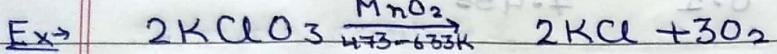
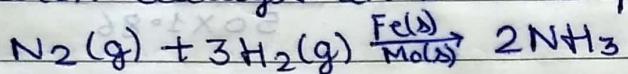


SURFACE CHEMISTRY

Catalysis: Substance which alter 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: Promoters are substances that enhance the activity of a catalyst. Ex → Mo (Molybdenum) acts as promoter for iron catalyst in Haber's process.

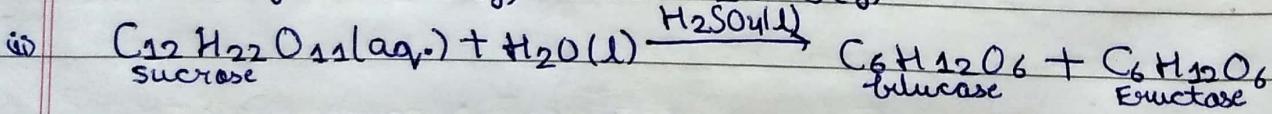
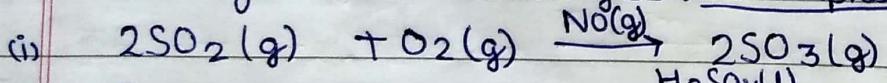


Toxins: Poisons or inhibitors are substance that decrease the activity of a catalyst. Ex → Carbon monoxide (CO) acts as poison for iron catalyst in Haber's process. Therefore it is necessary to remove CO when ammonia is obtained by Haber's process.

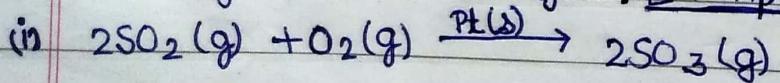
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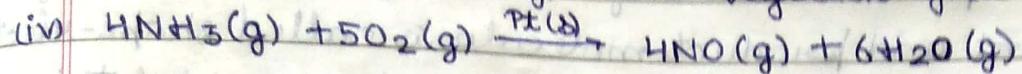
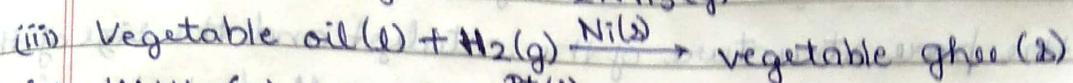
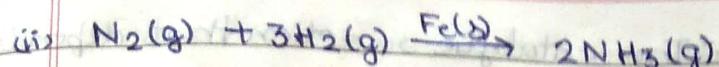
Types of Catalysis

1. Homogeneous catalysis: The process, in which reactants and catalysts are in the same phase, is called homogeneous catalysis. Examples →



2. Heterogeneous catalysis: The process in which the reactants and the catalyst are in different phase is known as heterogeneous catalysis. Examples →





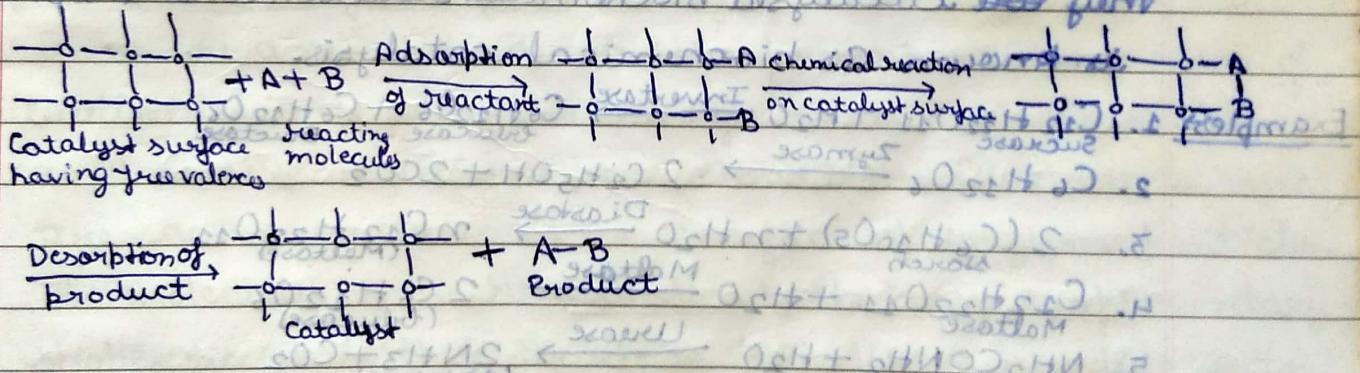
Adsorption theory of heterogeneous catalyst

The modern adsorption theory is the combination of intermediate compound formation theory and old adsorption theory. The mechanism involves five steps:-

- Diffusion of reactants to the surface of the catalyst.
- Adsorption of reactant molecules on the surface of catalyst.
- Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate.

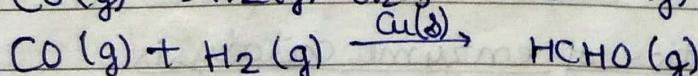
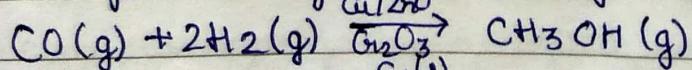
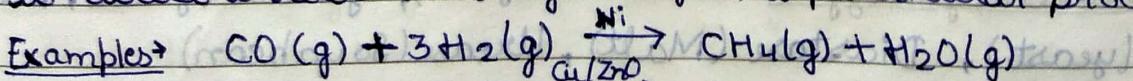
iv) Desorption of reaction products from the catalyst surface and thereby, making the surface available for more reaction to occur.

v) Diffusion of reaction products away from the catalyst's surface.



Activity of catalyst :- Activity of catalyst means its capacity to increase the speed of chemical reaction.

Selectivity of catalyst :- The selectivity of catalyst is its ability to direct a reaction to yield (give) a particular product.



Shape-Selective catalysis :- The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis. Zeolite are good shape-selective catalysts because of their honey comb-like structure.

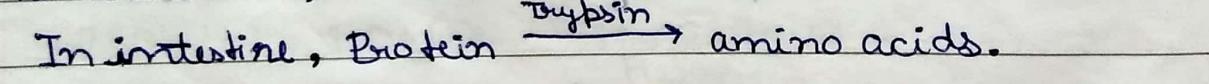
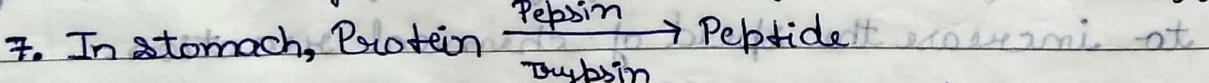
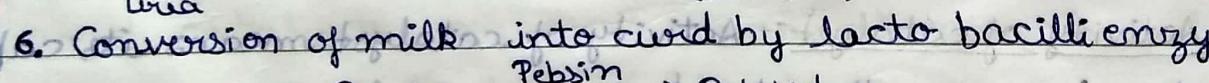
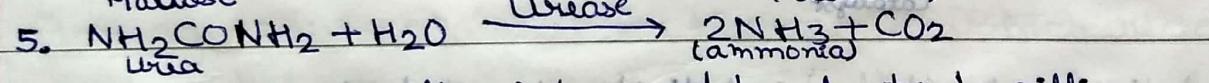
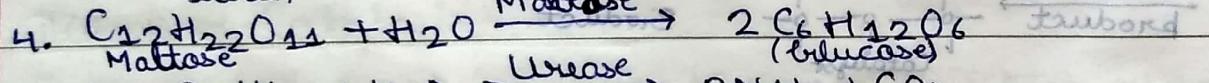
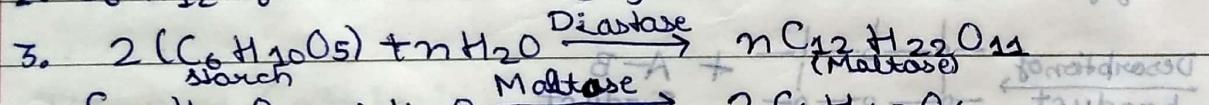
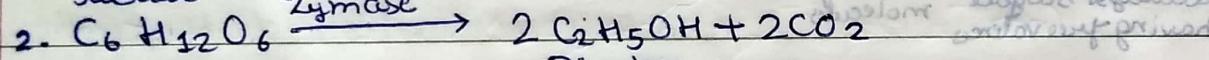
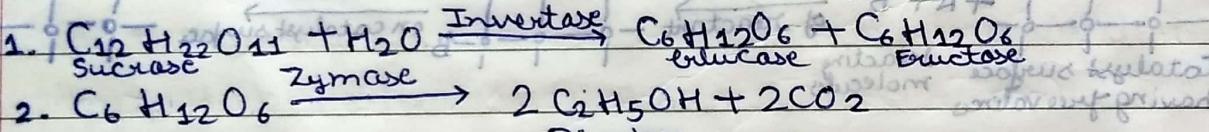
An important zeolite catalyst used in petroleum industry is ZSM-5. It converts alcohols directly into gasoline (Petrol) by dehydrating them to give a mixture of hydrocarbons.

Enzyme

Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. They are actually protein molecules of high molecular mass and form colloidal solutions in water.

Enzymes are termed as biochemical catalysts i.e., they catalysed biochemical reaction and the phenomenon is known as biochemical catalysis.

Example



Sources of enzyme :- Invertase (yeast), Zymase (yeast), Maltase (yeast), Diastase (Malt), Urease (soyabean)

Characteristics of enzyme catalysis

1. Enzymes are highly efficient (i.e. one molecule of an enzyme

may transform one million molecules of the reactant per minute).

2. Enzyme is specific in nature. Example: Enzyme urease catalysis the hydrolysis of urea only.
3. They are highly active under optimum temperature (298-310 K) and optimum pH (5-7).
4. The activity of enzymes is increased in the presence of certain substance, known as co-enzymes.

When a small non-protein (vitamin) is present along with an enzyme, the activity of catalyst is enhanced considerably. Activators are metal ions such as Na^+ , Co^{2+} , Cu^{2+} etc. When metal ions weakly bonded to enzyme molecules, increase activity of catalyst.

5. Enzymes are also inhibited and poisoned by presence of certain substances (drugs and medicines).

Mechanism of enzyme catalysis

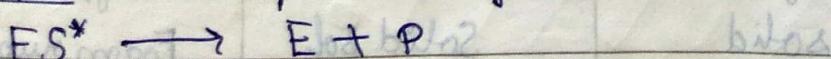
There are a number of cavities present on the surface of enzymes. These cavities are of characteristic shape and possess active groups such as NH_2 , COOH , OH etc. These are active centres on the surface of enzyme particles.

The molecules of the reactant which have complementary shape, fit into these cavities just like a key fits into a lock. An activated complex is formed which then decomposes to yield the products.

The enzyme-catalysed reactions may be considered to proceed in two steps-

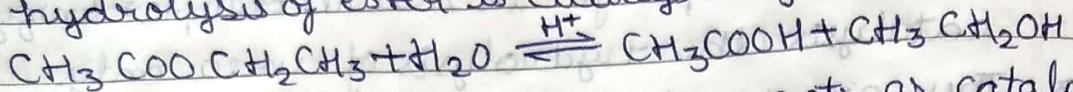
Step 1 → Binding of enzyme to substrate to form an activated complex. $E + S \rightarrow ES^*$

Step 2 → Decomposition of the activated complex to form product.



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

The hydrolysis of ester is catalysed by acid.



The acid produced in the reaction acts as catalyst (auto catalyst) for the reaction. Hence, the reaction becomes faster after some time.

Mixture

Homogeneous

(True solution)

Particle size less than 1nm

Appearance Transparent

Heterogeneous

Colloids

1nm - 100nm

Translucent

Suspension

more than 100nm

opaque

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

The range of diameters of colloidal particles is

between 1 and 1000 nm (10^{-9} to 10^{-6} m)

Classification of colloids

(A) Physical state of dispersed phase and dispersed medium.

S.No	Dispersion phase	Dispersion medium	Type of colloid	Examples
1.	Solid	Solid	Solid sol	coloured glasses, gemstone
2.	Solid	Liquid	Sol	Paints, starch sol
3.	Solid	Gas	Aerosol	Smoke, dust
4.	Liquid	Solid	Gels	Cheese, Butter, jellies
5.	Liquid	Liquid	Emulsion	Milk, hair cream
6.	Liquid	Gas	Aerosol	Fog, mist, cloud
7.	Gas	Solid	Solid sol	Foam rubber, Pumice stone
8.	Gas	Liquid	Foam	Froath, soap, leather

(B) Classification based on nature of interaction between dispersed phase and dispersion medium:-

1. Lyophilic or hydrophilic colloids

The word lyophilic means liquid-loving. Colloidal sols directly formed by mixing substances like gum, gelatine, starch etc. with a suitable liquid are called lyophilic sols.

Lyophilic sols are called reversible sols. This is because after precipitation, the sol can be reconstituted by simply remixing with dispersion medium.

Lyophilic sols are stable due to its high solvation power.

2. Lyophobic (or hydrophobic) colloids

The word lyophobic means liquid-hating substances like metals, their sulphides etc., when simply mixed with liquid do not form colloidal sol. Their sol can be prepared by special method. Such sols are called lyophobic sols.

Lyophobic sols are called irreversible sols. This is because, once precipitated, they do not give back the colloidal sol by simple addition of liquid. Lyophobic sols are unstable.

Types of particles of the dispersed phase

Colloids are classified as multimolecular, macromolecular and associated colloids.

1. Multimolecular colloids: On dissolution, a large no. of smaller molecules of a substance aggregate together to form species having size in the colloidal range. The species thus formed are called multimolecular colloids.

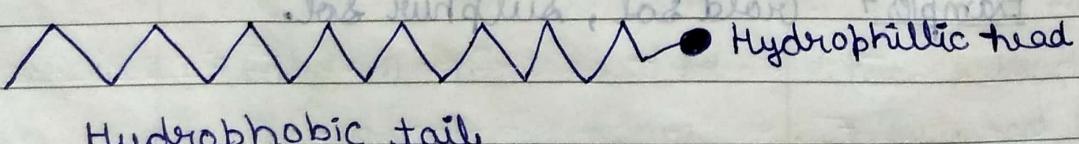
Examples → Gold sol, sulphur sol.

2. Macromolecular colloids :- Macromolecules in suitable solvents form solutions in which the size of the macromolecules may be in the colloidal range. Such colloids are called macromolecular colloids. These colloids are more stable. Examples? Starch, protein.

3. Associated colloids (Micelles) :- There are some substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations behave as normal strong electrolytes, but at higher concentration exhibit colloidal behaviour due to the formation of aggregates. The aggregated particles thus formed are called micelles. These are also known as associated colloids.
 * The formation of micelles takes place only above a temperature called Kraft temperature and above a particular conc. called critical micelle conc. (CMC). For soaps, the CMC is 10^{-4} mol L⁻¹.

Mechanism of mille formation

Soap is sodium or potassium salt of a higher fatty acid may be represented as $R\text{COO}^-\text{Na}^+$ [Example - sodium stearate $(\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-\text{Na}^+$]. When dissolved in water, it dissociates into RCOO^- and Na^+ ions. The RCOO^- ions consist of two parts - a long hydrocarbon chain (non polar tail) which is hydrophobic and a polar group COO^- (polar ionic head) which is hydrophilic.

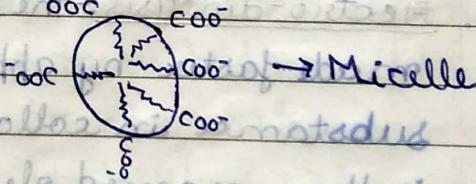


Hydrophobic tail

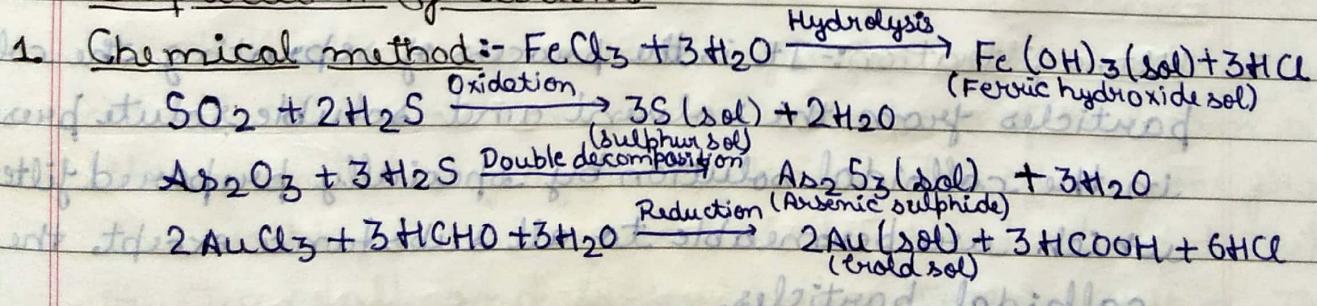
Therefore, RCOO^- ions are present on the surface with their COO^- groups in water and the hydrocarbon chains R- staying away from it and remain at the surface. But at C.M.C., the anions are pulled into the bulk of the solution and aggregate to form a spherical shape with their hydrocarbon chains pointing towards the centre of the sphere with COO^- part remaining outward on the surface of the sphere. An aggregate thus formed is known as ionic micelle. These micelles may contain as many as 100 such ions.

Cleansing action of soap

The cleansing action of soap is due to the fact that soap molecule form micelle around the oil droplet in such a way that hydrophobic part of the RCOO^- ions is in the oil droplet and hydrophilic part project out of the oil droplet like bristles. Since the polar groups can interact with water, the oil droplet surrounded by RCOO^- ions is now pulled in water and removed.



Preparation of colloids



2. Bredig's Arc Method :- Colloidal sols of metals such as gold, silver, platinum etc. can be prepared by this method.

In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium. The intense heat produced vapourises the metal which then condense to form particles of colloidal size.

3. Peptization: It is 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.

* During peptization, one of the ions of peptizing agent adsorbed on the surface of precipitate and develop net charge on precipitate particles.

Purification of colloidal solutions

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

2. Electro-dialysis: The process of dialysis is slow. It can be made faster by applying an electric field if the dissolved substance in colloidal sol is only electrolyte. The process is then named electro-dialysis.

3. Ultrafiltration: It is the process of separating the colloidal particles from the solvent and soluble solute present in the colloidal solution by specially prepared filters, which are permeable to all substance except the colloidal particles.

Colloidion: It is a 4% solution of nitrocellulose in a mixture of alcohol and ether. It is used to

reduced the size of pores of filter paper.

Properties of colloidal solutions

1. Colloidal particles being bigger aggregates, the no. of particles in a colloidal solution is small as compared to a true solution. Hence, value of colligative properties are small.
2. Colour:- The colour of colloidal solution depends on the wavelength of light scattered by the dispersed particles. The wavelength of light depends on the size and nature of particles. The colour of colloidal solution also changes with manner in which the observation receives the light.
For example:- A mixture of milk and water appears blue when viewed by the reflected light and red when viewed by transmitted light.
Finest gold sol is red in colour, as the size of particle increases, it appears purple, then blue and finally golden.
3. Brownian movement:- The zig-zag motion of colloidal particles in sols, is called Brownian movement. Brownian movement is due to unbalanced bombardment of the particles by the molecules of the dispersion medium. It is responsible for the stability of sols.
4. Tyndall effect:- If a beam of light is passed through a colloidal solution in dark, the path of the beam is illuminated by a bluish light. This effect was first observed by Faraday and later studied in detail by Tyndall and is termed as Tyndall effect. The bright cone of the light is called Tyndall cone. The tyndall effect is due to the fact that colloidal particles scatter light in all directions in space.

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

- Diameter of colloidal particles is not much smaller than the wavelength of the light used.
- The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.

Application:- Blue colour of sky.

5. Charge on colloidal particles:- Colloidal particles always carry an electric charge. The nature of this charge is the same on all particles.

Positively charged sols

Negatively charged sols

* Haemoglobin (+ve) [blood \rightarrow (-ve)]

* Metals sol [Au, Ag, Cu]

* Oxides (TiO_2 sol)

* Sol's of starch, gum, gelatin etc.

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

* Metallic sulphides (As_2S_3 , Cd)

* Hydrated metallic oxides

* Acid dye stuffs-

$Al_2O_3 \cdot nH_2O$, $Fe_2O_3 \cdot nH_2O$ etc.

eosin, congo red sols.

Cause of charge:- The charge on the sol particle is due to:-

1. Electron capture by sol particle during electrodispersion of metal.

2. Preferential adsorption of ions from solution.

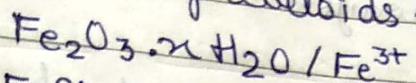
Examples:-

(a) When silver nitrate solution is added to KI sol, the precipitated AgI adsorbs I^- ions from dispersion medium and negatively charged colloidal solution formed AgI/I^- .

When KI solution is added to $AgNO_3$ solution, positively charged solution of colloids formed due to adsorption of Ag^+ ions from dispersion medium.

AgI/Ag^+ .

(B) If FeCl_3 is added to excess of hot water, a positively charged sol of colloids formed.



When FeCl_3 is added to NaOH , a negatively charged sol is formed. $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}/\text{OH}^-$,

Helmholtz electrical double layer.

When one type of ions of electrolyte are adsorbed on the surface of the colloidal particles, it forms a fixed layer. It attracts the counter-ions from the medium forming a second layer which is mobile and is called diffused layer. The double layer of opposite charges thus formed is called Helmholtz electrical double layer.

As a result, a difference of potential exists between the fixed layer and diffused layer. This potential difference is known as zeta potential or electrokinetic potential.

6. Electrophoresis: When electric potential is applied across two platinum electrodes dipping in a colloidal solution, the colloidal particles under an applied electric potential is called electrophoresis or cataphoresis.

Electroosmosis

When electrophoresis is prevented by some suitable means, it is observed that the dispersion medium start to move in an electric field. This phenomenon is known as electro osmosis.

Coagulation or Precipitation

The process of settling of colloidal particles is called Coagulation.

The coagulation of the lyophobic sols can be carried out in the following ways:

- (i) By electrophoresis
 - (ii) By mixing two oppositely charged sol
 - (iii) By Boiling
 - (iv) By persistent dialysis
 - (v) By addition of electrolytes: When excess of an electrolyte is added, the colloidal particles are precipitated. The reason is that colloids interact with ions carrying charge opposite to that present on themselves. This cause neutralisation leading to their coagulation.
- The ion responsible for neutralisation leading to their coagulation is called coagulating ion (or flocculating ion).

Hardy-Schulze rule: The greater the valence of the flocculating ion added, the greater is its power to cause precipitation.

This is known as Hardy-Schulze rule.

In the coagulation of a negative sol, the flocculating power is in the order $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$.

Similarly, in the coagulation of a positive sol, the flocculating power $\rightarrow [\text{Fe}(\text{CN})_6]^{4-} > \text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$

Coagulating Value

The minimum concentration of an electrolyte in milligrams per litre required to cause precipitation of a sol in two hours is called coagulating value.

The smaller the quantity needed, the higher will be the coagulating power of an ion.

Coagulation of Lyophilic sol

Lyophilic sols are more stable than lyophobic sols due to high solvation power.

Therefore, a lyophilic sol can be coagulated =

(i) by adding electrolyte.

(ii) by adding suitable solvent.

8. Protection of colloids

When Lyophilic sol is added to the Lyophobic sol, the Lyophilic particles form a layer around Lyophobic particles and thus protect the Lyophobic sol from electrolytes. Lyophilic colloids used for this purpose are called protective colloids.

Emulsions

Emulsions are liquid-liquid colloidal system. There are two types of emulsions:-

(i) Oil dispersed in water (O/W) type \Rightarrow Examples \rightarrow Milk, Vanishing cream.

(ii) Water dispersed in oil (W/O) type \Rightarrow Example \rightarrow Butter, cold cream.

Emulsifying agent

Emulsions are unstable. For stabilisation of an emulsion, a

third component called emulsifying agent is usually

added. The emulsifying agent forms an interfacial film between suspended particles and dispersion medium. Examples

Demulsification:- The process of separation of the constituent liquids of an emulsion is called demulsification.

Example \rightarrow Centrifuging, boiling, freezing etc.

Applications of emulsion

- (i) Milk
- (ii) Oily drugs
- (iii) Cleansing action of soap for washing clothes.
- (iv) Digestion of fats in intestines take place by process of emulsification.

Applications of colloid

1. Blue colour of sky: Dust particles along with water suspended in air scatter blue light which reaches our eyes and the sky looks blue to us.
2. Blood is a colloidal solution of albuminoid substance. The styptic action of Alum and FeCl_3 solution is due to coagulation of blood forming a clot which stops further bleeding.
3. River water is a colloidal solution of clay. Sea water contains a number of electrolytes. When river water meets the sea water, the electrolyte present in sea water coagulates the colloidal solution of clay resulting in its deposition with the formation of delta.
4. Smoke is a colloidal solution of solid particles such as carbon, arsenic compounds, dust etc. in air. The smoke, before it comes out from the chimney is led through 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. And the particles are settle down on the floor of the chamber. The precipitator is called Scott's precipitator.
5. Tanning:- Animal hide (Colloidal in nature), which has positively charged particles, is soaked in tannin (which contains negatively charged colloidal particles), mutual coagulation takes place. This results in the hardening of leather. This process is known as tanning.

6. Photography:- A colloidal solution of AgBr in gelatine is applied on glass plates or celluloid films to form sensitive plates in photography.
7. Artificial rain can be caused by spraying electrified or oppositely charged colloidal dust particles over a cloud. The colloidal water particles present in cloud will get neutralized and coagulate to form bigger water drops causing artificial rain.
8. Medecines:- Argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing Kalaazar. Colloidal gold is used for intramuscular injection because they have large surface area and are easily assimilated.

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