



12085CH05

Objectives

After studying this Unit, you will be able to

- describe interfacial phenomenon and its significance;
- define adsorption and classify it into physical and chemical adsorption;
- explain mechanism of adsorption;
- explain the factors controlling adsorption from gases and solutions on solids;
- explain adsorption results on the basis of Freundlich adsorption isotherms;
- appreciate the role of catalysts in industry;
- enumerate the nature of colloidal state;
- describe preparation, properties and purification of colloids;
- classify emulsions and describe their preparation and properties;
- describe the phenomenon of gel formation;
- list the uses of colloids.

Unit 5 Surface Chemistry

Some of the most important chemicals are produced industrially by means of reactions that occur on the surfaces of solid catalysts.

Surface chemistry deals with phenomena that occur at the surfaces or interfaces. The interface or surface is represented by separating the bulk phases by a hyphen or a slash. For example, the interface between a solid and a gas may be represented by solid-gas or solid/gas. Due to complete miscibility, there is no interface between the gases. The bulk phases that we come across in surface chemistry may be pure compounds or solutions. The interface is normally a few molecules thick but its area depends on the size of the particles of bulk phases. Many important phenomena, noticeable amongst these being corrosion, electrode processes, heterogeneous catalysis, dissolution and crystallisation occur at interfaces. The subject of surface chemistry finds many applications in industry, analytical work and daily life situations.

To accomplish surface studies meticulously, it becomes imperative to have a really clean surface. Under very high vacuum of the order of 10^{-8} to 10^{-9} pascal, it is now possible to obtain ultra clean surface of the metals. Solid materials with such clean surfaces need to be stored in vacuum otherwise these will be covered by molecules of the major components of air namely dioxygen and dinitrogen.

In this Unit, you will be studying some important features of surface chemistry such as adsorption, catalysis and colloids including emulsions and gels.

5.1 Adsorption

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

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

Adsorption in action

- (i) If a gas like O_2 , H_2 , CO , Cl_2 , NH_3 or SO_2 is taken in a closed vessel containing powdered charcoal, it is observed that the pressure of the gas in the enclosed vessel decreases. The gas molecules concentrate at the surface of the charcoal, i.e., gases are adsorbed at the surface.
- (ii) In a solution of an organic dye, say methylene blue, when animal charcoal is added and the solution is well shaken, it is observed that the filtrate turns colourless. The molecules of the dye, thus, accumulate on the surface of charcoal, i.e., are adsorbed.
- (iii) Aqueous solution of raw sugar, when passed over beds of animal charcoal, becomes colourless as the colouring substances are adsorbed by the charcoal.
- (iv) The air becomes dry in the presence of silica gel because the water molecules get adsorbed on the surface of the gel.

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

5.1.1 Distinction between Adsorption and Absorption

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

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

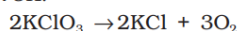
5.1.2 Mechanism of Adsorption

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

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

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

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



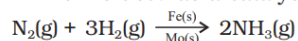
However, when a little of manganese dioxide is added, the decomposition takes place at a considerably lower temperature range, i.e., 473-633K and also at a much accelerated rate. The added manganese dioxide remains unchanged with respect to its mass and composition. In a similar manner, the rates of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

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

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

Promoters and poisons

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



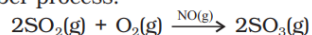
5.2.1 Homogeneous and Heterogeneous Catalysis

Catalysis can be broadly divided into two groups:

(a) *Homogeneous catalysis*

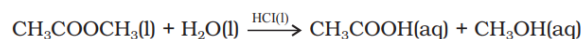
When the reactants products and the catalyst are in the same phase (i.e., liquid or gas), the process is said to be homogeneous catalysis. The following are some of the examples of homogeneous catalysis:

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



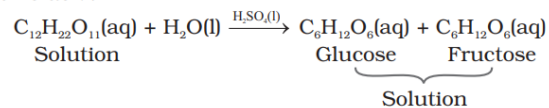
The reactants, sulphur dioxide and oxygen, and the catalyst, nitric oxide, are all in the same phase.

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



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

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

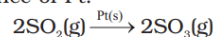


Both the reactants and the catalyst are in the same phase.

(b) Heterogeneous catalysis

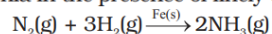
The catalytic process in which the reactants and the catalyst are in different phases is known as heterogeneous catalysis. Some of the examples of heterogeneous catalysis are given below:

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



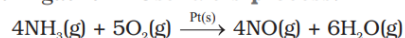
The reactant is in gaseous state while the catalyst is in the solid state.

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



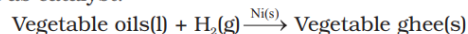
The reactants are in gaseous state while the catalyst is in the solid state.

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



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

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



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

5.3 Colloids

We have learnt in Unit 2 that solutions are homogeneous systems. We also know that sand in water when stirred gives a suspension, which slowly settles down with time. Between the two extremes of suspensions and solutions we come across a large group of systems called colloidal dispersions or simply colloids.

A colloid is a heterogeneous system in which one substance is dispersed (dispersed phase) as very fine particles in another substance called dispersion medium.

The essential difference between a solution and a colloid is that of particle size. While in a solution, the constituent particles are ions or small molecules, in a colloid, the dispersed phase may consist of particles of a single macromolecule (such as protein or synthetic polymer) or an aggregate of many atoms, ions or molecules. Colloidal particles are larger than simple molecules but small enough to remain suspended. Their range of diameters is between 1 and 1000 nm (10^{-9} to 10^{-6} m).

Colloidal particles have an enormous surface area per unit mass as a result of their small size. Consider a cube with 1 cm side. It has a total surface area of 6 cm^2 . If it were divided equally into 10^{12} cubes, the cubes would be the size of large colloidal particles and have a total surface area of $60,000\text{ cm}^2$ or 6 m^2 . This enormous surface area leads to some special properties of colloids to be discussed later in this Unit.

5.4 Classification of Colloids

Colloids are classified on the basis of the following criteria:

- (i) Physical state of dispersed phase and dispersion medium
- (ii) Nature of interaction between dispersed phase and dispersion medium
- (iii) Type of particles of the dispersed phase.

5.4.1 Classification Based on Physical State of Dispersed Phase and Dispersion Medium

Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gases, eight types of colloidal systems are possible. A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system. The examples of the various types of colloids along with their typical names are listed in Table 5.4.

Many familiar commercial products and natural objects are colloids. For example, whipped cream is a foam, which is a gas dispersed in a

Table 5.4: Types of Colloidal Systems

Dispersed phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid sol	Some coloured glasses and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, jellies
Liquid	Liquid	Emulsion	Milk, hair cream, butter
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather