Surface Chemistry

INTRODUCTION :

Surface chemistry is that branch of chemistry which deals with study of the phenomena occuring at the surface or interface, i.e. at the boundary separating two bulk phases. In this chapter our main emphasis will be on three important topics related to surface chemistry, viz., adsorption, colloids and emulsions.

- **Adsorption :** The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting into a higher concentration of the molecules on the surface is called adsorption. As a result of adsorption, there is a decrease of surface energy. The process of removal of an adsorbed substance from the surface on which it is adsorbed is called desorption. It is the reverse of adsorption and can be brought about by heating or by reducing the pressure.

- **Adsorbent and adsorbate :**The substance on the surface of which adsorption occurs is known as adsorbent. The substances that get adsorbed on the solid surface due to intermolecular attractions are called adsorbate.Charcoal, silica, gel, alumina gel are good adsorbents because they have highly porous structures and have large surface area. Colloids on account of their extremely small dimensions possess enoromous surface area per unit mass and are, therefore, also good adsorbents.

Examples of adsorption :

- **Adsorption of a gas by charcoal :** Finely divided activated charcoal has a tendency to adsorb a number of gases like ammonia, sulphur dioxide, chlorine, phosgene, etc. In this case, charcoal acts as an adsorbent while gas molecules act as adsorbate.

- **Adsorption of a dye by charcoal :** Animal charcoal is used for decolourising a number of organic substances in the form of their solutions. The discharge of the colour is due to the fact that the coloured component (generally an organic dye) gets adsorbed on the surface of the adsorbent (animal charcoal).

- **Sorption :** When both adsorption and absorption take place simultaneously.
  Eg : Dyes get adsorbed as well as absorbed in the cotton fibre i.e. sorption takes place.

Difference between adsorption and absorption :

The terms adsorption and absorption are different. Adsorption is a phenomenon in which there is higher concentration of another substance on the surface than in the bulk. On the other hand, absorption is a phenomenon in which the molecules of a substance are uniformly distributed throughout the body of other substance. For example, when silica gel is placed in the environment of water, it adsorbs the water vapour. The water vapour are present in high concentration at the surface of silica gel. On the other hand, when calcium chloride is placed in the environment of water, it absorbs water. The water vapour uniformly get distributed throughout the body of calcium chloride. Thus, silica gel adsorbs water vapour while anhydrous calcium chloride absorbs water.

- **Thermodynamics of adsorption :** Adsorption is an exothermic process. Therefore ΔH of adsorption is always negative. When a gas is adsorbed the entropy of the gas decreases i.e. ΔS is negative. Adsorption is thus accompanied by decrease in enthalpy as well as entropy of the system, for a process to be spontaneous requirement is that ΔG must be negative. On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if ΔH has sufficiently high negative value as $- T\Delta S$ is positive. Thus, in an adsorption process, which is spontaneous, ΔS is negative, and ΔH is also sufficiently negative and as a combination of these two factors, ΔG is negative.

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

- **Enthalpy of adsorption $\Delta H_{adsorption}$:** It is the amount of the heat released when 1 mole of an adsorbate gets adsorbed on a particular adsorbent at adsorption equilibrium. It depends upon the nature of both the adsorbate as well as adsorbent.

Types of adsorption : The adsorption is classified into two types :

(i) **Physical adsorption (i.e. physisorption) :** When the particles of the adsorbate are held to the surface of the adsorbent by the physical forces such as van der Waal's forces, the adsorption is called physical adsorption or vanderwaals adsorption.

(ii) **Chemical adsorption (i.e. chemisorption) :**
When the molecules of the adsorbate are held to the surface of the adsorbent by the chemical forces, the adsorption is called chemical adsorption.

Difference between physical adsorption and chemical adsorption

Physical Adsorption	Chemical Adsorption
● The forces between the adsorbate molecules and the adsorbent are weak van der Waal's forces.	The forces between the adsorbate molecules and the adsorbent are strong chemical forces.
● Low heat of adsorption of the order of 20-40 kJ mol^{-1}	High heat of adsorption of the order 80-240 kJ mol^{-1}
● Usually occurs at low temperature and decreases with increasing temperature.	It occurs at high temperature
● It is reversible.	It is irreversible.
● The extent of adsorption depends upon the ease of liquefication of the gas.	There is no correlation between extent of adsorption and the ease of liquefication of gas.
● It is less specific in nature, all gases are adsorbed on the surface of a solid to some extent.	It is highly specific in nature and occurs only when there is bond formation between adsorbent and adsorbate molecules.
● It forms multimolecular layers.	It forms mono-molecular layer.
● extent of adsorption (x/m) increases with pressure	extent of adsorption (x/m) increases with pressure

- **Competitive adsorption :** When an adsorbent is in contact with more than one species (adsorbate). There will be competition among them to get adsorbed on to the surface of the adsorbent. The one that is more strongly adsorbed gets deposited first in preference to the others. Further a strongly adsorbed substance may displace a weakly adsorbed substance.
  Ex. NH_3 can displace O_2 or N_2 from the surface of charcoal.

Adsorption of gases on solids :

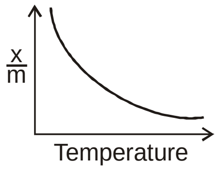
The extent of adsorption of a gas on a solid surface is affected by the following factors:

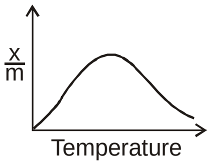
- **The nature of the gas (i.e. nature of the adsorbate).** The easily liquefiable gases such as HCl, NH_3, Cl_2 etc. are adsorbed more than the permanent gases such as H_2, N_2 and O_2. The ease with which a gas can be liquefied is primarily determined by its critical temperature. Higher the critical temperature (T_c) of a gas, the more easily it will be liquefied and, therefore, more readily it will be adsorbed on the solid.

Gas	SO_2	CH_4	H_2
T_C	330K	190 K	33 K

- **Nature of adsorbent.** The extent of adsorption of a gas depends upon the nature of adsorbent. Activated charcoal (i.e. activated carbon), metal oxides (silica gel and aluminium oxide) and clay can adsorb gases which are easily liquified. Gases such as H_2, N_2 and O_2 are generally adsorbed on finely divided transition metals Ni and Co.

- **Activation of adsorbent :**
  (a) Metallic adsorbents are activated by mechanical rubbing or by subjecting it to some chemical reactions.
  (b) To increase the adsorbing power of adsorbents, they are sub-divided into smaller pieces. As a results, the surface area is increased and therefore, the adsorbing power increases.
- **Effect of temperature :**Mostly the process of adsorption is exothermic and the reverse process or desorption is endothermic. If the above equilibrium is subjected to increase in temperature, then according to Le-Chaterlier's principle, with increase in temperature, the desorption will be favoured. Physical adsorption decreases continuously with increase in temperature whereas chemisorption increases initially, shows a maximum in the curve and then it decreases continuously.





The initial increase in chemisorption with increase in temperature is because of activation energy required.

This is why the chemical adsorption is also known as "**Activated adsorption".**

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

- **Effect of pressure.** The extent of adsorption of a gas per unit mass of adsorbent depends upon the pressure of the gas. The variation of extent of adsorption expressed as x/m (where x is the mass of adsorbate and m is the mass of the adsorbent) and the pressure is given as below. A graph between the amount of adsorption and gas pressure keeping the temperature constant is called an adsorption isotherm.

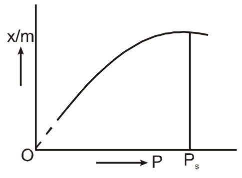


Figure-1

It is clear from the figure-1 that extent of adsorption (x/m) increases with pressure and becomes maximum corresponding to pressure P_s called equilibrium pressure. Since adsorption is a reversible process, the desorption also takes place simultaneously. At this pressure (P_s) the amount of gas adsorbed becomes equal to the amount of gas desorbed.

Freundlich Adsorption isotherm :

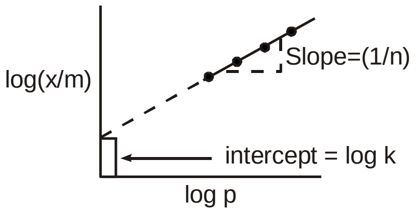
The variation of extent of adsorption (x/m) with pressure (P) was given mathematically by Freundlich.

- At low pressure the graph is almost straight line which indicates that x/m is directly proportional to the pressure. This may be expressed as :

  $(x/m) \alpha\ p$ or $(x/m) = kp$ where k is constant.
- At high pressure the graph becomes almost constant which means that x/m becomes independent of pressure. This may be expressed as :

  $(x/m) = \text{constant}$ or $(x/m)\ \alpha\ p^0$ (since $p^0 = 1$) or $(x/m) = kp^0$.
- Thus, in the intermediate range of pressure, x/m will depend upon the power of pressure which lies between 0 to 1, fractional power of pressure. This may be expressed as

  $(x/m)\ \alpha\ p^{1/n}$ or $(x/m) = kp^{1/n}$



Where n can take any whole number value which depends upon the nature of adsorbate and adsorbent. The above relationship is also called Freundlich's adsorption isotherm.

The constant k and n can be determined as explained below :

Taking logarithms on both sides of

Eq. $(x/m) = kp^{1/n}$ we get

$\log (x/m) = \log k + (1/n) \log p$.

☞ One of the drawbacks of Freundlich isotherm is that it fails at high pressure of the gas.

☞ This equation applicable only when adsorbate substance form unimolecular layer on adsorbent surface. i.e. chemical adsorption.

Adsorption from solutions : The process of adsorption can take place from solutions also. It is observed that solid adsorbents adsorb certain solutes from solution in preference to other solutes and solvents. For example, animal charcoal decolouries impure sugar solution by adsorbing colouring dye in preference to sugar molecules.

The extent of adsorption from solution depends upon the concentration of solute in the solution as given by Freundlich isotherm : $(x/m) = k(c)^{1/n}$ $(n \geq 1)$

where c is the equilibrium concentration of the solute in solution.

Temperature dependence here also is similar to that for adsorption of gases and in place of equilibrium pressure, we use equilibrium concentrations of the adsorbates in the solution.

Applications of adsorption :

- **In gas masks :** Activated charcoal is generally used in gas masks to adsorb poisonous and toxic gases from air. These masks are commonly used by the miners because there are poisonous gases like CO, CH_4 etc. in the atmosphere in coal mines.
- **In dyeing of cloths :** Mordants such as alums are used in dyeing of cloths. They adsorb the dye particles which, otherwise, do not stick to the cloths.
- **In dehumidizers :** Silica gel is commonly used to adsorb humidity or moisture from air.
- **Removal of colouring matter :** Many substances such as sugar, juice and vegetable oils are coloured due to the presence of impurities. They can be decolourised by placing them in contact with adsorbents like activated charcoal or fuller's earth.
- **Heterogeneous catalysis :** The phenomenon of adsorption is useful in the heterogeneous catalysis. The metals such as Fe, Ni, Pt, Pd, etc, are used in the manufacturing processes such as Contact process, Haber process and the hydrogenation of oils. Their use is based upon the phenomenon of adsorption.
- **Refining Petroleum :** Silica gel is used as adsorbent in petroleum refining.
- **Chromatography :** It is a method for separation of component and is based on preferential adsorption column is very common device used.
- **Creating vacuum :** High vacuum can be created by removing gas by adsorption.
- **Adsorption Indicators :** In volumetric analysis, adsorption indicator is used Surface of certain precipitates such as silver halide have the property of adsorbing some dye like eosin, fluorescein, etc In the case of precipitation titration ($AgNO_3$ vs NaCl) of the indicator is adsorbed at the end point producing a characteristic colour on the precipitate.
- **In froth floatation process :** (in metallurgy).
- **Softening of hard water :** Ion exchange resins used for softening of hard water is based upon selective and competive adsorption of ions on resins.

$$Na_2Z + Ca^{+2} \longrightarrow CaZ + 2\,Na^+$$

The organic polymers containing groups like –COOH, $-SO_3H$ and $-NH_2$ etc. possess the property of selective adsorption of ions from solution. These are quite useful in the softening of water.

Solved Examples

Example-1 A sample of charcoal weighing 6 g was brought into contact with a gas contained in a vessel of one litre capacity at 27ºC. The pressure of the gas was found to fall from 700 to 400 mm. Calculate the volume of the gas (reduced to STP) that is adsorbed per gram of the adsorbent under the condition of the experiment (density of charcoal sample is 1.5 g cm^3).

Solution. The adsorption is taking place in a closed vessel hence if pressure falls there is correspondingly increase in volume constant, excess of the volume of the gas would be adsorbed.

$$P_1V_1 = P_2V_2$$

$$V_2 = P_1\frac{V_1}{P_2} = 700 \times \frac{1000}{40} = 1750 \text{ mL.}$$

Actual volume of the flask = 1000 – volume of charcoal = $1000 - \frac{6.00}{1.50}$ = 996 mL.

Volume of the gas adsorbed = 1750 – 996 = 754 mL.

Volume of the gas adsorbed per gram at STP $\left(\text{Using } \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}\right)$

$$= \frac{125.67 \times 400 \times 273}{300 \times 760} = \mathbf{60.19\ mL.}$$

- **Catalysts :** Berzillus in 1835 used the word catalyst first time for some substance which alter rate of chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction and the phenomenon is known as catalysis.

  Eg : Potassium chlorate when heated at 653K to 873K, it gives O_2, When MnO_2 is used in this reaction the O_2 is quickly at the low temperature hence MnO_2 is a catalyst

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

- **Homogeneous Catalysis :** When catalysts and reactants are in same phase then the process is said to be homogeneous catalysis and

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

  (ii) $CH_3COOCH_3(\ell) \xrightarrow{HCl(\ell)} CH_3COOH(aq)$

  (iii) $\underset{}{C_{12}H_{22}O_{11}(aq.) + H_2O(\ell) \xrightarrow{H_2SO_4(\ell)} \underset{\text{Glucose}}{C_6H_{12}O_6(aq.)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq.)}}$

- **Heterogenous Catalysis :** When catalysts and reactants are in different phases, then process a know as heterogenous catalysis and catalyst is called heterogeneous catalyst

  Eg : (i) $2SO_3(g) + O_2(g) \xrightarrow{Pt(s)} 2SO_3(g)$

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

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

  (iv) Vegetable oils $(\ell) + H_2(g) \xrightarrow{Ni(s)}$ Vegetable ghee (s).

- **Types of Catalysis**

  (a) Positive Catalysis : A substance which increase the rate of chemical reaction is called positive catalyst and this process called positive catalysis.

  (i) $2SO_2(g) + O_2(g) \xrightarrow[\text{positive catalyst}]{Pt(s)} 2SO_3(g)$ (ii) $N_2(g) + 3H_2(g) \xrightarrow[\text{positive catalyst}]{Fe(s)} 2NH_3(g)$

  (b) Negative Catalysis : A substance which decrease the rate of chemical reaction is called negative catalyst and this process called negative catalysis.

  Eg : (i) $2H_2O_2 \xrightarrow[\text{negative catalyst}]{H_3PO_4 \text{ or glycerol}} 2H_2O + O_2$

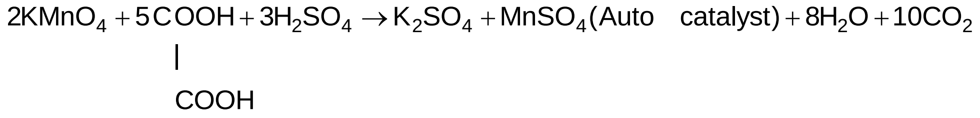
  (ii) Decomposition of chloroform reduces in the presence of 1% ethyl alcohol.

  $$CHCl_3 + \frac{1}{2}O_2 \xrightarrow[\text{negative catalyst}]{1\% \text{ ethyl alcohol}} COCl_2 + HCl$$

  (iii) T.E.L. is used as negative catalyst in petrol which reduce knocking.

(c) **Auto Catalysis :** When one of the reaction product behave as catalyst for that reaction and increase the rate of reaction then the phenomenon is called autocatalysis.
"Auto catalytic reactions are slow in the beginning but become increasingly rapid as the reaction proceeds.

Eg : (i) $CH_3COOC_2H_5 + HOH \rightarrow CH_3COOH(\text{Auto catalyst}) + C_2H_5OH$

(ii)


$$2KMnO_4 + 5\underset{\substack{|\\ COOH}}{COOH} + 3H_2SO_4 \rightarrow K_2SO_4 + MnSO_4(\text{Auto catalyst}) + 8H_2O + 10CO_2$$

(d) **Induced Catalyst :** When one reaction catalyse an other reaction than the phenomenon is called induced catalysis and that reaction is called induced catalyst.

- **Promoters/Activators :** Substance which themselves are not catalyst but its presence can increase the catalytic activity of catalyst. A promoters increase the number of active sites on the surface Eg :

(i) $N_2 + 3H_2 \xrightarrow[\text{Mo(promoter)}]{\text{Fe(catalyst)}} 2NH_3$

(ii) Vegetable Oil + H_2 $\xrightarrow[\text{Cu(promoter)}]{\text{Ni(catalyst)}}$ Vegetable ghee.

(iii) $CO + 2H_2 \xrightarrow[Cr_2O_3\text{(promoter)}]{\text{ZnO(catalyst)}} CH_3OH$

- **Catalytic Poisons/ Anti catalysts/ Catalyst Inhibitor :** Substance which themselves are not catalyst but whose presence decrease the activity of the catalyst. Poisoning is due to preferential adsorption of poison on the surface of the catalyst.

(i) $N_2 + 3H_2 \xrightarrow[CO/H_2S\text{(catalytic poisons)}]{\text{Fe(catalyst)}} 2NH_3$

(ii) $2SO_2 + O_2 \xrightarrow[As_2S_3\text{(catalytic poisons)}]{\text{Platinised asbestos (catalyst)}} 2SO_3$

(iii) Rosunmund Reactions : $RCOCl + H_2 \xrightarrow[BaSO_4\text{(poisons catalytst)}]{\text{Pd(catalyst)}} RCHO + HCl$

- **Characteristics of Catalysis :**

(i) A Catalyst remains unchanged in mass and chemical compositions at the end of reactions. However its physical state can be change. Eg :
Granular MnO_2 during decomposition of $KClO_3$ is left as powder at the end of the reaction.

(ii) Finely devided state of catalyst is more efficient for the reactions because surface area increases and more adsorption take place.

(iii) A small amount of catalyst is generally sufficient to catalyse almost unlimited reaction but in some cases the rate of reaction depends on amount of catalyst.

Exception : (a) In Friedal Craft reaction more amount of catalyst is required.
(b) Hydrolysis of ester in acidic and alkaline medium its rate of reaction is proportional to concentration of H^+ or OH^- ions.

(iv) A catalyst cannot initiate reaction. But some times the activation energy is so large that practically a reaction may not start until a catalyst lowers the activation energy significantly. For example, mixture of hydrogen and oxygen do not react at room temperature but the reaction occurs very rapid in presence of Pt black.

$$H_2 + O_2 \xrightarrow{\text{room temperature}} \text{No reaction}$$

$$H_2 + O_2 \xrightarrow{\text{Pt black}} H_2O.$$

(v) Catalyst are generally specific in nature. A substance which act as a catalyst in a particular reaction, fails to catalyse other reaction.

(vi) Catalyst cannot change equilibrium state but it help to attain equilibrium quickly.

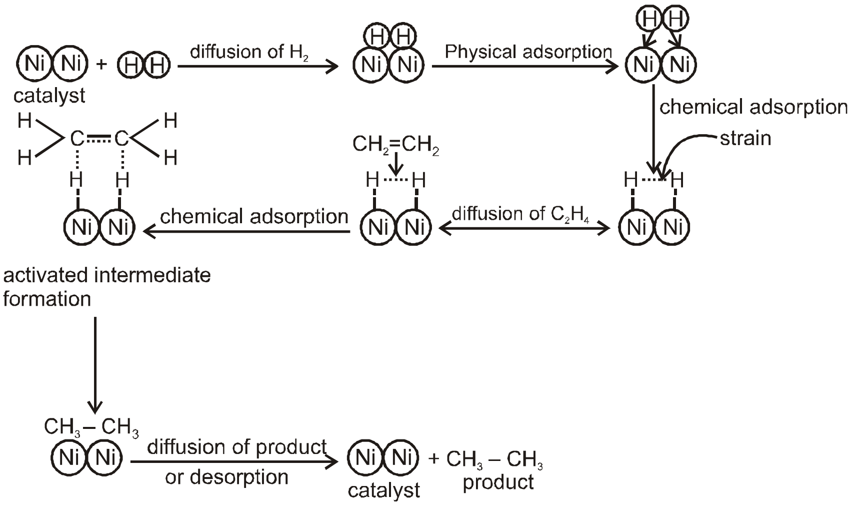
(vii) A catalyst does not change the enthalpy, entropy and free energy of a reaction.

(viii) Optimum temperature : There is a particular temperature at which the efficiency of a catalyst a maximum this temperature is known as optimum temperature. On either side the optimum temperature, the activity of catalyst decreases.

- **Adsorption Theory of Heterogeneous Catalyst :** This theory explain the mechanism of heterogeneous catalyst. This theory is combination of two theory, intermediate compound formation theory and the old adsorption theory, the catalytic activity is localised on the surface on the catalyst. The mechanism involve 5 steps.

(i) Diffusion of reactant to the surface of the catalyst.
(ii) Adsorption of reactant molecules on the surface of the catalyst.
(iii) Formation of activated intermediate.
(iv) Formation of reactions product on the catalyst surface.
(v) Diffusion of reactions product from the catalyst surface or desorption.

Examples :
Let us consider addition of H_2 gas to ethelene in presence of Ni catalyst, the reaction take places as follows.

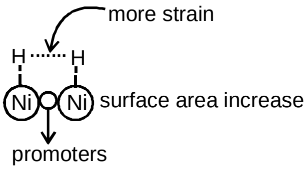


- **Factors Supporting Theory :**

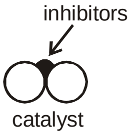
(i) This theory explain the role of active centre, more free valency which provide the more space for the more adsorption and concentration increases as a result increase in rate of reaction.

(ii) Rough surface has more active and pores there will be more free valency so more will be rate of reaction.

(iii) The theory explain centre action of promoters which occupied interstial void as a result surface area for the adsorption increases therefore rate of reaction increases.



(iv) The theory explain of function of poisons or inhibitors. In poisoning preferential adsorption of poisons take place on the catalyst, surface area for the adsorption on the catalyst decrease hence rate of reaction decreases.



Some Industrial Catalytic reactions

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

- **Colloid Solution :**

  Colloid State : A substance is said to be in colloidal state when the size of the particle of disperse phase is greater than particle of true solution and less than that of suspension solution particle, their range of diameters between 1 and 1000 nm (10^{-9} to 10^{-6} m).

  Colloid solution : It is a heterogeneous system consisting of 2 phase :

(1) Disperse Phase (D.P) : The phase which is dispersed through the medium is called dispersed phase or discontinuous phase or internal phase.

(2) Dispersion Medium (D.M) : A medium in which colloidal particles are dispersed is called dispersion medium. It is also known as continuous phase or outer phase or external phase.

Colloidal solution = D.P. + D.M.

Ex. In Gold sol, Gold is D.P and water is D.M.

- **Diffrenciating point of colloids :**

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

(2) The solution and colloid essentially differ from one another by particle size.

* In a solution, the 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.

(3) Colloidal particles are larger than simple molecules but small enough to remain suspended. They have a range of diameters between 1 and 1000 nm (10^{-9} to 10^{-6} m).

Classification of colloids :

1. On the basis of physical state of D.P. and D.M.

On the bases of physical state of D.P. and D.M. colloidal solution may be divided into eight system.

D P	D M	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, butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Liquid Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid Sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froath, whipped cream, soap lather.

* Solution of gas in gas is not a colloidal system because it form homogeneous mixture.

2. On the Basis of interaction of D.P. for D.M. : There are two types-

(i) Lyophilic colloids / liquid loving sols / intrinsic colloid. The colloidal solution in which the particles of the dispersed phase have a great affinity (or love) for the dispersion medium, are called lyophilic colloids. These solutions are easily formed and the lyophilic colloids are reversible in nature. In case water acts as the dispersion medium, the lyophilic colloid is called hydrophilic colloid. The common examples of lyophilic colloids are glue, gelatin, starch, proteins, egg albumin, rubber, etc.

(ii) Lyophobic colloids / solvent hating colloid / extrinsic colloid. The colloidal solutions in which there is no affinity between particles of the dispersed phase and the dispersion medium are called lyophobic colloids. Such solutions are formed with difficulty only by special methods. These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking and hence are not stable. Further, once precipitated, they do not give back the colloidal sol by simple addition of the dispersion medium. Hence these sols are also called irreversible sols. They need stabilising agents for their preservation. In case the dispersion medium is water, the lyophobic sol is called hydrophobic colloid. For example, the solution of metals like Ag and Au, hydroxides like Al $(OH)_3$, $Fe(OH)_3$, metal sulphides like As_2S_3 etc.

* **Lyophilic sols are more stable than lyophobic sols,** the additional stability is due presence of an envelope of the solvent layer (say water) around the colloidal particle, the process is known as hydration, To coagulate a hydrophilic sols we have to add a dehydrating agent in addition to electrolyte.

DISTINCTION BETWEEN LYOPHILIC AND LYOPHOBIC COLLOIDS

S.No.	Property	Lyophilic colloids	Lyophobic colloids
1	Ease of preparation	There are easily formed by direct mixing.	These are formed only by special methods
2	Reversible or irreversible nature	These are reversible in nature	These are irreversible in nature.
3	Particles nature	The particles of colloids are true molecules but are big in size	The particles are aggregates of many molecules
4	Stability	These are very stable	These are unstable and require traces of stabilizers
5	Action of electrolytes	No effect	The addition of small amount of electrolytes causes precipitation (called coagulation) of colloidal solution.
6	Charge on particles	The particles do not carry any charge.	The particles move in a specific direction either towards anode or cathode depending upon their charge in an electric field
7	Hydration	The particles of colloids are heavily hydrated due to the attraction for the solvent.	The particles of colloids are not appreciably hydrated.
8	Viscosity	The viscosity is higher and surface tension of the sols are lesser	The viscosity and surface tension are nearly the same as that of the dispersion medium.
9	Tyndall effect	They do no show tyndall effect	They show tyndall effect.

3. **On the basis of charge of on particles**

(i) positive Sol

(a) Metal Oxide & Hydroxide - SnO_2, TiO_2, Fe_2O_3, $Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$.

(b) Basic Dyes Methylene blue, vismark brown.

(ii) negative Sol -

(a) Metal sol - Ag, Au, Pt, Cu

(b) Acidic dye - congo red, eosin

(c) Sulphide Sol- CdS, HgS, As_2S_3, Sb_2S_3.

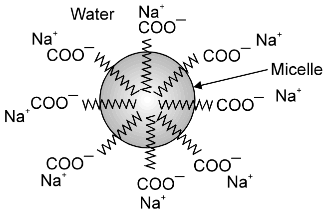
(d) Natural sol - Blood, clay, charcoal, latex rubber, dust particle in water, starch carbon particle in smoke, gum.

4. Other type of colloids : Multimolecular, macromolecular and associated colloids

- **Multimolecular colloids :** In this type, the particles consist of an aggregate of atoms or small molecules size less than 1 nm. For example, sols of gold atoms and sulphur (S_8) molecules. In these colloids, the particles are held together by van der Waal's forces.
- **Macromolecular colloids :** In this types, the particles of the dispersed phase are sufficiently big in size (macro) to be of colloidal dimensions. These macromolecules forming the dispersed phase are generally polymers having very high molecular masses. These colloids are quite stable and resemble true solutions in many respects. Naturally occuring macromolecules are starch, cellulose, proteins, enzymes, gelatin, etc.
- **Associated colloids (Micelles):** These are the substances which behave as normal strong electrolytes at low concentration but behave as colloidal particles at higher concentration. These associated particles are also called micelles. Ex. Soap.

Micelles : There are some substances which at low concentrations behave as normal strong electrolytes but at higher concentrations exhibit colloidal behaviour due to the formation of aggregated particles. The aggregated particles thus formed are called micelles. These are also known as associated colloids. The formation of micelles takes place only above a particular temperature called **Kraft Temperature** (T_k) and above a particular concentration called **Critical Micelle Concentration (CMC)**. On dilution, these colloids revert back to individual ions. Surface active agents such as soaps and synthetic detergents belong to this class. For soaps, the CMC is ~ 10^{-4} to 10^{-3} mol L^{-1}. These colloids have both lyophobic and lyophilic parts. Micelles may contain as many as 100 molecules or more.

Mechanism of micelle formation: Let us take the example of soap solutions. Soap is sodium salt of a higher fatty acid and may be represented as $RCOO^-Na^+$ e.g., sodium stearate viz.$CH_3(CH_2)_{16}COO^-\ Na^+$ which is a major component of many bar soaps. When dissolved in water, it dissociates into RCOO- and Na+ ions. The $RCOO^-$ ions, however, consist of two parts i.e., long hydrocarbon chain R (also called non-polar 'tail') which is hydrophobic (water repelling) and the polar group COO^- (also called polar-ionic 'head') which is hydrophilic (water loving). The $RCOO^-$ Ions are, therefore, present on the surface with their COO^- groups in water and the hydrocarbon chains R staying away from it, and remain at the surface, but at higher concentration these are pulled into the bulk of the solution and aggregate in a spherical form with their hydrocarbon chains pointing towards the centre with COO^- part remaining outward on the surface. An aggregate thus formed is known as **'Ionic micelle'**. These micelles may contain as many as upto 100 such ions.



Aggregation of $RCOO^-$ ions to form an ionic micelle.

Similarly, in case of detergents, e.g., sodium lauryl sulphate viz. $CH_3(CH_2)_{11}SO_4^-\ Na^+$, the polar group is – SO_4^- along with the long hydrocarbon chain. Hence, the mechanism of micelle formation is same as that of soaps.

Critical micelle concentration [CMC] : The minimum concentration required for micelle formation is called critical micelle concentration. Its value depends upon the nature of D.P. and D.M. For eg. Surface active agent (surfactants, which decrease the surface tension) like soaps and detergents form micelle beyond CMC (~10^{-3} mol/litre for soaps).

* Usually longer the hydrophobic chain, smaller is its CMC.

* Also CMC increase with decreasing polarity of the D.M.

* The micelles 'formation takes place only above a particular temperature called as Kraft Temperature (T_k).

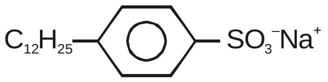
*At CMC, the micelles are spherical in shape, but that start flattening with increase in concentration and ultimately form sheet or film like structures which have a thickness of two molecules. These are called **lamelar micelles** or **McBain Micelles.**

Example of micelles :

(i) Sodium stearate $C_{17}H_{35}COO^-Na^+$(Soap).

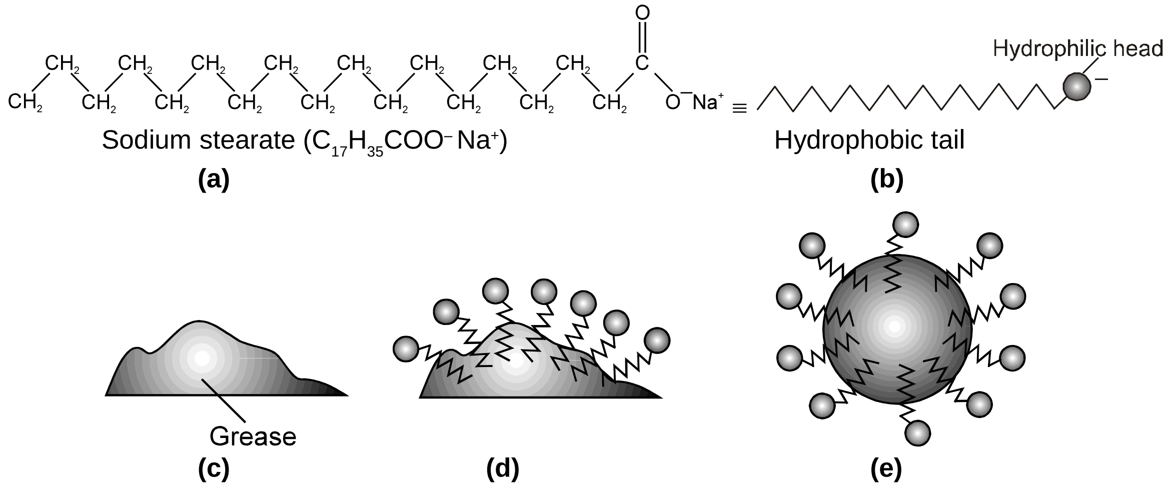
(ii) Sodium lauryl sulphate $CH_3\ [CH_2]_{11}\ SO_4^-\ Na^+$ (Detergent).

(iii) Cetyl trimethyl ammonium bromide (Detergent). $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$.

(iv) Sodium p-dodecylbenzenesulphonate (Detergent) : 

(v) Acidic (negative colloids) and basic (positive colloids) dyes.

The Cleansing Action of Soaps : It has been mentioned earlier that a micelle consists of a hydrophobic hydrocarbon like central core. The cleansing action of soap is due to these micelles, because oil and grease can be solubilised in their hydrocarbon, like centres which are not otherwise soluble in water. This is shown diagrammatically in Figure The dirt goes out along with the soap micelles.



Sodium stearate ($C_{17}H_{35}COO^- Na^+$)

Hydrophobic tail

Fig. : The cleansing action of soap.

(a) A sodium stearate molecule

(b) The simplified representation of the molecule that shows a hydrophilic head and a hydrophobic tail

(c) Grease (oily substance) is not soluble in water

(d) When soap is added to water, the non-polar tails of soap molecules dissolve in grease

(e) Finally, the grease is removed in the form of micelles containing grease.

***Surfactants :** They can be ionic as well as non-ionic. The ionic are soaps and detergent. The surfactant gets adsorbed at the interface between the dispersed droplets and dispersion medium in a form of mono molecular layer and lowers the interfacial tension between oil and water so as to facilitate the mixing of two liquids.

Preparation of lyophobic colloidal sols :

[A] Condensation methods :

In these methods particles of atomic or molecular size are induced to combine to form aggregates having colloidal dimensions. For this purpose chemical as well as physical methods can be applied.

(a) Chemical methods. Colloidal solutions can be prepared by chemical reactions leading to formation of molecules by double decomposition, oxidation, reduction or hydrolysis. These molecules then aggregate leading to formation of sols.

(i) Double decomposition : When a hot aqueous dilute solution of arsenous oxide (As_2O_3) is mixed with a saturated solution of H_2S in water, a colloidal sol of arsenous sulphide (As_2S_3) is obtained.

$$As_2O_3\text{(in hot water)} + 3H_2S \text{ (saturated solution in } H_2O) \xrightarrow{\text{Double decomposition}} As_2S_3\text{(sol)} + 3H_2O$$

(ii) Oxidation : A colloidal sol of sulphur is obtained by passing H_2S into a solution of sulphur dioxide.

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

Sulphur sol can also be obtained when H_2S is bubbled through Br_2 water or nitric acid (oxidizing agent).

(iii) Reduction : Colloidal sol of metals like gold, silver solution are obtained by following method.

$$2\,AuCl_3 + 3\,HCHO + 3H_2O \longrightarrow 2Au\text{(sol)} + 3HCOOH + 6HCl.$$

(purple of cassius)

(iv) Hydrolysis : A colloidal sol of metal hydroxides like $Al(OH)_3$ or $Cr(OH)_3$ is obtained by boiling a dilute solution of $FeCl_3$, $AlCl_3$ or $CrCl_3$.

$FeCl_3 + 3H_2O\ \ Fe(OH)_3$ (sol) + 3HCl ; $AlCl_3 + 3H_2O \longrightarrow Al(OH)_3$ (sol) + 3HCl

The colloidal sol of sillicic acid is also obtained by hydrolysis of dilute solution of sodium silicate with hydrochloric acid. $Na_4SiO_4 + 4HCl \longrightarrow Si(OH)_4$ (sol) + 4NaCl.

(b) Physical methods : The following physical methods are used to prepare the colloidal solutions.

(i) By Exchange of solvent : When a true solution is mixed with an excess of the other solvent in which the solute is insoluble but solvent is miscible, a colloidal sol is obtained. For example,

- when a solution of sulphur in alcohol is poured in excess of water, a colloidal sol of sulphur is obtained.
- when a solution of phenolphthalein in alcohol is poured in excess of water a white sol of phenolphthalein is found.
- Phenolphthalein, I_2 , sulphur sol can be prepared by this methods.

(ii) Excessive cooling : Molecules of certain substance condense together on excess cooling to form colloidal size particle. The colloidal sol of ice in an organic solvent such as $CHCl_3$ or ether can be obtained by freezing a solution of water in the solvent. The molecules of water which can no longer be held in solution separately combine to form particles of colloidal size.

[B] Dispersion Methods : In these methods large particles of the substance are broken into particles of colloidal dimensions in the presence of dispersion medium. These are stabilized by adding some suitable stabilizer. Some of the methods employed are given below :

(a) Electrical disintegration or Bredig's Arc method : This process involves dispersion as well as condensation. Colloidal sols of less reactive metals such as gold, silver, platinum, copper, lead etc., can be prepared by this method. In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium as shown in fig. The intense heat produced vaporises the metal, which then condenses to form particles of colloidal size by surrounding cooling mixture (ice).

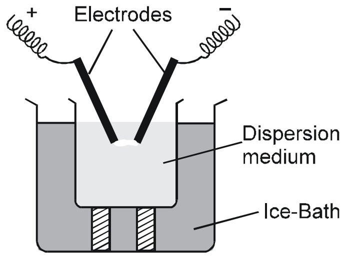


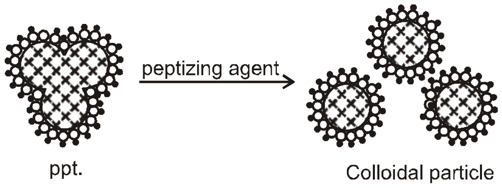
Fig. : Bredig's Arc method

*A slight trace of KOH is added in water to stabilized colloidal solutions.

(b) Peptization: The term has originated from the digestion of proteins by the enzyme pepsin. Peptization may be defined as (the process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte).

The electrolyte used for this purpose is called peptizing agent. This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol. During peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface.

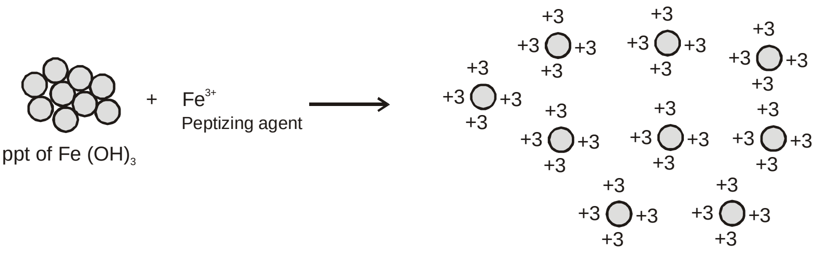
The ion adsorbed on the surface is common either with the anion or cation of the electrolyte. This causes the development of positive or negative charge on precipitates which ultimately break up into smaller particles having the dimensions of colloids.



For example :

(i) When freshly precipitated $Fe(OH)_3$ is shaken with aqueous solution of $FeCl_3$ (peptizing agent) it adsorbs Fe^{3+} ions and thereby breaks up into small-sized particles.

$FeCl_3 \longrightarrow Fe^{3+} + 3Cl^-$; $Fe(OH)_3 + Fe^{3+} \longrightarrow Fe(OH)_3 \mid Fe^{3+}$



Charge Colloidal particals of Fe $(OH)_3$

(ii) Freshly prepared stannic oxide on treatment with a small amount of dilute hydrochloric acid forms a stable colloidal sol of stannic oxide, SnO_2 ; Sn^{4+} .

$SnO_2 + 4HCl \rightarrow Sn^{4+} + 2H_2O + 4Cl^-$; $SnO_2 + Sn^{4+} \rightarrow SnO_2 / Sn^{4+}$.

(iii) Freshly precipitated silver chloride can be converted into a colloidal sol by adding a small amount of hydrochloric acid, AgCl : Cl^- .

(iv) Cadmium sulphide can be peptised with the help of hydrogen sulphide, CdS : S^{2-} .

Purification of Colloidal Sols : The colloidal sols obtained by various methods are impure and contain impurities of electrolytes and other soluble substances. These impurities may destabilise the sol. Hence, they have to be removed. A very important method of removal of soluble impurities from sols by a semipermeable membrane is known as dialysis.

A. Dialysis : It is a process of removing a dissolved substance from a colloidal solution by means diffusion through suitable membrane. Since particles in true solution (ions or smaller molecules) can pass through animal membrane or parchment paper or cellophane sheet but colloidal particle do not, the appratus used for this purpose is called Dialyser.

A bag of suitable membrane containing the colloidal solutions is suspended in a vessel through which fresh water continously flow. The molecules and ions (crystalloids) diffuse through membrane into the outer water & pure colloidal solution is left behind.

Movement of ions across the membrane can be expedited by applying electric potential through two electrodes as shown in fig.

This method is faster than simple dialysis and is known as **Electrodialysis.**

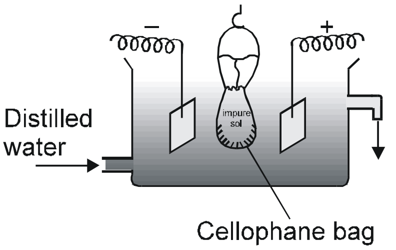


Fig. : An apparatus for electrodialysis.

*The most important applications of dialysis is in the purification of blood in the artificial kidney machine. In case of kidney failure, blood cannot be purified. under such condition, the blood is separated from dissolved toxic impurities by dialysis and re-introduced in the bloods stream.

*Dialysis is not applicable for non-electrolytes like glucose, sugar, etc.

B. Ultra Filtration : In this method, colloidal sols are purified by carrying out filtration through special type of graded filters called ultra-filters. These filter papers allow only the electrolytes to pass through. These filter papers are made of particular pore size by impregnating with colloidal solution and subsequently hardened by soaking in formaldehyde collodion. In order to accelerate the filtration through such filter papers, increased pressure or section is employed.

Solved Examples

Example-2 When SO_2 is bubbled into H_2S gas, colloidal sol is formed. What type of colloidal sol is it ?

Solution. $2H_2S + SO_2 \longrightarrow 2H_2O + 3S$ (colloidal).

Lyophobic colloidal sol of sulphur is formed.

Example-3 A reddish brown positively charged sol is obtained by adding small quantity of $FeCl_3$ solution to freshly prepared and well washed $Fe(OH)_3$ precipitate. How does it take place ?

Solution. It is due to adsorptions of Fe^{3+} ions on the surface of $Fe(OH)_3$ which gives colloidal sol.

$Fe(OH)_3$ (ppt.) + Fe^{3+} (ions adsorbed) $\longrightarrow$ $[Fe(OH)_3]Fe^{3+}$ (colloidal sol).

Example-4 Suppose we have a cube of 1.00 cm length. It is cut in all three directions, so as to produce eight cubes, each 0.50 cm on edge length. Then suppose these 0.50 cm cubes are each subdivided into eight cubes 0.25 cm on edge length, and so on. How many of these successive subdivisions are required before the cubes are reduced in size to colloidal dimensions of 100 nm.

Solution. We find that every division in two equal halves also reduces the size of edge lengths to one half.

In first subdivision 1 cm is reduceds to 0.5 cm = $\frac{1}{2}$ cm.

In second subdivision 0.5 cm is reduced to 0.25 cm = $\frac{1}{4}$ cm = $\left(\frac{1}{2}\right)^2$ cm

In n subdivision 1 cm is reduced to $\left(\frac{1}{2}\right)^n$. Size of colloidal particles lies between 1 to 1000 mm.

Thus to make n subdivision required particle size may be attained.

$$\left(\frac{1}{2}\right)^n = 100 \text{ nm} = 100 \times 10^{-9} \text{ m} = 100 \times 10^{-7} \text{ cm.}$$

$\therefore$ n log 2 = 5

n × 0.3010 = 5.

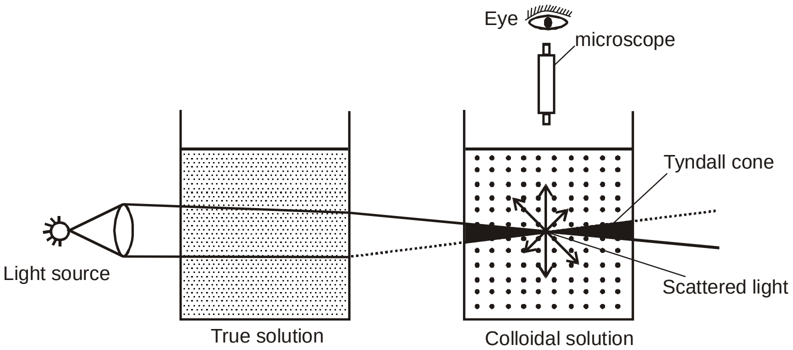
n = $\frac{5}{0.3010}$ = 16.61 **= 17 subdivisions are required for dimension of 100 nm.**

Important properties of colloidal sols :

- **Heterogeneous character :** Colloidal sols are heterogeneous in character as they consist of two phases. (a) dispersed phase and (b) dispersion medium.
- **Visibility :** Due to scattering caused by the colloidal particles, it will appear as a bright spot moving randomly.
- **Filterability :** Colloidal particles pass through an ordinary filter paper. However, the particle do not pass through other fine membranes.

- **Colligative Properties :** Colloidal sols show the colligative properties viz. relative lowering of vapour pressure, elevation in boiling point, depression in freezing point and osmotic pressure. However, due to high average molecular masses of colloidal particles, mole fraction of the dispersed phase is very low. Hence, the values of the colligative properties observed experimentally are very small. Only osmotic pressure measurements are used in determining the molecular mass of polymers.

- **Optical Properties-Tyndall effect :** Tyndall, in 1869, observed that if a strong beam of light is passed through a colloidal sol placed in a dark place, the path of the beam gets illuminated. This phenomenon is called Tyndall effect, which is due to the scattering of light by the colloidal particles. The illuminated path of beam is called Tyndall cone. This phenomenon is due to scattering of light from the surface of colloidal particles. In a true solution there are no particles of sufficiently large diameter to scatter light & hence the beam is invisible.



*The intensity of scattered light depends on the difference between the refractive indice of the D.P and D.M., In lyophobic colloids, this difference is appreciable and therefore the tyndal effect is quite well defined but in lyophilic sols the difference is very small and the tyndal effect is very weak. Thus in sols of silicic acid, blood serum, albumin, etc. there is little or no tyndal effect.

Example of Tyndall Effect

→ Blue colour of sky and sea water.

→ Visibility of tail of comets.
→ Light thrown from a projector in cinema hall.
→ Appearance of dust particle in a semi darked room.

- **Application of Tyndall Effect :**

(i) In making ultramicroscopes.
(ii) In finding heterogenity of solution.

Solved Examples

Example-5 Under what conditions is Tyndal effect observed ?

Solution. Tydalls effect is applicable when :

(a) The diameter of the dispersed particles is not much smaller than the wavelength of the light used.

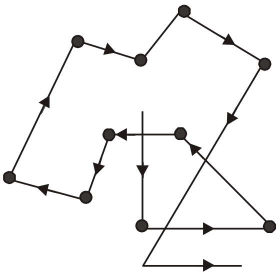
(b) The refractive indices of the dispersed phase and the dispersion medium must differ greatly in magnitude.

Example-6 In the lower layer of the atmosphere, there is a great deal of dust. When the weather is fine, it is possible to see the magnificent red colour of the setting sun. What have these observation to do with colloids ?

Solution. Dust in the atmosphere is often colloidal. When the sun is low down on the horizon, light from it has to pass through a great deal of dust to reach your eyes. The blue part of the light is scattered away from your eyes. You see the red part of the spectrum, which remains. Red sunsets are the Tyndall effect on a large scale.

● Mechanical Properties :

Brownian movement: Robert Brown, a botanist, discovered in 1827 that pollen grains placed in water do not remain at rest but move about continuously and randomly. Later on, this phenomenon was observed in case of colloidal particles when they were seen under an ultramicroscope. The particles were seen to be in constant zig-zag motion as shown in fig. This zig-zag motion is called Brownian movement.



(Fig. Brownian movement)

Brownian movement arises because of the impact of the molecules of the dispersion medium with the colloidal particles. It has been postulated that the impact of the molecules of the dispersion medium on the colloidal particle are unequal leading to zig-zag motion. However, as the size of the particle increases, the effect of the impacts average out and the Brownian movement becomes slow. Ultimately, when the dispersed particle becomes big enough to acquire the dimensions of suspension, no Brownian movement is observed.

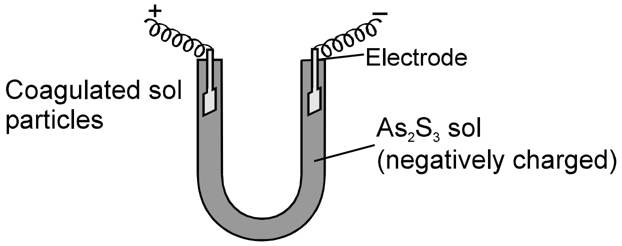
- **Factors Affecting Brownian Movement :**

(i) If particles is large then brownian movement becomes less.
(ii) Brownian movement increases with increasing temperature.
(iii) The brownian movement does not change with time & remains same for months or even for a year.

- **Important :**

(i) In confirmation of kinetic energy.
(ii) Determination of Avogadro numbers.
(iii) Stability of colloidal solution : Brownian movement does not allow the colloidal particles to settle down to gravity & thus is responsible for their stability.

- **Electrical Properties (Electrophoresis) :** The particles of the colloids are electrically charged and carry positive or negative charge. The dispersion medium has an equal and opposite charge making the system neutral as a whole. Due to similar nature of the charge carried by the particles, they repel each other and do not combine to form bigger particles. That is why, a sol is stable and particles do not settle down. Arsenious sulphide, gold, silver and platinum particles in their respective colloidal sols are negatively charged while particles of ferric hydroxide, aluminium hydroxide are positively charged. The existence of the electric charge is shown by the phenomenon of electrophoresis. It involves the 'movement of colloidal particles either towards the cathode or anode, under the influence of the electric field'. The apparatus used for electrophoresis as shown in fig.



(Fig. : A set up for electrophoresis.)

The colloidal solution is placed in a U-tube fitted with platinum electrodes. On passing an electric current, the charged colloidal particles move towards the oppositely charged electrode. Thus, if arsenic sulphide sol is taken in the U-tube, in which negatively charge particle of arsenic sulphide move towards the anode.

*Earlier this process was called cataphoresis because most of the colloidal sols studied at that time were positively charged and moved towards cathode.

- **Isoelectric point :** The H^+ concentration at which the colloidal particles have no charge is known as the isoelectric point. At this point stability of colloidal particles becomes very less & do not move under influence of electric field.

- $Fe(OH)_3$ sol prepared by the hydrolysis of $FeCl_3$ solution adsorbs Fe^{3+} and this is positively charged.

$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH_3) + 3HCl$; $Fe(OH)_3 + FeCl_3 \rightarrow Fe(OH)_3 \mid Fe^{3+} : 3Cl^-$

Fixed part Diffused part.

Positive charge on colloidal sol is due to adsorption of Fe^{3+} ion (common ion between $Fe(OH)_3$ and $FeCl_3$).

- As_2S_3 colloidal sol is obtained when As_2O_3 is saturated with H_2S :

$As_2O_3 + 3H_2S \rightarrow As_2S_3 + 3H_2O$.

As_2S_3 adsorbs S^{2-} ions (common between H_2S and As_2S_3 and thus is negatively charged).

$As_2S_3 + H_2S \rightarrow As_2S_3 \mid S^{2-} : 2H^+$.

- AgI in contact with $AgNO_3$ forms positively charged colloidal sol due to adsorption of Ag^+ ion.

$AgI + AgNO_3 \rightarrow [AgI]Ag^+ : NO_3^-$, AgI in contact with KI forms negatively charged colloidal sol due to adsorption of I^- ion $AgI + KI \rightarrow AgI \mid I^- : K^+$.

- SnO_2 in acidic medium forms positively charged colloidal sol due to adsorption of Sn^{4+} formed.

$SnO_2 + 4H^+ \rightarrow Sn^{4+} + 2H_2O$ $SnO_2 + Sn^{4+} \rightarrow SnO_2 \mid Sn^{4+}$

SnO_2 in alkaline medium forms negatively charged colloidal sol due to adsorption of SnO_3^{2-} formed.

$SnO_2 + 2OH^- \rightarrow SnO_3^{2-} + H_2O$ $SnO_2 + SnO_3^{2-} \rightarrow SnO_2 \mid SnO_3^{2-}$

- **Electric Double Layer Theory or Helm-holtz Electric double layer :**

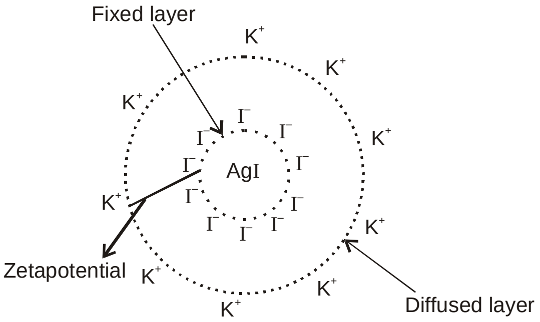
The surface of colloid particles acquire a positive or negative charge by the selective (preferential) adsorptions of common ions carrying positive or negative charge respectively to form first layer. This layer attract counter ions from D.M. form a second layer. The combination of two layers of opposite charge around the colloidal particle is called Helm-holtz electric double layer. The first layer of ions is firmely held and is termed as fixed layer while the second layer is mobile which is termed as diffused layer. The charge of opposite ions of fixed and diffused layer double layer results in a difference in potential between two opposite charge layer is called the electrokinetic potential or zetapotential which can be given by

Example :

When silver nitrate solution is added to KI solution, the precipitation of AgI adsorb iodide ions from the D.M with the formation of fixed layer and negatively charged colloidal solution form, however when KI solution is added to $AgNO_3$ solution positive charge sol result due to the adsorbs of Ag^+ ions from D.M.

AgI/I^-	AgI/Ag^+
Negative charged	Positively charged.

This fixed layer attracts counter ions from the medium forming a second layer.



Solved Examples

Example-7 Classify the following sols according to theirs charges :

(a) gold sol (b) ferric hydroxide sol (c) gelatine (d) blood

(e) sulphur (f) arsenious sulphide (g) titanium oxide.

Solution. Negatively charged colloidal sol : (a), (c), (d), (e), (f).

positively charged colloidal sol : (b), (g).

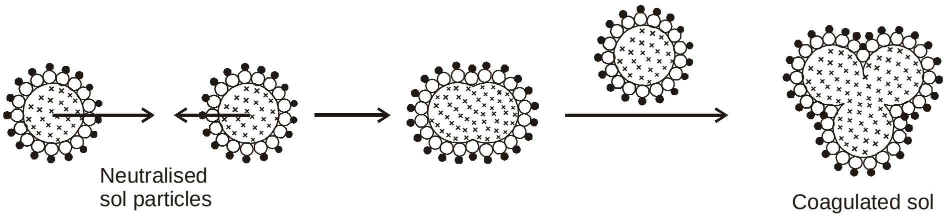
Example-8 SnO_2 forms positively charged colloidal sol in acidic medium and negatively charged colloidal sol in basic medium. Explain ?

Solution. SnO_2 is amphoteric reacting with acid and base both. In acidic medium (say HCl) Sn^{4+} ion is formed which is preferentially adsorbed on SnO_2 giving positively charged colloidal sol :

$$SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O \quad ;$$

$$SnO_2 + SnCl_4 \longrightarrow [SnO_2]Sn^{4+}(\text{positively charged}) + 4Cl^-.$$

- **Coagulation/Flocculation :** The presence of small amounts of appropriate electrolytes is necessary for the stability of the colloids. However, when an electrolyte is added in larger concentration; the particles of the sol take up the ions which are oppositely charged and thus get neutralised. The neutral particles then start aggregating giving particles of larger size which are then precipitated. **This process of aggregation of colloidal particles into an insoluble precipitate by the addition of some suitable electrolyte is known as coagulation.** At lower concentration of electrolytes, the aggregation of particles is called flocculation that can be reversed on shaking while at higher concentration of electrolyte, coagulation takes place and the same cannot be reversed simply by shaking. The stability of the lyophobic colloids is due to presence of charge on colloidal particles. If, somehow, the charge is removed, the particles will come near to each other to form aggregates and settled down under the force of gravity.



Coagulation of lyophobic sols can be carried out by the following methods.

(i) By electrophoresis

(ii) By mutual precipitation : It is a process in which oppositely charged sol are mixed in proper proportion to neutralise the charge of each other causing coagulation of both the sol.

Example : Positively charged $Fe(OH)_3$ and negatively charged As_2S_3 colloidal particle containing sol on mixing get coagulated.

(iii) By Prolonged Dialysis : On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely and the colloidal unstable and ultimately coagulate.

(iv) By Boiling : Sols such as sulphur and silver halides dispersed in water may be coagulated by boiling because increased collisions between sol particle and the water molecule removed the adsorbed electrolytes. This takes away the charge from the particles and helps them to coagulate.

(v) By cooling : Certain sol can also be coagulated by lowering temperature. For example, accumulation of cream on the surface of milk on cooling. This is because at lower temperature the dispersion medium molecules do not exert sufficient force on to the dispersed particles and hence the Brownian motion becomes less effective.

(vi) By the addition of electrolyte : When excess of an electrolyte is added, the colloidal particles are precipitated.

Coagulation value or Flocculation value : It needs to be noted that the coagulation of a colloidal solution by an electrolyte does not take place until the added electrolyte has certain minimum concentration in the solution. **The minimum concentration of electrolyte in millimoles required to cause coagulation of one litre of colloidal solution is called coagulation value.** It is express in terms of millimoles/litre.

$$\text{Coagulation value} = \frac{\text{millimoles of electrolyte}}{\text{volume of sol in litre}}$$

- **Comparision of relative coagulating power of two electrolyte for the same colloidal solution :**
  The coagulation value decrease with increase in charge of the coagulating ion.

$$\text{Coagulating power} \propto \frac{1}{\text{coagulation value}}.$$

$$\frac{\text{coagulating power of electrolyte A}}{\text{coagulating power of electrolyte B}} = \frac{\text{coagulation value B}}{\text{coagulation value A}}.$$

- **Hardy-Schulze Rule :** According to this rule greater is the valency of coagulating ion, greater its power to cause precipitation. This is known as Hardy-Schulze.

In case of positive charged sol, the coagulating power of anion is in the order of $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^-$

In case of negative charged sol, the coagulating power of cation is in the order of $Al^{3+} > Ba^{2+} > Na^+$.

- The coagulating power of bivalent ion is 20-80 times higher than monovalent ion and coagulating power of trivalents is many times more than bivalent.

Solved Examples

Example-9 The particles of a particular colloidal solution of arsenic trisulphide (As_2S_3) are negatively charged. Which 0.0005 M solution would be most effective in coagulating this colloidal solution. KCl, $MgCl_2$, $AlCl_3$ or Na_3PO_4? Explain.

Solution. Since As_2S_3 is a negatively charged colloidal sol hence positively charged ion will cause its coagulation. By Hardy-Schulze rule "greater the charge on ion, greater the coagulating power to coagulate oppositely charged colloidal sol", hence out of K^+, Mg^{2+}, Al^{3+} and Na^+, Al^{3+} would be most effective.

Protective colloidal sols : Lyophilic colloidal sols are much more stable than lyophobic colloidal sols. This is due to the extensive solvation of lyophilic colloidal sols, which forms a protective layer outside it and thus prevents it from forming associated colloids. Lyophobic sols can easily precipitate by addition of small amount of an electrolyte. They can be prevented from coagulation by previous addition of some lyophilic colloid. This is due to formation of a protective layer by lyophilic sols outside lyophobic sols. Process of protecting the lyophobic colloid solution from precipitation by an electrolyte due to previous addition of some lyophilic colloid is called protection of colloid and lyophilic colloidal sols are called protective sols.
Eg : Gelatin, Sodium caseinate, Egg albumin, Gum arabic, Potato starch etc.,
Gelatin (lyophilic) protects gold sol (lyophobic) colloids is expressed in terms of gold number.

Gold Number : Zpsigmondy (1901) introduce a term called gold number it is defined as ''the minimum amount of the protective colloid in milligrams which when added to 10 ml of a standard gold sol is just sufficient to prevent a colour change from red to blue on the addition of 1 ml of 10% sodium chloride solution. It may be noted that smaller of the gold number, greater will be protecting power of the protective colloid.

$$\text{Protecting power} \propto \frac{1}{\text{gold number}}.$$

$$\text{Gold Number} = \frac{\text{weight of lyophilic sol in mg} \times 10}{\text{volume of gold sol in mL}}$$

The gold numbers of a few protective colloids are as follows :

Gelatin	Haemoglobin	Egg albumin	Gum arabic	Dextrin	Starch
0.005 - 0.01	0.03 - 0.07	0.1 - 0.2	0.15 - 0.25	6 – 6.2	20 - 25

Uses of protective action :
(i) Gelatin is added in the preparation of ice cream to protect the particle of ice.
(ii) Protargol and Argyrol, is a silver sol protected by organic material used as eye drop.

Applications of Colloids : Colloids including emulsions find a number of uses in our daily life and industry. Some of the uses are given below.

- **In medicines :** A wide variety of medicinal and pharmaceutical preparations are emulsions. Colloidial medicines are easily adsorbed by the body tissue because of large surface area.
  * **Colloidal antimony** is used in curing **kalaazar.**
  * **Milk of magnesia,** an emulsion, is used for **stomach disorder.**
  * **Colloidal gold** is used for **intramuscular injection.**
  * **Colloidal sulphur** are used as **Germicides.**
  * **Argyrol** is a silver sol used as an **eye lotion.**
  * **Colloidal $Fe(OH)_3$** is given to **arsenic poisoning** patients as it adsorbs arsenic and then gets omited out.
- **Tanning :** Animal hides are colloidal in nature. Which contain positive charge colloidal particles of protein. This hide is kept in a tank containing tannic acid, which contains negatively charge colloidal particle. Therefore, mutual coagulation takes place this results in hardening of leather, this process is termed as tanning of leather. Chromium salts are also used in place of tannic acid.
- **Photographic plate & Film :** Photographic plate or films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films. Gelatin prevent the coagulation of colloidal particle of AgBr.
- **Rubber plating :** The negatively charged rubber particles from rubber sol are deposited on wares and handles of different tools. Rubber gloves are formed by rubber plating on suitable templates.
- **Sewage disposal :** Sewage water contains charged colloidal particles of dirt, rubbish, etc., and these do not settle down easily. The particles can be removed by discharging them at electrodes. Dirty water is passed through a tunnel fitted with metallic electrodes which are maintained at high potential difference. The particles migrate to the oppositely charged electrode, lose their charge and get coagulated. The deposited matter is used as a manure and the water left behind is used for irrigation.

- **Cottrell smoke precipitator :**
  Smoke is a dispersion of negatively charged colloidal particles of carbon in air and can be made free of these colloidal particles by passing it through cottrell precipitator as shown in fig. installed in the chimney of an industrial plant. It consists of two metal discs charged to a high potential. The carbon particles get discharged and precipitate, while gases come out from the chimney.

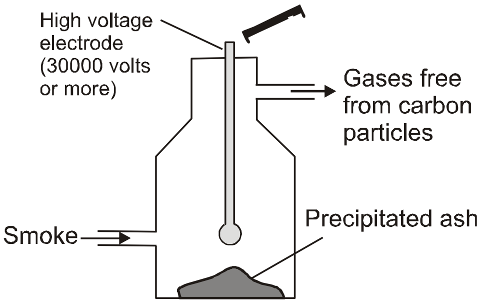


Fig. : Cottrell smoke precipitator.

- **Formation of deltas :** The river water contains colloidal particles of sand and clay which carry negative charge. The sea water contains +ve ions such as Na^+, Mg^{2+}, Ca^{2+}, etc. As the river water meets sea water, these ions discharge the sand or clay particle which are precipitated in the form of delta.
- **Artificial rain :** Cloud consists of charge particle of water disperse in air. Rain is caused by aggregation of these minute particles, artificial rain can be done by throwing electrified sand or AgI from aeroplanes, colloidal H_2O particle present in cloud will get coagulated by these sand or AgI particles to form bigger water drops causing rain.
- **Stop bleeding from a cut :** Blood is a colloidal solution containing a –ve charge colloidal particle (Albuminoid), bleeding can be stopped by use of alum or $FeCl_3$ solution. The addition of Al^{3+} or Fe^{3+} causes coagulation of blood, so bleeding stops.

EMULSIONS :

Pair of immiscible liquid is called emulsion. Emulsion are unstable and some time they are separated into two layers on keeping still, for the stabilising of an emulsion, a third component is added called emulsifying-Agent form an interfacial film between D.P. and D.M.

Emulsion droplets are bigger than sol particles and can be seen under an ordinary microscope and sometimes even with a magnifying glass.

Example : Milk is an emulsion in which liquid fat is D.P. and liquid water is D.M. and **casein** is emulsifying agent.

☞ **Demulsification :** The separation of an emulsion into its constituent liquids is called demulsification. Various techniques employed for this are freezing, boiling, centrifugation, electrostatic precipitation or chemical methods which destroys the emulsifying agents.

Demulsification can be brought about by :

(i) Freezing
(ii) Heating
(iii) Centrifugal action (Separation of cream of milk done by centrifugation).
(iv) Removal of emulsifiers by adding a better solvent for them like alcohol, phenol etc, called demulsifiers.

Types of emulsions : Depending on the nature of the dispersed phase, the emulsions are classified as :

(a) Oil in water emulsions (b) Water in oil emulsions

(a) Oil in water emulsions (o/w) : This type of emulsions is formed when oil D.P. and water D.M.

Ex. :- Milk and vanishing cream are oil - in - water type emulsions.

(b) Water in oil emulsions (w/o) : This type of emulsions is formed when water is D.P. and oil is D.M.

Ex. : - Cold cream and cod liver oil.

[B] Applications of emulsions :

- Disinfactants like phenyl, dettol when mixed with water form emulsion.
- Digestion of fat in small intestine occurs easily due to emulsion.
- In metallurgical process the concentration of ore by froath floatation method is based upon emulsion.
- Milk is an emulsion of liquid fat in water in which casein emulsifying agent.

- Cleansing action of soap is due to formation of emulsions. Soaps and detergents emulsify the grease along with the adhering dirt and carry them away in the wash water.
- For concentrating ores, the finely powdered ore is treated with an oil. Oil forms emulsion with the ore particles. When air is bubbled into the mixture, emulsion containing the particles of the mineral are carried to the surface.

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. Which of the following is (are) lyophobic colloids ?

(A) Gold sol (B) $As_2 S_3$ sol (C) Starch sol (D) $Fe(OH)_3$ sol

Sol. (ABD)

Gold sol, As_2S_3 and $Fe(OH)_3$ are lyophobic colloid.

Therefore, (A, B, D) are correct options.

2. The presence of colloidal particles of dust in air imparts blue colour to the sky. This is due to

(A) Absorption of the light (B) Scattering of the light

(C) Reflection of the light (D) None of these

Sol. (B)

Due to scattering of the light.

Therefore, (B) is correct option.

3. The volume of nitrogen gas U_m (measured at STP) required to cover a sample of silica gel with a mono-molecular layer is 129 cm^3 g^{-1} of gel. Calculate the surface area per gram of the gel if each nitrogen molecule occupies 16.2×10^{-20} m^2.

Ans. 561.8 cm^3

Sol. 22400 cm^3 of N_2 at STP contain = 6.022×10^{23} molecules

$\therefore$ 129 cm^3 of N_2 at STP will contain = $\dfrac{6.022\times10^{23}\times129}{22400}$ = 3.468×10^{21} molecules

Area occupied by a single molecule = 16.2×10^{-20} m^2

$\therefore$ Area occupied by 3.468×10^{21} molecules of nitrogen = $(16.2 \times 10^{-20}) \times (3.468 \times 10^{21})$ m^2 = 561.8 m^2.

4. Which of the following has minimum gold number ?

(A) Potato starch (B) Gum arabic (C) Gelatin (D) Albumin

Sol. (C)

Gelatin has minimum gold number.

Therefore, (C) is correct option.

5. Which of the following are correctly matched ?

(A) Butter-gel (B) Milk-emulsion (C) Fog-aerosol (D) Dust-solid sol

Sol. (A, B, C) are correct matches.

6. Explain the adsorption of nitrogen on iron.

Sol. When nitrogen gas is brought in contact with iron at 83 K, it is physisorbed on iron surface as nitrogen molecules, N_2.As the temperature is increased the amount of nitrogen adsorbed decreases rapidly and at room temperature, practically there is no adsorption of nitrogen on iron. At 773 K and above, nitrogen is chemisorbed on the iron surface as nitrogen atoms.

7. How do size of particles of adsorbent, pressure of gas and prevailing temperature influence the extent of adsorption of a gas on a solid ?

Sol. (a) Smaller the size of the particles of the adsorbent, greater is the surface area and hence greater is the adsorption

(b) At constant temperature, adsorption first increases with increase of pressure and then attains equilibrium.

(c) In physical adsorption, it decreases with increase of temperature but in chemisorption, first it increases and then decreases.

8. How is adsorption of a gas is related to its critical temperature ?

Sol. Higher is the critical temperature of a gas, greater the van der Waal's forces of attraction and hence greater is the adsorption.

9. Physical adsorption is essentially quite appreciable :

(A) at room temperature
(B) at higher temperature
(C) at lower temperature
(D) none of these

Sol. (C)

Rate of physical adsorption decreases with increase in temperature (exothermic process).

Therefore, (C) is correct option.

10. What type of colloidal sols are formed in the following ?

(i) Through cooled water, vapours of sulphur are passed.

(ii) White of an egg is mixed with water.

Sol. (i) Sulphur molecules associate together to form molecular sols.

(ii) Macromolecular sol because protein molecules present in the white of the egg are macromolecules & are soluble in water.

11. What happens when persistent dialysis of a colloidal solution is carried out.

Sol. The stability of a colloidal sol is due to the presence of a small amount of the electrolyte. On persistent dialysis, the electrolyte is completely removed. As a result, the colloidal sol becomes unstable and gets coagulated.