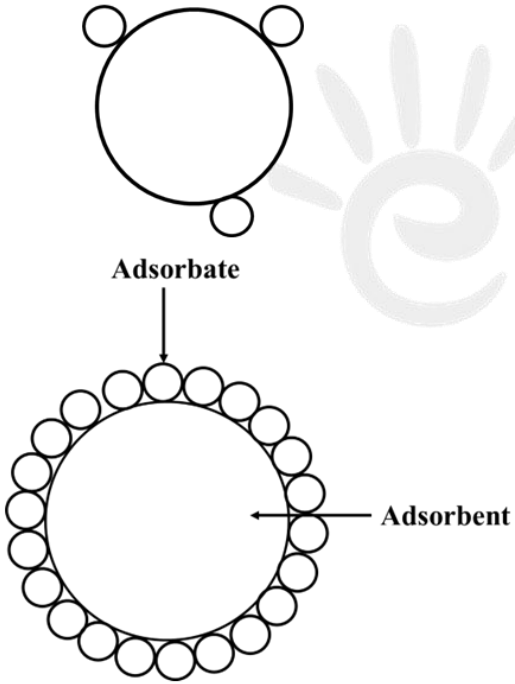
Surface chemistry deals with phenomenon that occur at the surfaces or interfaces.

Adsorption

The tendency of accumulation of molecular species at the surface than in the bulk of a solid (or liquid) is termed adsorption.

The molecular species or substance which concentrates or accumulates at the surface is termed adsorbate and the material on whose surface the adsorption has taken place is called adsorbent.

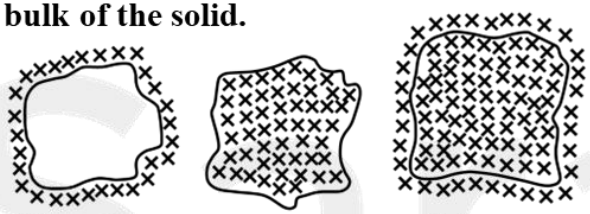


MIND MAP

Surface Chemistry

Distinction Between Adsorption And Absorption

In adsorption the concentration of the adsorbate increases only at the surface of the adsorbent, while in absorption the concentration is uniform throughout the bulk of the solid.



Adsorption is always exothermic but absorption may be endothermic or exothermic.

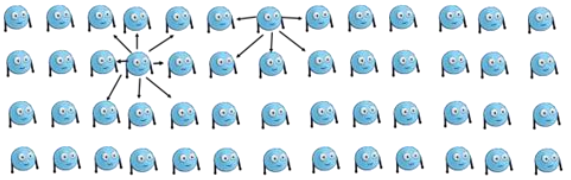
In absorption as well as adsorption, the concentration or partial pressure of absorbate or adsorbate decreases.

Solids, particularly in finely divided state, have large surface area and therefore Charcoal, Silica gel, Alumina gel, Clay, Colloids, metals in finely divided state etc. act as good adsorbents.

Mechanism of Adsorption

Inside the adsorbent all the force acting between the particles are mutually balanced but on the surface the particles are not surrounded by atoms or molecules of their kind on all sides and hence they possess unbalanced or residual attractive force.

These forces of the adsorbent are responsible for attracting the adsorbate particle on its surface.



This amounts to decrease in the entropy of the gas after adsorption i.e., ΔS is negative.

Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system.

For a process to be spontaneous the thermodynamic requirement is that, at constant temperature and pressure, ΔG must be negative i.e., there is a decrease in Gibbs energy.

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

As the adsorption proceeds, ΔH becomes less and less negative ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero.

At this state equilibrium is attained.

Types of Adsorption

Physical adsorption or Physisorption

In this adsorption, accumulation of gas on the surface of a solid occurs on account of weak Van der Waals' force.

Chemical adsorption or Chemisorption

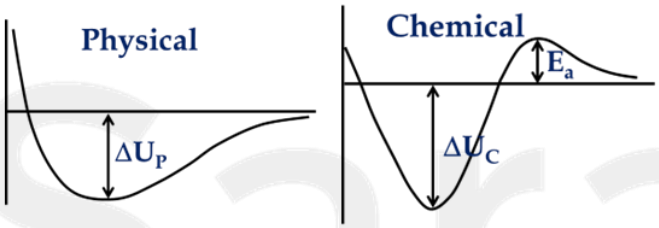
When the gas molecules or atoms are held to the solid surface by chemical bonds covalent or ionic in nature.

MIND MAP

Surface Chemistry

Chemisorption has a high energy of activation and is often referred to as activated adsorption.

Due to higher Ea it is called activated adsorption.



Note

(i) Chemical adsorption is irreversible.

(ii) Chemical adsorption is more exothermic & hence its Ea should be less but the reality is reversed due to requirement of bond cleavage.

(iii) A physical adsorption at low temperature may pass into Chemisorption as the temperature is increased.

Difference between Physisorption and Chemisorption

PHYSICAL ADSORPTION

1. It is caused by weak forces.
2. It is not specific.
3. It is reversible.
4. It depends on the nature of gas. More easily liquifiable gases are adsorbed readily.
5. No appreciable activation energy is involved.

CHEMICAL ADSORPTION

It is caused by chemical bond formation.

It is highly specific (Bond formation is necessary)

It is irreversible.

It depends on the nature of gas. Gases which form compounds with the adsorbent exhibit chemisorption.

High activation energy is involved.

Difference between Physisorption and Chemisorption

PHYSICAL ADSORPTION

6. Low temperature is favourable. It decreases with increase of temperature.
7. Enthalpy of adsorption is low (20 - 40 kJ mol^{-1})
8. High pressure is favourable. Decrease of pressure causes desorption.
9. It forms multilayers on adsorbent surface under high pressure.

CHEMICAL ADSORPTION

High temperature is favourable. It increases with the increase in temperature upto certain limit.

Enthalpy of adsorption is high (80 - 240 kJ mol^{-1})

High pressure is favourable. Decrease of pressure does not cause desorption.

It forms unimolecular layer.

Freundlich Adsorption Isotherm

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

MIND MAP

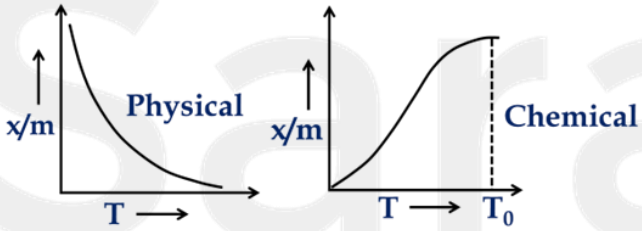
Surface Chemistry

Where 'x' is the mass of the gas adsorbed and mass 'm' of the adsorbent at a pressure P.

k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature.

x : mass of adsorbate

M : mass of adsorbent



Langmuir's Adsorption Isotherm

He derived the condition of equilibrium theoritically assuming that adsorbtion is

(a) Monolayered

(b) Uniform at solid surface

(c) Adsorbate particles do not interact with each other at the surface.

$$M(S) + X(g) \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} M{-}X(s)$$

At any instant

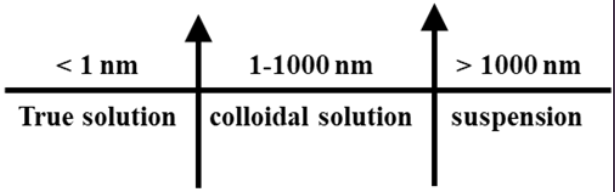
Rate of adsorption, $r_a \mu P \propto (1 - \theta)$

$\therefore r_a = K_a P(1 - \theta)$

where q = site occupied

Colloids

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



MIND MAP

Surface Chemistry

Phase of Colloids

A colloidal system is heterogeneous in character.

It consists of two phases, namely a dispersed phase and a dispersion medium.

(a) Dispersed Phase

It is the component present in small proportion and is just like a solute in a true solution.

For example, in the colloidal state of Sulphur in water, Sulphur acts as a dispersed phase.

(b) Dispersion Medium

It is normally the component present in excess and is just like a solvent in a solution.

Classification of Colloids

(A) Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gaseous, eight types of colloidal system are possible.

A gas mixed with another gas forms a homogeneous mixture and not a colloidal system.

Types of Colloidal Systems

Dispersed phase	Dispersion medium	Type of colloid	Examples
Solid	Solid	Solid sol	Some coloured glasses and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese, butter, jellies

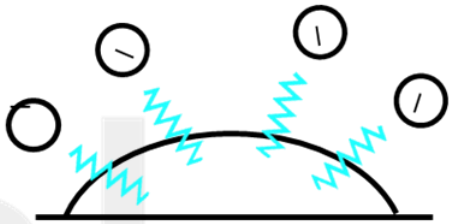
Dispersed phase	Dispersion medium	Type of colloid	Examples
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap lather

Cleansing Action of Soaps

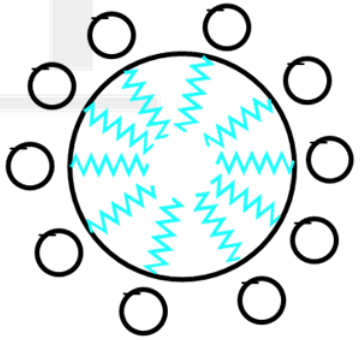
The cleansing action of Soap is due to the fact that Soap molecules form micelle around the oil droplet in such a way that hydrophobic part of the stearate ions is in the oil droplet and hydrophilic part projects out of the grease droplet like the bristles.

Since the polar groups can interact with water, the oil droplet surrounded by stearate ions is now pulled in water and removed from the dirty surface.

Grease on cloth



Stearate ions arranging around the grease droplet



Grease droplet surrounded by stearate ions (micelle formed)

MIND MAP

Surface Chemistry

Peptization

Peptization may be defined as the process of converting a precipitate into colloidal solution 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.

During Peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface. This causes the development of positive or negative charge on precipitates, which ultimately break up into smaller particles of the size of a colloid.

A few examples of sols obtained by Peptization are

(i) Freshly prepared Ferric hydroxide on treatment with a small amount of Ferric Chloride solution at once forms a dark reddish brown solution.

Ferric Chloride acts as a peptizing agent.

(ii) Freshly precipitated Silver Chloride can be converted into a colloidal solution by a small amount of Hydrochloric acid.

(iii) Cadmium Sulphide can be peptized with the help of Hydrogen Sulphide.

Condensation Methods

By Exchange of Solvents

If a solution of Sulphur or Phosphorus prepared in alcohol is poured into water, a colloidal solution of Sulphur or Phosphorus is obtained due to low solubility of Sulphur or Phosphorus in water.

By Change of Physical State

Colloidal solutions of certain elements such as Mercury and Sulphur are obtained by passing their vapour through cold water containing a stabilizer (an Ammonium salt or a Citrate).

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.

$$As_2O_3 + 3H_2S \xrightarrow[\text{decomposition}]{\text{Double}} As_2S_3\ (Sol) + 3H_2O$$

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

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

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

MIND MAP

Surface Chemistry

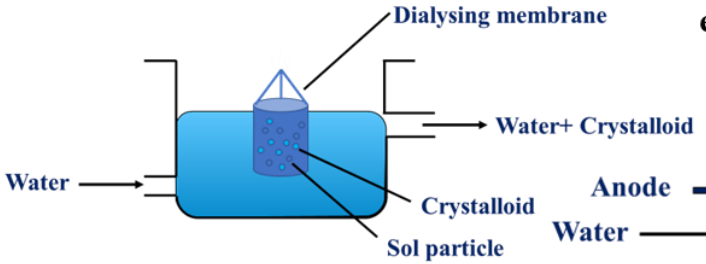
Purification of Colloidal Solutions

Dialysis

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

Since, particles (ions or smaller molecules) in a true solution can pass through animal membranes (bladder) or parchment paper or cellophane sheet but not the colloidal particles.
The membrane can be used for dialysis.

The molecules and ions diffuse through membrane into the outer water and pure colloidal solution is left behind.



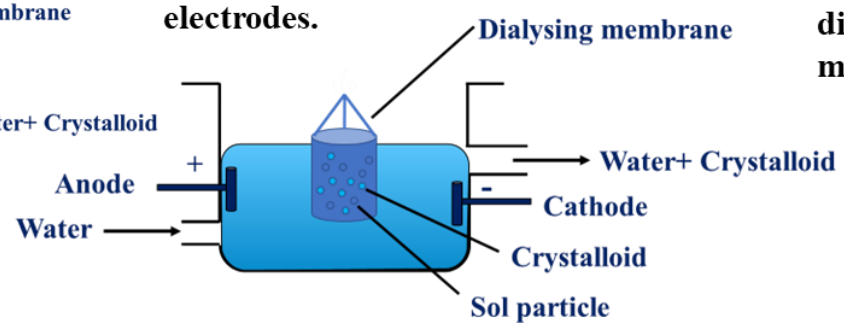
Electro-dialysis

Ordinarily, the process of dialysis is quite slow.
It can be made faster by applying an electric field if the dissolved substance in the impure colloidal solution is the only electrolyte.

The process is then named electro-dialysis.

The colloidal solution is placed in a bag of suitable membrane while water is taken outside.

Electrodes are fitted in the compartment as the ions present in the colloidal solution migrate out to the oppositely charged electrodes.



Ultrafiltration

Ultrafiltration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially prepared filters, which are permeable to all substances except the colloidal particles.

Colloidal particles can pass through ordinary filter paper because the pores are too large.

Surface Chemistry

Properties of Colloidal Solution

Physical Properties

Colloidal solutions are heterogeneous in nature consisting of two phases, the dispersed phase and the dispersion medium.

Colloidal solutions are quite stable, as the colloidal particles remain suspended in the dispersion medium indefinitely. Thus there is no effect of gravity on the colloidal particles.

Mechanical Properties

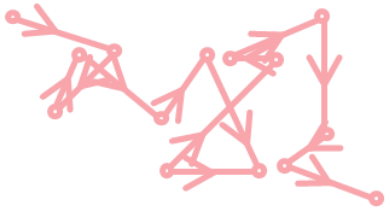
Brownian Movement

When a colloidal solution is viewed under an ultra microscope, the colloidal particles are seen continuously moving in a zigzag path. This kinetic activity of particles suspended in the liquid is called Brownian movement.

Cause of Movement

The Brownian movement has been explained to be due to the unbalanced bombardment of the particles by the molecules of the dispersion medium.

The Brownian movement has a stirring effect which does not permit the particles to settle and thus, is responsible for the stability of sols.



Brownian movement

MIND MAP

Surface Chemistry

Optical Properties (Tyndall Effect)

When a strong and converging beam of light is passed through a colloidal solution, its path becomes visible (bluish light) when viewed at right angles to the beam of light.

This effect is called Tyndall effect.

The light is observed as a bluish cone which is called Tyndall cone.

The Tyndall effect is due to scattering of light by the colloidal particles.

Charge of Colloidal Particles

a) When Silver Nitrate solution is added to Potassium Iodide solution, the precipitated Silver Iodide adsorbs Iodide ions from the dispersion medium and negatively charged colloidal solution results.

However, when KI solution is added to $AgNO_3$ solution, positively charged solution results due to adsorption of Ag+ ions from dispersion medium.

AgI/I^- AgI/Ag^+

Negatively charged Positively Charged

b) If $FeCl_3$ is added to excess of hot water, a positively charged solution of Hydrated Ferric Oxide is formed due to adsorption of Fe^{3+} ions.

However, when Ferric Chloride is added to NaOH a negatively charged solution is obtained with adsorption of OH^- ions.

$Fe_2O_3.xH_2O/Fe^{3+}$ $Fe_2O_3.xH_2O/OH^-$

Positively charged Negatively charged

The two electrical properties of colloidal solutions are

a) Electrophoresis or Cataphoresis

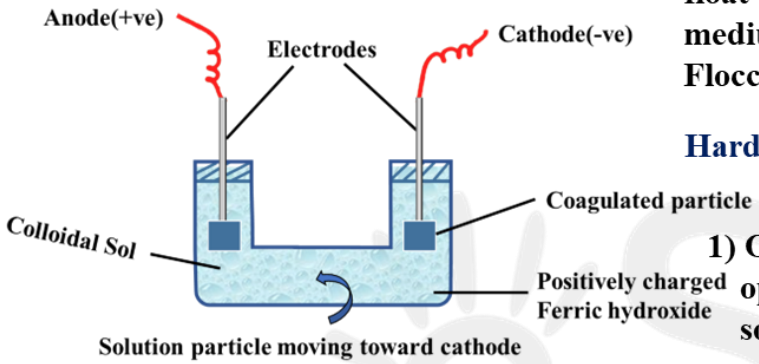
b) Electro-osmosis

MIND MAP

Surface Chemistry

Electrophoresis or Cataphoresis

The phenomenon involving the migration of colloidal particles under the influence of electric field towards the oppositely charged electrode, is called Electrophoresis or Cataphoresis.



Electro-osmosis

The phenomenon involving the migration of the dispersion medium and not the colloidal particles under the influence of an electric field is Electro-osmosis.

Coagulation

This process by means of which the particles of the dispersed phase in a solution are precipitated is known as Coagulation.

If the coagulated particles instead of settling at the bottom of the container, float on the surface of the dispersion medium, the coagulation is called Flocculation.

Hardy-Schulze Rule

1) Only the ions carrying charge opposite to the one present on the solution particles are effective to cause coagulation, e.g., the negative charged solution is best coagulated by cations and a positive solution is coagulated by anions.

2) The charge on coagulating ion influences the coagulation of solution in general, the coagulating power of the active ion increases with the valency of the active ion.

Hardy-Schulze law is stated as follows

"Higher is the valency of the active ion, greater will be its power to precipitate the solution."

Thus, coagulating power of cations is in the order of $Al^{3+} > Ba^{2+}$ or $Mg^{2+} > Na^{+}$ or K^{+}.

Similarly, to coagulate the positively charged solution the coagulating power of anion is in the order of $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}$.

Emulsion

An emulsion is a colloidal solution of a liquid.

Catalysis

Substances, which accelerate the rate of a chemical reaction and themselves remain chemically and quantitatively unchanged after the reaction, are known as Catalysts, and the phenomenon is known as Catalysis.

Promoters And Poisons

Promoters are substances that enhance the activity of a catalyst while poisons decrease the activity of a catalyst.