

# Surface Chemistry

## basic concepts

The chemistry which deals with the boundary separating two bulk phases is termed as **surface chemistry**. The boundary is also called surface or interface. Solid–solid, solid–liquid interfaces are known. As gases are completely miscible they do not form any interfaces. Interface is only a few molecules thick but its area is dependent on the particle size of the bulk phases. Important applications of surface chemistry are: corrosion, electrode processes, adsorption, heterogeneous catalysis.

- Adsorption:** The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid leading to a higher concentration on the surface in comparison to the bulk is called adsorption. Examples are: (i) water vapours on silica gel, (ii)  $H_2$ ,  $O_2$ ,  $NH_3$  on activated charcoal.
  - ➔ **Adsorbate:** The substance accumulating at the surface of the solid during adsorption is called adsorbate.
  - ➔ **Adsorbent:** The surface on which adsorption occurs is called adsorbent.
  - ➔ **Desorption:** The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption.
- Absorption:** It is the phenomenon in which a substance is uniformly distributed throughout the bulk, *i.e.*, it is the penetration of the substance through the surface into the bulk of the solid. **Example:** water vapours are absorbed by anhydrous  $CaCl_2$ .
- Sorption:** Sometimes the adsorbate dissolves into adsorbent. Initially, the adsorbate appears on the surface of adsorbent and later passes into the body of adsorbent. Thus, adsorption changes into absorption. Such side by side occurrence of absorption and adsorption, is called sorption.
- Types of Adsorption:** There are mainly two types of adsorption:
  - ➔ **Physical adsorption:** If the force of attraction between the adsorbate and adsorbent are van der Waals' forces, then the adsorption is called physical adsorption or physisorption.
  - ➔ **Chemical adsorption:** If the force of attraction between the particles of adsorbate and adsorbent are almost of the same strength as the chemical bond, the adsorption is called chemical adsorption or chemisorption.
- Enthalpy or Heat of Adsorption:** It may be defined as the enthalpy change when one mole of an adsorbate is adsorbed at the surface of adsorbent. It is low in case of physical adsorption and high in case of chemisorption.
- Adsorption Isotherm:** When extent of adsorption  $x/m$  (where  $x$  is the amount of adsorbate,  $m$  is mass of adsorbent) is plotted against pressure at a constant temperature, curve thus obtained is known as adsorption isotherm.
  - ➔ **Adsorption Isobar:** A plot of extent of adsorption ( $x/m$ ) vs. temperature at constant pressure is called adsorption isobar.

➔ **Adsorption Isostere:** The straight line, showing variation of pressure ( $p$ ) with temperature ( $T$ ) for a given quantity of adsorption is called adsorption isostere.

7. **Freundlich Adsorption Isotherm:** It gives the relationship between magnitude of adsorption ( $\frac{x}{m}$ ) and pressure at a constant temperature (Fig. 5.1). It can be expressed as

$$\frac{x}{m} = k p^{1/n} \quad (n > 1) \quad \dots(i)$$

where  $x$  is the amount of gas adsorbed by  $m$  grams of adsorbent at a pressure  $p$ ,  $k$  and  $n$  are constants.

Taking logarithm of equation (i)

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

A plot of  $\log \frac{x}{m}$  vs  $\log p$  is a straight line (Fig. 5.2).

The slope of straight line gives the value of  $\frac{1}{n}$  and

intercept is  $\log k$ . This isotherm explains the behaviour of adsorption approximately.  $\frac{1}{n}$  can have any value between 0 and 1.

(i) When  $\frac{1}{n} = 0$ ,  $\frac{x}{m} = k$ , which shows that adsorption is independent of pressure.

(ii) When  $\frac{1}{n} = 1$ ,  $\frac{x}{m} = kp$ ,  $\frac{x}{m} \propto p$ , adsorption varies directly as pressure.

Both the above observations have been verified.

The experimental isotherm always seems to approach saturation at high pressure. It cannot be explained by Freundlich isotherm. Thus, Freundlich isotherm fails at high pressure.

➔ **Adsorption from Solution**

Freundlich adsorption isotherm between  $\frac{x}{m}$  (mass of solute adsorbed per gram of the adsorbent) and the equilibrium concentration  $C$  is given by the expression

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

$\log \frac{x}{m} = \frac{1}{n} \log C + \log k$ . Plot of  $\log \frac{x}{m}$  vs  $\log C$  is a straight line.

➔ **Saturation Pressure:** The pressure beyond which adsorption becomes independent of pressure is called saturation pressure.

8. **Applications of Adsorption:**

(i) **Gas masks:** Activated charcoal or mixture of adsorbents is used in gas masks so that all toxic gases are preferably adsorbed and the air for breathing is purified.

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

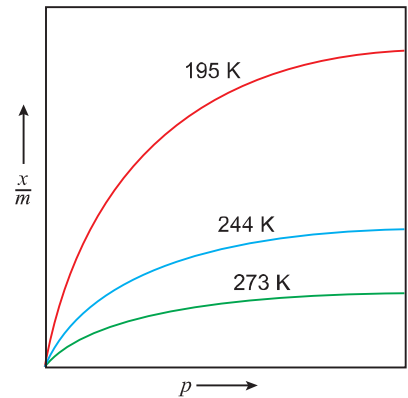


Fig. 5.1: Adsorption isotherm

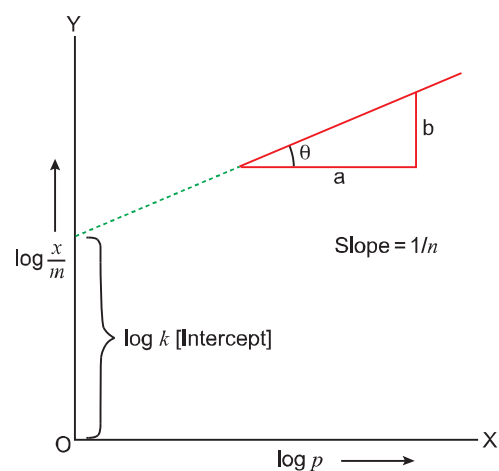


Fig. 5.2: Freundlich isotherm

- (iii) **Heterogeneous catalysis:** Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. For example, use of finely divided iron in the manufacture of ammonia and finely divided nickel in the hydrogenation of vegetable oil.
- (iv) **Removal of colouring matter from solutions:** Animal charcoal removes colours of solutions by adsorbing coloured impurities.
- (v) **Control of humidity:** Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.
- (vi) **In curing diseases:** A number of drugs are used to kill germs by getting adsorbed on them.
- (vii) **Adsorption indicators:** Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. In precipitation titration, the indicator is adsorbed at the endpoint producing a characteristic colour on the precipitate.
- (viii) **Chromatographic analysis:** It is based on the phenomenon of adsorption and finds a number of application in analytical and industrial fields.
- (ix) **Separation of inert gases:** A mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures. This is due to the difference in degree of adsorption of gases by charcoal.

9. **Catalyst:** A catalyst is a substance which influences the speed of a chemical reaction without itself undergoing any chemical change at the end of the reaction and the phenomenon is known as catalysis.

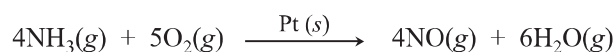
Catalysis is of two types:

(a) Heterogeneous catalysis

(b) Homogeneous catalysis

(a) **Heterogeneous catalysis:** When the catalyst is in a different phase from that of reactants, the phenomenon is known as heterogeneous catalysis.

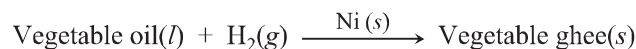
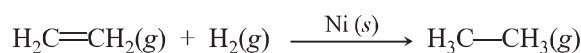
Examples: (i) Oxidation of ammonia to nitric oxide.



(ii) Contact process for the manufacture of sulphuric acid.



(iii) Hydrogenation of unsaturated organic compounds.



### Adsorption Theory of Heterogeneous Catalysis:

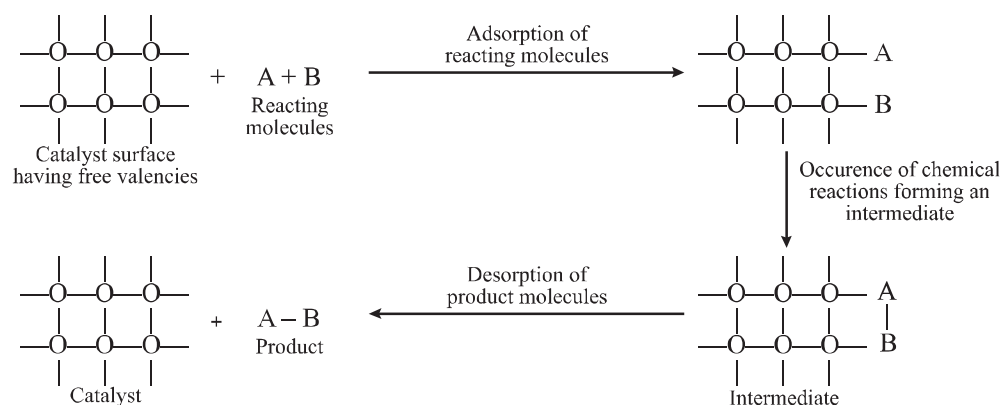


Fig. 5.3: Adsorption of reacting molecules, formation of intermediate and desorption of products

Modern theory has five steps:

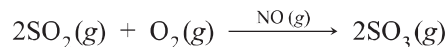
- Diffusion of reactants on the surface of catalyst.

- Adsorption of reactant molecules on the surface of catalyst.
- Chemical reaction takes place on the surface of heated catalyst through formation of intermediates.
- Desorption of product molecules from the surface of catalyst.
- Diffusion of products away from the surface of catalyst (Fig. 5.3).

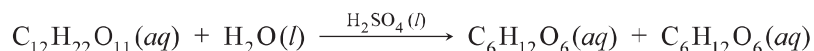
**(b) Homogeneous catalysis:** When the catalyst is present in the same phase as that of reactants, the phenomenon is known as homogeneous catalysis.

**Examples:**

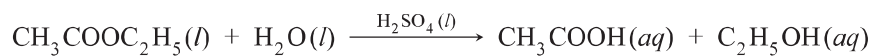
(i) Oxidation of  $\text{SO}_2$  into  $\text{SO}_3$  in the presence of nitric oxide (NO)



(ii) Inversion of sugarcane



(iii) Hydrolysis of ester

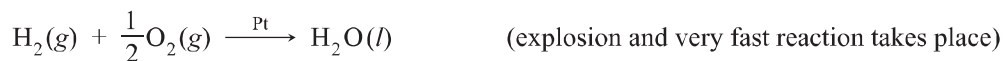


## 10. Characteristics of Catalytic Reactions

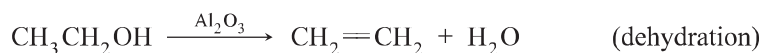
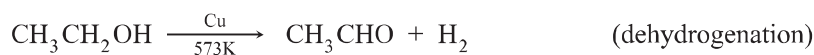
- A catalyst remains unchanged in mass and chemical composition at the end of the reaction.
- A small quantity of catalyst is generally needed to produce almost unlimited reactions.
- A catalyst cannot, in general, initiate a reaction.
- A catalyst is more effective when it is finely divided.
- A catalyst is specific in its action.
- Change of temperature changes the rate of a catalytic reaction as it would do for the same reaction without a catalyst.
- A catalyst does not alter the final position of equilibrium, although it decreases the time required to establish it.

## 11. Important Features of Solid Catalyst

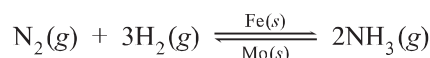
**Activity of a catalyst:** The ability of a catalyst to increase the rate of a reaction is called activity of a catalyst. For example, a mixture of hydrogen and oxygen does not react at all under normal conditions. However, in the presence of platinum as a catalyst they react with explosive violence.



**Selectivity of a catalyst:** It is the ability of a catalyst to direct a reaction to yield a particular product. For example, both dehydrogenation and dehydration of ethanol are possible. But, in presence of a suitable catalyst, only one reaction is made to occur.



**12. Catalytic Promoters:** A substance which, though itself not a catalyst, promotes the activity of a catalyst is called a promoter of a catalyst. In fact, a promoter is a catalyst for a catalyst. For example, molybdenum acts as a promoter for iron catalyst in the manufacture of ammonia by Haber's process.



**13. Shape-Selective Catalysis:** The catalytic reaction which depends upon the pore structure of the catalyst and the size of the reactant and product molecules is known as shape-selective catalysis. Zeolites exhibit shape-selective catalysis because of their honeycomb-like structures.

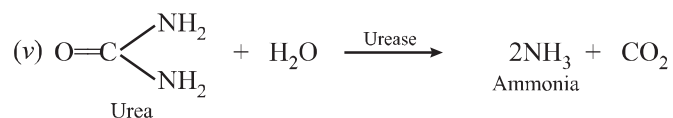
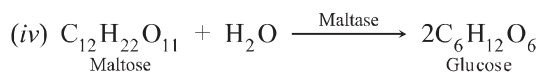
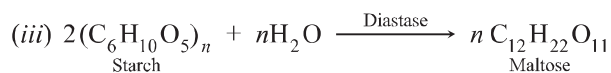
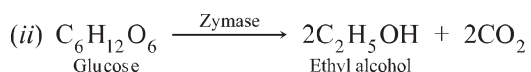
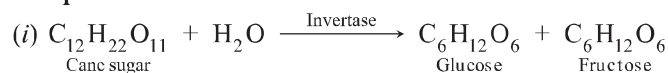
➔ **Zeolites or Shape-Selective Catalysts:** Zeolites are microporous aluminosilicate having the general formula  $M_{x/n} [(AlO_2)_x(SiO_2)_y] \cdot mH_2O$  where  $n$  is the charge on the metal ion  $M^{n+}$ . They have honeycomb-like structures. Before being used they are heated in vacuum so that water of hydration is lost. As a result they become porous. The pore size is in the range of 260-740 pm. The catalytic reactions taking place in zeolites depends upon the size and shape of reactant and product molecules as well as the pores and cavities of zeolites, that is why zeolites are called shape-selective catalysts. Zeolites have found usage as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. An important zeolite catalyst is ZSM-5. It converts alcohols directly into gasoline by dehydration.

**14. Enzyme Catalysis:** Enzymes are complex nitrogenous organic compounds produced in living cells of plants and animals. Chemically, enzymes are globular proteins with high molar mass ranging from 15,000 to 1,000,000  $g\ mol^{-1}$ . They are also called biocatalyst as they catalyse a large number of chemical reactions that occur in the bodies of plants and animals to maintain their life process.

**Characteristics:**

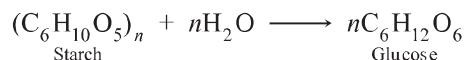
- (i) Enzymes form a colloidal solution in water and hence they are very active catalysts.
- (ii) Like inorganic catalysts they cannot disturb the final state of equilibrium of a reversible reaction.
- (iii) They are highly specific in nature, *i.e.*, one catalyst cannot catalyse more than one reaction.
- (iv) They are highly specific to temperature. The optimum temperature of their activity is 35°C to 40°C. They are deactivated at higher temperatures.
- (v) Their activity is increased in the presence of certain substances, known as co-enzymes.
- (vi) A small quantity of enzyme catalyst is sufficient for a large change.
- (vii) The enzyme activity can be reduced by the presence of certain compounds known as inhibitors. The use of many drugs is based on their action as enzyme inhibitors in the body.

**Examples:**

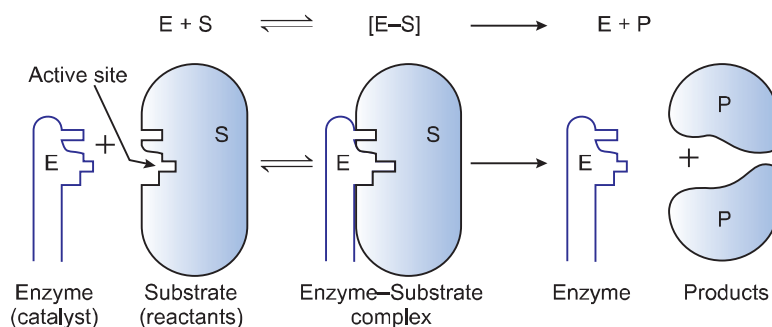


(vi) In stomach, enzyme pepsin converts proteins into peptides, whereas in intestines, pancreatic trypsin converts proteins into amino acids by hydrolysis. These amino acids are absorbed by blood and are used in the building of tissues.

(vii) Ptyalin enzyme present in human saliva converts starch into glucose.



### ➔ Mechanism of Enzyme Catalysed Reaction



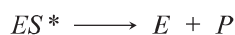
**Fig. 5.4:** Mechanism of enzyme catalysed reaction

The enzyme catalysed reactions may be considered to proceed in two steps (Fig. 5.4).

(i) Binding of enzyme to substrate to form an activated complex.



(ii) Decomposition of the activated complex to form the product.



## 15. Catalysis in Industry

**Table 5.1:** Some Industrial Catalytic Process

Process	Catalyst
(i) Haber's process for the manufacture of ammonia $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$	Finely divided iron, molybdenum as promoter; conditions: 200 bar pressure and 723-773 K temperature. Now-a-days, a mixture of iron oxide, potassium oxide and alumina is used.
(ii) Ostwald's process for the manufacture of nitric acid. $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$ $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $4NO_2(g) + 2H_2O(g) + O_2(g) \longrightarrow 4HNO_3(aq)$	Platinised asbestos; temperature 573 K.
(iii) Contact process for the manufacture of sulphuric acid. $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$ $SO_3(g) + H_2SO_4(aq) \longrightarrow H_2S_2O_7(l)$ <p style="text-align: center;">Oleum</p> $H_2S_2O_7(l) + H_2O(l) \longrightarrow 2H_2SO_4(aq)$	Platinised asbestos or vanadium pentoxide ( $V_2O_5$ ); temperature 673-723 K.

**16. Colloidal Solution:** A colloidal solution is a heterogeneous system in which a definite substance is distributed in the form of very small particles (diameter between  $10^{-4}$  and  $10^{-7}$  cm) as dispersed phase in another substance called the dispersion medium.

Dispersed phase + Dispersion medium = Dispersed system (Colloidal solution)

**Examples:** glue, ink, smoke, etc.

**Dispersed phase:** The phase of colloid particles is called dispersed phase. This is like a solute in the solution (homogeneous mixtures).

**Dispersion medium:** The medium in which dispersed particles are dispersed is called dispersion medium. This is like a solvent in true solutions (particle size less than  $10^{-9}$  m). If water being the medium, colloids are called hydrosols.

**Crystalloids:** The substances whose aqueous solutions can pass the semipermeable membrane are called crystalloids.

## 17. Classification of Colloids Based on Physical State of Dispersed Phase and Dispersion Medium

Table 5.2: Different Types of Colloidal Systems

Dispersed Phase	Dispersion Medium	Type of Colloid	Examples
Gas	Gas	No colloidal solution	—
Gas	Liquid	Foam	Froth, whipped cream, soap lather
Gas	Solid	Solid sol	Pumice stone, foam rubber
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide spray
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Solid	Gel	Cheese, butter, jellies
Solid	Gas	Aerosol	Smoke, dust
Solid	Liquid	Sol	Paints, cell fluids, gold sol, $\text{Fe}(\text{OH})_3$ sol, etc.
Solid	Solid	Solid sol	Some coloured glasses, gems and precious stones

Sols are called hydrosols, benzosols and alcosols according to their dispersion medium water, benzene and alcohol, respectively.

## 18. Classification Based on the Nature of Interaction between Dispersed Phase and Dispersion Medium

(i) **Lyophobic sols:** Particles of dispersed phase have no affinity for dispersion medium, rather they hate dispersion medium. They are not easily prepared and need stabilizing agents for their preservation. They are irreversible. **Examples:** sols of gold, silver,  $\text{Fe}(\text{OH})_3$ ,  $\text{As}_2\text{O}_3$ , etc. They are also called extrinsic colloids.

(ii) **Lyophilic sols:** Particles of dispersed phase have great affinity for the dispersion medium. They are self-stabilized because of strong attractive forces operating between the suspended particles and the dispersion medium. They are reversible in nature. **Examples:** gums, gelatin, starch, albumin, etc. They are also known as intrinsic colloids.

## 19. Classification Based on Type of Particles of the Dispersed Phase

(i) **Macromolecular colloids:** Macromolecules in suitable solvents form solution, where size of the macromolecules may fall within the colloidal range. The system showing such characteristics are called macromolecular colloids. The colloids are quite stable and in many respect they resemble true solutions. **Examples** of naturally occurring macromolecules are starch, cellulose, proteins and those of man-made macromolecules are nylon, polythene, polystyrene, synthetic rubber, etc.

(ii) **Multimolecular colloids:** A large number of atoms or smaller molecules (diameter  $< 1$  nm) of a substance on dissolution aggregate together to form species having size in the colloidal range. Such species are called multimolecular colloids. **Examples:** a sulphur sol consist of particles containing thousands of  $\text{S}_8$  sulphur molecules, a platinum or gold sol may have particles of various sizes having many atoms.

(iii) **Associated colloids (micelles):** There are certain substances which at low concentrations behave like normal strong electrolytes but at higher concentration behave as colloidal solutions due to the formation of aggregated particles. Such colloids are called associated colloids and aggregated particles are called micelles. **Examples:** soaps and detergents.

20. **Surface Active Agents:** Those substances which tend to concentrate on the surface of solutions and therefore, lower the surface tension are called surface active agents, e.g., soaps and detergents.

➔ **Critical Micelle Concentration (CMC):** It is the lowest concentration of the surfactant (soap solution) at which micelle formation takes place.

- ➔ **Kraft temperature:** Formation of micelles takes place only above a particular temperature called Kraft temperature.

## 21. Preparation of Colloidal Solutions

**1. Dispersion method:** In this method bigger suspension particles (greater than  $10^{-4}$  cm) are broken down into smaller particles of colloidal size ( $10^{-4}$  to  $10^{-7}$  cm).

(i) **Mechanical dispersion:** A colloidal mill is used. Useful in manufacturing dye stuffs, printing inks, paints, varnishes and dental creams.

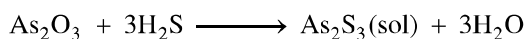
(ii) **Electrodispersion:** An arc is produced between rods of metals immersed in water containing KOH, surrounded by ice-cold water. KOH is added to stabilise the sol. Ag, Au, Pt, Cu sols are prepared in this manner. The method is known as Bredig's arc method.

(iii) **Dispersion by third substance (Peptization):** The process of passing a precipitate into a colloidal solution by adding an electrolyte is called peptization. In this process, dispersion medium (liquid) breaks up the precipitate into a colloidal state. Cellulose nitrate is peptised by organic solvents such as ethyl alcohol. The commercial name of the product is collodion. **Example:** fresh precipitate of  $\text{Fe}(\text{OH})_3$  gets easily dispersed into the colloidal solution of  $\text{Fe}(\text{OH})_3$  by adding  $\text{FeCl}_3$  solution.

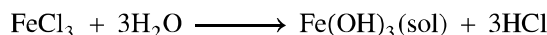
**2. Condensation methods:** In this case we start with molecular-sized particles of the substance and then build them to particles of colloidal dimensions. The different methods are:

(a) **By chemical reaction:**

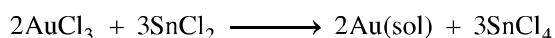
(i) **Double decomposition:** Sulphides of metal are usually prepared by this method.



(ii) **Hydrolysis:** A red sol of  $\text{Fe}(\text{OH})_3$  is obtained by adding some ferric chloride to a beaker of boiling water.



(iii) **Reduction:** Colloidal gold, known as purple of cassius is prepared by reducing auric chloride by stannous chloride.



(iv) **Oxidation:** Colloidal solutions of non-metals like sulphur, selenium and iodine may be obtained by oxidation.



(b) **By exchange of solvent, i.e., by lowering of solubility:** A substance is dissolved in a solvent and the solution is poured into another solvent in which it is less soluble. For example, sulphur sol is formed by pouring its solution in  $\text{CS}_2$  into water.

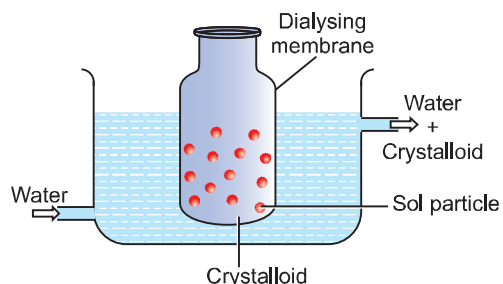
(c) **By excessive cooling:** A colloidal solution of ice in an organic solvent like chloroform or ether can be prepared by excessive cooling of water in these solvents.

(d) **By cathodic reduction:** When lead salts are electrolysed, a sol of lead is obtained at cathode.

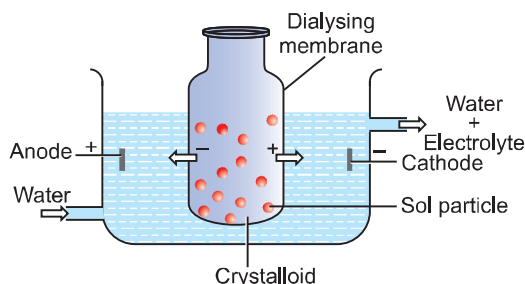
## 22. Purification of Colloidal Solutions:

(a) **Dialysis:** It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane. In this process, a bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flowing. The molecules and ions diffuse through membrane into the water outside and pure colloidal solution is left behind [Fig. 5.5(a)]. The dialysis can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is only an electrolyte. This process is called **electrodialysis** [Fig. 5.5(b)].





**Fig. 5.5(a): Dialysis**



**Fig. 5.5(b): Electro dialysis**

- (b) **Ultrafiltration:** Ultrafiltration is a process of separating the colloidal particles from the solvent and soluble solute particles present in the colloidal solution by specially prepared filters which are permeable to all substances except the colloidal particles. An ultra-filter paper may be prepared by soaking the filter paper in a collodion solution (a 4% solution of nitrocellulose in a mixture of alcohol and ether), hardening by formaldehyde and then finally drying it. Other filter media commonly used are unglazed porcelain and finely sintered glass. Ultrafiltration is a slow process. To speed up the process, pressure or suction is applied.

### 23. Properties of Colloids:

- (a) **Brownian movement:** When a colloidal solution is viewed under a powerful microscope, the colloidal particles appear to be in a state of continuous zig-zag motion all over the field of view. This zig-zag motion of colloidal particles in the dispersion medium is called Brownian movement after the name of its discoverer Robert Brown.

This motion is independent of the nature of the colloidal particles. It is more rapid when the size of the particles is small and solution is less viscous. Brownian movement is believed to be due to unequal bombardment of colloidal particles by the molecules of the dispersion medium. Since with increase of particle size the chances of unequal bombardment decreases, the Brownian movement too disappears.

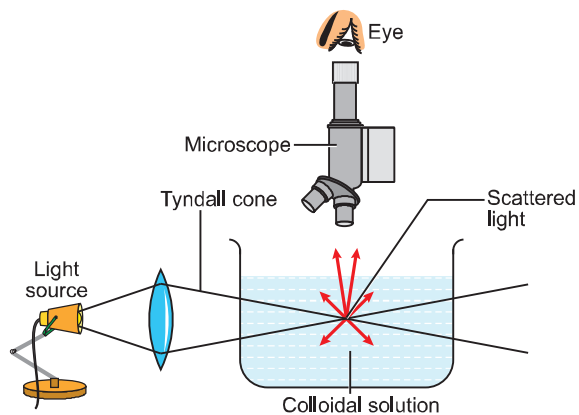
- (b) **Tyndall effect:** When a strong converging beam of light is passed through a colloidal solution placed in a dark room, the path of beam gets illuminated with a bluish light when viewed at right angles to the direction of the passage of light. This phenomenon is known as Tyndall effect (Fig. 5.6). The Tyndall effect is due to scattering of light by colloidal particles.

Tyndall effect is observed only when the following two conditions are satisfied:

- (i) The diameter of the dispersed particles is not much smaller than the wavelength of the light used; and
- (ii) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.

Tyndall effect is used to distinguish between a colloidal and true solution.

- (c) **Colour:** The colour of colloidal solution depends on the wavelengths of light scattered by the dispersed particles. The wavelength of light further depends on the size and nature of the particles. The colour of the colloidal solution also changes with manner in which the observer receives the light. For example, a mixture of milk and water appears red when viewed by the transmitted light and blue when viewed by the reflected light.

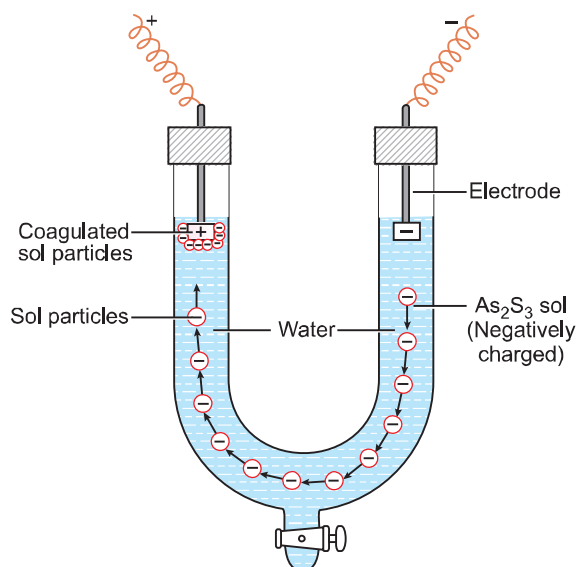


**Fig. 5.6: Tyndall Effect**

**(d) Charge on colloidal particles :** A list of some common sols with the nature of the charge on their particle is given in the table below:

S.No.	Positively Charged Sols	Negatively Charged Sols
(i)	Hydrated metallic oxides, <i>e.g.</i> , $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , $\text{CrO}_3 \cdot x\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ , etc.	Metal particles, <i>e.g.</i> , gold, silver, copper sols.
(ii)	Basic dyes like methylene blue sol.	Acidic dyes like eosin, Congo red sols.
(iii)	Haemoglobin.	Sols of starch, gum, gelation, clay, charcoal, etc.
(iv)	Oxides, <i>e.g.</i> , $\text{TiO}_2$ sol.	Metallic sulphides, <i>e.g.</i> , $\text{As}_2\text{S}_3$ , $\text{Sb}_2\text{S}_3$ , $\text{CdS}$ sols.

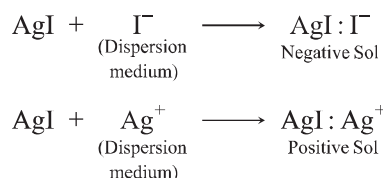
- **Origin of charge:** There have been number of views regarding the origin of charge on colloidal particles such as:
  - Due to friction between colloidal particles and molecules of dispersion medium.
  - Dissociation of molecules followed by aggregation of ions.
  - Due to electron capture during electrodispersion of metals.
  - Due to preferential adsorption of ions from solution and/or due to formulation of electrical double layer.



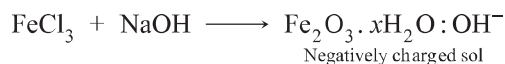
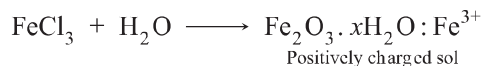
**Fig. 5.7: Electrophoresis**

Preferential adsorption of ions is the most accepted view. According to this view the charge on colloidal particles is due to preferential adsorption of ions present in the dispersion medium. The ions preferred by colloidal particles are those which are common with their own lattice. A few examples are given below:

- If silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide adsorbs iodide ions from the dispersion medium and negatively charged sol results. However, when silver iodide is formed by adding potassium iodide to silver nitrate solution, positively charged sol results due to adsorption of  $\text{Ag}^+$  ions from dispersion medium.



- (ii) When ferric chloride is added to excess of hot water, a positively charged sol of hydrated ferric oxide is formed due to adsorption of  $\text{Fe}^{3+}$  ions. However, if ferric chloride is added to NaOH a negatively charged sol is obtained due to adsorption of  $\text{OH}^-$  ions.



**Helmholtz electro-kinetic electrical double layer:** When positive or negative ions of the electrolytes are adsorbed on the surface of colloidal particles, it forms a fixed layer. It attracts the counter-ions from the dispersion medium to form a second layer which is mobile and is called diffused layer. The combination of the two layers of opposite charges around the colloidal particle thus formed is called Helmholtz electrical double layer.

**Electro-kinetic potential or zeta potential:** The potential difference between the fixed layer and the diffused layer of opposite charges is called electro-kinetic potential or zeta potential.

- (e) **Electrophoresis:** The movement of colloidal particles towards oppositely charged electrode in an electric field is called electrophoresis (Fig. 5.7). If the movement of colloidal particles takes place towards the cathode, the phenomenon is called cataphoresis.
- (f) **Electroosmosis:** When electrophoresis, *i.e.*, movement of particles is prevented by some suitable means, it is observed that the dispersion medium begins to move in the electric field. This phenomenon is known as electroosmosis.
- (g) **Stability of a sol:** The stability of the lyophobic sols is due to the presence of similar charge on colloidal particles. Lyophilic sols are more stable than lyophobic sols as the stability of lyophilic sol is due to two factors. These are same charges and solvation of the colloidal particles.
- (h) **Coagulation:** The process of aggregation of colloidal particles into an insoluble precipitate by the addition of suitable electrolyte is called coagulation.
- **Hardy and Schulze rules:**
    - (i) The ions carrying charge opposite to that of sol particles are effective in bringing about the coagulation of sol.
    - (ii) Coagulating power of the electrolyte is directly proportional to the fourth power of the valency of the ions causing coagulation.
  - **Coagulating value:** The minimum concentration of an electrolyte in millimoles per litre required to cause precipitation of a sol in two hours is called coagulating value. The smaller the quantity needed, the higher will be the coagulating power of an ion.
  - **Coagulation of lyophobic sol is done by**
    - (i) addition of electrolytes.
    - (ii) electrophoresis.
    - (iii) boiling.
    - (iv) mixing two oppositely charged sols.
    - (v) persistent dialysis.
  - **Coagulation of lyophilic sol is done by**
    - (i) adding an electrolyte.
    - (ii) adding a suitable solvent. When solvents such as alcohol and acetone are added to hydrophilic sols, dehydration of dispersed phase occurs. Under this condition, a small quantity of electrolyte can bring about coagulation.

- **Gold number:** The number of milligrams of protective colloids which must be added to 10 mL of given gold sol so that it is just prevented from coagulation by addition of 1 mL of 10% NaCl solution. The smaller the gold number, the higher is the protecting power of lyophilic colloids.
- 24. Emulsions:** Emulsions are colloidal systems in which both the dispersed phase and dispersion medium are liquids. There are two types of emulsions:
- (i) **Oil in water (O/W) type emulsions:** In such emulsions, oil is the dispersed phase and water is the dispersion medium, *e.g.*, milk, vanishing cream.
  - (ii) **Water in oil (W/O) type emulsions:** In such emulsions, water is the dispersed phase and oil is the dispersion medium, *e.g.*, butter, cod liver oil.
    - ➔ **Emulsifiers:** These are the substances which help in stabilising emulsions. The emulsifier forms a film around every drop of the dispersed phase and hence, prevents drops from coming together. The emulsifiers for O/W emulsions are proteins, gums, natural and synthetic soaps, etc. and for W/O emulsions are heavy metal salts of fatty acids, long chain alcohols, lampblack, etc.
    - ➔ **Demulsification:** The process of decomposing an emulsion into its constituent liquids is called demulsification. It is carried out by centrifugation, freezing, boiling or chemical methods which destroy the emulsifying agents.
- 25. Colloids Around Us**
- (i) **Blue colour of the sky:** Dust particles along with water suspended in air scatter blue light which reaches our eyes and the sky looks blue to us.
  - (ii) **Clouds:** Clouds are aerosols having small droplets of water suspended in air.
  - (iii) **Blood:** Blood is colloidal solution of an albuminoid and the stoppage of bleeding on applying ferric chloride solution is due to coagulation of blood forming a clot.
  - (iv) **Food articles:** Milk, butter, ice-creams, fruit juices, etc. are of colloidal nature.
  - (v) **Formation of delta:** River water is colloidal solution of clay. Sea water contains a number of electrolytes. As soon as the river water comes in contact with the sea water, the electrolytes present in sea water coagulate the colloidal solution of clay resulting in its deposition with the formation of delta.
- 26. Application of Colloids:**
- (i) **Medicines:** Most of the pharmaceutical preparation are colloidal in nature. For example, colloidal antimony is used in curing Kala-azar, argyrol used as an eye lotion is silver sol protected by gelatin, milk of magnesia is an emulsion used for stomach trouble, colloidal gold and calcium are used for intra-muscular injection.
  - (ii) **Industrial products:** Paints, ink, rubber, synthetic plastics, graphite lubricants, cement, etc. are all colloidal solutions.
  - (iii) **Tanning:** When a hide, which contain positively charged particles is soaked in tannin, which has negatively charged particles, mutual coagulation takes place. It results in the hardening of leather. This process is known as tanning.
  - (iv) **Purification of drinking water:** The water from river contains negatively charged clay particles. On addition of alum which yields trivalent  $\text{Al}^{3+}$  ions in solution, the negative charge on clay particles is neutralised and consequently, they precipitate out and settle down at the bottom. The clear water is left at the top and can be decanted off.

## NCERT Textbook Questions

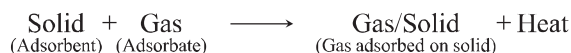
### NCERT Intext Questions

**Q. 1. Write any two characteristics of chemisorption.**

- Ans.** (i) Chemisorption is highly specific and it will occur only if there is some possibility of bonding between adsorbent and adsorbate.  
(ii) As chemisorption involves compound formation therefore it is usually irreversible in nature.

**Q. 2. Why does physisorption decrease with increase of temperature?**

**Ans.** Physisorption is an exothermic process:



According to Le Chatelier's principle, if we increase the temperature, equilibrium will shift in the backward direction, *i.e.*, gas is released from the adsorbed surface.

**Q. 3. Why are powdered substances more effective adsorbent than their crystalline forms?**

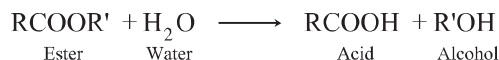
**Ans.** Powdered substances have greater surface area as compared to their crystalline forms. Greater the surface area, greater is the adsorption.

**Q. 4. In Haber's process hydrogen is obtained by reacting methane with steam in presence of NiO as catalyst. This process is known as steam reforming. Why is it necessary to remove CO when ammonia is obtained by Haber's process?**

**Ans.** CO acts as catalytic poison and must be removed.

**Q. 5. Why is the ester hydrolysis slow in the beginning and becomes faster after some time?**

**Ans.** The ester hydrolysis takes place as follows:



The acid produced in the reaction acts as catalyst (autocatalyst) for the reaction. Hence, the reaction becomes faster after sometime.

**Q. 6. What is the role of desorption in the process of catalysis?**

**Ans.** The reaction products formed on the catalyst surface get detached from the surface as a result of desorption, thereby making the surface available again for more reaction.

**Q. 7. What modification can you suggest in the Hardy-Schulze law?**

**Ans.** This law does not take into account the size of the ion. The smaller the size of anion, greater will be its polarising power. Thus, the law can be modified in terms of polarising power of the flocculating ion. The modified law states that, the greater the polarising power of the flocculating ion, the greater is its power to cause precipitation.

**Q. 8. Why is it essential to wash the precipitate with water before estimating it quantitatively?**

**Ans.** Some amount of the electrolytes mixed to form the precipitate remains adsorbed on the surface of the particles of the precipitate. Hence, it is essential to wash the precipitate with water to remove the sticking electrolytes (or any other impurities) before estimating it quantitatively.

### NCERT Textbook Exercises

**Q. 1. Distinguish between the meaning of the term adsorption and absorption. Give one example of each.**

**Ans.**

S.No.	Adsorption	Absorption
(i)	It is a surface phenomenon. Adsorbate molecules are held at the surface of adsorbent.	Absorption occurs in the bulk of absorbing substance.
(ii)	The concentration of the adsorbate at the adsorbent surface is much more than that in the bulk.	Absorbed material is uniformly distributed throughout the bulk. Thus, concentration is same throughout.
(iii)	Initially, rate of adsorption is rapid. It decreases slowly till equilibrium is attained. <b>Example:</b> Water vapours on silica gel.	Absorption occurs with uniform rate. <b>Example:</b> Water vapours are absorbed by anhydrous $\text{CaCl}_2$ .

**Q. 2. What is the difference between physisorption and chemisorption?** [CBSE 2019 (56/5/2)]

OR

**Give three points of differences between physisorption and chemisorption.** [CBSE 2020 (56/1/1)]

OR

**Write two differences between physisorption and chemisorption.** [CBSE 2020 (56/3/1)]

Ans.

S.No.	Physisorption	Chemisorption
(i)	It arises because of van der Waals' forces.	It is caused by chemical bond formation.
(ii)	It is not specific in nature.	It is highly specific in nature.
(iii)	It is reversible in nature.	It is irreversible.
(iv)	It depends on the nature of gas. More easily liquefiable gases are adsorbed readily.	It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption.
(v)	Enthalpy of adsorption is low (20-40 kJ mol <sup>-1</sup> ) in this case.	Enthalpy of adsorption is high (80-240 kJ mol <sup>-1</sup> ) in this case.
(vi)	Low temperature is favourable for adsorption. It decreases with increase of temperature.	High temperature is favourable for adsorption. It increases with the increase of temperature.
(vii)	No appreciable activation energy is needed.	High activation energy is sometimes needed.
(viii)	It results into multimolecular layers on adsorbent surface under high pressure.	It results into unimolecular layer.

**Q. 3. Give reason why a finely divided substance is more effective as an adsorbent.**

[CBSE (F) 2013; 2019 (56/4/2)]

Ans. Powdered substances have greater surface area as compared to their crystalline forms. Greater the surface area, greater is the adsorption.

**Q. 4. What are the factors, which influence the adsorption of a gas on a solid?**

Ans. The extent of adsorption of a gas on a solid surface depends on following factors:

- The nature of gas
- Surface area of adsorbent
- Pressure
- Temperature
- Activation of adsorbent.

**Q. 5. What is an adsorption isotherm? Describe Freundlich adsorption isotherm.**

Ans. Refer to Basic Concepts Points 6 and 7.

**Q. 6. What do you understand by activation of adsorbent? How is it achieved?**

Ans. Activation of adsorbent means, increasing the adsorbing power of an adsorbent. This can be done by increasing the surface area of the adsorbent which can be achieved in any of the following ways:

- By removing the gases adsorbed, *i.e.*, wood charcoal can be activated by heating it between 650 K and 1330 K in vacuum or super-heated steam.
- By breaking the adsorbent into small pieces.
- By making the surface of adsorbent rough.

**Q. 7. What role does adsorption play in heterogeneous catalysis?**

[CBSE 2020 (56/5/1)]

Ans. In heterogeneous catalysis, generally the reactants are gaseous whereas the catalyst is a solid. The reactant molecules are adsorbed on the surface of the solid catalyst by physical adsorption or chemical adsorption. As a result, the concentration of the reactant molecules on the surface increases and hence the rate of reaction increases. Alternatively, one of the reactant molecules undergoes fragmentation on the surface of the solid catalyst producing active species which react faster. The product molecules in either case have no affinity for the solid catalyst and are desorbed, making the surface free for fresh adsorption. This theory is called adsorption theory.

**Q. 8. Why is adsorption always exothermic?**

**Ans.** As the adsorption progresses, the residual forces at the surface decreases resulting in the decrease of surface energy which appears as heat.

**Q. 9. How are the colloidal solutions classified on the basis of physical states of the dispersed phase and dispersion medium?**

**Ans.** Refer to Basic Concepts Point 17.

**Q. 10. Discuss the effect of pressure and temperature on the adsorption of gases on solids.**

**Ans. Effect of pressure on adsorption:** At constant temperature, the extent of adsorption of a gas ( $x/m$ ) on a solid increases with pressure. A graph between  $x/m$  and the pressure  $p$  of a gas at constant temperature is called adsorption isotherm.

(i) At lower range of pressure,  $x/m$  is directly proportional to the applied pressure.

$$\frac{x}{m} \propto p^1 \quad \text{or} \quad \frac{x}{m} \propto kp$$

(ii) At high pressure range, the extent of adsorption of a gas ( $x/m$ ) is independent of the applied pressure, *i.e.*,

$$\frac{x}{m} \propto p^0 \quad \text{or} \quad \frac{x}{m} = k$$

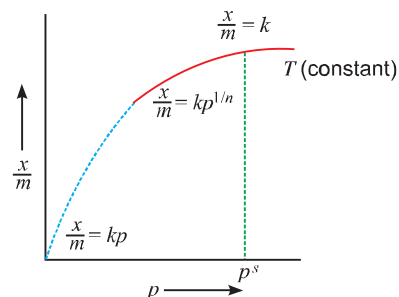
(iii) At intermediate pressure range, the value of  $x/m$  is proportional to a fractional power of pressure, *i.e.*,

$$\frac{x}{m} \propto p^{1/n} \quad \text{or} \quad \frac{x}{m} = kp^{1/n} \quad \dots(i)$$

where  $1/n$  is a fraction. Its value may be between 0 and 1.

$$\log \left( \frac{x}{m} \right) = \log k + \frac{1}{n} \log p \quad \dots(ii)$$

**Effect of temperature on adsorption:** Adsorption is generally temperature dependent. Mostly adsorption processes are exothermic and hence adsorption decreases with increasing temperature. However, for an endothermic adsorption process, adsorption increases with increase in temperature.



**Q. 11. What are lyophilic and lyophobic sols? Give one example of each type. Why is hydrophobic sol easily coagulated?**

**Ans.** For first and second part refer to Basic Concepts Point 18.

The stability of hydrophobic sol is only due to the presence of charge on the colloidal particles. If charge is removed, by addition of suitable electrolytes, the particles will come nearer to each other to form aggregate, *i.e.*, they will coagulate and settle down. The stability of hydrophilic sol is due to charge as well as solvation of the colloidal particles. Both the factors have to be removed to bring about their coagulation.

**Q. 12. What is the difference between multimolecular and macromolecular colloids? Give one example of each. How are associated colloids different from these two types of colloids? [CBSE Delhi 2010]**

**Ans. Multimolecular colloids:** In this type of colloids, colloidal particles are aggregates of atoms or molecules each having size less than 1 nm, *e.g.*, sulphur sol, gold sol. Multimolecular colloids are generally lyophobic in nature.

**Macromolecular colloids:** In this type of colloids, colloidal particles are themselves large molecules of colloidal dimensions, *e.g.*, starch, proteins, polythene, etc. Macromolecular colloids are generally lyophilic in nature.

**Associated colloids:** There are certain substances which at low concentrations behave as normal electrolyte, but at higher concentrations exhibit colloidal behaviour due to the formation of aggregates. Such colloids are known as associated colloids, *e.g.*, soaps and detergents.

**Q. 13. What are enzymes? Write in brief the mechanism of enzyme catalysis.**

**Ans.** Refer to Basic Concepts Points 14.

**Q. 14. How are colloids classified on the basis of**

- (i) physical states of components,
- (ii) nature of dispersed phase, and
- (iii) interaction between dispersed phase and dispersion medium.

**Ans.** (i) Refer to Basic Concepts Point 17.  
(ii) Refer to Basic Concepts Point 19.  
(iii) Refer to Basic Concepts Point 18.

**Q. 15. Explain what is observed when**

- (i) when a beam of light is passed through a colloidal solution.
- (ii) an electrolyte, NaCl is added to hydrated ferric oxide sol.
- (iii) electric current is passed through a colloidal sol.

[CBSE (AI) 2011]

**Ans.** (i) Scattering of light by the colloidal particles takes place and the path of light becomes visible (Tyndall effect).  
(ii) The positively charged colloidal particles of Fe(OH)<sub>3</sub> get coagulated by the oppositely charged Cl<sup>-</sup> ions provided by NaCl.  
(iii) On passing direct current, colloidal particles move towards the oppositely charged electrode where they lose their charge and get coagulated.

**Q. 16. What are emulsions? What are their different types? Give example of each type.** [CBSE (AI) 2014]

**Ans.** Refer to Basic Concepts Point 24.

**Q. 17. How do emulsifiers stabilise emulsions? Name two emulsifiers.**

**Ans.** The emulsifier forms a film around every drop of the dispersed phase and hence, prevents drops from coming together. The emulsifiers for O/W emulsions are proteins, gums, natural and synthetic soaps, etc. and for W/O emulsions are heavy metal salts of fatty acids, long chain alcohols, lampblack, etc.

**Q. 18. Action of soap is due to emulsification and micelle formation. Comment.**

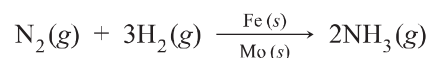
**Ans.** The cleansing action of soap such as sodium stearate is due to the fact that soap molecules form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles. Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface. Thus, soap helps in emulsification and washing away of oils and fats.

**Q. 19. Give four examples of heterogeneous catalysis.**

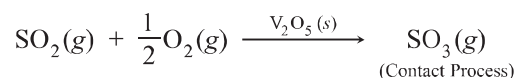
**Ans.** A catalyst in different phase than that of the reactants in a reaction is called heterogeneous catalyst and this phenomenon is called heterogeneous catalysis. In heterogeneous catalysis, catalyst is generally a solid and reactants are usually gases (or sometimes liquids).

Some important industrial reactions which are heterogeneous catalytic reactions are given below:

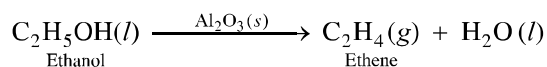
- (i) Synthesis of ammonia from nitrogen and hydrogen in the presence of iron as a catalyst.



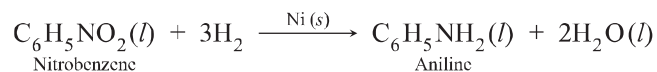
- (ii) Manufacture of sulphur trioxide (SO<sub>3</sub>) by the oxidation of sulphur dioxide (SO<sub>2</sub>) in the presence of vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) as a catalyst.



- (iii) Dehydration of ethanol by alumina (Al<sub>2</sub>O<sub>3</sub>).



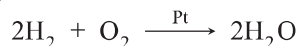
- (iv) Reduction of nitrobenzene in the presence of nickel catalyst.



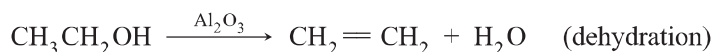
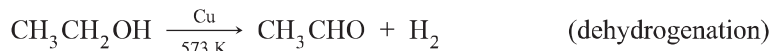


**Q. 20. What do you mean by activity and selectivity of catalysts?**

**Ans. Activity of catalyst:** The ability of a catalyst to increase the rate of a reaction is called its activity. For example, a mixture of hydrogen and oxygen does not react at all, however, in the presence of platinum as a catalyst the mixture reacts with explosive violence to form water.



**Selectivity of catalyst:** It is the ability of a catalyst to direct a reaction to yield a particular product. For example, both dehydrogenation and dehydration of ethanol are possible. But in presence of a suitable catalyst only one reaction is made to occur.

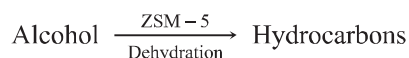


**Q. 21. Describe some features of catalysis by zeolites.**

**Ans.** Features of catalysis by zeolites:

- (i) Zeolites are hydrated aluminosilicates which have a three-dimensional network structure containing water molecules in their pores.
- (ii) To use them as catalysts, they are heated so that water of hydration present in the pores is lost and the pores become vacant.
- (iii) The size of the pores varies from 260 to 740 pm. Thus, only those molecules can be adsorbed in these pores and catalysed whose size is small enough to enter these pores. Hence, they act as molecular sieves or shape-selective catalysts.

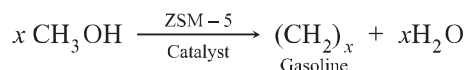
An important catalyst used in petroleum industry is ZSM-5 (Zeolite sieve of molecular porosity 5). It converts alcohols into petrol by dehydrating them to form a mixture of hydrocarbons.



**Q. 22. What is shape-selective catalysis?**

[CBSE Delhi 2010, 2011, 2012; 2020 (56/3/1)]

**Ans.** Shape-selective catalysis is chemical reaction in which the rate depends on the pore size of the catalyst, and also on the shape and size of the reactant and product molecules. A shape-selective catalyst has a variety of active sites of different shape and size. Zeolite acts as a shape-selective catalyst. In the crystal of a zeolite, the pore size usually varies from 260 pm to 740 pm. If the reactant molecules are too large they cannot fit into pores of zeolite and no reaction takes place. On the other hand, if the reactant molecules are too small, they would just slip through the pores in the catalyst without any interactions. ZSM-5 is used as shape-selective catalyst to produce gasoline of high octane number from methanol.



where  $x$  varies from 5 to 10. ZSM-5 stands for zeolite sieve of molecular porosity-5.

**Q. 23. Explain the following terms:**

- |                     |                     |
|---------------------|---------------------|
| (i) Electrophoresis | (ii) Coagulation    |
| (iii) Dialysis      | (iv) Tyndall effect |

**Ans.** (i) Refer to Basic Concepts Point 23 (e).  
(ii) Refer to Basic Concepts Point 23 (h).  
(iii) Refer to Basic Concepts Points 22 (a).  
(iv) Refer to Basic Concepts Points 23 (b).

**Q. 24. Give four uses of emulsions.**

**Ans.** Four uses of emulsions are:

- (i) The concentration of sulphide ore by froth floatation process is based on emulsification.
- (ii) Cleansing action of soap and detergents is due to the formation of an emulsion between dirt and soap solution.
- (iii) Milk is an emulsion of fat in water.