SURFACE CHEMISTRY

Adsorption physisorption and chemisorptions: factors affecting adsorption of gases on solids

- The surface are a solid is referred to as the atoms present in the top most layer of the solid but not in the interior or bulk of the solid.
- The solid surface area includes the atoms present up to a depth of 100 nm only.
- "The phenomenon of attracting and subsequently accumulating the molecules of a substance by a liquid or solid on its surface is called adsorption.
- The molecules present on the surface of a substance are of greater energy than the molecules present in the bulk of the substance.
- The molecules in the bulk are attracted by more number of the molecules and the molecules on the surface are attracted by less number of other molecules, of the same substance
- The surface molecules show greater tendency to attract the molecules of other substances and allow than to settle on its surface
- During adsorption, there is always a decrease in residual forces of surface i.e. there is decrease in surface energy which appears as heat. There fore Adsorption is an exothermic process.

- During process of adsorption, freedom movement become restricted i.e. entropy of system decreases. .
- Adsorption is thus accompanied by decrease in enthalpy and entropy of the system.
- But adsorption process is spontaneous, the thermodynamic requirement for this is must be negative
- On the basis of equation can be negative it has sufficiently high negative value as is positive
- As the adsorption proceed, becomes less and less negative ultimately becomes equal to zero. At this state equilibrium is reached.

<u>Applications of Adsorption:</u>

- **Production of high vacuum:** The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum.
- **Gas masks: Gas mask:** (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.
- **Control of humidity:** Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.
- Removal of coloring matter from solutions: Animal charcoal removes colours of solutions by adsorbing colored impurities.
- **<u>Absorption</u>**: - The phenomenon by which the molecules of a substance are attracted and uniformly distributed into the bulk of another solid or liquid substance is called "absorption".
- Eg : i) Ink gets absorbed into the bulk of a piece of chalk.
- ii) Water molecules are absorbed into anhydrous calcium chloride
- H_2 gas kept in contact with finely divided palladium metal is absorbed by metal. The absorption of H_2 gas by 'Pd' is known as occlusion
- A sponge placed in water absorbs water into it.
- Absorption is bulk phenomenon while adsorption is surface phenomenon.
- The substance getting adsorbed on the surface of other substance is called "adsorbate"
- Activated charcoal is prepared by heating charcoal at 623K-1273K in vacuum or in the presence of an inert gas

- The adsorption that occurs due to week Vander-Waal forces between adsorbate and adsorbent is called physical adsorption or

ADSORPTION

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- Activated charcoal is prepared by heating charcoal at 623K-1273K in vacuum or in the presence of an inert gas
- The adsorption that occurs due to week Vander Waal forces between adsorbate and adsorbent is called physical adsorption or physisorption.

The adsorption that occurs due to chemical bonding between adsorbent and adsorbate is called chemisorption.

Factors affecting adsorption:

a)<u>Nature of adsorbate :</u>

i) Easily liquefiable gases like HCl, CO_2 , NH_3 and SO_2 with higher critical temperature can be more easily adsorbed than gases like H_2, N_2, O_2 etc which have lower critical temperature.

ii) Greater the critical temperature of a gas, greater is its liquifiability and greater the case of its adsorption and vice versa.

iii) T_C values of H_2, CH_4,SO_2 are 253 of adsorbent and to what extent an adsorbent is finely divided.

ii) Greater the specific area of solid, the greater its capacity to adsorb the molecules of

b) <u>Specific area of adsorbent:</u>

1) The surface area of an adsorbent provided by one gram of an adsorbent is called its specific area. It depends on the porous nature of adsorbent and to what extent an adsorbent is finely divided.

ii) Greater the specific area of solid, the greater its capacity to adsorb the molecules of adsorbate.

(iii) Finely divided and porous material has greater surface area hence greater extent of adsorption so these are used in heterogeneous catalytic reactions.

c) <u>Pressure of the adsorbate gases :</u> (Isotherms):

i) The extent of adsorption of gas on a solid surface changes depending on

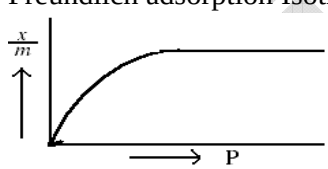
a) Type of adsorption

b) The pressure of the gas at equilibrium state

The extent of adsorption of a gas on a solid is expressed in terms of the ratio
where: x = no.of adsorbate moles adsorbed at adsorption equilibrium.
m = mass of the adsorbent.

* The graphs obtained with on y–axis and 'pressure' on x–axis is called isotherms.

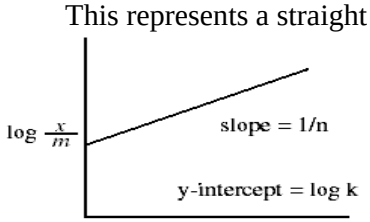
* Freundlich adsorption Isotherm is given by: (n >1)
* Freundlich adsorption Isotherm gives a graph as below:



The logarithmic expression of Freundlich adsorption isotherm is :

$$\log\frac{x}{m} = \log K + \frac{1}{n}\log P.$$

This represents a straight line



* Freundlich adsorption isotherms can not explain adsorption at high pressures.
* Langmuir adsorption isotherm explains well the adsorption at all pressures.
* Langmuir adsorption isotherm is given by

$$\frac{x}{m} = \frac{aP}{1+bP}$$

where 'a' and 'b' are Langmuir parameters.

* At very high pressure the isotherm becomes: $\frac{x}{m} = \frac{a}{b}$ Constant. ——— (1)
* At very low pressure the isotherm becomes: $\frac{x}{m}$ = aP ———(2) ,
* The inverse form of Langmuir isotherm may be written as : $\frac{m}{x} = \frac{b}{a} = \frac{1}{aP}$ ——— f
* "m/x" on y – axis, "1/p" on x – axis gives a straight line with slope '1/a' and y – intercept b/a, from which the parameters 'a' and 'b' can be obtained.
* Equation '1' suggests that at. very high pressures after all the surface area is covered the 'x/m' remains constant and indicates no further adsorption is possible however high pressure is applied further.

Langmuir adsorption isotherm:

* A solid surface is considered homogeneous. But it contains a fixed number of adsorption sites on the surface of it.
* Each such site adsorbs a single molecule. This means that adsorption is confined to a mono molecular layer.
* Adsorption is considered as an equilibrium process comprising of vaporization and condensation occurring simultaneously at a given temperature.
* At equilibrium the rate of evaporation is equal to rate of condensation
* Rate of evaporation is proportional to the area of the surface covered by the adsorbed gas Rate area covered.

  Rate of evaporation = $K_d \times \theta *$

  Rate of condensation is proportional to the product of the pressure of the gas and area uncovered on adsorbent.

  Rate $\propto$ P x area uncovered.

  Rate of condensation = $K_a p(1-\theta)$

  At equilibrium both rates are equal $K_d\theta = K_a p(1-\theta)$

  If θ is covered fraction of the surface

  $\theta = \frac{bp}{1+bp}$ Where $b = \frac{k_a}{k_d}$

  $\frac{X}{m} = \frac{k_b p}{1+bp}$; $\frac{X}{m} = \frac{ap}{1+bp}$

* Where x = mass of a gas adsorbed

  m = mass of adsorbent

  a = kb, b = ka/kd, p = pressure.

  The above equation is called Langmuir adsorption Isotherm.

d) Effect of temperature:

i) Adsorption being an exothermic process is generally formed by low temperature. But in case of endothermic chemisorptions processes high temperature supports adsorptions to certain extent.

ii) At 463K, N_2 is physically adsorbed on Iron metal. But at 723K iron nitric is formed due to chemisorptions

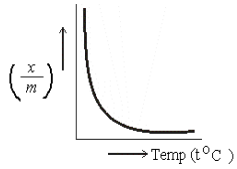
iii) Physisorption takes place at low temp while chemisorptions takes place at high temperature.

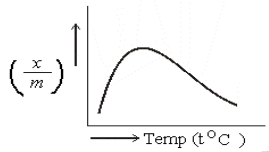
iv) As temperature rises physical adsorption may change into chemisorptions in $CaCl_2$, N_2 on Iron metal, (or) desorption may also take place in case noble gases on activated charcoal.

v) Physical adsorption equilibrium follows Lech atelier's principal

vi) The graphs showing the variation of x/m with temperature are known as adsorption isobars. These are used to distinguish physical and chemical adsorption.

vii) **Physical Adsorption Chemical Adsorption**





21. During adsorption S becomes negative. Hence to make "G" negative H must be negative according to the thermodynamic relation

G = H - TS.

22. **Adsorption in solutions:**

The solute present in a solution may be adsorbed on the surface of a suitable adsorbent.

Freundlich and Langmuir isotherms are applicable in case of adsorption in solutions as well. The isotherms may be written as :

a) Freundlich adsorption Isotherm: $\frac{x}{m} = KC^{\frac{1}{n}} (n > 1)$

b) Langmuir adsorption Isotherm:

, where $\frac{x}{m} = \frac{aC}{1+bC}$

C = Equilibrium Concentration of solution.

c) Freshly prepared metal hydrolysis are good adsorbing agents for dye stuffs solutions.

CATALYSIS HOMOGENOUS AND HETEROGENEOUS ACTIVITY AND SELECTIVITY, ENZYME CATALYSIS

- The term catalyst was first proposed by Berzelius in 1836.
- A catalyst is a substance that increases the rate of a chemical reaction to which it is added, without itself being consumed in the reaction.
- catalyst can be recovered unchanged chemically at the end of the reaction
- The action of a catalyst in changing the rate of a chemical reaction is called catalysis.
- Some examples of catalystic reactions

The manufacture of NH_3 (g) from N_2 (g) and H_2(g) (Haber's process). Mixture of Fe and Mo is used as catalyst)

$$N_2(g) + 3H_2(g) \xrightleftharpoons{Fe+Mo} 2NH_3(g)$$

The manufacture of H_2SO_4 by contact process from $SO_2.V_2O_5$ or Pt is used as catalyst.

$$2SO_2\,(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

In the lead chamber process, nitric oxide (NO) is used as catalyst

$$2SO_2\,(g) + O_2(g) \xrightarrow{NO} 2SO_3(g)$$

The thermal decomposition of $KClO_3$ to give KCl and $O_2.MnO_2$ is used as catalyst

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2(g)$$

Ostwald's process of preparation of HNO_3 from NH_3 Platinum is used as catalyst.

$$2NH_3\,(g) + 2O_2\,(g) \xrightarrow{pt} 2NO\,(g) + 3H_2O\,(g)$$

- Characteristics of Catalysts :

A catalyst does not initiate a reaction but will only increase the speed of a chemical reaction.

A catalyst remains chemically unaffected at the end of the reaction

- A small quantity of the catalyst is sufficient to affect the huge quantities of reactants.

For example, one milligram of fine platinum powder is enough to cause the combination of 2.5 liters of a mixture of H_2 and O_2 to form water.

- A catalyst does not effect the position of equilibrium in case of reversible reactions. But it helps to attain the equilibrium quickly. It catalyses both the forward and the backward reactions.
- There must be an optimum temperature at which the efficiency of the catalyst is maximum.
- A catalyst may get poisoned (lose its activity) by the presence of even traces of other substances.
- The substance which destroys or reduces the activity of the catalyst is known as catalytic poison. The phenomenon is called catalytic poisoning
- For example, As_2O_3 acts as a poison for platinum in the contact process of manufacture of H_2SO_4.
- Iron acts as a catalyst in the Haber's process of manufacture of NH_3. The catalyst iron is poisoned by H_2S.
- Platinum is poisoned by CO in the oxidation reaction of $H_2$to H_2O
- A substance which promotes the activity of the catalyst, to which it is added in small amounts, is called a promoter or activator. The process is known as activation.
- The promoter may be spoken of as 'catalyst for a catalyst'.

For example, molybdenum (Mo) is promoter to the catalyst iron in the Haber process.

- Copper when added to Nickel increase its catalytic activity in hydrogenation of oils.
- Finely divided substances function as more effective catalysts than the coarsely divided substances.

For example, finely divided nickel functions as a good catalyst in the hydrogenation of oils.

- The presence of a foreign substance which retards the rate of a reaction is called a negative catalyst or inhibitor. The phenomenon is negative catalysis.

For example, Decomposition of $H_2O_2$is retarded by the presence of glycerol

$$2H_2O_2 \xrightarrow{glycerol} 2H_2O + O_2$$

- Change of temperature may alter the rate of a catalytic reaction. Some catalysts may lose their catalytic activity at higher temperatures. Catalysts thus function at optimum temperatures.
- Catalysis is classified into two types based on the physical state of the catalyst and the reactants: Homogeneous catalysis and Heterogeneous catalysis.
- In a homogeneous catalysis, the Catalyst and the reactants are in the same phase.
- Many homogeneous catalyzed reactions occur in the gaseous phase as well as in the liquid phase.

- Examples of homogeneous catalysis :
- Gaseous phase homogeneous catalysis :
  1) $2SO_2(g) + O_2(g) \xrightarrow{NO_{(g)}} 2SO_3(g)$
  2) $2CO\ (g) + O_2(g) \xrightarrow{NO_{(g)}} 2\ CO_2(g)$
  3) $CH_3CHO\ (g) \xrightarrow{I_2(g)} CH_4(g) + CO(g)$
- Liquid phase homogeneous catalysis :
  d) $2H_2O_2(l) \xrightarrow{I^-(aq)} 2H_2O\ (l) + O_2(g)$

$$CH_3COOC_2H_5\ (l) + H_2O(l) \xrightarrow{H^+(l)\ or\ OH^{-1}(l)} CH_3COOH_{(l)} + C_2H_5OH_{(l)}$$

$$C_{12}H_{22}O_{11}\ (l) + H_2O\ (l) \xrightarrow{H^+(l)} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

- In heterogeneous catalysis, the catalyst is in a different phase from that of the reactants.

In many heterogeneous catalytic reactions, generally the catalyst is a solid and the reactants are either liquids or gases.

The catalysts commonly used are transition metals or metal oxides.

Example: Pt, Ni, Cu, Fe, Mo and the oxides such as Fe_2O_3, ZnO, V_2O_5 and molybdenum oxide

Some examples of heterogeneous catalytic reactions:

Gaseous phase reactions:

Oxidation of SO_2 (g) to SO_3 (g) in the manufacture of sulphuric acid by the contact process

Platinum or vanadium pentoxide is used as catalyst.

$$2SO_2\ (g) + O_2\ (g) \xrightarrow{Pt(s)} 2SO_3\ (g)$$

Synthesis of ammonia gas from N_2 (g) and H_2 (g) by Haber's process Iron is used as catalyst.

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

Oxidation of NH_3 (g) to NO (g) in the presence of $Fe_2O_3(s) + Bi_2O_3(s)$ in the manufacture of HNO_3.

$$4NH_3\ (g) + 5O_2\ (g) \xrightarrow{Fe_2O_3(s)+Bi_2O_3(s)} 4NO + 6H_2O$$

Liquid phase heterogeneous catalysis:

Decomposition of aqueous solution of liquid H_2O_2 to water and O_2.Manganese dioxide (s) or Platinum in colloidal form is used as catalyst.

$$2H_2O_2\ (l) \xrightarrow[MnO_2]{pt} 2H_2O + O_2$$

- **Activity:** It is the ability of the catalyst to speed up enormously the chemical reaction.

A mixture of H_2 and O_2 can be stored indefinitely without any reaction occurring in the mixture in the absence of a catalyst.

The same mixture of H_2 and O_2 in the presence of the catalyst platinum gives water with explosive Violence.

- **Selectivity:** It is the ability of a catalyst to direct the reaction to yield particular products only.

Example:

When ethyl alcohol is passed over hot $Al_2O_3(s)$ ethene is formed. (Dehydration)

$$C_2H_5OH \xrightarrow{Al_2O_3} C_2H_4 + H_2O$$

But when ethyl alcohol is passed over hot copper metal, it gives acetaldehyde. (Dehydrogenation)

$C_2H_5OH \xrightarrow{Cu} CH_3CHO + H_2O$

- The action of a catalyst is explained by two different theories.

Intermediate compound formation theory

The adsorption theory

Intermediate Compound formation theory: According to this theory

The chemical combination of the catalyst with one or more of the reactants to form an Intermediate compound

The decomposition of the intermediate compound (unstable) alone or it reacts with other reactant Or reactants to give the products with the regeneration of the catalyst

$2SO_2 + O_2 \xrightarrow{NO} 2SO_3$

The mechanism is

$2NO + O_2 \rightarrow 2NO_2$

(Catalyst) (Intermediate Compound)

$2NO_2 + 2SO_2 \xrightarrow{NO} 2SO_3 + 2NO$ (Regenerated Catalyst)

$2CO + O_2 \xrightarrow{NO} 2CO_2$

$2NO + O_2 \rightarrow 2NO_2$

$2NO_2 + 2CO \rightarrow 2CO_2 + 2NO$

- Adsorption theory: This mechanism is operative in heterogeneous catalytic reactions occurring on solid catalysts.

Example : The process of hydrogenation of C_2H_4 to give C_2H_6 on nickel catalyst.

A catalyst lowers the activation energy of the reaction by providing a new path way.

When one of the intermediates formed in a reaction itself acts as a catalyst for the reaction, the catalysis is called autocatalysis.

Some examples are

Oxidation of oxalic acid by acidified $KMnO_4$

$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 10CO_2$

Mn^{2+} ions are formed initially in the reduction of $KMnO_4$ by oxalic acid. These Mn^{2+} ions act as an autocatalyst and increase the rate of the further reaction.

Decomposition of arsene

$2AsH_3 \rightarrow 2As + 3H_2$

Arsenic is formed initially and this catalyses the further reaction. Hence the rate of reaction increases.

COLLOIDAL STATE: DISTINCTION BETWEEN TRUE SOLUTIONS, COLLIODS AND SUSPENSIONS, LYOPHILLIC, LYOPHOBIC, MULTI MOLECULAR, AND MACROMOLECULAR COLLOIDS

- Thomas Graham (1861) divided soluble substances into two classes, ‘crystalloids’ and ‘colloids’, according to their powers of diffusion across vegetable or animal membranes.
- Substances such as salts, sugar, Urea, acids and bases which diffuse rapidly, through the membrane were known as crystalloids, on account of the fact they are rapidly obtained in the crystalline form.

- Amorphous substances like gelatin, albumin, glue and gums, starch which exhibit little tendency or no tendency to diffuse, through the membrane were known as colloids.
- They were colloids because of their gluey nature.
- The so-called colloids like gelatin, starch, gum etc are also crystalline in nature, but not amorphous as thought by Graham.
- It is also observed that substances which behave as crystalline under some experimental conditions, also behave as colloids under different experimental conditions.
- Now days any substance can be brought into the 'Colloidal state' under suitable experimental conditions.
- Solutions of chemical substances are broadly classified into true solutions and colloidal solutions.
- These two types of solutions differ greatly in their properties. This difference in their properties is attributed to the particle size of the solute in these solutions.

TRUE SOLUTION

a. When a common salt (NaCl) is added to water and the contents are shaken well, a clear homogeneous solution is formed. Na^+ and Cl^- ions are uniformly dispersed in water. It is called a true solution.
b. The size of the particles in true solution is less than 1m. ($1m=10^{-9}m$)
c. True solutions are clear as water and transparent to light.
d. The particles of solute in a true solution are either single molecules or ions.
e. These cannot be separated by filtration.
f. Even on long standing the particles in a true solution do not settle under gravity or not separated by centrifugation.
g. A true solution is an intimate homogeneous binary mixture of solute and solvent.

COLLOIDAL SOLUTION

a. A colloidal solution is a heterogeneous binary system in which a disperse phase (solute) of 1m-1 size is dispersed in a continuous dispersion medium (solvent).
b. A colloidal solution is a heterogeneous system, consisting of a disperse phase and the dispersion medium.
c. In a colloidal solution, each particle is contained with in its boundary which separates it from the continuous dispersion medium.
d. The surface of the disperse phase particle is large.
e. Colloidal particles do not settle down even on long standing provided they are pure.
f. Colloidal solutions pass through filter paper easily but slowly through parchment paper.
g. The colloidal solutions scatter light and exhibit a phenomenon known as Tyndall effect.
h. The external appearance of colloidal solution opaque
i. The components of colloidal solution can be separated by ultra filtration, and partially possible by filtration
j. The dispersal phase in colloidal solution is settled down by centrifugation.

- When sand or powdered glass is mixed with water and the contents are shaken well, a coarse suspension of sand or glass in water is formed.
- The size of the particles in a coarse suspension is greater than 1.

- The filter papers soaked in a solution of gelatin or of colloidion and subsequently hardened by soaking in formaldehyde are called ultra filters.
- The pores in ultra filter paper are small. The filtration through this paper is known as ultra filtration.
- When starch paste is added to hot water and the contents are shaken well, a colloidal solution is formed.
- The substance distributed in a dispersion medium as colloidal particles in a hetero-genous system of colloidal solution is known as disperse phase.
- The continuous phase of the heterogeneous colloidal solution, in which the colloidal particles are dispersed is known as dispersion medium.
- Types of colloids: colloids are classified into 8 types based on the physical states of the dispersion medium and dispersed phase.
- Smoke :
  - It is an aerosol
  - It is a lyophobic colloid
  - Carbon particles are dispersed in air.
  - Carbon particles - Disperse phase
  - Air (gas) - Dispersion medium
- Cloud :
- It is an aerosol
- It is a lyophobic colloid
- It is a colloidal suspension of droplets of water (liquid) in air.
- Droplets of water - Disperse phase
- Air (gas) - Dispersion medium.
- Blood :
- It is an aqua sol or hydrosol.
- It is a colloidal suspension of albuminoidal substances in water.
- Albuminoidal substances (RBC erythrocytes) WBC (leucocytes) blood platelets -Disperse phase.
- Water containing some inorganic ions and organic molecules is the dispersion medium.
- Milk :
- It is an emulsion.
- It is oil in water (o/w) type emulsion.
- It is a liquid in a liquid colloidal solution.
- Droplets of liquid fat are dispersed in water.
- Milk is quite stable.
- Butter fat droplets (liquid) - Disperse phase
- Water (liquid) - Dispersion medium.
- Impure blood is purified by kidneys through dialysis.
- Addition of $FeCl_3$ to bleeding wound causes coagulation of blood to form a clot.
- On addition of large quantities of electrolytes starch sol is coagulated.
- Starch sol is prepared by adding starch paste to hot water with constant stirring.
- Starch Solution :
- It is an aqua sol or hydrosol.
- It is lyophilic colloid.
- It is a colloidal solution of starch molecules in water.
- Starch (solid) - Disperse phase

- Water (liquid) - Dispersion medium.
- It is a solid in liquid sol.
- Milk on coagulation gives emulsified fat (casein).
- Milk cream is separated from milk by centrifugation.
- The curdling of milk when it sours is an example of coagulation of milk.
- Milk sugar lactose ferments to lactic acid in souring. This coagulates milk.
- Gold sol :
- It is an aqua sol or hydrosol
- It is lyophobic sol
- It is a colloidal solution of gold particles (solid) in water.
- Gold particles (solid) - Disperse phase.
- Water (liquid) - Dispersion medium.
- It is solid in liquid sol.
- It is coagulated by adding small amounts of electrolytes.
- It is prepared by Bredig arc method.
- Gold sol is stabilised by the presence of an alkali.
- The gold sol is coloured blue if the particle size is big and red in colour when the particle size is small.
- If the dispersion medium is air, the sols are named as aerosols.
- If the dispersion medium is water, the sols are named as hydrosols.
- A great affinity exists between the disperse phase and the dispersion medium in lyophilic or hydrophilic sols.
- Examples of lyophilic sols are starch solution, aqueous protein solution, polymer solution in some organic solvents.
- Not much affinity exists between the disperse phase and the dispersion medium in lyophobic or hydrophobic sols.
- Examples of lyophobic sols are aqueous metal sols, aqueous sols of metal sulphides and oxides, gold sol, AS_2S_3 Sol, $Fe(OH)_3$ sol etc.
- Depending upon the nature of solvent being water, alcohol or benzene, sols may be called as hydrosols, alcosols or benzosols respectively.

Emulsion

- An emulsion is a colloidal system in which both the dispersed phase and the dispersion medium are liquids.
- Milk is a naturally occurring emulsion in which the liquid fat (Granules) is dispersed in water.
- A dispersion of finely divided liquid droplets in another liquid dispersion medium is known as emulsion.
- Generally one of the liquids is water and the other is a liquid immiscible with water. The other liquid immiscible with water is referred to as oil.
- Emulsions are classified into two classes.
- Oil in water (O/W) emulsion
- Water in oil (W/O) emulsion
- In oil in water type emulsions, the dispersed phase is oil and the dispersion medium is water.

- Milk and vanishing cream are the examples of this type.
- In water in oil type emulsion, the disperse phase is water and the dispersion medium is oil.
- Examples :
- Stiff greases: Water is dispersed in lubricating oils.
- Cod-liver oil : Water is dispersed in cod-liver oil.
- Cold cream: Water is dispersed in liquid fat.
- Oil in water and water in oil emulsions are generally not stable.
- If the emulsion is kept aside for some time, the droplets of the dispersed phase (oil or water) get aggregated and separate out as a separate layer.
- The third substance added in small amounts to an emulsion to make the emulsion stable is known as emulsifying agent or emulsifier.
- The emulsifier reduces the surface tension on the side of one liquid and the other roll into droplets.
- The emulsifying agent is usually a soap, a sulphate detergent, a hydrophilic colloid (like gelatin, egg albumin, carbon powder)
- Soap emulsifies Kerosene in water emulsion.
- Egg albumin emulsifies an olive oil in water emulsion.
- Solid mercuric iodide emulsifies water in benzene emulsion.
- Soap emulsifies O/W type emulsion
- Casein emulsifies oil in water(milk) emulsion.
- Solutions of soaps and detergents at low concentrations behave as normal or true solutions of strong electrolytes.
- Solutions of soaps and detergents exhibit colloidal properties at higher concentrations due to formation of aggregated particle called 'micelles'. They are also called associated colloids.
- Micelles contain generally as many as 100 or more molecules of the substance forming the micelle.

  Sodium stearate ($C_{17}H_{35}COONa$) is an example which forms micelles or associated colloid.

  The stearate ion $CH_3(CH_2)_{15}CH_2COO^-$ contains a hydrophobic group (alkyl group end) and an hydrophilic group (carboxylate ion end).

  Soaps are sodium salts of higher fatty acids. For example sodium stearate $CH_3(CH_2)_{16}COO^- Na^+$ is a salt of 18 carbon fatty acid.
- The stearate ions associate themselves in higher concentrations to form ionic micelles.

  A colloidal sized particle (aggregate) formed in water by the association of normal simple molecules, each having a hydrophobic end and a hydrophilic end is micelle.
- For example, stearate ions ($CH_3\ (CH_2)_{16}\ COO$) to water. The COO^- group has an affinity for water.
- The COO^- group is called hydrophilic group and is called "head" of the stearate anion.
- A colloid in which the dispersed phase consists of micelles or aggregated colloidal particles is an associated colloid.
- Sodium lauryl sulphate is synthetic detergent present in laundry soap, tooth pastes and shampoos.
- $CH_3(CH_2)_{10}CH_2OSO_3^- Na^+$ (or) $C_{12}H_{25}O\ SO_3^-\ Na^+$

  This detergent has a hydrophilic sulphate group (OSO_3^-) and a hydrophobic dodecyl alkyl group ($C_{12}H_{25}$) which are called anionic detergents
- The cleaning action of soap is based on the solubilization of grease or dirt on the cloth into micelle. This is known as emulsification of grease.

- The cleaning action of soap is due to affinity of soap anions to water.
- The hydrocarbon chain of the anion has an affinity for grease, oil or dirt. This is the hydrophobic part of ion and is called 'tail' of the anion.
- The 'tail' part dissolves the grease deposit or dirt and encapsulates to form micelles. These micelles are then removed by water in washing process.
- The main function of soap is therefore to convert the oily and greasy dirt on the cloth or human body into large colloidal particles (micelle or emulsion)
- Soap functions as an emulsifying agent in the cleaning process.
- The action of soap is valid to all synthetic detergents.
- Repulsion of like charges - COO^- or - OSO_3^- on grease micelle prevents them to come together.
- The hydrocarbon chains (tails) are in the interior of the micelle and - COO^- or - OSO_3^- ions are on the surface.
- The grease or dirt is adsorbed into the interior of the micelle which behaves as liquid hydrocarbon. The dirt thus is removed into the micelle from the cloth.
- Applications of emulsions :

i) In washing process of clothes and crockery
ii) In the digestion of fats in intestines. A little amount of fat in the intestines forms soap with alkaline solution of intestines. This soap emulsifies the rest of the fat.
iii) As lotions, creams and ointments in pharmaceuticals and cosmetics.
iv) As drugs of oily type in the form of emulsions to facilitate their easy absorption.
v) In the metallurgy, concentration of ores is carried out through emulsification process.
vi) In the conversion of cream into butter by churning. This is breaking of emulsion of fats in water.
vii) In natural oil wells, oils and water form emulsions. Hence de-emulsification is necessary.

Preparation of colloidal solutions: Lyophobic sols and lyophilic sols are prepared by different methods.

Preparation of lyophobic sols - The methods employed are:

a) Condensation methods
b) Dispersion methods.

Chemical methods:

1) Double Decomposition :

$$As_2O_3 + 3H_2S \rightarrow As_2S_3(sol) + 3H_2O$$

2) Oxidation :

$$2H_2S + SO_2 \rightarrow 2H_2O + S \downarrow$$

3) Reduction:

$AgNO_3$ + Tannic acidAg Sol

$AuCl_3$ + Tannic acid Au Sol

3) Hydrolysis :

$$FeCl_3 + 3H_2O \rightarrow \underset{\text{Red sol (Positive in nature)}}{Fe(OH)_3} + 3HCl$$

Sols of chromium and aluminium can also be prepared by this method.

5) Change of solvent - When ethanolic solution of **sulphur** is added to an excess of water, the sol of **sulphur** is obtained. This is physical method.

Dispersion methods: Here a lump of the substance is broken down to colloidal size in presence of dispersion medium and suitable stabilizer.

Mechanical Dispersion: In this method colloid mill, ball mill or ultrasonic disintegrator is used.

Bredig's arc method (Electrical disintegration) : An arc is struck between two metal electrodes of silver, gold or platinum held at the surface of cold water containing traces of alkali when sol of metal is obtained.

By Peptization: The process of conversion of a precipitated substance into colloidal solution by the addition of a small amount of electrolyte is called peptization.

The electrolyte used for the peptization process is called peptizing agent.

(i) Ferric hydroxide $Fe(OH)_3$ is peptized by ferric chloride giving positive sol. of $[Fe(OH)_3]Fe^{3+}$

(ii) Silver chloride *AgCl* is peptized by *HCl* giving negative sol of $(AgCl)Cl^-$

(iii) Cadmium sulphide CdS is peptized by H_2S giving negative sol of $[CdS]S^{--}$

(iv) Cellulose nitrate is peptized by a mixture of ethanol and water. The product obtained is called "COLLODION".

Purification of Colloidal Solutions

Definition: The process of removal of impurities from colloidal solution is known as purification of colloids.

Colloidal solutions can be purified by the following methods.

a) Dialysis b) Electro dialysis c) ultra filtration

Protective Colloids & Gold number :

* Lyophobic sols are less stable than lyophilic colloids
* On addition of electrolytes lyophobic colloids are precipitated. This phenomenon is called coagulation or flocculation
* Positively charged colloid is coagulated by negative ion and negatively charged colloid is coagulated by the positive ion of the added salt
* The coagulating effect is more when the charge of the ion is more
* A lyophobic sol can be protected from coagulation by adding a lyophilic colloid to the lyophobic sol
* The lyophilic sol added is called protective colloid or protective agent
* Zigmondy introduced the term gold number to measure the protective power of different colloids
* Weight in milligrams of a protective colloid which checks the coagulation of 10 ml of a given gold solution on adding 1 ml of a 10 % solution of sodium chloride is called **gold number**
* Smaller the gold number of a lyophilic colloid, greater is its protective power
* In the given examples

  Gelatin is the most effective protective colloid and starch is the least effective protective colloid
* Gold numbers of some protective colloids

PROTECTIVE COLLOID GOLD NUMBER

Gelatin	0.005-0.01
Hemoglobin	0.03 - 0.07
Casein	0.01 - 0.02
Albumin	0.1 - 0.2
Gum Arabic	0.15 - 0.25
Potato Starch	25

Properties of colloids:

The charge on the colloidal particle (disperse phase) is usually taken as the charge of the colloid

Properties are classified into three types:

1. Optical properties (size of the colloidal particles)
2. Kinetic properties (random motion of the particles)
3. Electrical properties (charge on the colloidal particle)
4. Colour.
5. Colligative properties.

Tyndal effect

* It is an optical property
* The phenomena of the scattering of light by the colloidal particles is called Tyndall effect
* The illuminated beam or cone formed by the scattering of light by the sol particles is referred as Tyndal beam or tyndall cone.
* Tyndall effect is observed only when

i) The diameter of the dispersed particles is not much smaller than the wave length of light used

ii) The refractive indices of the dispersed phase and dispersion medium differ greatly in magnitude

Examples:

1) Blue appearance of sky and sea water
2) Visibility of tails of comets

BROWNIAN MOVEMENT (KINETIC PROPERTY)

* The continuous rapid zig - zag movement executed by colloidal particle in a liquid dispersion medium is called Brownian motion.
* All colloidal particles in colloidal solution exhibits Brownian motion. This is due to bombardment of the particles of the dispersion medium on the particles of dispersed phase.
* Brownian motion is independent of the nature of colloid but depends on the size of the particles and viscosity of solution
* Smaller the size and lesser the viscosity, faster is the motion of colloidal particles
* Brownian movement increases with rise in temperature.

Coagulation of colloidal solution

1. The precipitation of colloidal particles by adding a suitable electrolyte is called coagulation (or) flocculation.
2. The particles of the colloidal solutions possess electrical charge i.e., positive or negative
3. Because of the presence of charge on the colloidal particles, this can be converted into precipitation by the addition of electrolyte (oppositely chargedaion)

4. The ion which responsible for the coagulation of colloid solution is known as effective ion or active ion.
5. The effectiveness of an ion or electrolyte in causing coagulation is dependent on the charge sign and charge magnitude. This fact is enunciated by Hardy and Schulze.

Hardy - Schulze law:

1. The ion with charge opposite to the charge of the colloidal particles is effective in coagulating the colloid

2. Greater the charge of the ion, greater is the coagulating ability of the ion

Positive colloids are coagulated by negative ions or anions of the salt added.

a) $Cl^{-} < SO_4^{-2} < PO_4^{-3}$

b) $[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > C\bar{l}$

Negative colloids are coagulated by positive ions or cations of the salt added.

a) $K^{+} < Ba^{+2} < Al^{+3}$

Blood is positively charged sol (pH=7.4) and is coagulated by alum, $Al_2(SO_4)_3$. These salts lower the pH and denaturate globular proteins.

Flocculation value - The minimum concentration in mill moles per liter required to cause the precipitation of a sol in 2 hours. The smaller the flocculation value, the higher is the precipitating power of an ion.

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