zero

(D) No change takes place.

(7) By which other name the adsorption of gases on the solid surface is known ?

(A) Evaporation (B) Surface tension

(C) Condensation (D) Sorption

(8) What is the substance that is adsorbed called ?

(A) Adsorbent (B) Adsorbate (C) Absorsent (D) Absorbite

(9) Which of the following substances is not an adsorbent ?

(A) Sugar (B) Clay (C) Silica gel (D) Alumina

(10) What type of attraction forces are present between adsorbent and adsorbate in physisorption ?

(A) van der Waals (B) Strong chemical (C) Gravitation (D) Metallic bond.

(11) Which statement is correct for physical adsorption ?

(A) It is slow or fast process

(B) The value of adsorption enthalpy is low

(C) Unimolecalar layer is formed on the adsorbent

(D) Generally results at high temperature.

(12) What is used for the electronic instruments so that they may not be spoiled by moisture ?

(A) Alumina (B) Silica gel (C) Iron powder (D) Animal charcoal.

(13) Which of the following gaseous molecule has maximum physical adsorption enthalpy ?

(A) Ne (B) H_2O (C) H_2 (D) C_2H_6

(14) Mention the Freundlich adsorption isotherm.

(A) $\frac{x}{m} = Kp^{n}$ (B) $\frac{x}{m} = Kp^{n^2}$ (C) $\frac{x}{m} = Kp^{\frac{1}{n}}$ (D) $\frac{m}{x} = pK^{n}$

(15) Which equation is applicable to Langmuir adsorption isotherm at low pressures ?

(A) $\frac{x}{m} = \frac{b}{a}$ (B) $\frac{x}{m} = ap$ (C) $\frac{x}{m} = \frac{1}{n}p$ (D) $\frac{x}{m} = \frac{a}{b}$

(16) Which of the following is applicable to Langmuir adsorption isotherm when derived ?

(A) The random motion of molecules of gas

(B) Kinetic theory of gases

(C) Magnitude of adsorption of gas

(D) All the given

(17) What is called the substance which increases the rate of chemical reaction but does not take part in the reaction ?

(A) Adsorbent (B) Catalyst (C) Adsorbate (D) Reactant

(18) Which type of catalyst is used in obtaining SO_3 gas required in obtaining sulphuric acid by Lead chamber process ?

(A) Homogeneous catalyst (B) Heterogeneous catalyst
(C) Catalyst is not used (D) Vanadium pentoxide

(19) Which catalyst is used in the reaction of preparing vegetable ghee from vegetable oil ?

(A) Iron powder (B) Zinc powder
(C) Raney nickel (D) Vanadium pentoxide

(20) On what does the shape-selective catalytic reaction depend ?

(A) Molecules of product (B) Size of reactant
(C) Porosity of catalyst (D) All the given.

(21) What are enzymes made up of ?

(A) Carbohydrates (B) Lipids (C) Vitamin (D) Proteins

(22) If sand is dissolved in water, shaken and kept for some time, the sand settles down. The phenomenon is called :

(A) Colloid solution (B) True solution (C) Suspension (D) Dispersion

(23) What is the colloid in which both dispersion medium and dispersed phase are in solid state called ?

(A) Emulsion (B) Gel (C) Aerosol (D) Solid sol.

(24) Which of the following colloid is reversible ?

(A) Lyophilic (B) Lyophobic (C) Hydrophilic (D) Both (A) and (C)

(25) What type of colloid is sulphur (S_8) dissolution ?

(A) Associated colloid (B) Micelle
(C) Multimolecular colloid (D) Macromolecular colloid

(26) Which choice is correct for micelle ?

(A) Is a combination of emulsion and gel
(B) Is an adsorbate catalyst
(C) Is an ideal solution
(D) Is an associate of colloids.

(27) At critical micelle concentration, the molecules on the surface...

(A) Decompose (B) Associate
(C) Dissociate (D) Completely soluble.

(28) What is the correct effective coagulating order of ions for positively charged colloid of $Fe(OH)_3$?

(A) $PO_4^{3-} > Cl^- > SO_4^{2-}$ (B) $PO_4^{3-} > SO_4^{2-} > Cl^-$
(C) $Cl^- > SO_4^{2-} > PO_4^{3-}$ (D) $SO_4^{2-} > PO_4^{3-} > Cl^-$

(29) Which of the following colloidal sol can not be prepared by Bredig's arc method ?

(A) Sulphur (B) Silver (C) Gold (D) Platinum

(30) With which property of colloid Tyndall effect is associated ?

(A) Mechanical (B) Colligative (C) Optical (D) Electrical

(31) By which name the zigzag motion of colloidal particle in the dispersion medium is known ?

(A) Brownian movement (B) Tyndall motion

(C) Vibrational motion (D) Mechanical motion.

(32) By which instrument the existence of positive or negative electric charge of colloid is determined ?

(A) Electrophoresis (B) Microscope

(C) Ultrasonic dispersant (D) Voltmeter.

(33) Which of the following is oil/water (oil in water) emulsion ?

(A) Cold cream (B) Vanishing cream

(C) Butter (D) Cod liver oil

(34) Which of the following is water/oil (water in oil) emulsion ?

(A) Cold cream (B) Butter milk (C) Milk (D) Vanishing cream

(35) Which of the following substances is an emulsifier ?

(A) Common salt (B) Urea (C) Oil (D) Soap

(36) Which of the following is a multimolecular colloid ?

(A) Wax (B) Latex-rubber (C) Silicones (D) All the given

(37) From which of the following effects the colloidal system is free ?

(A) Gravitational effect (B) Effect of added electrolyte

(C) Effect of heat (D) Effect of applied electrical field.

(38) At isoelectric point the colloid…

(A) Stabilizes (B) Peptizises

(C) Does not possess electrical charge (D) Can not be coagulated

(39) By which method ferric hydroxide colloid is prepared ?

(A) Hydrolysis (B) Peptization

(C) Double decomposition (D) Oxidation

(40) The dimension of colloid particles is........

(A) Less than that of true solution

(B) Between true solution and suspension

(C) More than that of suspended particles

(D) Can be of any dimension

2. Answer the following questions is brief :

(1) Give definition of adsorption

(2) Give definition of colloid. Give one example.

(3) Write the name of any one enzyme and its function.

(4) What is meant by emulsion ? Give example.

(5) Give three examples of reversible colloids.

(6) Write formula of Langmuir adsorption isotherm.

(7) What is micelle ? Explain its formation.

(8) Give names of three factors that affect adsorption.

(9) Give name of purification method for colloid.

(10) How adsorption is useful for protection against effect of poisonous gases ?

3. Answer the following questions :

(1) Explain giving suitable example : adsorption, adsorbate, adsorbent.

(2) Mention three differences between physical and chemical adsorption.

(3) Why the granular or powder form substance is considered good adsorbent ?

(4) Explain the factors affecting adsorption of gaseous adsorbate on solid adsorbent.

(5) What is meant by adsorption isotherm ? Explain.

(6) Explain giving examples homogeneous and heterogeneous catalysis.

(7) Give explanation of micelle. Explain critical micelle concentration.

(8) Write Freundlich adsorption isotherm and explain the terms involved in it .

(9) Write two chemical methods for preparation of colloids.

(10) Explain the difference amongst true solution, suspension and colloid.

(11) Write types of colloid and give one example of each.

(12) What is meant by emulsion ? Explain its types giving examples.

(13) Explain the terms : (i) Peptization (ii) Emulsification

(14) Explain the terms : (i) Tyndall effect (ii) Brownian movement.

(15) What is meant by shape selective catalysis ? Explain.

4. Answer the following questions in detail :

(1) Explain giving examples the terms : dispersion medium, dispersing phase.

(2) How are colloids classified on the basis of dispersing phase ?

(3) How catalysis occurs by zeolite ?

(4) Explain Hardy-Schulze rules.

(5) "Colloid is not a substance but a state of substance." Discuss.

(6) Write five examples of the biochemical reactions occurring by use of specific enzymes.

(7) Write short notes : (i) Coagulation (ii) Electrophoresis

(8) Mention types of emulsion and describe the tests for their identification.

(9) Describe the methods to prepare colloids of sulphur and gold.

(10) Write short notes : (i) Tyndall effect (ii) Brownian movement

(11) Explain the working of enzyme catalyst by lock-key model.

(12) Explain purification of colloid by electrodialysis.

(13) Write short note on Cottrell smoke precipitator.

(14) Mention uses of colloids in different fields.

(15) Write short notes : (i) Bredig's arc method (ii) Colloid mill.

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UNIT

3

d- and f-Block Elements

3.1 Introduction

We have obtained the information about modern periodic table for classification of elements in standard 11 (semester I). In addition to this, we have also studied in detail the s- and p-block elements during semesters I to III. We know, the elements in modern periodic table are classified into s-, p-, d- and f-blocks and 1 to 18 groups. The elements of groups 1 and 2 and the groups 13 to 18 are known as s-block and p-block elements respectively; while elements of rest of the ten groups, group no 3 to 12 are called d-block elements because the last electron of the elements, enter into the available d-orbital. The position of these elements is between s-block and p-block elements. The properties of d-block elements show transition between the properties of representative elements of periodic table i.e. most electropositive elements of s-block (metal elements) and least electropositive elements of p-block (nonmetals, metalloids and metals). Hence, they are known as **transition elements.** This means that those elements have their properties which intermediate between those of s- and p-block elements. The two horizontal rows at the bottom of the modern periodic table are called f-block elements because the last electron enters into the available f-orbitals. Th (Z= 90) has got the electronic structure [Rn] $5f^0 6d^2 7s^2$. In Th, the last electron is not filled in f-orbital although the experimental results support the elements as f-block elements. Thus, it is included in f-block elements. These elements being part of the transition series of transition elements of periods 6 and 7; are called **innertransition elements.**

3.2 Transition Elements – Elements of d-Block

The elements which in their ground state or any one of its oxidation state, have incompletely filled d-orbitals with electrons are called the transition elements. The elements whose ground state or any of its oxidation state have vacant 3d-orbitals are called **first transition series elements,** if 4d-orbitals are incompletely filled then **second transition series elements** and

5d-orbitals incompletely filled with electrons then they are called **third transition series elements.** In each of these series there are ten elements. Fourth transition series corresponding to the filling of 6d-orbital begins with actinium (Z = 89) followed by element with atomic number 104 (Rf) onwards. Regarding fourth transition series, the research is continuing at present.

3.2.1 Electronic Configuration and Oxidation States of Transition Elements :

The general electronic configuration of transition elements is $(n-1)d^{1-10}ns^{1-2}$. Generally the stability of half filled or completely filled orbital is relatively more. Because of this the electronic configuration of Cr is considered $[Ar]3d^54s^1$ instead of $[Ar]3d^44s^2$. In the same way the electronic configuration of Cu is considered $[Ar]3d^{10}4s^1$ instead of $[Ar]3d^94s^2$. It is necessary here to note that the difference between energies of 3d and 4s orbital, is very less, hence this becomes possible.

When ions are formed from first transition series elements, the electron entering last in 3d-orbital is not removed first but both the electrons of 4s orbital are removed first and then the electrons of 3d-orbital are removed; because the electrons in the outermost orbital have relatively less attraction towards the nucleus in comparison to the electrons in the inner orbital. It is important to note here that the orbit having higher value of principal quantum number is considered as the outermost orbital. Thus, between the 3d-orbital (n = 3) and 4s-orbital (n = 4), 4s-orbital will be outermost orbital. Similarly, when ions are formed from the elements of second transition series, the electron of 5s-orbital is removed first and then the electron of 4d-orbital when ions of third transition elements, the electron is removed first from 6s-orbital and then the electron from 5d-orbital is removed; the electronic configuration of elements of first transition series in the ground state and their oxidation states are shown in table 3.1.

Table 3.1. The electronic configuration of first transition series in ground state and their oxidation states

Element	Atomic Number	Electronic configuration	Oxidation state
Sc	21	$[Ar]3d^14s^2$	(+3)
Ti	22	$[Ar]3d^24s^2$	+2, +3, (+4)
V	23	$[Ar]3d^34s^2$	+2, +3, (+4), +5
Cr	24	$[Ar]3d^54s^1$	(+2), (+3), +4, +5, (+6)
Mn	25	$[Ar]3d^54s^2$	(+2), +3, +4, +5, +6, (+7)
Fe	26	$[Ar]3d^64s^2$	(+2), (+3), +4, +5, +6
Co	27	$[Ar]3d^74s^2$	(+2), (+3), +4
Ni	28	$[Ar]3d^84s^2$	(+2), +3, +4
Cu	29	$[Ar]3d^{10}4s^1$	+1, (+2)
Zn	30	$[Ar]3d^{10}4s^2$	(+2)

Note: Stable oxidation state is shown in parenthesis.

The electronic configuration of Cu in ground state in first transition series is $[Ar]3d^{10}4s^1$. In it 3d-orbital is completely filled with electrons but electronic configuration of Cu^{2+} is $[Ar]3d^9$. Here, 3d-orbitals are incompletely filled with electrons and so Cu is considered transition element. The electronic configuration of Zn in ground state is $[Ar]3d^{10}4s^2$. In it, 3d-orbital is completely filled with electrons. In addition, the electronic configuration of Zn^{2+} is $[Ar]3d^{10}$. Here, also, the 3d-orbital is completely filled. Hence **Zn is not considered as a transition element.** The electronic configuration of elements of second transition series in the ground state and their oxidation states are shown in table 3.2.