5 Surface Chemistry

LESSON AT A GLANCE

- **Adsorption:** The formation of a layer of gas on the surface of a solid, or less frequently, of a liquid. There are two types depending on the nature of the forces involved. In chemisorption a single layer of molecules, atoms, or ions is attached to the adsorbent surface by chemical bonds. In physisorption adsorbed molecules are held by the weaker van der Waals' forces.
- **Adsorbate:** The substance adsorbed is known as adsorbate.
- **Adsorbent:** Substance on which adsorption takes place is known as adsorbent.
- **Physisorption:** Adsorbate is held to the adsorbent by weak van der Waals' forces.
- **Chemisorption:** Adsorbate is held to the adsorbent by strong chemical bond.
- **Factors affecting adsorption:** The extent of adsorption of a gas on a solid depends upon nature of gas, nature of solid, surface area of the solid, pressure of gas and temperature of gas.
- **Adsorption isotherm:** The relationship between extent of adsorption (x/m) and pressure of gas at constant temperature is known as adsorption isotherm.
- **Catalyst:** A catalyst is a substance which enhances the rate of chemical reaction without itself getting used up in the reaction.
- The phenomenon of using catalyst is known as catalysis.
- **Homogeneous catalysis:** In this process catalyst is in the same phase as on the reactants.
- **Heterogeneous catalysis:** Catalyst is in a different phase from that of the reactants.

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- **Colloidal solutions:** Colloidal solutions are in intermediate between true solutions and suspension.

  Size of the particles ranges from 1 to 1000 nm.
- **Coagulation:** Process of changing the colloidal particles in a sol into insoluble precipitate by addition of some suitable electrolyte is known as coagulation.
- **Emulsions:** Emulsions are colloidal systems in which both dispersed phase and dispersion medium are liquids.
- **Desorption:** The process of removing an adsorbed substance from a surface on which it is adsorbed is called desorption.
- **Sorption:** When adsorption and absorption takes place simultaneously, it is called sorption, *e.g.* dying of cotton fabrics. The dye is adsorbed on the surface of the cotton fibre but after it is dyed, the fibre dye gets uniformed throughout.
- **Promoters:** Promoters are the substances that enhance the activity of a catalysts.

  For example, in Haber's process for the manufacture of ammonia, molybdenum is used as a promoter which increases the activity of iron used as a catalyst.

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

- **Catalytic Poisons (Inhibitors):** Those substances which decrease the activity of catalyst are called catalytic poisons or inhibitors. *e.g.* arsenic acts as catalytic poison in the manufacture of sulphuric acid by contact process.
- **Colloids:** A colloid is a heterogeneous system in which one substance is dispersed as very fine particles in another substance called dispersion medium colloidal particles one larger than simple molecules but small enough to remain suspended.

  Their range of diameters is between (10^{-9} to 10^{-6} m).

  Colloids are classified on the basis of following criteria:

  (*i*) Physical state of dispersed phase and dispersion medium.

  (*ii*) Nature of interaction between dispersed phase and dispersion medium

  (*iii*) Type of particles of the dispersed phase

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TEXTBOOK QUESTIONS SOLVED

5.1 *Distinguish between the meaning of the terms adsorption and absorption. Give one example of each.*

Ans. In adsorption the substance is retained at the surface of the other substance while in absorption it is distributed uniformly throughout the other substance.

Example: Water is adsorbed by silica gel but is absorbed by anhydrous calcium chloride.

5.2 *What is the difference between physisorption and chemisorption?*

Ans.

Physisorption	Chemisorption
1. Non-specific in nature.	1. Highly specific in nature. It can occur between specific pairs of adsorbent and adsorbate where there is possibility of bond formation between them.
2. Reversible in nature. Desorption occurs on decreasing the pressure of the adsorbate gas and/or increasing the temperature.	2. Irreversible in nature. The compound formed between adsorbent and adsorbate can not be broken by changing temperature or pressure.
3. It arises due to van der Waals' forces.	3. It arises due to chemical bond formation.
4. It depends upon nature of gas. More easily liquifiable gases are adsorbed more readily.	4. It depends upon the nature of adsorbent and adsorbate both.
5. Enthalpy of adsorption is low (20–40 kJ mol^{-1}).	5. Enthalpy of adsorption is high (80–240 kJ mol^{-1}).
6. It is favoured at low temperature.	6. It is favoured at high temperature.
7. Multimolecular layer is formed.	7. Unimolecular layer is formed.

5.3 *Give reason why a finely divided substance is more effective as an adsorbent.*

Ans. It is because finely divided substance has a large surface area.

5.4 *What are the factors which influence the adsorption of a gas on a solid?*

Ans. The factors that influence adsorption are the following:

(*i*) *Nature of adsorbate:* Easily liquifiable gases like H_2S, NH_3, SO_2 are adsorbed more readily than the ones which are difficult to liquify like H_2, N_2, O_2, etc.

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(ii) *Nature of adsorbent and their surface area:* Porous substancess like charcoal and silica gel are better adsorbents than non-porous substance. In finely divided state, adsorbing power of any substance is much more than in a more compact form.

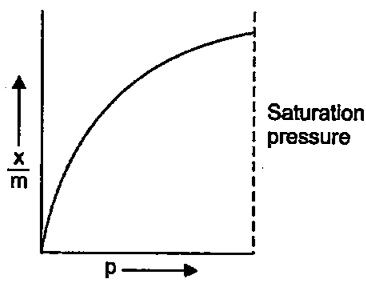
(iii) *Pressure of the adsorbate gas:* At a constant temperature, the adsorption of a gaseous adsorbate increases with increase in pressure. The effect is more pronounced at low pressures.

(iv) *Temperature:* Low temperature favours adsorption. As temperature increases, the adsorption decreases.

5.5 *What is an adsorption isotherm? Describe Freundlich adsorption isotherm.*

Ans. An adsorption isotherm depicts the effect of pressure of adsorbate gas on its adsorption at a constant temperature.

Freundlich adsorption isotherm. Freundlich in 1909 gave an empirical relationship between the quantity of gas adsorbed by unit mass of the solid adsorbent and pressure of particular temperature. The relationship can be expressed by:



$$\frac{x}{m} = k \cdot P^{1/n} \ (n>1)$$

x = mass of the gas adsorbed

m = mass of the adsorbent at pressure P

n and k = Constant which depends on the nature of the adsorbent and the gas at a particular temperature.

5.6 *What do you understand by activation of adsorbent? How is it achieved?*

Ans. Activation of adsorbent means increasing its adsorbing power. It is achieved by one or more of the following steps:

(i) *By finely dividing the adsorbent:* When adsorbent is finely divided, its particle size decreases and surface area per unit mass increases. This increases the adsorbing power of the adsorbent.

(ii) *By making the surface rough:* When surface of adsorbent is made rough, its surface area as well as adsorbing power increases. It can be achieved in many ways, like

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mechanical rubbing of the surface, chemical action of a suitable reagent and *electro-deposition* of metal on a strip of its own (*e.g.*, electroplating of platinum on the surface of platinum strip).

(*iii*) *By making the surface of adsorbent free of any adsorbate:* At room temperature, the surface of any adsorbent is partially covered by atmospheric gases or other substance that come in its contact. These can be removed by heating the adsorbent and then cooling it in absence of adsorbates. For example, charcoal is activated by heating it in superheated steam or in vaccum.

5.7 *What role does adsorption play in heterogeneous catalysis?*

Ans. In hetrogeneous catalysis, the reactant molecules diffuse to the surface of the catalyst and get adsorbed on it. An intermediate is formed in the adsorbed state which involves less activation energy than that of uncatalysed reaction. The intermediate is converted into products which get desorbed and diffuse away making the surface available for more reaction to occur. Thus, the catalyst increases the rate of reaction by decreasing the activation energy.

5.8 *Why is adsorption always exothermic?*

Ans. During adsorption there is always decrease in residual forces of the adsorbent. This decreases the surface energy which appears as heat. Thermodynamically, there is always decrease in entropy (ΔS = – ve) during adsorption because the freedom of adsorbate molecules to move randomly is restricted. Adsorption occurs spontaneously, therefore, ΔG must be negative at constant temperature and pressure since $\Delta G = \Delta H - T\Delta S$. This can happen only if ΔH is sufficiently high negative so that it can more than compensate for the term $-T\Delta S$ which is positive.

5.9 *How are the colloidal solutions classified on the basis of physical states of the dispersed phase and dispersion medium?*

Ans. Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gases, eight types of colloidal systems are possible A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system.

Many familiar commercial products and natural objects are colloids.

For example: Whipped cream in a foam, which is a gas dispersed in a liquid.

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Most biological fluids are aqueous sols (Solids dispersed in water)

	Dispersed Phase	*Dispersion Medium*	*Types of Colloids*	*Examples*
1.	Solid	Solid	Solid sol	Some coloured glasses, gem stoves,
2.	Solid	Liquid	Sol	Paints, colloids
3.	Solid	Gas	Aerosol	Smoke, dust
4.	Liquid	solid	Gel	Cheese, butter
5.	Liquid	Liquid	Emulsion	Milk, hair creame,
6.	Liquid	Gas	Aerosol	Fog, mist, cloud.
7.	Gas	Solid	Solid sol	Pumic stone, foam rubber.
8.	Gas	Liquid	Foam	Fork, whipped cream, soap leather.

5.10 *Discuss the effect of pressure and temperature on the adsorption of gases on solids.*

Ans. Effect of temperature: Studying the adsorption of any particular gas by some particular adsorbent it is observed that the adsorption decreases with increase of temperature and vice versa. **For example:** One gram of charcoal adsorbs about 10 cm^2 of N_2 at 273 K, 20 cm^3 at 244 K and 45 cm^3 at 195 K.

The decrease of adsorption with increase of temperature may be explained as follows:

$$\text{Gas (Adsorbate)} + \text{Solid (Adsorbent)} \underset{\text{Evaporation}}{\overset{\text{Condensation}}{\rightleftharpoons}} \text{Gas adsorbed on solid} + \text{Heat}$$

Applying the Chatelier's principle, it can be seen that increase of temperature decreases the adsorption and vice-versa.

Effect of pressure: At constant temperature the adsorption of a gas increases with increase of pressure. It is observed that at 100 temperature, the adsorption of a gas increases very rapidly as the pressure is increased from small values.

5.11 *What are lyophillic and lyophobic sols? Give one example of each type. Why are hydrophobic sols easily coagulated?*

Ans. Lyophilic Sols: Colloidal sols directly formed by mixing substances like gums gelatine, starch, rubber *etc.*, with

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a suitable liquid (The dispersion medium) are lyophilic sols.

An important characteristic of these sols is that if the dispersion medium is separated from the dispersed phase (say by evaporation) the sol can be reconstituted by simply remixing with the dispersion medium. That is why these sols are also called reversible sols. These sols are quite stable and cannot be easily coagulated.

Lyophobic sols: Their colloidal sol can be prepared by only special methods. These sols are readily precipitated on the addition of small amounts of electrolytes, by heating or by shaking and hence are not stable.

Lyophobic sols are not very stable and are stabilised by the presence of similar charges on their particles and the repulsive forces between the charged particles prevent them from coalescing. This charge can be easily removed by addition of a small amount of an electrolyte or electrophoresis or by mixing two oppositely charged sols. They can also be coagulated by boiling or persistent dialysis which removes the charges.

5.12 *What is the difference between multimolecular and macromolecular colloids? Give one example of each. How are associated colloids different from these two types of colloids?*

Ans. Multimolecular colloids are formed by aggregation of large number of molecules, for example, sols of gold or silver contain particles consisting of large number of their atoms. Macromolecular colloids consist of particles of colloidal size (1–1000 nm), *e.g.*, polythene. Associated colloids are made of substances which are strong electrolytes at low concentrations which dissociate in their solutions. Above a certain concentration, large number of their ions combine and form micelles of colloidal size. Soaps are examples of this type.

5.13 *What are enzymes? Write in brief the mechanism of enzyme catalysis.*

Ans. 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. They are very effective catalysts, catalyse numbers reactions, especially those connected with natural processes.

The enzymes are, thus termed as biochemical catalysts.

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Many enzymes have been obtained in pure crystalline state from living cells.

The following are some of the examples of enzyme-catalysed reactions:

(*i*) **Inversion of cane sugar:** The Invertase enzyme converts cane sugar into glucose and fructose.

$$\underset{\text{cane sugar}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{Fructose}}{C_6H_{12}O_6(aq)}$$

(*ii*) **Conversion of glucose into ethyl alcohol:** The zymases enzyme converts glucose into ethyl alcohol and carbon dioxide.

$$C_6H_{12}O_6(aq) \xrightarrow{\text{Zymase}} 2C_2H_5OH(aq) + 2CO_2(q)$$

Mechanism of enzyme catalysis: There are number of cavities present on the surface of colloidal particles of enzymes. These cavities are of characteristic shape and possess active groups such as $-NH_2$, $-COOH$, $-5H$, $-OH$ *etc.*, These are actually the active centres on the surface of enzyme particles. The molecules of the reactant (substrata) which have complementary shape, fit into these cavities just like a key fits into a lock. On account of the presence of active groups, an activated complex is formed which then decomposes to yield the products.

Thus, the enzyme-catalysed reactions may be considered to proceed in two steps:

Step I: Binding of enzyme to substrate to form an activated complex.

$$E + S \longrightarrow ES^{\neq}$$

Step II: Decomposition of the activated comply to form the product

$$ES^{\neq} \longrightarrow E + P$$

5.14 *How are colloids classified on the basis of*

(*i*) *physical states of components,*

(*ii*) *nature of dispersion medium, and*

(*iii*) *interaction between dispersed phasee and dispersion medium?*

Ans. (*i*) Depending upon the physical states of components eight types of colloidal system are possible.

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The examples of the various types of colloids along with their typical names arelisted below:

	Dispersed Phase	*Dispersion Medium*	*Types of Colloids*	*Examples*
1.	Solid	Solid	Solid sol	some coloured glasses, gem stones,
2.	Solid	Liquid	Sol	paints, cellfluids.
3.	Solid	Gas	Aerosol	smoke, dust
4.	Liquid	solid	Gel	cheese, butter
5.	Liquid	Liquid	Emulsion	milk, hair cream,
6.	Liquid	Gas	Aerosol	fog, mist, cloud.
7.	Gas	Solid	Solid sol	pumice stone, foam rubber.
8.	Gas	Liquid	Foam	froth, whipped cream soap leather.

(*ii*) Depending upon the type of the particles of the dispersed phase, colloids are classified as: Multimolecular macromolecular and associated colloids.

(*a*) ***Multimolecular colloids***: The colloids in which the colloidal particles consist of aggregates of atoms or small molecules with diameters of cells than 1 *nm* are called multimolecular colloids

For Example: A gold sol may contain particles of various sizes having several atoms of gold, a sulphur sol consists of particles containing about a thousand of 58 molecules. They are held together by van der waals' forces.

(*b*) ***Macromolecular colloids***: These are the colloids in which the dispersed particles are themselves large molecules (usually polymers).

Since these molecules have dimensions comparable to those of colloidal particles, their dispersions are called macromolecular colloids

Example: Proteins, starch and cellulose form macromolecular colloids.

(c) ***Associated colloids (Micelles)***: Those colloids which behave as normal strong electrolyse at low concentration but show colloidal properties at higher

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concentrations due to the formation of aggregated particles of colloidal dimensions.

Such substances are also referred to as associated colloids.

(*iii*) Depending upon the nature of interaction between the dispersed phase and the dispersion medium colloidal sols are divided into two types:

(*a*) ***Lyophilic colloids*:** (Solvent attracting) Colloidal sols directly formed by mixing substances like gum, gelatine, starch, rubber etc. with a suitable liquid are called lyophilic sols. They are reversible sols. They are quite stable and cannot be easily coagulated.

(*b*) ***Lyophobic colloids*:** (Solvent repelling) Substances like metals, their sulphides etc. when simply mixed with the dispersion medium do not form the colloidal sols. Their colloidal sols can be prepared only by special methods. These sols are readily precipitated on the addition of small amounts of electrolytes by heating or by shaking and hence are not stable. These sols are also called irreversible sol.

5.15 *Explain what is observed*

(*i*) *when a beam of light is passed through a colloidal sol.*

(*ii*) *an electrolyte, NaCl is added to hydrated ferric oxide sol.*

(*iii*) *electric current is passed through a colloidal sol.?*

Ans. (*i*) When beam of light is passed through a colloidal sol, Tyndall effect is observed and the path of beam becomes visible due to scattering of light.

(*ii*) When the elctrolyte NaCl is added to the sol of hydrated ferric oxide, the charge on the colloidal particles is neutralised by the oppositely charged ions provided by NaCl resulting in its coagulation.

(*iii*) On passing electric current through a colloidal sol, electrophoresis occurs and sol particles move towards oppositely charged electrode and get coagulated.

5.16 *What are emulsion? What are their different types? Give example of each type.*

Ans. Emulsions are colloidal system in which dispersed phase and dispersion medium both are liquids. Types: (1) Oil in water type, *example, milk.*

(2) Water in oil type, *example, butter.*

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5.17 *What is demulsification? Name two demulsifiers.*

Ans. Demulsification is the process of breaking up of an emulsion. It can be done by freezing or centrifugation.

5.18 *Action of soap is due to emulsification and micelle formation. Comment.*

Ans. Cleansing action of soaps is due to the fact that their molecules form micelle around oil droplets such that they completely surround it with their polar ends projecting outwardly. The oil droplets surrounded by stearate ions are pulled away from cloth into water forming emulsion which is washed away. Thus the cleansing action of soaps involves micelle formation and emulsification both.

5.19 *Give four examples of heterogeneous catalysis.*

Ans. (*i*) Oxidation of sulphur dioxide into sulphur trioxide in the presence of pt.

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

(*ii*) Combination between dinitrogen and dihydrogen to form ammonia in the presence of finely divided ion in Haber's process.

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

The reactants are in gaseous state while the catalyst is in the solid state.

(*iii*) Oxidation of ammonia into nitric oxide in the presence of platinum gauze in Ostwald's process.

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

The reactants are in gaseous state while the catalyst is in the solid state.

(*iv*) Hydrogenation of vegetable oils in the presence of finely divided nickel as catalyst.

$$\text{vegetable oils}(l) + H_2(g) \xrightarrow{Ni(s)} \text{vegetable ghee (s)}$$

One of the reactants is in liquid state and the other in gaseous state while the catalyst is in the solid state.

5.20 *What do you mean by activity and selectivity of catalysts?*

Ans. *Activity* of a catalyst is its effectiveness or efficiency as catalyst and depends upon strength of chemisorption of reactants which should be optimum, neither too weak nor too strong. Selectivity of a catalyst is its ability to result in formation of a particular product.

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5.21 *Describe some features of catalysis by zeolites.*

Ans. Zeolites are good shape-selective catalysts because of their honey-comb like structures. They are microporous alumno silicates with three dimensional network of silicates in which some silicon atoms are replaced by aluminium atoms giving Al–O–Si framework.

Zeolites are being very widely used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation. An important zeolite catalyst used in the petroleum industry is ZSN – 5. It converts alcohols directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons.

5.22 *What is shape selective catalysis?*

Ans. 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. Zeolites are good shape-selective catalysts because of their honey-comb-like structures.

5.23 *Explain the following terms:*

(*i*) *Electrophoresis* (*ii*) *Coagulation*

(*iii*) *Dialysis* (*iv*) *Tyndall effect*

Ans. (*i*) ***Electrophoresis*:** The movement of colloidal particles under an applied electric potential is called electrophoresis. Positively charged particles move towards the cathode while negatively charged particles move towards anode.

(*ii*) ***Coagulation*:** The stability of the lyophobic sols is due to the presence of charge on colloidal particles. If somehow, the charge is removed, the particles will come nearer to each other to form aggregates and settle down under the force of gravity.

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

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

(*a*) By electrophoresis

(*b*) By mixing two oppositely charged sols.

(c) By boiling.

(*d*) By persistent dialysis.

(*e*) By addition of electrolytes.

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(*iii*) ***Dialysis***: It is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane. Since particles (ions or smaller molecules) in a true solution can pass through animal membrane (bladder) or parchment paper or cellophane sheet but not the colloidal particles, the membrane can be used for dialysis.

The apparatus used for this purpose is called dialyser. A bag of suitable membrane containing the colloidal solution is suspended in a vessel through which fresh water is continuously flowing. The molecules and ions diffuse through membrane into the outer water and pure colloidal solution is left behind.

(*iv*) ***Tyndall effect***: This effect was first observed by Faraday and later studied in detail by Tyndall and is termed as Tyndall effect.

The tyndall effect is due to the fact that colloidal particles scatter light in all directions in space. This scattering of light illuminates the path of beam in the colloidal dispersion. Tyndall effect is observed only when the following two conditions are satisfied:

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

(*ii*) The retractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.

5.24 *Give four uses of emulsions.*

Ans. (*i*) Synthetic paints for painting of walls are emulsions.

(*ii*) Cleansing action of soaps and detergents is based on the formation of *oil in water* type emulsions.

(*iii*) Photographic films and plates are made by applying a coating of an emulsion of light sensitive silver bromide in gelatine.

(*iv*) Digestion of fat in our body occurs through its emulsification in intestines.

5.25 *What are micelles? Give an example of a micellers system.*

Ans. Micelles are also known as associated colloids.

They behave as normal strong electrolyte at low concentrations but show colloidal properties at higher concentration due to the formation of aggregated particles of colloidal dimension.

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Surface active agents like soap and synthetic detergents belong to this class.

5.26 *Explain the terms with suitable examples:*

(*i*) *Alcosol* (*ii*) *Aerosol* (*iii*) *Hydrosol*

Ans. (*i*) *Alcosol:* It is a colloidal system in which particles of a solid (dispersed phase) are dispersed in alcohol (dispersion medium), *e.g.*, colloidal solutions of silver or gold in alcohol.

(*ii*) *Aerosol:* Aerosols are colloidal solutions in which a solid or a liquid is dispersed in a gaseous medium, *e.g.*, smoke or fog.

(*iii*) *Hydrosol:* Hydrosols are colloidal solutions in which a solid is dispersed in water, *e.g.*, mud.

5.27 *Comment on the statement that "colloid is not a substance but a state of substance".*

Ans. The statement that "colloid is not a substance but a state of substance" is correct. Any substance can attain this state under suitable conditions when size of its particles is in the range 1 nm-1000 nm and it is dispersed in a suitable medium. Sulphur is ordinarily a crystalloid but can become a colloid under suitable conditions. Soaps and detergents form true solutions when dilute but colloidal solution when their concentration is increased beyond a certain value (critical micelle concentration).

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