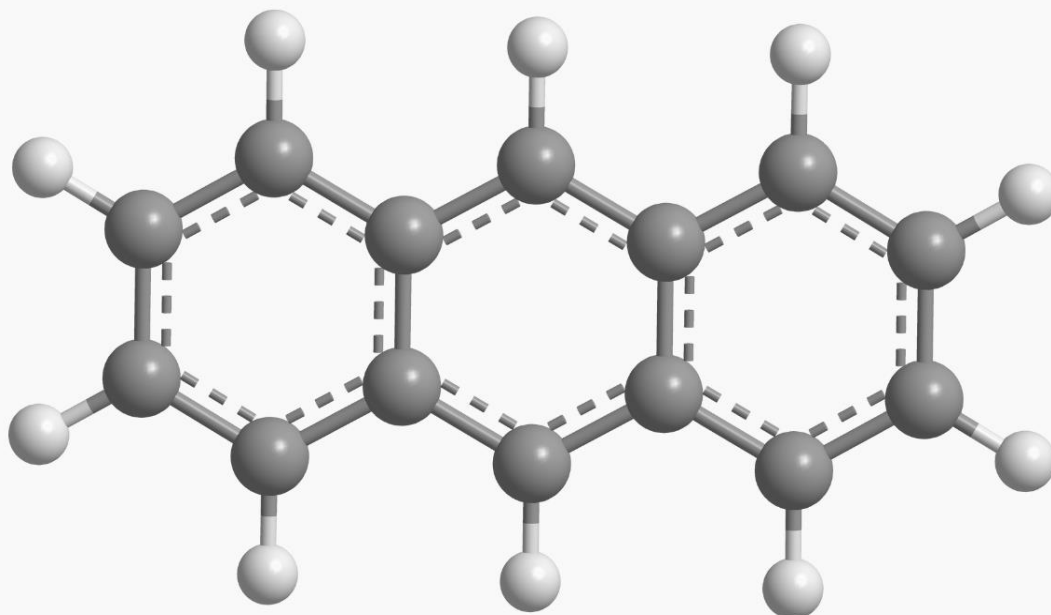


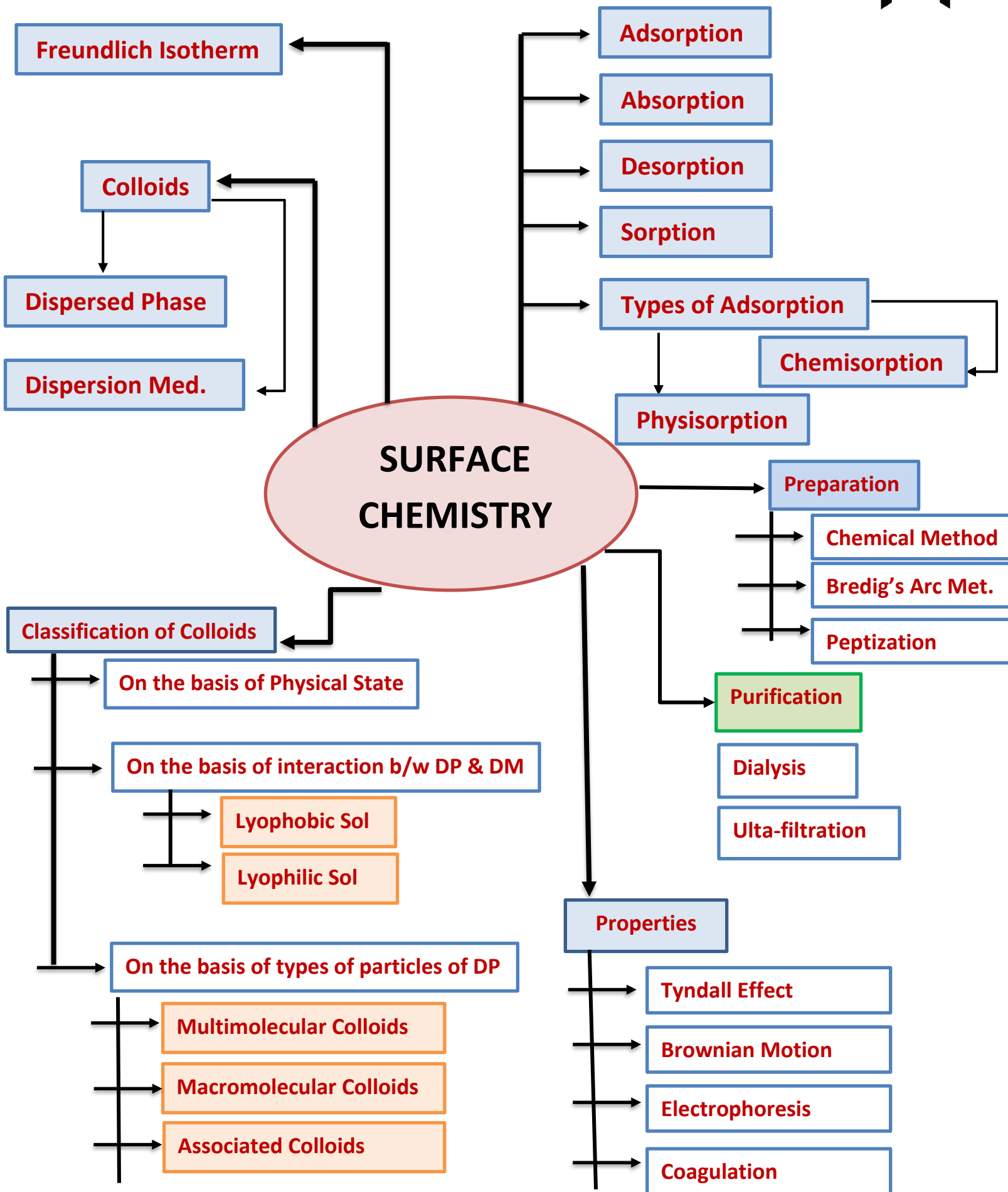
MBC

MRIDUL BHAIYA CLASSES

Chapter

SURFACE CHEMISTRY



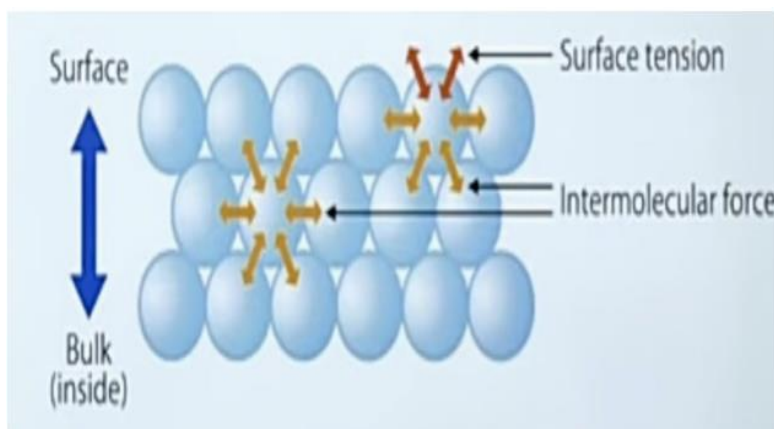
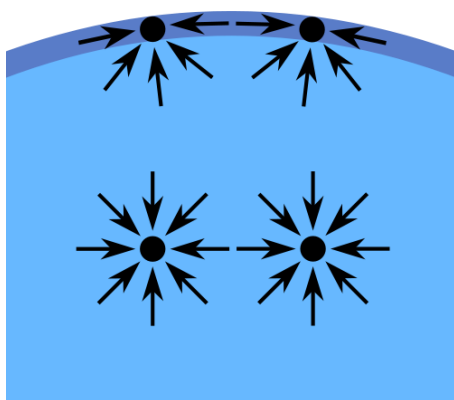


SURFACE CHEMISTRY

Surface Chemistry deals with the phenomena that occurs at the surface or the interfaces.

The surface or interface is represented by separating the bulk phases by a hyphen or slash

- **Interface between a solid and gas :**
Solid – gas or Solid/gas
- **Interface between liquid and liquid :**
Liquid/Liquid
- **But there is no interface between two gases, due to complete miscibility.**



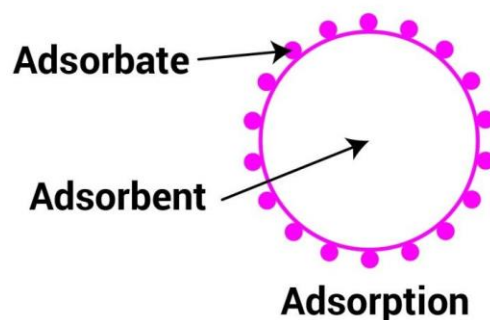
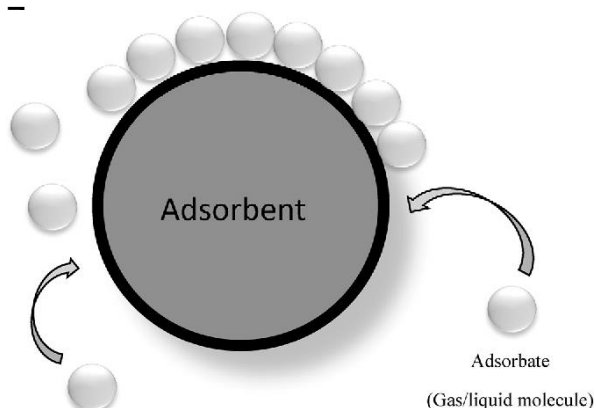
Molecules on surface experiences unbalanced attractive forces resulting in a net inward pull. This produces surface tension.

Molecules in bulk phases experiences balanced forces from all the direction and are in state of equilibrium.

Adsorption : The accumulation of molecular species at the surface rather than in bulk of a solid or liquid termed Adsorption.

Adsorbate : The molecular species or substance which concentrates or accumulates at the surface is termed Adsorbate.

Adsorbent : The material on the surface of which the adsorption takes place is called Adsorbent. E.g. : Silica Gel, Charcoal, Colloids



Absorption

The substance is uniformly distributed throughout the bulk of solid.



Desorption

The process of removing an adsorbed substance from a surface.

Adsorption

The substance is concentrated only at the surface and does not penetrate rough surface to the bulk of absorbent.



Sorption

When adsorption and absorption takes place simultaneously.

THEMODYNAMIC OF ADSORPTION

Why is adsorption always exothermic ?

During adsorption there is always a decrease in residual forces of surface, there is a decrease in surface energy, which appears as heat.

That's why adsorption is an exothermic process. $\Delta H = -ve$

After adsorption randomness of the system decreases.

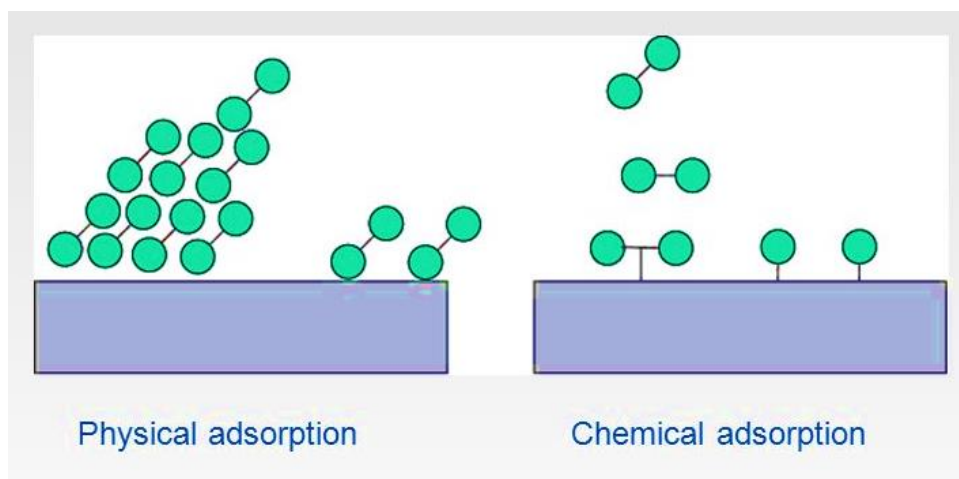
So for adsorption $\Delta S = -ve$.

For adsorption, thermodynamic requirement is that at constant T and P, ΔG must be negative. [$\Delta G = -ve$]

$$\Delta G = \Delta H - T\Delta S$$

Types of Adsorption :-

- i) **Physical Adsorption** : When the particles of adsorbate are held to the surface of adsorbent by physical forces such as **Vander Waal's Forces**. Then adsorption is called Physical Adsorption.
- ii) **Chemical Adsorption** : When the molecules of adsorbate are held to the surface of the adsorbent by **Chemical Attraction (bond)**.





Q. Difference between Physisorption and Chemisorption

Ans:

Physisorption

- Example – Adsorption of SO_2 on charcoal.
- Lack of Specificity – A given surface of an adsorbent does not show any preference for a particular gas.
- It arises due to Vander Waal Forces.
- It is reversible in nature.
- As the surface of adsorbent increases, Physisorption increases.
- Enthalpy of adsorption is low due to weak force of attraction between adsorbent and adsorbate.

Chemisorption

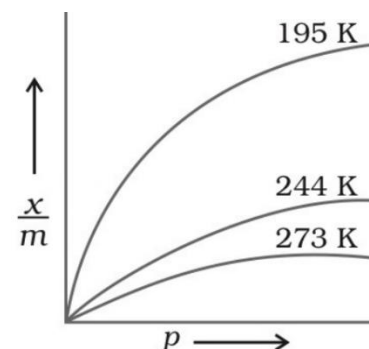
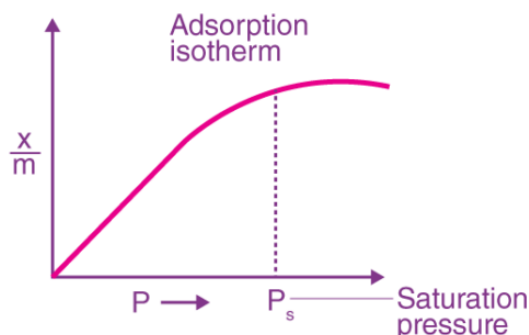
- Example – Adsorption of H_2 on Platinum.
- High Specificity – It will only occur if there is some possibility.
- It is caused by chemical bond formation.
- It is irreversible nature.
- As the surface of adsorbent increases, Chemisorption increases.
- Enthalpy of adsorption is relatively high due to bond formation.
[Strong attractive force]

ADSORPTION ISOTHERMS

The graph between amount of gas adsorbed and pressure at **constant temperature** is known as adsorption isotherms.

X – mass of gas adsorbed

M – mass of adsorbent



FREUNDLICH ADSORPTION ISOTHERMS

Empirical relationship between quantity of gas adsorbed and pressure at constant temperature.

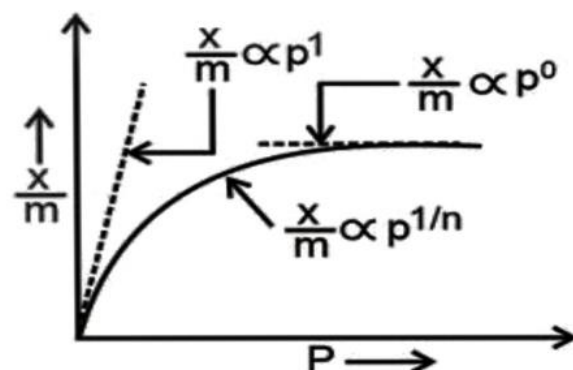
$$\frac{x}{m} = kp^{1/n}$$

$$\left[0 < \frac{1}{n} \leq 1 \right]$$

K and n are constants which depends on nature of adsorbent and gas.

From Graph :

- As temperature increases extent of adsorption decreases.
- At low pressure : $\frac{x}{m} \propto P^1$
- At high pressure : $\frac{x}{m} \propto P^0$



Curve seems to approach saturation at high pressure.

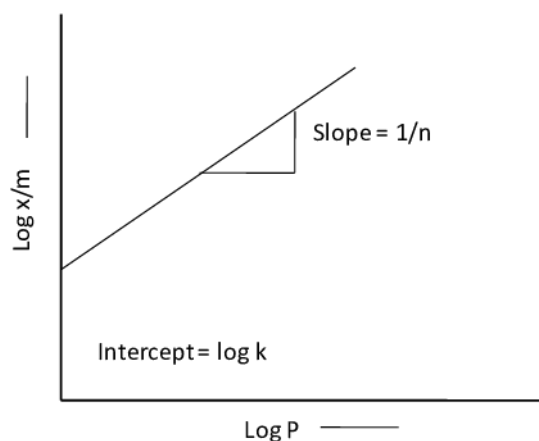
- At moderate pressure : $\frac{x}{m} \propto P^{1/2}$

$$\text{Taking log of } \frac{x}{m} = k p^{1/n} \quad : \quad \log \frac{x}{m} = \log k + \frac{1}{n} \log p$$

$$y = c + m \cdot x$$

$$\text{Slope [m]} = \frac{1}{n}$$

$$\text{Intercept [c]} = \log k$$



ADSORPTION FROM SOLUTION PHASE

Solids can absorb solutes from solutions. Freundlich equation approximately describes the behaviour of adsorption from solution with a difference that instead of pressure, concentration of solution is taken into account.

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

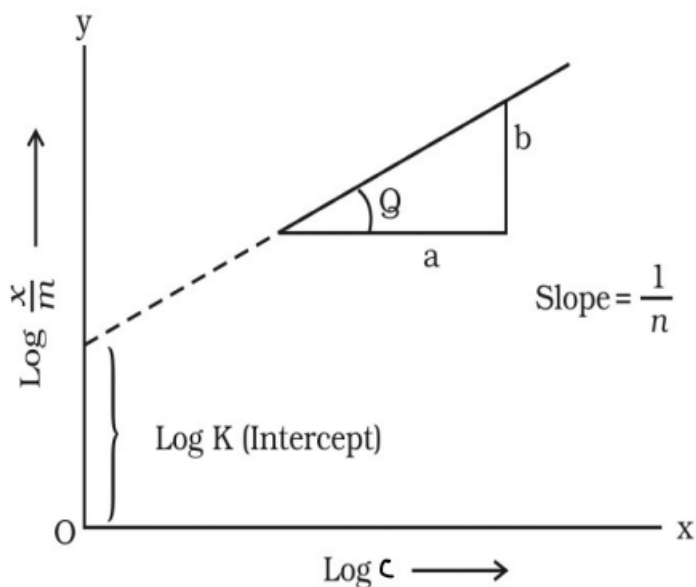
$$\log \frac{x}{m} = \frac{1}{n} \log c + \log k$$

$$y = mx + c$$

$$\rightarrow \frac{x}{m} = k c^{1/n}$$

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

$$y = mx + c$$



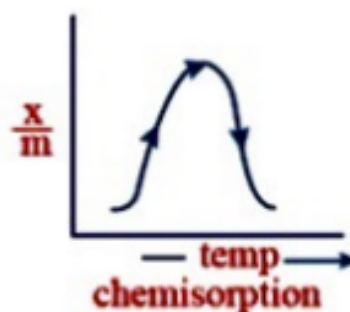
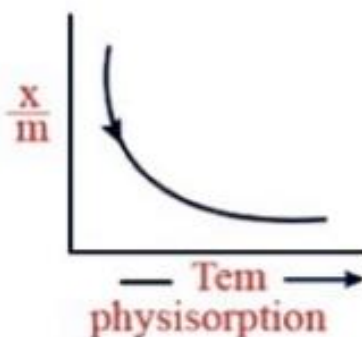
Q. What is the Effect of temperature on Physisorption and Chemisorption ?

A. Chemisorption first increases and then decreases with increase in temperature. As temperature increases, Physisorption decreases.

As temperature \uparrow es



Physisorption \downarrow es

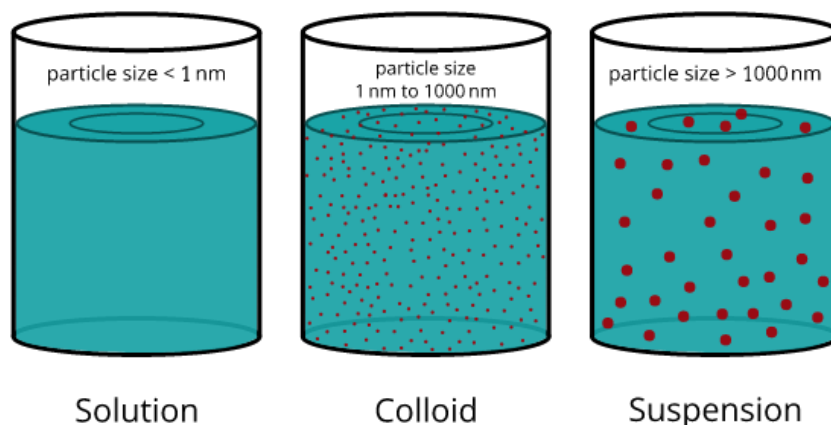


COLLOIDS

The colloidal solutions are intermediate between true solutions and suspensions.

Colloidal Solution = Dispersed Phase (Solute) + Dispersion Medium (Solvent)

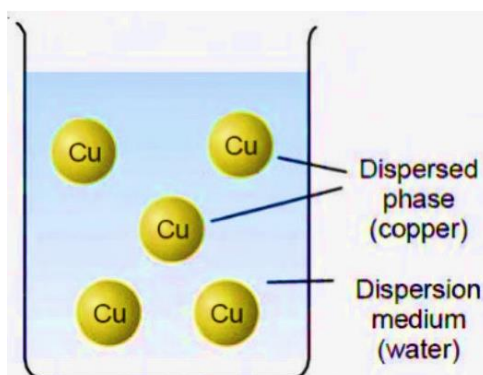
Size of colloidal particles = 1 to 1000nm



Dispersed Phase : The phase which is distributed (or dispersed) through the medium is called Dispersed Phase. (DP)

Dispersion Medium : A medium in which colloidal particles are dispersed is called continuous phase or Dispersion medium (DM)

For example : **Gold Sol** – Gold Particles are D.P and water is D.M





CLASSIFICATION OF COLLOIDS

I.) On the Basis of Physical State of DP and DM :- [Most important]

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

II.) On the basis of interaction between DP and DM :

Lyophilic Colloids

- Lyophilic means liquid loving.
- Colloidal Solution in which the particles of DP (Solute) have great affinity for Dispersion medium (Solvent).
- Example : Glue, gelatin, starch, protein with a suitable liquid.
- It is a reversible sol means that if DM is separated from DP, the sol can be reconstituted by simply mixing of DM and DP.
- It is a stable colloid. It can not be precipitated easily

Lyophobic Colloids

- Lyophobic means liquid hating.
- Colloidal Solution in which the particles of the DP (Solute) have no affinity for Dispersion Medium (Solvent).
- Example – Solution of metals [Ag, Au]
– Gold Sol
- It is an irreversible sol means that it can not be prepared just by mixing of DP and DM. It can be prepared only by special methods.
- It is an unstable colloid. So this sol need stabilising agent for preservation



III.) On the basis of types of particles of the DP :

a. Multimolecular Colloids : On dissociation, a large number of atoms or molecules of a substance aggregate together to form species having size in colloidal range. The species thus formed are called multimolecular colloid.

Example – Gold Sol and Sulphur $[S_8]$ sol

b. Macromolecular Colloids : Macromolecules [Polymers] in suitable solvents form solution in which the size of macromolecules may be in colloidal range. Such systems are called Macromolecular Colloids.

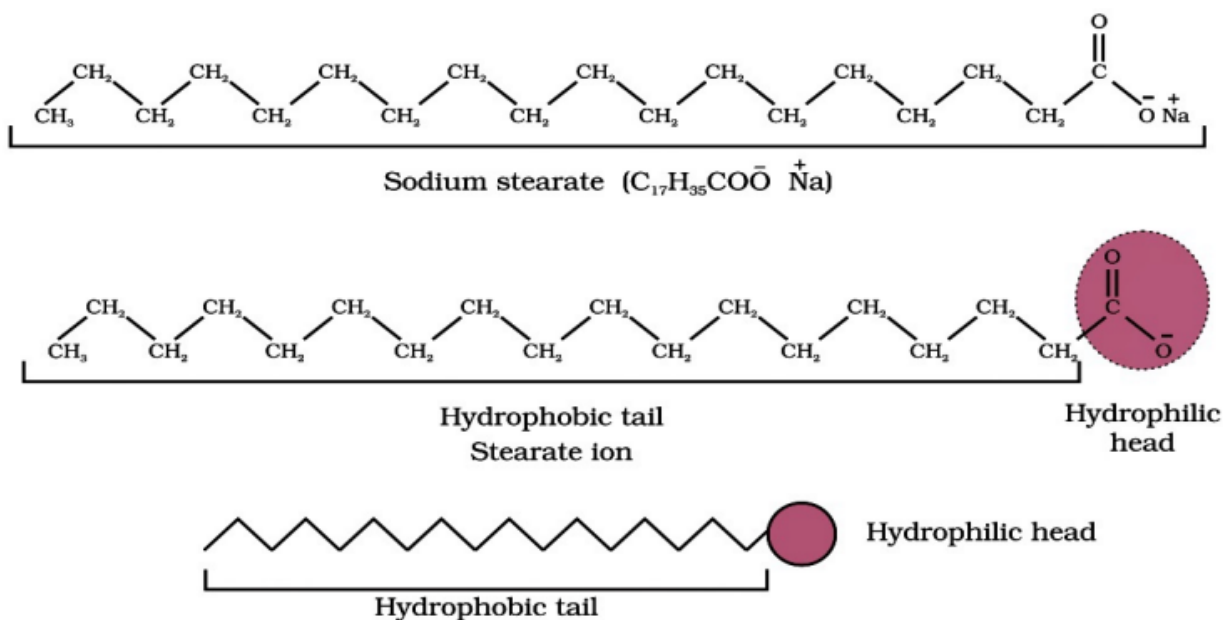
Example – Polymers [like starch, cellulose, proteins, enzymes, polythene etc.]

c. Associated Colloids : There are some substances which at low concentrations behave as normal strong electrolytes. But at higher concentrations exhibit colloidal behaviour due to formation of aggregates.

- The aggregated particles are called micelles or associated colloids
Ex – Soap/Detergents
- The formation of micelles takes place only above a particular temperature called **Kraft temperature (T_k)** and above a particular concentration called CMC means **Critical micelle concentration**.

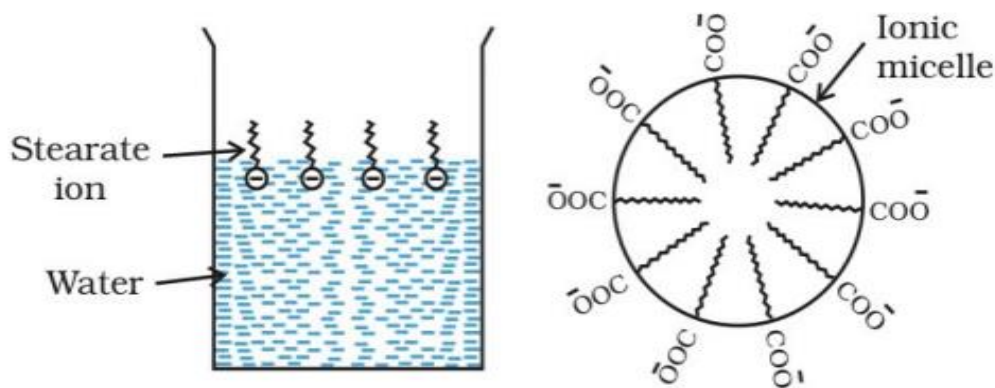
Mechanism of Micelle formation :

- To understand the mechanism, let us take example of soap solution.
- Soap : Sodium or Potassium Stearate
- Sodium stearate has two parts



- i.) Hydrophobic part [Water repelling] : A long hydrocarbon Chain (Non-polar tail)
- ii.) Hydrophilic part [Water loving] : $-\text{COO}^-$ group (polar ionic head) [$\text{C}_{17}\text{H}_{35}^-$]

→ The $\text{C}_{17}\text{H}_{35}\text{COO}^-$ ions are present on the surface with their COO^- group in water and the hydrocarbons chains [$\text{C}_{17}\text{H}_{35}$] staying away from it and remain at the surface.



→ But at CMC, the anions are pulled into the bulk of solution and aggregate to form a spherical shape with their hydrocarbons chains pointing

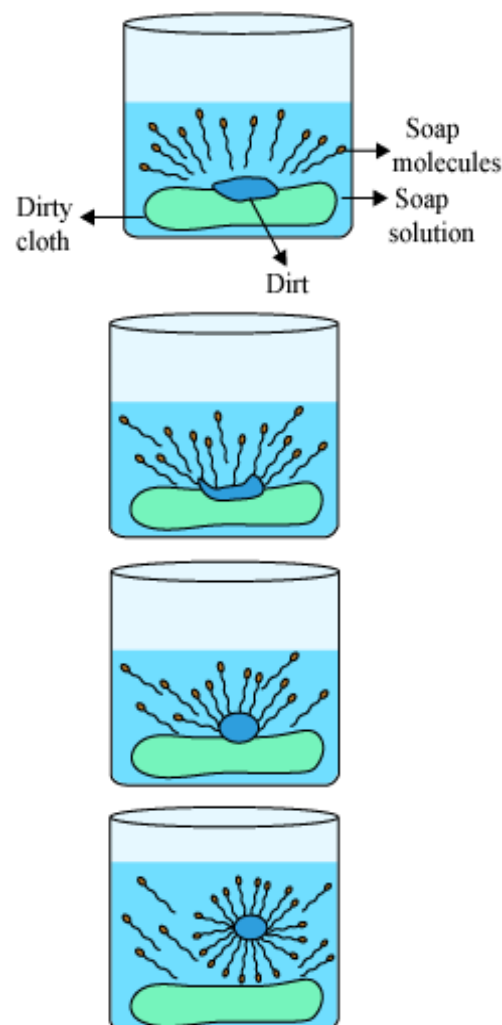
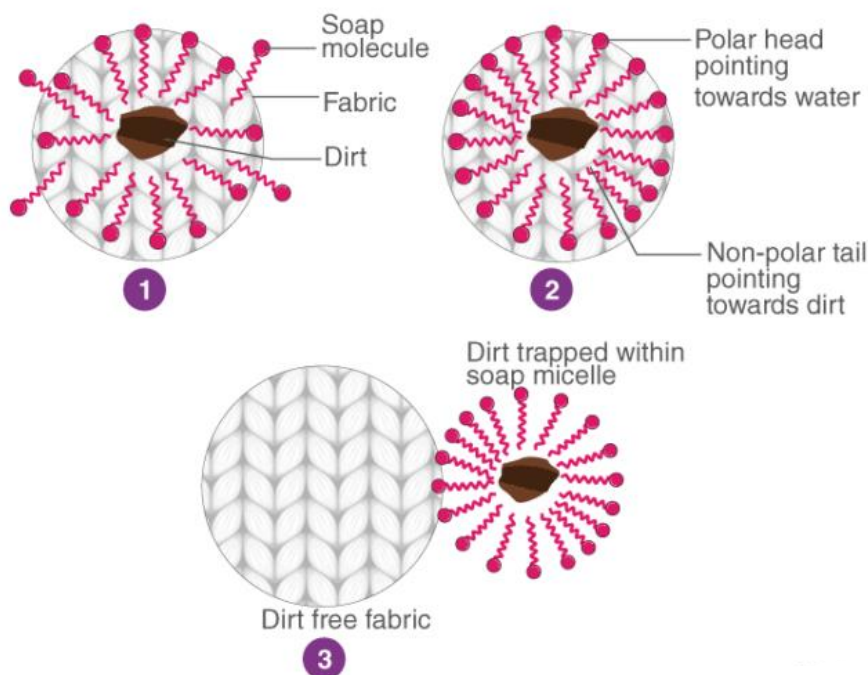
towards the centre of sphere with COO^- part remaining outward on the surface of sphere. This spherical aggregate is known as **ionic micelle**.

- **Detergents** : Sodium Lauryl sulphate $[\text{CH}_3(\text{CH}_2)_{11}\text{SO}_4^- \text{Na}^+]$

Cleaning action of Soap : The cleaning action of soap is due to the fact that soap particles form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in oil droplet and hydrophilic part projects out of the grease droplet. Because hydrophilic part is outside of oil droplet, so it can interact with water due to polarity.

- The oil droplet surrounded by stearate ions is now pulled in water and removed from dirty surface.

CLEANSING ACTION OF SOAPS AND DETERGENTS



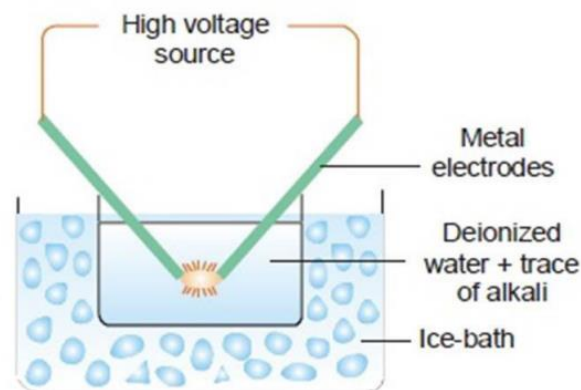
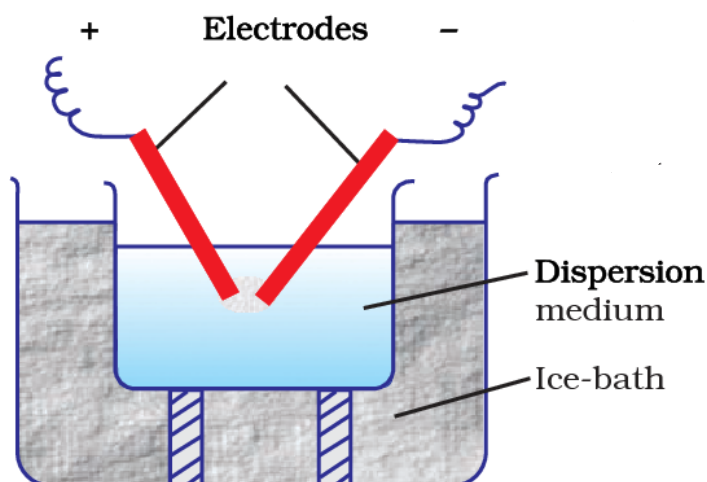
PREPARATION OF COLLOIDS

1. Chemical Methods :

- **Double Decomposition** : $\text{As}_2\text{O}_3 + \text{H}_2\text{S} \longrightarrow \text{As}_2\text{S}_3 (\text{sol}) + 3\text{H}_2\text{O}$
[Arsenic Sulphide sol]
- **Oxidation** : $\text{SO}_2 + 2\text{H}_2\text{S} \longrightarrow 3\text{S} + \text{H}_2\text{O}$
[Sulphur Sol]
- **Reduction** : $2\text{AuCl}_3 + 3\text{HCHO} + 3\text{H}_2\text{O} \longrightarrow 2\text{Au} + \text{HCOOH} + 6\text{HCl}$
[Gold Sol]
- **Hydrolysis** : $\text{FeCl}_3 + 3\text{H}_2\text{O} \longrightarrow \text{Fe}(\text{OH})_3 + 3\text{HCl}$
[Ferric Hydroxide Sol]

2. Bredig's Arc Method : [Electrical Disintegration]

By using electric arc, we can disintegrate (Vapourise) the metal electrode [gold, silver, platinum etc]. Which then condensate to form particles of colloidal size. This process involves dispersion as well as condensation

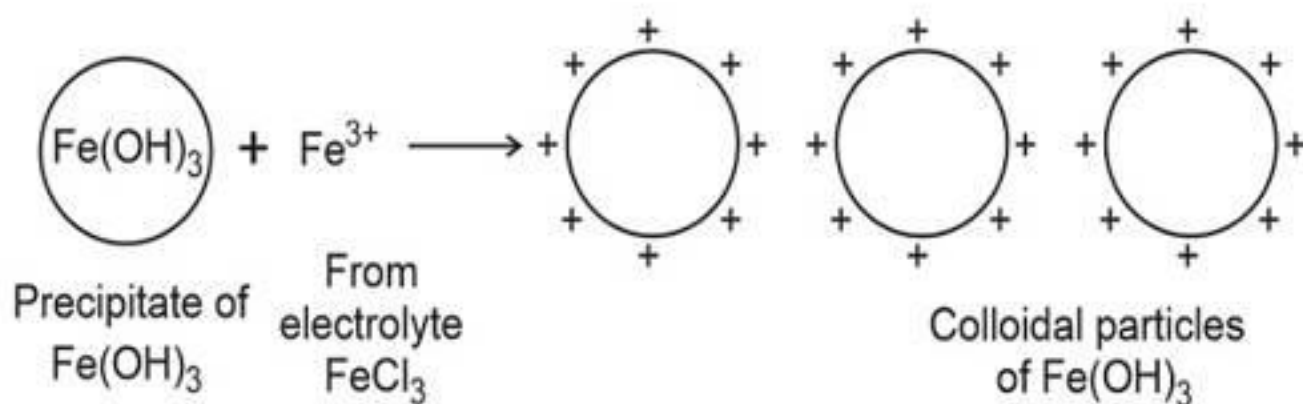


Bredig's Arc method.

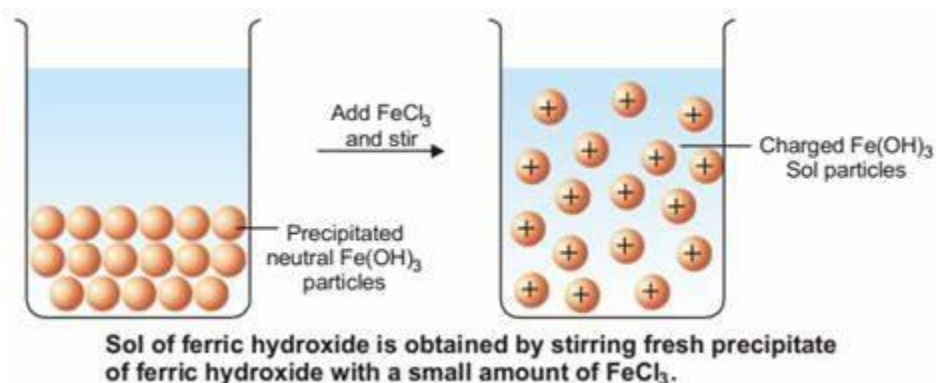
3. Peptization : Process of converting a precipitate into colloidal sol, by shaking it with DM in presence of a small amount of electrolyte.

- The electrolyte used for this purpose is called **peptizing agent**.
- During peptization the ppt adsorbs one of the ions of electrolyte on its surface. This causes the development of positive or negative charge on ppt, which ultimately break up into smaller particles of size of a colloid.

Ppt + Electrolyte = Colloidal Solution



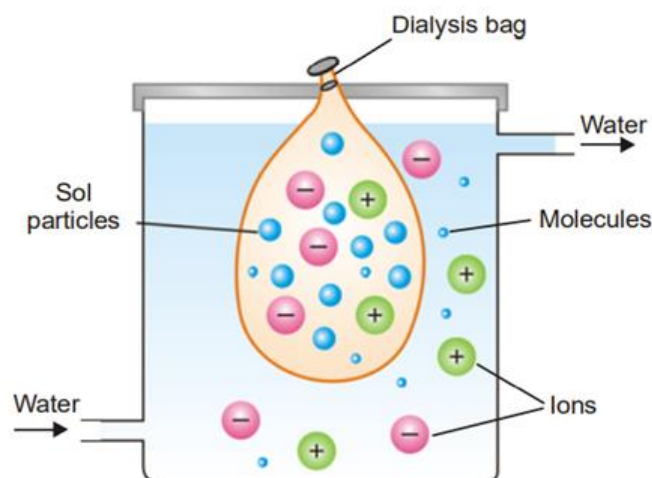
Preparation of colloidal sol by peptization



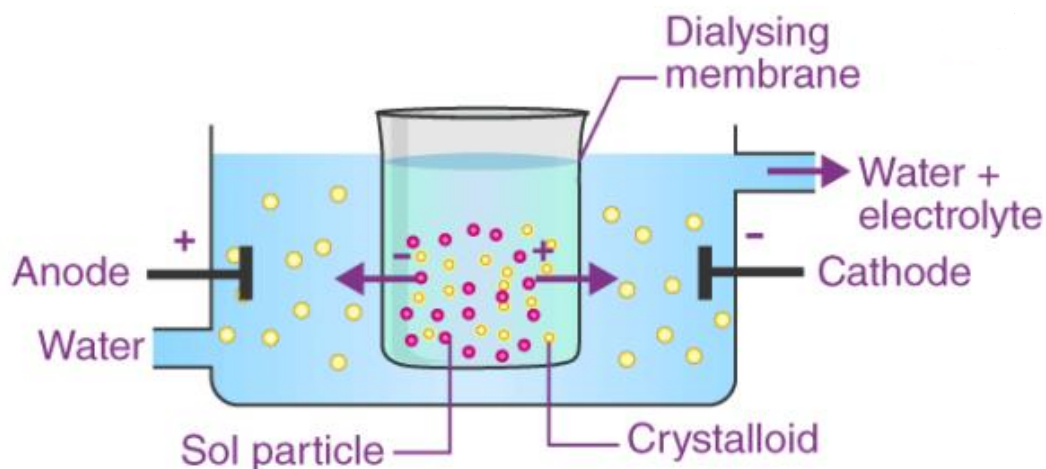
PURIFICATION OF COLLOIDS

1. **Dialysis** : It is process of removing a dissolved substance from a colloidal solution by means of diffusion through suitable membrane.

- True solution can pass through this membrane but not colloidal particles
- A bag of semipermeable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuous flowing. The molecule and ions diffuse through membrane into the outer water and pure colloidal solution is left behind.

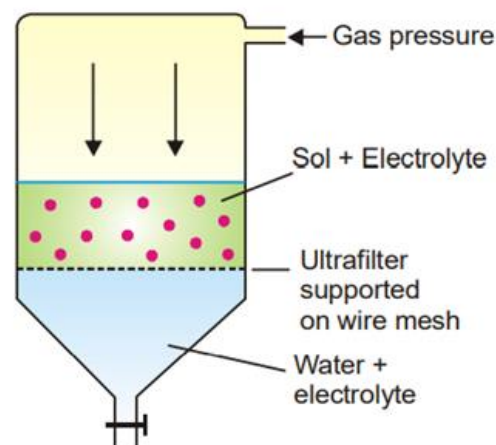


2. **Electro-Dialysis** : Dialysis can be made faster by applying an electric field



3. **Ultra-Filtration** : Ordinary filter paper have very large pore size. So it can pass both impurities and colloidal particles.

- In such condition, we use ultrafiltration paper which is designed in such a way that it can allow only the true solution to pass through. The pure colloid left on filter paper.



PURIFICATION OF COLLOIDS

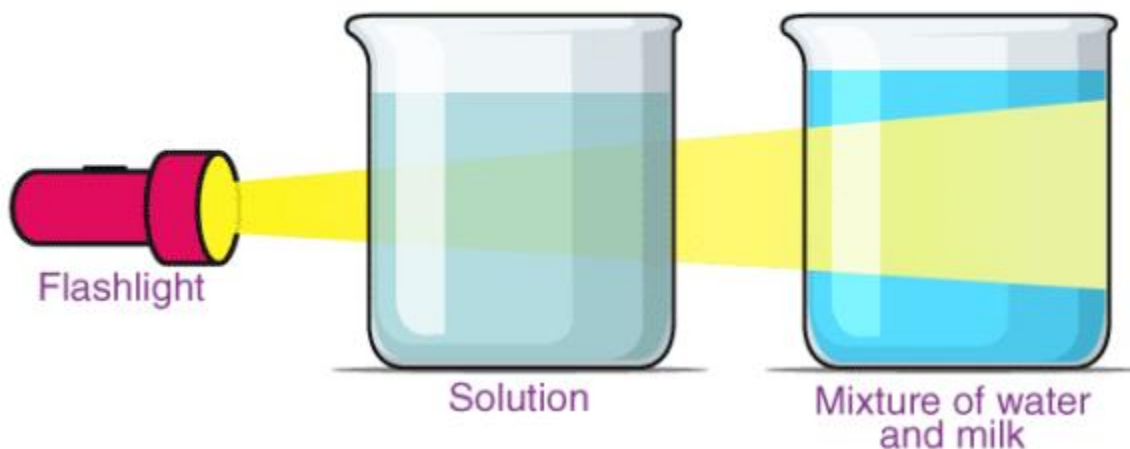
1. Optical Property : [Tyndall Effect]

- Scattering of light by colloidal particles is called Tyndall Effect.
- This scattering of light illuminates the path of beam in colloidal solution.

Condition for Tyndall Effect :

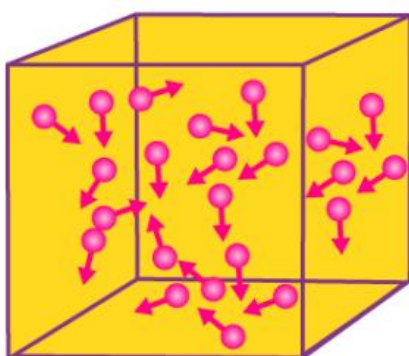
- Size of the colloidal particles should be approximately similar to the wavelength of light used.
 - The difference in refractive indices of D.P and D.M should be large.
- As the size of particles changes colour of colloidal solution changes.

TYNDALL EFFECT

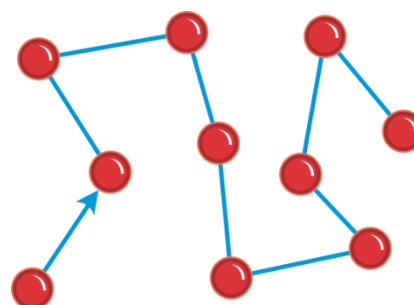


2. Brownian Motion : [Kinetic Property]

- Continuous random motion | zig-zag motion of the colloidal particles is known as Brownian motion.
- The Brownian movement has been explained to be due to the unbalanced bombardment of the particles by the molecules of the DM.
- This motion stabilizes the colloidal solution as it does not allow the DP to settle down.



Brownian Movement



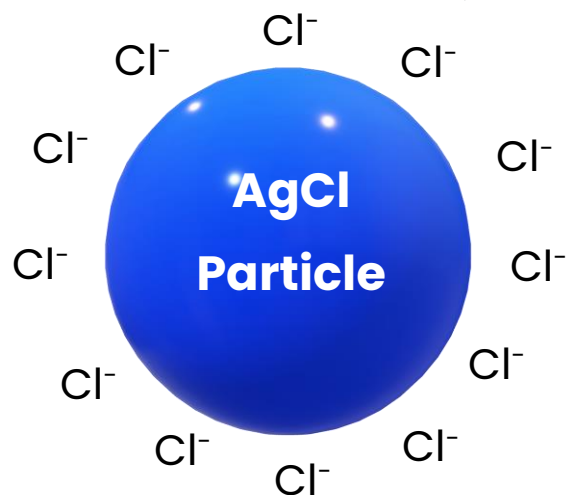
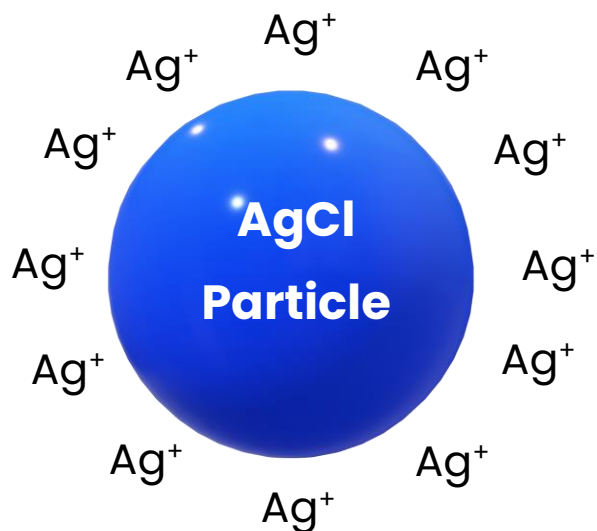
Brownian Movement
of a Particle

3. Electrical Properties :

Charge on colloidal particles :

Colloidal particles always carry an electric charge. The nature of this charge is same for all the particles in a given colloidal solution.

- Preferential adsorption of ions create charge on colloidal particles.
- The charge on sol particles originates by selective adsorption of ions common to the particles from the dispersion medium.
- In some cases, particles may absorb the anions or cations whichever are in excess and acquire the corresponding charge.
- $\text{AgNO}_3 + \text{KCl} \longrightarrow \text{AgCl} \xrightarrow{\text{KCl}} \text{AgCl/Cl}^-$
(Excess)
- $\text{AgNO}_3 + \text{KCl} \longrightarrow \text{AgCl} \xrightarrow{\text{AgNO}_3} \text{AgCl/Ag}^+$
(Excess)



Positively charged sols

Hydrated metallic oxides, e.g., $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, $\text{CrO}_3 \cdot x\text{H}_2\text{O}$ and $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, etc.

Basic dye stuffs, e.g., methylene blue sol.

Haemoglobin (blood)

Oxides, e.g., TiO_2 sol.

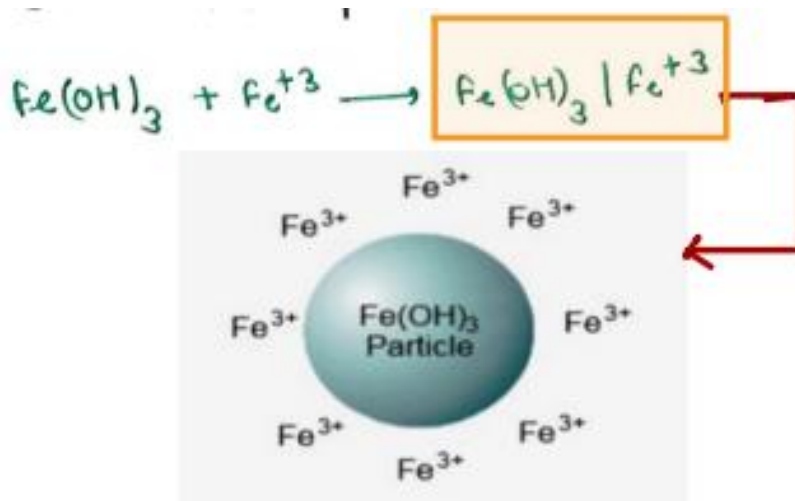
Negatively charged sols

Metals, e.g., copper, silver, gold sols.

Metallic sulphides, e.g., As_2S_3 , Sb_2S_3 , CdS sols.

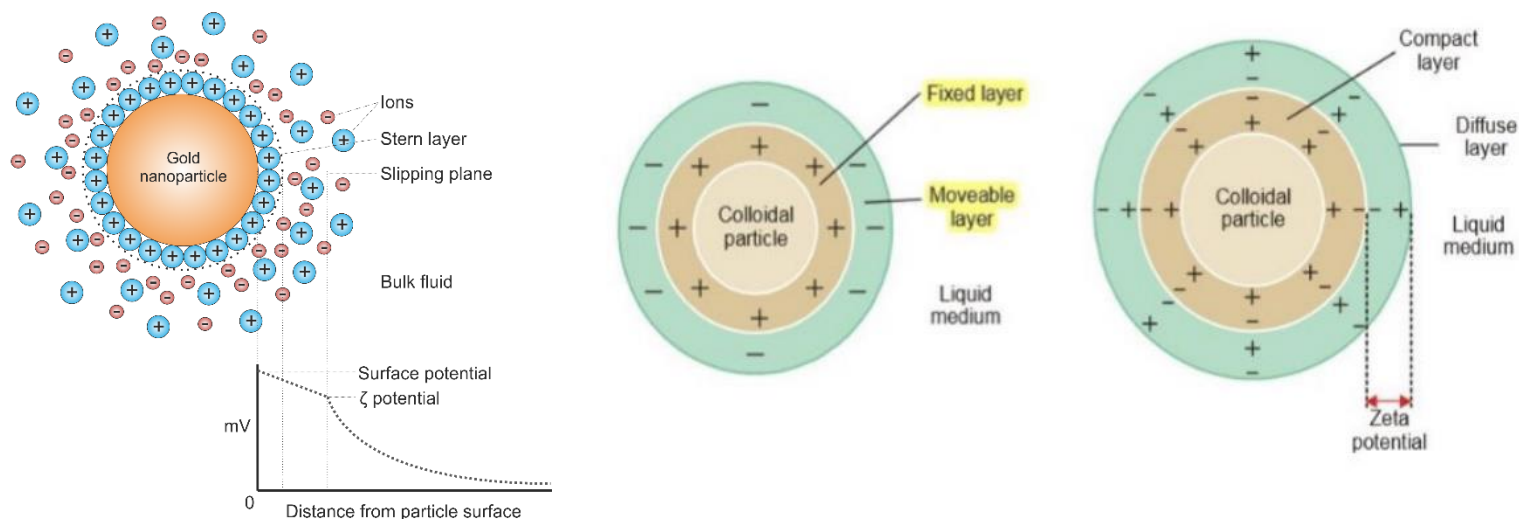
Acid dye stuffs, e.g., eosin, congo red sols.

Sols of starch, gum, gelatin, clay, charcoal, etc.



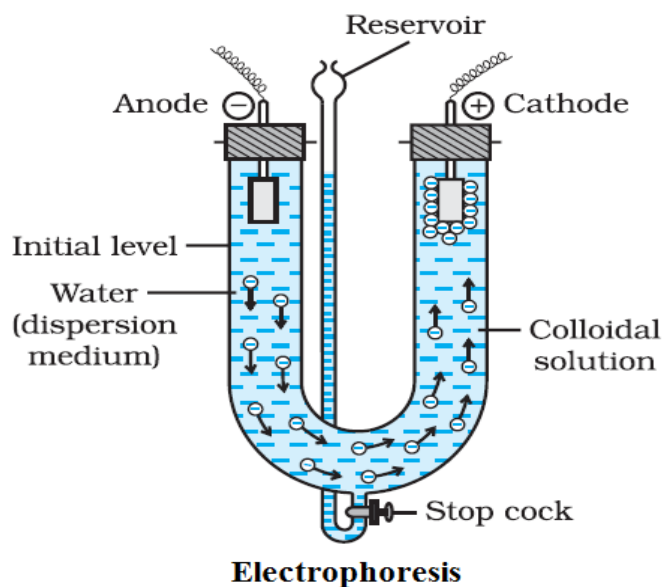
Zeta Potential [ElectroKinetic Potential]

Potential difference between fixed layer and diffused layer = Zeta Potential



Electrophoresis : The existence of charge on colloidal particles is confirmed by electrophoresis experiment.

- The movement of sol particles under electric potential is called cataphoresis or electrophoresis.
- +ve particles moves towards cathode.
- -ve particles moves towards anode.



4.Coagulation : [Precipitation]

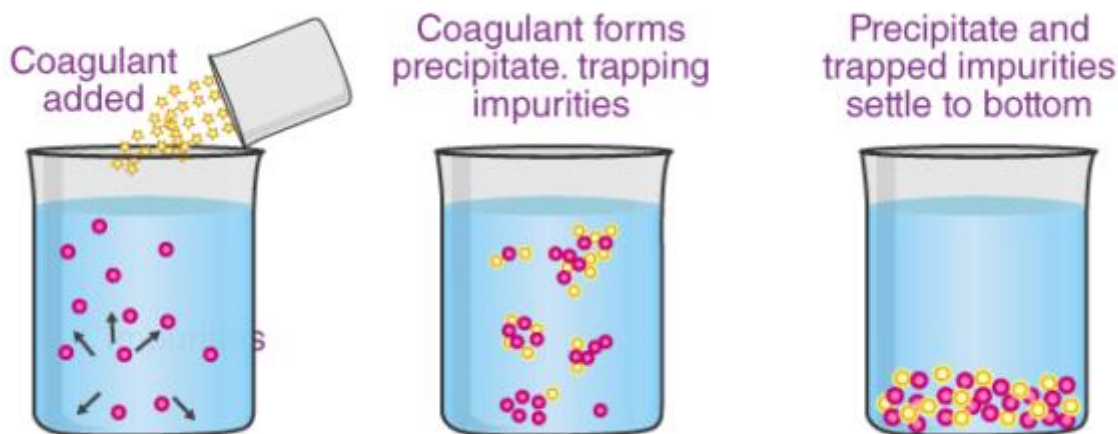
The process of settling of colloidal particles is called coagulation of the sol.

- The stability of lyophobic sols is due to the presence of charge on colloidal particles. If charge is removed by some method, the particles



will come nearer to each other to form aggregates and settle down under the force of gravity.

- Coagulation of lyophobic sols can be carried out by following ways :
 1. By Electrophoresis
 2. By Boiling
 3. By addition of electrolyte
 4. By mixing of two oppositely charged sols



Hardy – Schulze Law

The precipitating effect of an ion on D.P of opposing charge increases with charge of ion.

$$\text{Coagulation Power} \propto \text{Charge on ion}$$

For +vely charged sol [$\text{Fe}(\text{OH})_3$ sol] : Order of Coagulation power : $[\text{Fe}(\text{CN})_5]^{4-} > \text{SO}_4^{2-} > \text{Cl}^-$

For -vely charged sol [Gold sol] : Order of Coagulation power : $\text{Al}^{+3} > \text{Ba}^{+2} > \text{Na}^+$

Coagulation Value : Minimum concentration of an electrolyte [milimoles per litre] required to cause precipitation of a sol is called coagulation value.

$$\text{Coagulation Power} \propto \frac{1}{\text{Coagulation Value}}$$



Protections of Colloids :

Lyophilic sols are more stable than lyophobic sols because lyophilic sols are extensively solvated by DM.

- Due to its stability, Lyophilic sols are used to protect the lyophobic sols from precipitation [Coagulation]. Lyophilic sols form a protective layer around lyophobic sol particles and thus protect from electrolyte.

Gold Number : Protective power of lyophilic sol is expressed in terms of gold number.

- The no. of milligrams of a hydrophilic colloids that will just prevent the precipitation of 10ml of a gold sol, on the addition of 1ml of 10% NaCl solution.

$$\text{Protecting Power} \propto \frac{1}{\text{Gold Number}}$$

EMULSION

These are liquid – liquid colloidal systems.

In other words an emulsion may be defined as a dispersion / distribution of finely divided liquid droplets in another liquid.

There are two types of emulsions

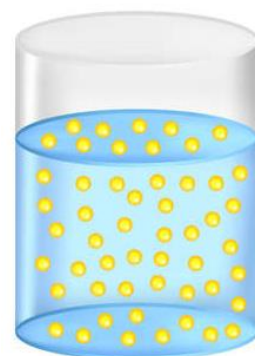
1. Oil in water type [O/W type]

DP – Oil

DM – Water

Example : Milk, Cream, Soaps, Gums

OIL IN WATER (O/W)
EMULSION





2. Water in Oil Type [W/O type]

DP – Water

DM – Oil

Example : Heavy metals salts of fatty acids.

WATER IN OIL (W/O)
EMULSION



Emulsifying Agent :

Water and oil are immiscible and they form unstable emulsion or sometime they separate in two layers. To stabilise the emulsion and to make them homogenous, we add emulsifying agent.

Example : Soap/Detergent : Emulsifiers

Casein (Protein) in milk : Emulsifying agent.

- Emulsions can be broken into constituent liquids by heating, freezing and centrifuging etc. This process is called **De-emulsification**.

Question : Leather gets hardened after tanning, why ?

Answer : Because colloidal nature of animal – skin having positively charged particles whereas tannin consists of negatively charged colloidal particles, which when combine leather get hardened.

Question : Why are medicines more effective in colloidal state ?

Answer : Because they have large surface area per unit mass. So they are easily assimilated in the body.

Question : Some substance can act both as Colloid and Crystalloids. Explain?

Answer : When size of the particles lies between 1 to 1000 nm \Rightarrow Colloid.

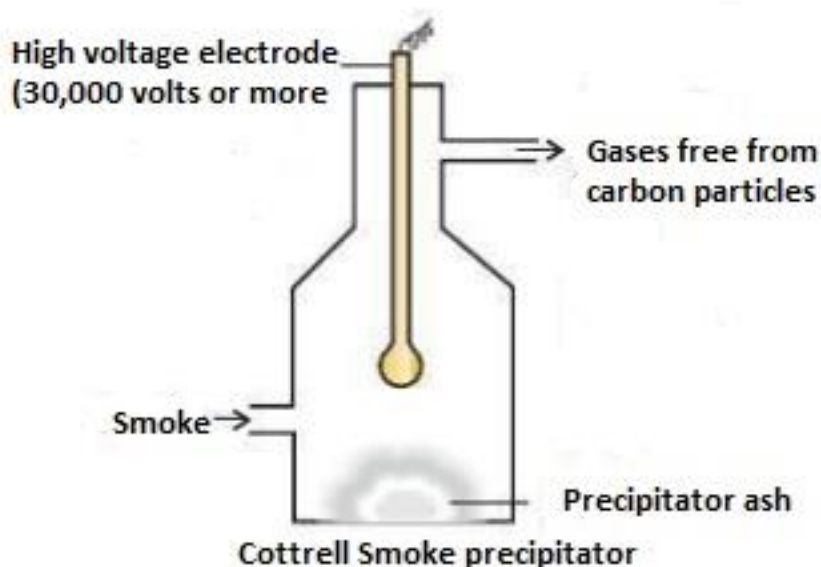
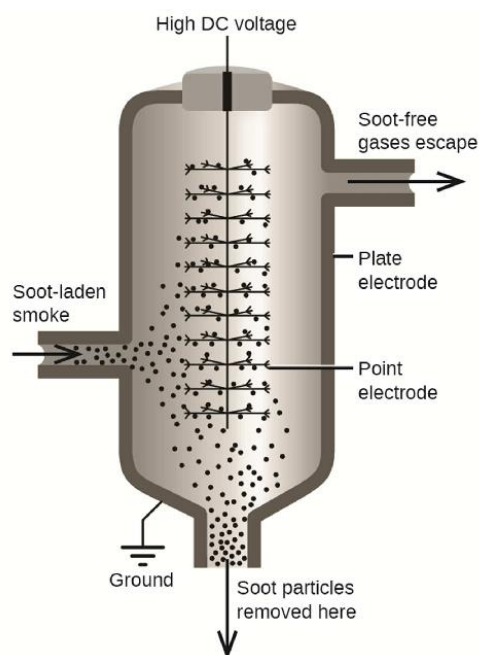
When size of the particles is less than 1 nm (true solution range) \Rightarrow Crystalloids

Example : NaCl in water : Colloid ; NaCl in benzene : Crystalloid

APPLICATION OF COLLOIDS

1. Electrical Precipitation of Smoke : Smoke is a colloidal solution of solid particles such as carbon arsenic compounds, dust etc in air

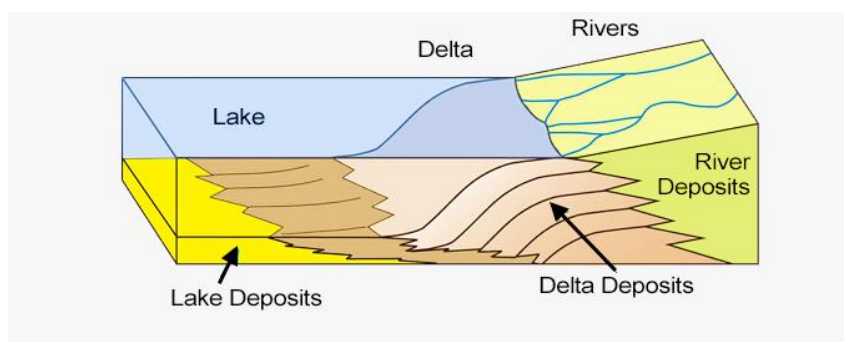
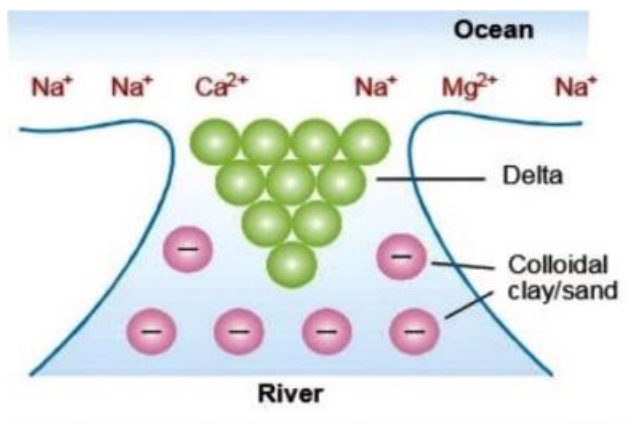
Cottrell Precipitator : A chamber containing plates having a charge opposite to that carried by smoke particles. The particles on coming in contact with these plates lose their charge and get precipitated.



2. Coagulation of Blood : Blood is a colloidal particle which get precipitated by using alum (Electrolyte)

Formation of Delta :

Due to precipitation of clay (which is colloidal in nature), delta's are formed at junction of river and sea.



Question : Why is a finely divided substance more effective as an adsorbent ?

Answer : Because finely divided substance has more surface area, so more adsorption occurs.



This Chapter Ends here !! But not your work

Go to Practice Questions, Solve Dpps attend MCQs and revise the notes
after some 2nd 4th and 7th day

To get 95+ you have to keep on revising what you studied.

[Remember Consistency and HardWork Gives Great Result]

NOTES MADE BY



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