الجامعة التكنولوجية

قسم الهندسة الكيمياوية

المرحلة الثانية

الكيمياء الفيزياوية

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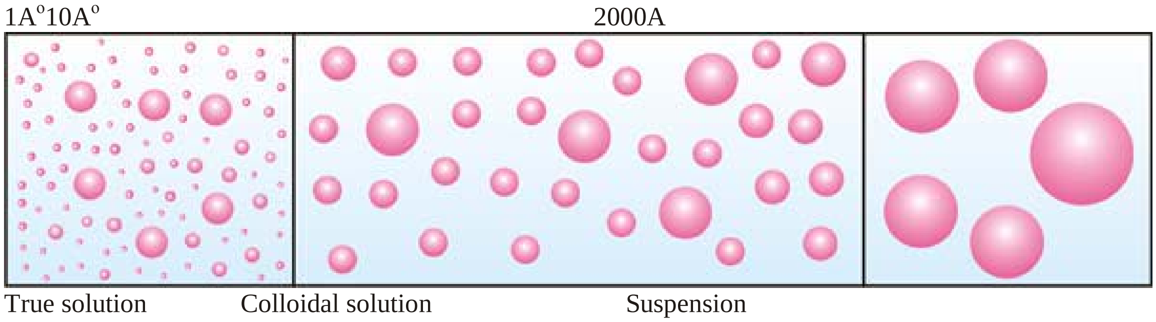
Colloid

Thomas Graham (1861) studied the ability of dissolved substances to diffuse into water across a permeable membrane. He observed that crystallinesubstances such as sugar, urea, and sodium chloride passed through themembrane, while others like glue, gelatin and gum arabic did not.

The former he called crystalloids and the latter colloids (Greek, kolla = glue ; eidos = like). Graham thought that the difference in the behavior of‘crystalloids’ and ‘colloids’ was due to the particle size. Later it was realised that any substance, regardless of its nature, could be converted into a colloid by subdividing it into particles of colloidal size.

In a true solution as sugar or salt in water, the solute particlesare dispersed in the solvent as single molecules or ions. Thusthe diameter of the dispersed particles ranges from 1Å to 10 Å.

On the other hand, in a suspension as sand stirred intowater, the dispersed particles are aggregates of millions ofmolecules. The diameter of these particles is of the order 2,000 Å or more.



Particle size (indicated by diameter) range of true solution, colloidal dispersion, and suspension

The colloidal solutions or colloidal dispersions are intermediate between true solutions andsuspensions.In other words, the diameter of the dispersed particles in a colloidal dispersion is morethan that of the solute particles in a true solution and smaller than that of a suspension.

When the diameter of the particles of a substance dispersed in a solvent ranges from about 10Å to 2,000 Å, the system is termed a colloidal solution, colloidal dispersion, or simply a colloid.The material with particle size in the colloidal range is said to be in the ***colloidal state.***

Types of colloidal systems

As we have seen above, a colloidal system is made of two phases. The substance distributed as the colloidalparticles is called the **Dispersed phase.** The second continuous phase in which the colloidal particles are dispersed is called the **Dispersion medium.** For example, for a colloidal solution of copper in water, copper particles constitute the dispersed phase and water the dispersion medium.

As stated above, a colloidal system is made of a dispersed phase and the dispersion medium. Because either the dispersed phase or the dispersion medium can be a gas, liquid or solid, there are eight types of colloidal systems possible. A colloidal dispersion of one gas in another is not possible since the two gases would give a homogeneous molecular mixture.

Type Name	Dispersed Phase	Dispersion medium	Examples
Foam	gas	liquid	whipped cream, shaving cream, soda-water
Solid foam	gas	solid	froth cork, pumice stone, foam rubber
Aerosol	liquid	gas	for, mist, clouds
Emulsion	liquid	liquid	milk, hair cream
Solid emulsion (gel)	liquid	solid	butter, cheese
Smoke	solid	gas	dust, soot in air
Sol	solid	liquid	paint, ink, colloidal gold
Solid sol	solid	solid	ruby glass (gold dispersed in glass), alloys.

The name given to the colloid depends on the two phases involved. A **sol** is a dispersionof a solid in a liquid (such as clusters of gold atoms in water) or of a solid in a

solid (such as ruby glass, which is a gold-in-glass sol, and achieves its colour by lightscattering). An **aerosol** is a dispersion of a liquid in a gas (like fog and many sprays) ora solid in a gas (such as smoke): the particles are often large enough to be seen with amicroscope. An **emulsion** is a dispersion of a liquid in a liquid (such as milk).

A further classification of colloids is as **lyophilic**, or solvent attracting, and **lyophobic**,

solvent repelling. If the solvent is water, the terms **hydrophilic** and **hydrophobic**, respectively, are used instead. Lyophobic colloids include the metal sols.

Lyophiliccolloids generally have some chemical similarity to the solvent, such as -OH groupsable to form hydrogen bonds. A **gel** is a semirigid mass of a lyophilic sol in which allthe dispersion medium has penetrated into the sol particles.

In this chapter we will restrict our study mainly to the colloidal systems which consist of a solidsubstance dispersed in a liquid. These are frequently referred to as **Sols** or **Colloidal solution.**

Thecolloidal solutions in water as the dispersion medium are termed **Hydrosols or Aquasols.** When thedispersions medium is alcohol or benzene, the sols are referred to as **Alcosols** and **Benzosols**respectively.

Sols are colloidal systems in which a solid is dispersed in a liquid.

These can be subdivided into two classes :

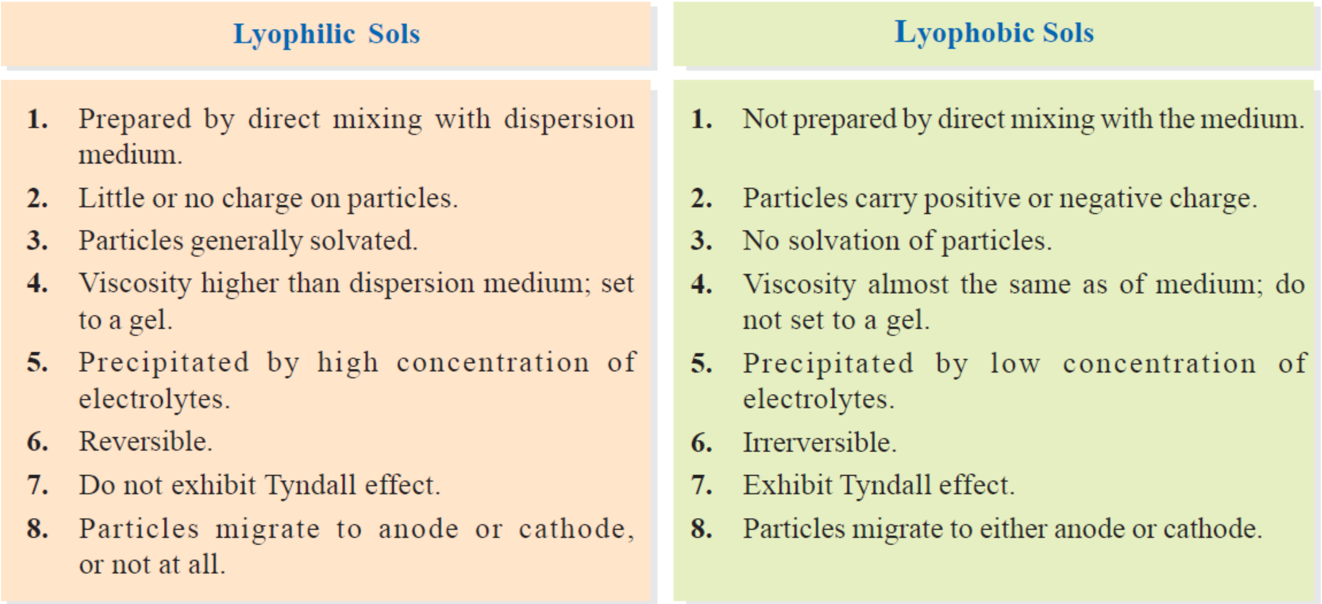
(*a*) Lyophilic sols (solvent-loving)

(*b*) Lyophobic sols (solvent-hating)

*Lyophilic sols are those in which the dispersed phase exhibits a definite affinity for the mediumor the solvent.*The examples of lyophilic sols are dispersions of starch, gum, and protein in water.

Lyophobic sols are those in which the dispersed phase has no attraction for the medium or thesolvent.The examples of lyophobic sols are dispersion of gold, iron (III) hydroxide and sulphur in water.

The affinity or attraction of the sol particles for the medium, in a lyophilic sol, is due to hydrogenbonding with water. If the dispersed phase is a protein (as in egg) hydrogen bonding takes placebetween water molecules and the amino groups (-NH-, -NH_2) of the protein molecule. In a dispersionof starch in water, hydrogen bonding occurs between water molecules and the -OH groups of thestarch molecule. ***There are no similar forces of attraction when sulphur or gold is dispersed inwater.***



Lyophilic Sols	Lyophobic Sols
1. Prepared by direct mixing with dispersion medium.	**1.** Not prepared by direct mixing with the medium.
2. Little or no charge on particles.	**2.** Particles carry positive or negative charge.
3. Particles generally solvated.	**3.** No solvation of particles.
4. Viscosity higher than dispersion medium; set to a gel.	**4.** Viscosity almost the same as of medium; do not set to a gel.
5. Precipitated by high concentration of electrolytes.	**5.** Precipitated by low concentration of electrolytes.
6. Reversible.	**6.** Irrerversible.
7. Do not exhibit Tyndall effect.	**7.** Exhibit Tyndall effect.
8. Particles migrate to anode or cathode, or not at all.	**8.** Particles migrate to either anode or cathode.

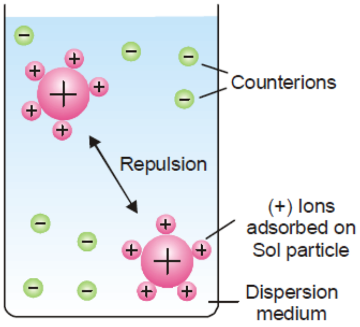
****The phenomenon of the scattering of light by the sol particles is called Tyndall effect***

****The continuous rapid zig-zag movement executed by a colloidal particle in the dispersion medium is called Brownian movement or motion.***

Electrical properties of Sols

I. The sol particles carry an electric charge

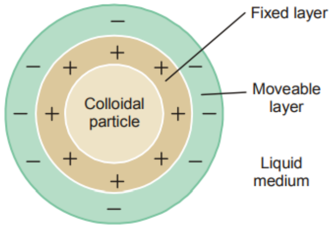
The most important property of colloidal dispersions is that all the suspended particles possess either a positive or a negative charge. The mutual forces of repulsion between similarly charged particles prevent them from aggregating and settling under the action of gravity (This gives stability to the sol). The sol particles acquire positive or negative charge by preferential adsorption of positive or negative ions from the dispersion medium. For example, a ferric hydroxide sol particles are positively charged because these adsorb Fe^{3+} ions from ferric chloride($FeCl_3$) used in the preparation of the sol. Since the sol as a whole is neutral, the charge on the particle is counterbalanced by oppositely charged ions termed **counterions** (in this case Cl^-) furnished by the electrolyte in medium.



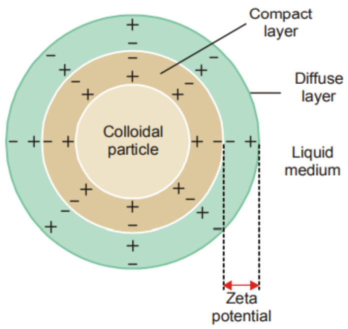
Adsorption of ions from dispersion medium gives charge to Sol particleswhich do not settle on account of mutual repulsions.

Electrical Double layer:

The surface of colloidal particle acquires a positive charge by selective adsorption of a layer of positive ions around it. This layer attracts counter ions from the medium which form a second layer of negative charges. The combination of the two layer of +ve and –ve charges around the sol particle was called Helmholtz Double layer. Helmholtz thought that positive charges next to the particle surface were fixed, while the layer of negative charges along with the medium were mobile.



Helmholtz double layer.



The electrical double layer (Stern).

More recent considerations have shown that the double layer is made of :

(a) a Compact layer of positive and negative charges which are fixed firmly on the particle surface.**(b)** a Diffuse layer of counter ions (negative ions) diffused into the medium containing positive ions. The combination of the compact and diffuse layer is referred to as the **Stern Double layer** after the colloid chemist who first realised its significance. The diffuse layer is only loosely attached to the particle surface and moves in the opposite direction under an applied electric field. Because of the distribution of the charge around the particle, there is a difference in potential between the compact layer and the bulk of solution across the diffuse layer. This is called Electrokinetic or **Zeta potential**.

The presence of the double layer accounts for the electrical properties :

(i) Cataphoresis; and (ii) Electro-osmosis of colloids. It has been made possible to estimate the magnitude of the zeta potential with the help of these properties. We have explained the theory of electrical double layer taking example of a positive sol. Our considerations could well be applied to a negative sol with the interchange of the disposition of positive and negative ions.

II. Electrophoresis:

If electric potential is applied across two platinum electrodes dipping in a hydrophilic sol, the dispersed particles move toward one or the other electrode.

The movement of sol particles under an applied electric potential is called electrophoresis or cataphoresis. If the sol particles migrate toward the positive electrode, they carry a negative charge. On the other hand, if they move toward the negative electrode, they are positively charged. Thus by noting the direction of movement of the sol particles, we can determine whether they carry a positive or negative charge.

The phenomenon of electrophoresis can be demonstrated by placing a layer of As_2S_3 sol under two limbs of a U-tube. When a potential difference of about 100 volts is applied across the two platinum electrodes dipping in deionised water, it is observed that the level of the sol drops on the negative electrode side and rises on the positive electrode side. This shows that As_2S_3 sol has migrated to the positive electrode, indicating that the particles are negatively charged. Similarly, a sol of ferric hydroxide will move to the negative electrode, showing that its particles carry positive charge.

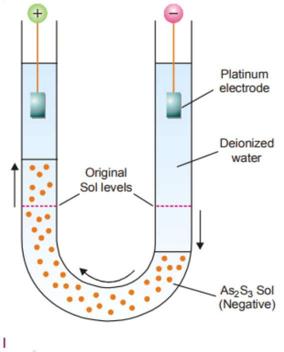


Illustration of Electro-osmosis.

Electrophoresis of a Sol.

Applications:

Some important applications of electrophoresis are:
(1) Removal of smoke from chimney gases;
(2) Removal of suspended impurities;
(3) Electro-plating of rubber on metal surfaces from latex (a sol);
(4) painting of metal parts of cars from colloidal pigments

III. Electro-osmosis

A sol is electrically neutral. Therefore the dispersion medium carries an equal but opposite charge to that of the dispersed particles. Thus the medium will move in opposite direction to the dispersed phase under the influence of applied electricpotential. When the dispersed phase is kept, stationary, the medium is actually found to move to the electrode of opposite sign that its own.

The movement of the dispersion medium under the influence of applied potential is known as electroosmosis.

Electro-osmosis is a direct consequence of the existence of zeta potential between the sol particles and the medium. When the applied pressure exceeds the zeta potential, that *diffuse layer* moves and causes electro-osmosis.

The phenomenon of electro-osmosis can be demonstrated by using a U-tube in which a plug of wet clay (a negative colloid) is fixed. The two limbs of the tube are filled with water to the same level. The platinum electrodes are immersed in water and potential applied across them. It will be observed that water level rises on the cathode side and falls on anode side. This movement of the medium towards the negative electrode, shows that the charge on the medium is positive. Similarly, for a positively charged colloid electro-osmosis will take place in the reverse direction.

Technically the phenomenon has been applied in the removal of water from peat, in dewatering of moist clay and in drying dye pastes.

IV. Coagulation or Precipitation

We know that the stability of a lyophobic sol is due to the adsorption of positive or negative ions by the dispersed particles. The repulsive forces between the charged particles do not allow them to settle. If, somehow, the charge is removed, there is nothing to keep the particles apart from each other. They aggregate (or flocculate) and settle down under the action of gravity.

The flocculation and settling down of the discharged sol particles is called coagulation orprecipitation of the sol.

How coagulation can be brought about?

The coagulation or precipitation of a given sol can be brought about in four ways :

(*a*) By addition of electrolytes
(*b*) By electrophoresis
(*c*) By mixing two oppositely charged sols
(*d*) By boiling

(*a*) **By addition of Electrolytes.** When excess of an electrolyte is added to a sol, the dispersedparticles are precipitated. The electrolyte furnishes both positive and negative ions in the medium.The sol particles adsorb the oppositely charged ions and get discharged. The electrically neutralparticles then aggregate and settle down as precipitateA negative ion (anion) causes the precipitation of a positively charged sol, and *vice versa*. Theeffectiveness of an anion or cation to precipitate a sol, will naturally depend on the magnitude of thecharge or valence of the effective ion. From a study of the precipitating action of various electrolyteson particular sol, Hardy and Schulze gave a general rule.Hardy-Schulze Rule states that **the precipitating effect of an ion on dispersed phase of oppositecharge increases with the valence of the ion.**

The higher the valency of the effective ion, the greater is its precipitating power. Thus forprecipitating an As_2S_3 sol (negative), the precipitating power of Al^{3+} , Ba^{2+}, Na^+ ions is in the order : $Al^{3+} > Ba^{2+} > Na^+$

Similarly, for precipitating $Fe(OH)_3$ sol (positive), the precipitating power of cations$[Fe(CN)_6]^{3-}$, SO_4^{-2}, $Cl^-$is in the order: $[Fe(CN)_6]^{3-} > SO4^{2-} > Cl^-$

The precipitation power of an electrolyte or ion is experimentally determined by finding theminimum concentration in millimoles per liter required to cause the precipitation of a sol in 2 hours.

This is called the **Flocculation value.** The smaller the flocculation value the higher the precipitatingpower of an ionratio for the mono-, di-, and trivalent anion or cation are approximately 1 : 40 : 90 for $Fe(OH)_3$ sol and1 : 70 : 500 for the As_2S_3 sol.

(*b*) **By Electrophoresis.** In electrophoresis the charged sol particles migrate to the electrode ofopposite sign. As they come in contact with the electrode, the particles are discharged and precipitated.

(*c*) **By mixing two oppositely charged sols.** The mutual coagulation of two sols of oppositecharge can be effected by mixing them. The positive particles of one sol are attracted by the negativeparticles of the second sol. This is followed by mutual adsorption and precipitation of both the sols.

Ferric hydroxide (+ve sol) and arsenious sulphide (–ve sol) form such a pair.

(*d*) **By boiling.** Sols such as sulphur and silver halides dispersed in water, may be coagulated by

boiling. Increased collisions between the sol particles and water molecules remove the adsorbedelectrolyte. This takes away the charge from the particles which settle down.

V. Protective action of sols

Lyophobic sols are readily precipitated by small amounts of electrolytes. However these sols areoften stabilized by the addition of lyophilic sols.**The property of lyophilic sols to prevent the precipitation of a lyophobic sol is called *protection.***

The lyophilic sol used to protect a lyophobic sol from precipitation is referred to as a ***Protectivecolloid*.**

Example. If a little gelatin (hydrophilic colloid) is added to a gold sol (hydrophobic sol), the latteris protected. The 'protected gold sol' is no longer precipitated on the addition of sodium chloride.

Explanation. The particles of the hydrophobic sol adsorb the particles of the lyophilic sol. Thusthe lyophilic colloid forms a coating around the lyophobic sol particles. The hydrophobic colloid,therefore, behaves as a hydrophilic sol and is precipitated less easily by electrolytes.

Gold number

The lyophilic colloids differ widely in their powers of protection. The protective action ofdifferent colloids is measured in terms of the **'Gold number'** introduced byZsigmondy. The goldnumber is defined as ***: the number of milligrams of a hydrophilic colloid that will just prevent the precipitation of 10 ml of a gold sol on the addition of 1 ml of 10 per cent sodium chloride solution.***

The onset of precipitation of the gold sol is indicated by a colour change from red to blue whenthe particle size just increases.The smaller the gold numberof a hydrophilic colloid, the greater is its protective power. Gelatin has a small gold number and is an

effective protective colloid. Starch has a very high value, which shows that it is an ineffectiveprotective colloid.

EMULSIONS

These are liquid-liquid colloidal systems. In other words, **an emulsion may be defined as adispersion of finely divided liquid droplets in another liquid.**

Generally one of the two liquids is *water* and the other, which is immiscible with water, isdesignated as *oil*. Either liquid can constitute the dispersed phase.

Types of Emulsions

There are two types of emulsions.

Oil-in-Water type (O/W type) ; (*b*) **Water-in-Oil type (W/O type)**

Examples of Emulsions

(1) Milk is an emulsion of O/W type. Tiny droplets of liquid fat are dispersed in water.

(2) Stiff greases are emulsions of W/O type, water being dispersed in lubricating oil.

Preparation of Emulsions

The dispersal of a liquid in the form of anemulsion is called **emulsification.** This can bedone by agitating a small proportion of oneliquid with the bulk of the other. It is betteraccomplished by passing a mixture of the twoliquid through a colloid mill known as**homogenizer.**

The emulsions obtained simply by shakingthe two liquids are unstable. The droplets ofthe dispersed phase coalesce and form aseparate layer. To have a stable emulsion, smallamount of a third substance called the**Emulsifier** or **Emulsifying agent** is addedduring the preparation. This is usually a soap,synthetic detergent, or a hydrophilic colloid.

Role of Emulsifier

The emulsifier concentrates at the interface and reduces surface tension on the side of oneliquid which rolls into droplets. Soap, for example, is made of a long hydrocarbon tail (oil soluble)with a polar head —COO–Na+ (water soluble). In O/W type emulsion the tail is pegged into the oildroplet, while the head extends into water. Thus the soap acts as go-between and the emulsifieddroplets are not allowed to coalesce.

Properties of Emulsions

(1) ***Demulsification***: Emulsions can be broken or ‘demulsified’ to get the constituent liquids byheating, freezing, centrifuging, or by addition of appreciable amounts of electrolytes. They are alsobroken by destroying the emulsifying agent. For example, an oil-water emulsion stabilized by soap isbroken by addition of a strong acid. The acid converts soap into insoluble free fatty acids.

(2) ***Dilution***: Emulsions can be diluted with any amount of the dispersion medium. On the otherhand the dispersed liquid when mixed with it will at once form a separate layer. This property ofemulsions is used to detect the type of a given emulsion.

Gels:

A gel is a jelly-like colloidal system in which a liquid is dispersed in a solid medium.

For example, when a warm sol of gelatin is cooled,it sets to a semisolid mass which is a gel. Theprocess of a gel formation is known as **Gelation.**

Explanation. Gelation may be thought of aspartial coagulation of a sol. The coagulating solparticles first unite to form long thread-likechains. These chains are then interlocked to forma solid framework. The liquid dispersion mediumgets trapped in the cavities of this framework.

The resulting semisolid porous mass has a gelstructure. A sponge soaked in water is anillustration of gel structure.

Two types of Gels

Gels may be classified into two types :

(*a*) **Elastic gels** are those which possess the property of elasticity. They change their shape onapplying force and return to original shape when the force is removed. Gelatin, starch and soaps areexamples of substances which form elastic gels.

Elastic gels are obtained by cooling fairly concentrated lyophilic sols. The linkages between themolecules (particles) are due to electrical attraction and are not rigid.

(*b*) **Non-elastic gels** are those which are rigid *e.g.*, silica gel. These are prepared by appropriatechemical action. Thus silica gel is produced by adding concentrated hydrochloric acid to sodiumsilicate solution of the correct concentration. The resulting molecules of silicic acid polymerize toform silica gel. It has a network linked by covalent bonds which give a strong and rigid structure.

Properties of Gels

(1) **Hydration:** A completely dehydrated elastic gel can be regenerated by addition of water. Butonce a nonelastic gel is freed from moisture, addition of water will not bring about gelation.

(2) **Swelling.** Partially dehydrate elastic gels imbibe water when immersed in the solvent. Thiscauses increase in the volume of the gel and process is called **Swelling.**

(3) **Syneresis:**Many inorganic gels on standing undergo shrinkage which is accompanied byexudation of solvent. This process is termed **Syneresis.**

(4) **Thixotropy:**Some gels are semisolid when at rest but revert to liquid sol on agitation. Thisreversible sol-gel transformation is referred to as **Thixotropy.** Iron oxide

and silver oxide gels exhibitthis property. The modern thixotropic paints are also an example.

APPLICATIONS OF COLLOIDS

Colloids play an important role in our daily life and industry. A knowledge of colloid chemistry isessential to understand some of the various natural phenomena around us. Colloids make up some

of our modern products. A few of the important applications of colloids are listed below.

(1) Foods

Many of our foods are colloidal in nature. Milk is an emulsion of butterfat in water protected bya protein, casein. Salad dressing, gelatin deserts, fruit jellies and whipped cream are other examples.Ice cream is a dispersion of ice in cream. Bread is a dispersion of air in baked dough.

(2) Medicines

Colloidal medicines being finely divided, are more effective and are easily absorbed in oursystem. Halibut-liver oil and cod-liver that we take are, in fact, the emulsions of the respective oils inwater. Many ointments for application to skin consist of physiologically active components dissolvedin oil and made into an emulsion with water. Antibiotics such as penicillin and streptomycin areproduced in colloidal form suitable for injections.

(3) Non-drip or thixotropic paints

All paints are colloidal dispersions of solid pigments in a liquid medium. The modern *nondrip orthixotropic paints* also contain long-chain polymers. At rest, the chains of molecules are coiled andentrap much dispersion medium. Thus the paint is a semisolid gel structure. When shearing stress isapplied with a paint brush, the coiled molecules straighten and the entrapped medium is released. Assoon as the brush is removed, the liquid paint reverts to the semisolid form. This renders the paint‘non-drip’.

(4) Electrical precipitation of smoke

The smoke coming from industrial plants is a colloidal dispersion of solid particles (carbon,arsenic compounds, cement dust) in air. It is a nuisance and pollutes the atmosphere. Therefore,before allowing the smoke to escape into air, it is treated by

Cottrell Precipitator

The smoke is let past a series of sharp points charged to a high potential (20,000 to 70,000 V). Thepoints discharge high velocity electrons that ionise molecules in air. Smoke particles adsorb thesepositive ions and become charged. The charged particles are attracted to the oppositely chargedelectrodes and get precipitated. The gases that leave the *Cottrell precipitator* are thus freed fromsmoke. In addition, valuable materials may be recovered from the precipitated smoke. For example,arsenic oxide is mainly recovered from the smelter smoke by this method.

(5) Clarification of Municipal water

The municipal water obtained from natural sources often contains colloidal particles. The processof coagulation is used to remove these. The sol particles carry a negative charge. When aluminiumsulphate (*alum*) is added to water, a gelatinous precipitate of hydrated aluminium hydroxide (*floc*) isformed,

$$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+$$

$$Al(OH)^{3+} + 4H_2O + H^+ \longrightarrow Al(OH)_3(H_2O)_4$$

The positively charged *floc* attracts to it negative sol particles which are coagulated. The *floc*along with the suspended matter comes down, leaving the water clear.

(6) Formation of Delta

The river water contains colloidal particles of sand and clay which carry negative charge. Thesea water, on the other hand, contains positive ions such as Na^+, Mg^{2+}, Ca^{2+}. As the river water meetssea water, these ions discharge the sand or clay particles which are precipitated as **delta.**

(7) Artificial Kidney machine

The human kidneys purify the blood by dialysis through natural membranes. The toxic wasteproducts such as urea and uric acid pass through the membranes, while colloidal-sized particles ofblood proteins (haemoglobin) are retained. Kidney failure, therefore, leads to death due to accumulationof poisonous waste products in blood . Now-a-days, the patient’s blood can be cleansed by shuntingit into an ‘artificial kidney machine’. Here the impure blood is made to pass through a series of*cellophane tubes* surrounded by a washing solution in water. The toxic waste chemicals (urea, uricacid) diffuse across the tube walls into the washing solution. The purified blood is returned to thepatient. The use of artificial kidney machine saves the life of thousands of persons each year.

(8) Adsorption indicators

These indicators function by preferentialadsorption of ions onto sol particles. Fluorescein(Na^+Fl) is an example of adsorption indicatorwhich is used for the titration of sodium chloridesolution against silver nitrate solution.When silver nitrate solution is run into asolution of sodium chloride containing a littlefluorescein, a white precipitate of silver chlorideis first formed. At the end-point, the whiteprecipitate turns sharply pink.

Explanation. The indicator fluorescein is adye (Na^+Fl^-) which gives coloured anion Fl^- inaqueous solution. The white precipitate of silverchloride formed by running $AgNO_3$ solution intoNaCl solution is partially colloidal in nature.

(*a*) *Before the end-point,* Cl^- ions are inexcess. The AgCl sol particles adsorb these ionsand become negatively charged. The negative$AgCl/Cl^-$ particles cannot adsorb the colouredfluorescein anions (Fl^-) due to electrostaticrepulsion. Thus the precipitate remains white.

(*b*) *After the end-point*, Ag+ ions become in excess. AgCl sol particles adsorb these andacquire positive charge. The positive AgCl/Ag+ particles now attract the coloured fluorescein anions(Fl^-) and turn rose-red.

Thus the end-point is marked by white precipitate changing to pink.

(9) Blue colour of the sky

This is an application of Tyndall effect. The upper atmosphere contains colloidal dust or iceparticles dispersed in air. As the sun rays enter the atmosphere, these strike the colloidalparticles. The particles absorb sunlight and scatter light of blue colour (4600–5100Å). The light thatis incident at earth's surface is considerably reddened due to the removal of most of the blue light inthe upper atmosphere.