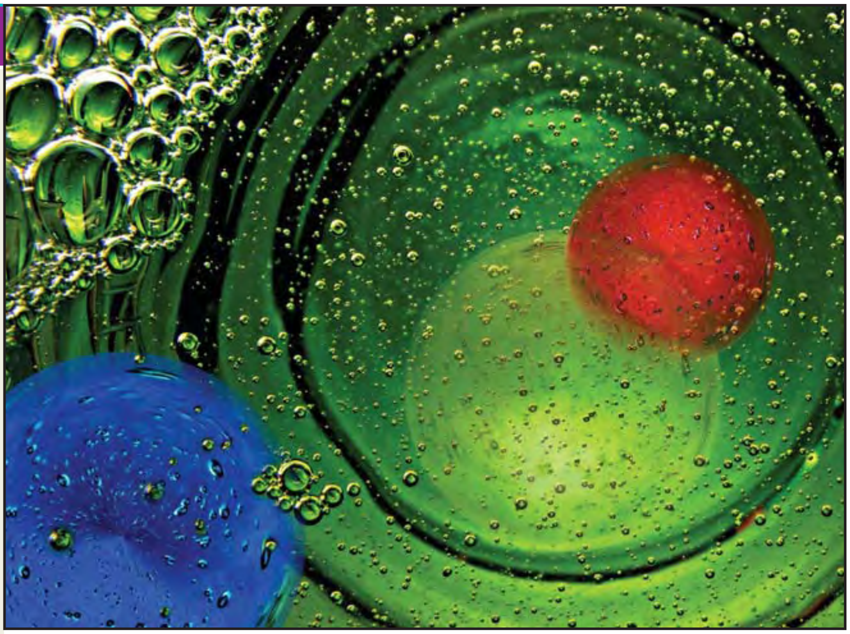
22

CHAPTER

Colloids

CONTENTS



Thomas Graham (1861) studied the ability of dissolved substances to diffuse into water across a permeable membrane. He observed that crystalline substances such as sugar, urea, and sodium chloride passed through the membrane, 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.**

WHAT ARE COLLOIDS ?

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

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

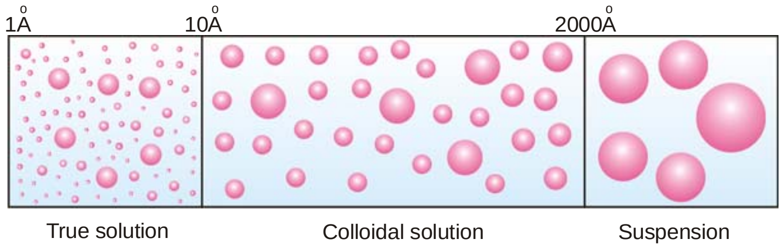


Figure 22.1
Particle size (indicated by diameter) range of true solution, colloidal dispersion, and suspension.

The colloidal solutions or colloidal dispersions are intermediate between true solutions and suspensions. In other words, the diameter of the dispersed particles in a colloidal dispersion is more than 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 10 Å 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.**

Figure 22.2
Common examples of colloids.

The colloidal particles are not necessarily corpuscular in shape. In fact, these may be rod-like, disc-like, thin films, or long filaments. For matter in the form of corpuscles, the diameter gives a measure of the particle size. However, in other cases one of the dimensions (length, width and thickness) has to be in the colloidal range for the material to be classed as colloidal. Thus in a broader context we can say :

A system with at least one dimension (length, width, or thickness) of the dispersed particles in the range 10 Å to 2,000 Å, is classed as a colloidal dispersion.

TYPES OF COLLOIDAL SYSTEMS

As we have seen above, a colloidal system is made of two phases. The substance distributed as the colloidal particles 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.

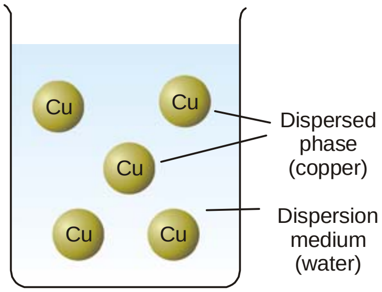


Figure 22.3
A colloidal system of copper in water

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.

The various types of colloidal systems are listed in Table. 22.1.

In this chapter we will restrict our study mainly to the colloidal systems which consist of a solid substance dispersed in a liquid. These are frequently referred to as **Sols** or **Colloidal solution.** The colloidal solutions in water as the dispersion medium are termed **Hydrosols or Aquasols.** When the dispersions medium is alcohol or benzene, the sols are referred to as **Alcosols** and **Benzosols** respectively.

TABLE 22.1. TYPES OF COLLOIDAL SYSTEMS

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.

LYOPHILIC AND LYOPHOBIC SOLS OR COLLOIDS

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 medium or 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 the solvent.

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 hydrogen bonding with water. If the dispersed phase is a protein (as in egg) hydrogen bonding takes place between water molecules and the amino groups (–NH–, $–NH_2$) of the protein molecule. In a dispersion of starch in water, hydrogen bonding occurs between water molecules and the – OH groups of the starch molecule. **There are no similar forces of attraction when sulphur or gold is dispersed in water.**

CHARACTERISTICS OF LYOPHILIC AND LYOPHOBIC SOLS

Some features of lyophilic and lyophobic sols are listed below.

(1) Ease of preparation

Lyophilic sols can be obtained straightaway by mixing the material (starch, protein) with a suitable solvent. The giant molecules of the material are of colloidal size and these at once pass into the colloidal form on account of interaction with the solvent.

Lyophobic sols are not obtained by simply mixing the solid material with the solvent.

(2) Charge on particles

Particles of a hydrophilic sol may have little or no charge at all.

Particles of a hydrophobic sol carry positive or negative charge which gives them stability.

(3) Solvation

Hydrophilic sol particles are generally solvated. That is, they are surrounded by an adsorbed layer of the dispersion medium which does not permit them to come together and coagulate. Hydration of gelatin is an example.

There is no solvation of the hydrophobic sol particles for want of interaction with the medium.

(4) Viscosity

Lyophilic sols are viscous as the particle size increases due to solvation, and the proportion of free medium decreases. Warm solutions of the dispersed phase on cooling set to a gel *e.g.*, preparation of *table jelly*.

Viscosity of hydrophobic sol is almost the same as of the dispersion medium itself.

(5) Precipitation

Lyophilic sols are precipitated (or coagulated) only by high concentration of the electrolytes when the sol particles are dissolved.

Lyophobic sols are precipitated even by low concentration of electrolytes, the protective layer being absent.

(6) Reversibility

The dispersed phase of lyophilic sols when separated by coagulation or by evaporation of the medium, can be reconverted into the colloidal form just on mixing with the dispersion medium. Therefore this type of sols are designated as **Reversible sols.**

On the other hand, the lyophobic sols once precipitated cannot be reformed merely by mixing with dispersion medium. These are, therefore, called **Irreversible sols.**

(7) Tyndall effect

On account of relatively small particle size, lyophilic sols do not scatter light and show no Tyndall effect. Lyophobic sol particles are large enough to exhibit tyndall effect.

(8) Migration in electronic field

Lyophilic sol particles (proteins) migrate to anode or cathode, or not at all, when placed in electric field.

Lyophobic sol particles move either to anode or cathode, according as they carry negative or positive charge.

COMPARISON OF LYOPHILIC AND LYOPHOBIC SOLS

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.

PREPARATION OF SOLS

Lyophilic sols may be prepared by simply warming the solid with the liquid dispersion medium *e.g.*, starch with water. On the other hand, lyophobic sols have to be prepared by special methods. These methods fall into two categories :

(*a*) Dispersion Methods in which larger macro-sized particles are broken down to colloidal size.

(*b*) Aggregation Methods in which colloidal size particles are built up by aggregating single ions or molecules.

DISPERSION METHODS

In these methods, material in bulk is dispersed in another medium.

(1) Mechanical dispersion using Colloid mill

The solid along with the liquid dispersion medium is fed into a Colloid mill. The mill consists of two steel plates nearly touching each other and rotating in opposite directions with high speed. The solid particles are ground down to colloidal size and are then dispersed in the liquid to give the sol. 'Colloidal graphite' (a lubricant) and printing inks are made by this method.

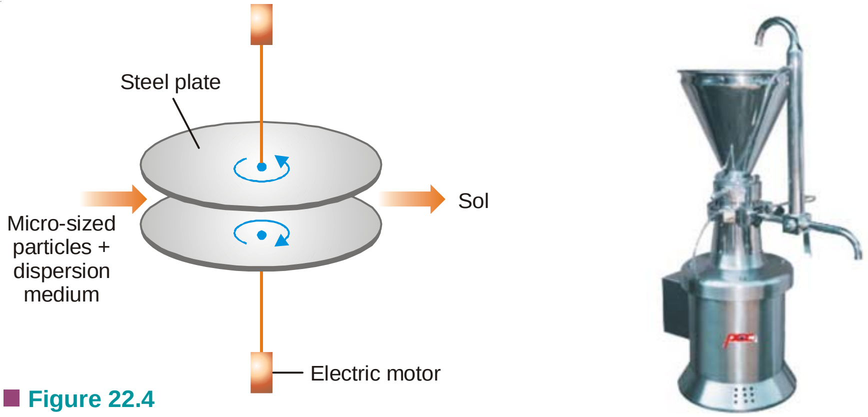


Figure 22.4
A Colloid mill.

Recently, mercury sol has been prepared by disintegrating a layer of mercury into sol particles in water by means of ultrasonic vibrations.

(2) Bredig's Arc Method

It is used for preparing hydrosols of metals *e.g.*, silver, gold and platinum. An arc is struck between the two metal electrodes held close together beneath *de-ionized* water. The water is kept cold by immersing the container in ice/water bath and a trace of alkali (KOH) is added. The intense heat of the spark across the electrodes vaporises some of the metal and the vapour condenses under water. Thus the atoms of the metal present in the vapour aggregate to form colloidal particles in water. Since the metal has been ultimately converted into sol particles (*via* metal vapour), this method has been treated as of dispersion.

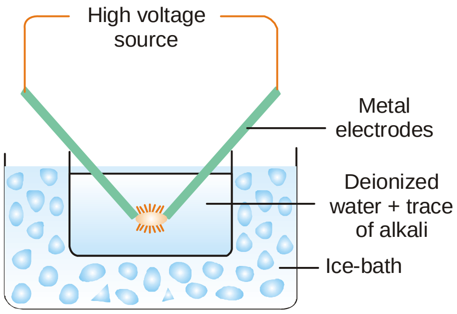


Figure 22.5
Bredig's Arc method.

Non-metal sols can be made by suspending coarse particles of the substance in the dispersion medium and striking an arc between iron electrodes.

(3) By Peptization

Some freshly precipitated ionic solids are dispersed into colloidal solution in water by the addition of small quantities of electrolytes, particularly those containing a common ion. The precipitate adsorbs the common ions and electrically charged particles then split from the precipitate as colloidal particles.

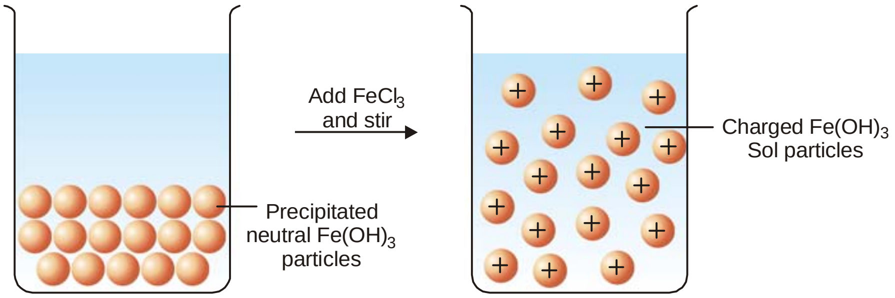


Figure 22.6
Sol of ferric hydroxide is obtained by stirring fresh precipitate of ferric hydroxide with a small amount of $FeCl_3$.

The dispersal of a precipitated material into colloidal solution by the action of an electrolyte in solution, is termed peptization. The electrolyte used is called a peptizing agent.

Peptization is the reverse of coagulation of a sol.

Examples of preparation of sols by peptization

(1) **Silver chloride,** Ag^+Cl^-, can be converted into a sol by adding hydrochloric acid (Cl^- being common ion.)

(2) **Ferric hydroxide,** $Fe(OH)_3$, yields a sol by adding ferric chloride (Fe^{3+} being common ion).

AGGREGATION METHODS

These methods consists of **chemical reactions or change of solvent** whereby the atoms or molecules of the dispersed phase appearing first, coalesce or aggregate to form colloidal particles. The conditions (temperature, concentration, etc.) used are such as permit the formation of sol particles but prevent the particles becoming too large and forming precipitate. The unwanted ions (spectator ions) present in the sol are removed by dialysis as these ions may eventually coagulate the sol.

The more important methods for preparing hydrophobic sols are listed below :

(1) Double Decomposition

An arsenic sulphide (As_2S_3) sol is prepared by passing a slow stream of hydrogen sulphide gas through a cold solution of arsenious oxide (As_2O_3). This is continued till the yellow colour of the sol attains maximum intensity.

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3\,(sol) + 3H_2O$$

Excess hydrogen sulphide (electrolyte) is removed by passing in a stream of hydrogen.

(2) Reduction

Silver sols and gold sols can be obtained by treating dilute solutions of silver nitrate or gold chloride with organic reducing agents like tannic acid or methanal (HCHO)

$$AgNO_3 + \text{tannic acid} \longrightarrow \text{Ag sol}$$

$$AuCl_3 + \text{tannic acid} \longrightarrow \text{Au sol}$$

(3) Oxidation

A sol of sulphur is produced by passing hydrogen sulphide into a solution of sulphur dioxide.

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

In qualitative analysis, sulphur sol is frequently encountered when H_2S is passed through the solution to precipitate group 2 metals if an oxidizing agent (chromate or ferric ions) happen to be present. It can be removed by boiling (to coagulate the sulphur) and filtering through two filter papers folded together.

(4) Hydrolysis

Sols of the hydroxides of iron, chromium and aluminium are readily prepared by the hydrolysis of salts of the respective metals. In order to obtain a red sol of ferric hydroxide, a few drops of 30% ferric chloride solution is added to a large volume of almost boiling water and stirred with a glass rod.

$$FeCl_3 + 3H_2O \longrightarrow \underset{\text{red sol}}{Fe(OH)_3} + 3HCl$$

(5) Change of Solvent

When a solution of *sulphur* or *resin* in ethanol is added to an excess of water, the sulphur or resin sol is formed owing to decrease in solubility. The substance is present in molecular state in ethanol but on transference to water, the molecules precipitate out to form colloidal particles.

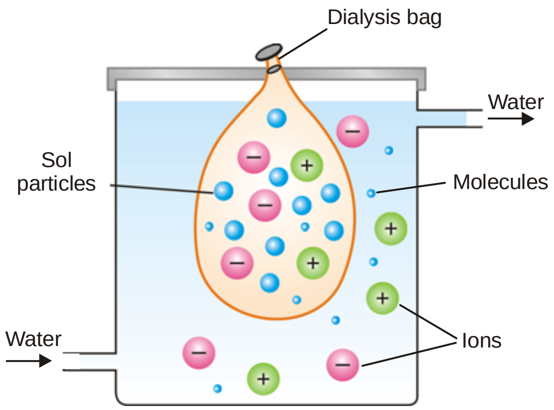
PURIFICATION OF SOLS

In the methods of preparation stated above, the resulting sol frequently contains besides colloidal particles appreciable amounts of electrolytes. To obtain the pure sol, these electrolytes have to be removed. This purification of sols can be accomplished by three methods :

(*a*) Dialysis
(*b*) Electrodialysis
(*c*) Ultrafiltration

Dialysis

Animal membranes (bladder) or those made of parchment paper and cellophane sheet, have very fine pores. These pores permit ions (or small molecules) to pass through but not the large colloidal particles. When a sol containing dissolved ions (electrolyte) or molecules is placed in a bag of permeable membrane dipping in pure water, the ions diffuse through the membrane. By using a continuous flow of fresh water, the concentration of the electrolyte outside the membrane tends to be zero. Thus diffusion of the ions into pure water remains brisk all the time. In this way, practically all the electrolyte present in the sol can be removed easily.



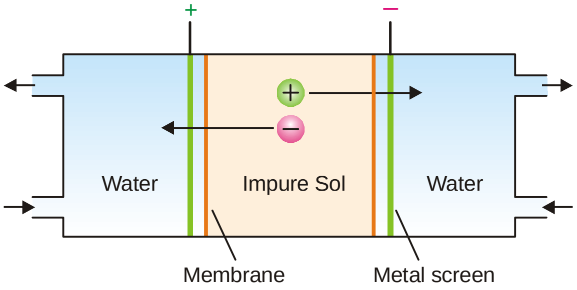
■ Figure 22.7
Dialysis of a sol containing ions and molecules.

The process of removing ions (or molecules) from a sol by diffusion through a permeable membrane is called Dialysis. The apparatus used for dialysis is called a **Dialyser.**

Example. A ferric hydroxide sol (red) made by the hydrolysis of ferric chloride will be mixed with some hydrochloric acid. If the impure sol is placed in the dialysis bag for some time, the outside water will give a white precipitate with silver nitrate. After a pretty long time, it will be found that almost the whole of hydrochloric acid has been removed and the pure red sol is left in the dialyser bag.

Electrodialysis

In this process, dialysis is carried under the influence of electric field (Fig. 22.8). Potential is applied between the metal screens supporting the membranes. This speeds up the migration of ions to the opposite electrode. Hence dialysis is greatly accelerated. Evidently **electrodialysis is not meant for nonelectrolyte impurities** like sugar and urea.



■ Figure 22.8
Electrodialysis.

Ultrafiltration

Sols pass through an ordinary filter paper, Its pores are too large to retain the colloidal particles. However, if the filter paper is impregnated with collodion or a regenerated cellulose such as *cellophane* or *visking*, the pore size is much reduced. Such a modified filter paper is called an **ultrafilter.**

The separation of the sol particles from the liquid medium and electrolytes by filtration through an ultrafilter is called ultrafiltration.

Ultrafiltration is a slow process. Gas pressure (or suction) has to be applied to speed it up. The colloidal particles are left on the ultrafilter in the form of slime. The slime may be stirred into fresh medium to get back the pure sol. By using graded ultrafilters, the technique of ultrafiltration can be employed to separate sol particles of different sizes.

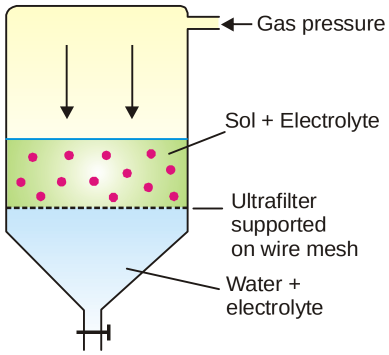


Figure 22.9
Ultrafiltration.

PROPERTIES OF SOLS–THEIR COLOUR

The colour of a hydrophobic sol depends on the wavelength of the light scattered by the dispersed particles. The wavelength of the scattered light again depends on the size and the nature of the particles. This is fully borne out from the following date in case of silver sols.

COLOUR OF Ag-SOL	PARTICLE DIAMETER
Orange-yellow	6×10^{-5} mm
Orange-red	9×10^{-5} mm
Purple	13×10^{-5} mm
Violet	15×10^{-5} mm

The colour changes produced by varying particles size have been observed in many other cases.

OPTICAL PROPERTIES OF SOLS

(1) Sols exhibit Tyndall effect

When a strong beam of light is passed through a sol and viewed at right angles, the path of light shows up as a hazy beam or cone. This is due to the fact that sol particles absorb light energy and then emit it in all directions in space. This 'scattering of light', as it is called, illuminates the path of the beam in the colloidal dispersion.

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

The illuminated beam or cone formed by the scattering of light by the sol particles is often referred as **Tyndall beam** or **Tyndall cone.**

The hazy illumination of the light beam from the film projector in a smoke-filled theatre or the light beams from the headlights of car on a dusty road, are familiar examples of the Tyndall effect. If the sol particles are large enough, the sol may even appear turbid in ordinary light as a result of Tyndall scattering.

True solutions do not show Tyndall effect. Since ions or solute molecules are too small to scatter light, the beam of light passing through a true solution is not visible when viewed from the side. Thus Tyndall effect can be used to distinguish a colloidal solution from a true solution.

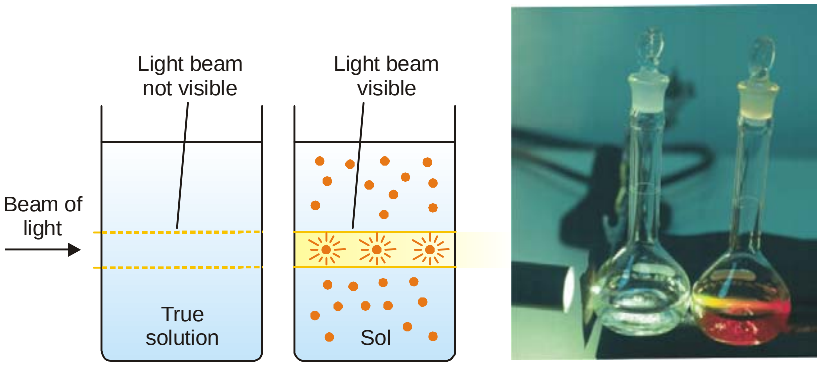


Figure 22.10
Tyndall effect (Illustration).

Figure 22.11
Tyndall effect in nature.

(2) Ultramicroscope shows up the presence of individual particles

Sol particles cannot be seen with a microscope. Zsigmondy (1903) used the Tyndall phenomenon to set up an apparatus named as the **ultramicroscope.** An intense beam of light is focussed on a sol contained in a glass vessel. The focus of light is then observed with a microscope at right angles to the beam. Individual sol particles appear as bright specks of light against a dark background (dispersion medium). It may be noted that under the ultramicroscope, the actual particles are not visible. It is the larger halos of scattered light around the particles that are visible. **Thus an ultramicroscope does not give any information regarding the shape and size of the sol particles.**

(3) Sol particles can be seen with an Electron microscope

In an electron microscope, beam of electrons is focussed by electric and magnetic fields on to a photographic plate. This focussed beam is allowed to pass through a film of sol particles. Thus it is possible to get a picture of the individual particles showing a magnification of the order of 10,000. With the help of this instrument, we can have an idea of the size and shape of several sol particles including paint pigments, viruses, and bacteria. These particles have been found to be spheriod, rod-like, disc-like, or long filaments.

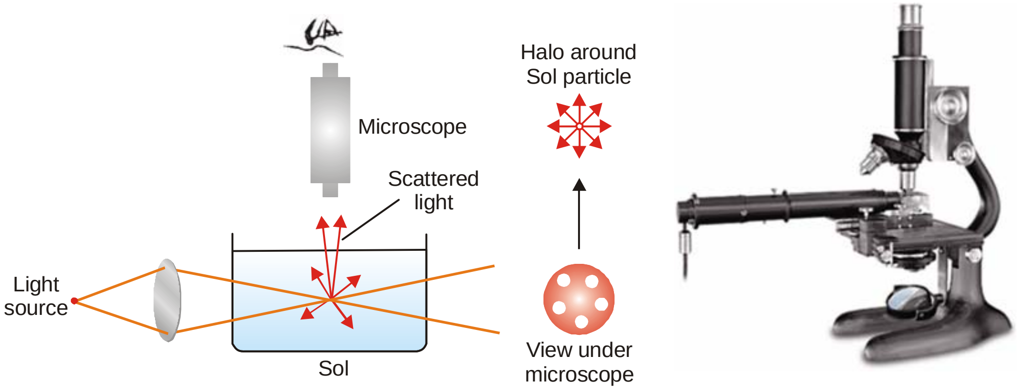


Figure 22.12
Principle of the Ultramicroscope.

KINETIC PROPERTIES OF SOLS

Brownian Movement

When a sol is examined with an ultramicroscope, the suspended particles are seen as shining specks of light. By following an individual particle it is observed that the particle is undergoing a constant rapid motion. It moves in a series of short straight-line paths in the medium, changing directions abruptly.

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

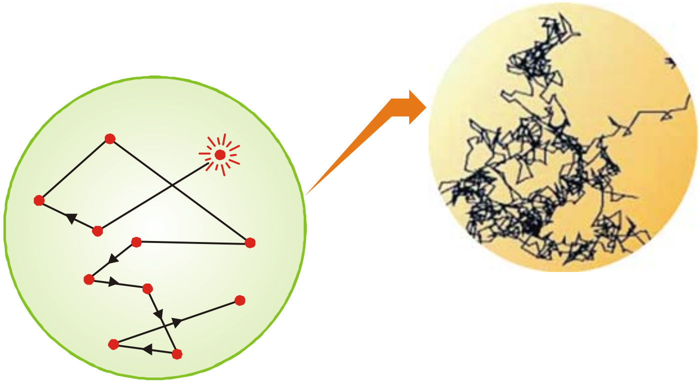


Figure 22.13
An illustration of Brownian movement.

This phenomenon is so named after Sir Robert Brown who discovered it in 1827.

Suspension and true solutions do not exhibit Brownian movement.

Explanation of Brownian movement. The explanation of Brownian movement was advanced by Albert Einstein around 1955 by mathematical considerations based on the kinetic molecular theory. According to him, at any instant a colloidal particle was being struck by several molecules of the dispersion medium. The movement of the particle was caused by unequal number of molecules of the medium striking it from opposite directions. When more molecules struck the particle on one side than on another, the direction of movement changed. Fig. 22.14 illustrates how a colloidal particle is knocked about in a zig-zag path by molecules of the dispersion medium.

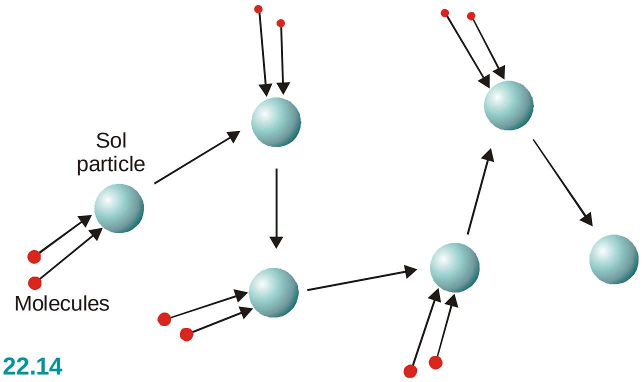


Figure 22.14
The bombardment on the sides of the colloidal particles by molecules of dispersion medium causes the random movement of the particle.

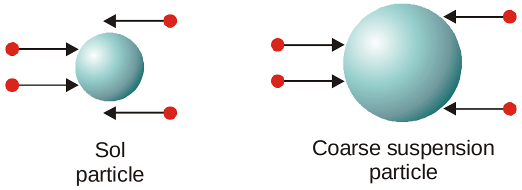


Figure 22.15
Illustration showing how Brownian movement vanishes in coarse suspensions.

In a suspension, the suspended particles being very large the probability of unequal bombardments diminishes. The force of the molecules hitting the particle on one side is cancelled by the force of collisions occurring on the other side. Hence they do not exhibit Brownian movement.

The phenomenon of Brownian movement is an excellent proof of the existence of molecules and their ceaseless motion in liquids. It also explains how the action of gravity, which would ordinarily cause the settling of colloidal particles, is counteracted. The constant pushing of the particles by the molecules of the dispersion medium has a stirring effect which does not permit the particles to settle.

ELECTRICAL PROPERTIES OF SOLS

(1) The sol particles carry an electric charge

The most important property of colloidal dispersions is that all the suspended particles posses 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.

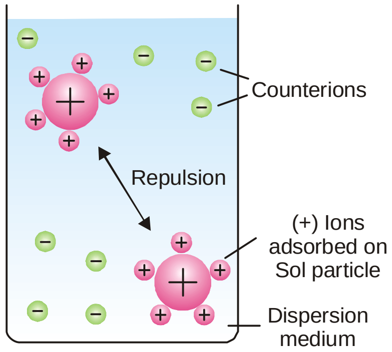


Figure 22.16
Adsorption of ions from dispersion medium gives charge to Sol particles which do not settle on account of mutual repulsions.

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 counterions 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.

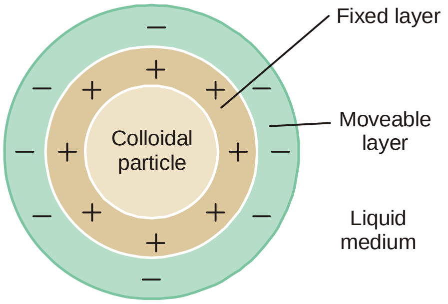


Figure 22.17
Helmholtz double layer.

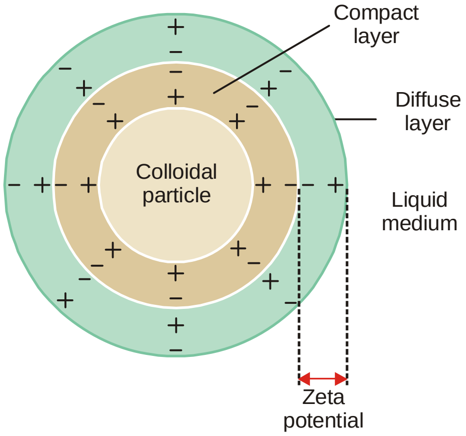


Figure 22.18
The electrical double layer (Stern).

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 counterions (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 by **Electrokinetic** or **Zeta potential.** The presence of the double layer accounts for the electrical properties : (*a*) Cataphoresis; and (*b*) 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.

(2) 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.

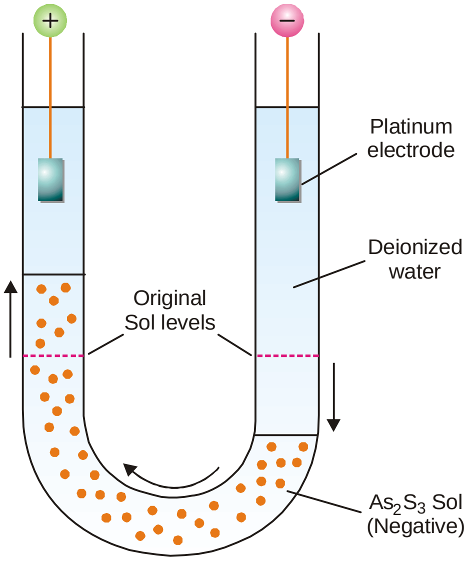


Figure 22.19
Electrophoresis of a Sol.

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 (Fig. 22.19). 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.

Using water as the dispersion medium, the charge on the particles of some common sols determined by electrophoresis is given below.

NEGATIVELY CHARGED	POSITIVELY CHARGED
(1) Metals *e.g.*, Au, Ag, Pt	(1) Ferric hydroxide
(2) Arsenic sulphide	(2) Aluminium hydroxide
(3) Starch	(3) Basic dyes
(4) Clay	(4) Haemoglobin

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.

(3) 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 electric potential. 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 electro-osmosis.

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 (Fig. 22.19). 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

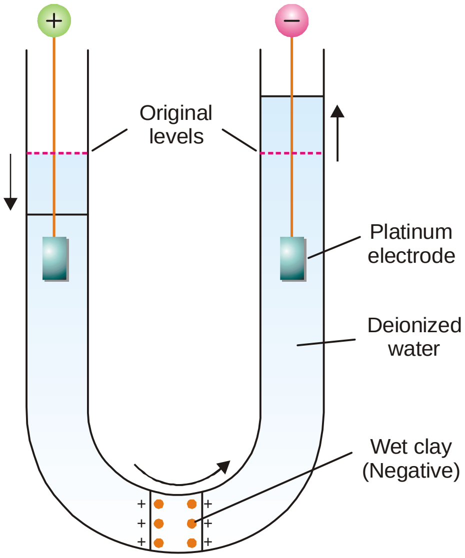


Figure 22.20
Illustration of Electro-osmosis.

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.

(4) 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, some how, 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 or precipitation 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 dispersed particles 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 neutral particles then aggregate and settle down as precipitate (Fig. 22.21).

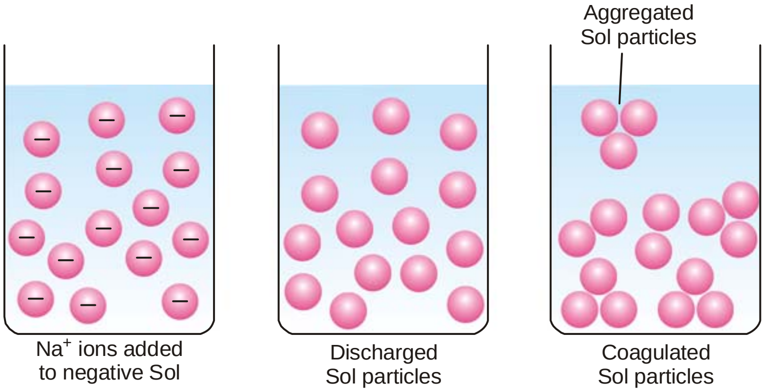


Figure 22.21
Coagulation of a Sol (illustration).

A negative ion (anion) causes the precipitation of a positively charged sol, and *vice versa*. The effectiveness of an anion or cation to precipitate a sol, will naturally depend on the magnitude of the charge or valence of the effective ion. From a study of the precipitating action of various electrolytes on particular sol, Hardy and Schulze gave a general rule.

Hardy-Schulze Rule states that **the precipitating effect of an ion on dispersed phase of opposite charge increases with the valence of the ion.**

The higher the valency of the effective ion, the greater is its precipitating power. Thus for precipitating 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.

$$[Fe(CN)_6]^{3-} > SO_4^{2-} > Cl^-$$

The precipitation power of an electrolyte or ion is experimentally determined by finding the minimum concentration in millimoles per litre 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 precipitating power of an ion.

TABLE 22.2. FLOCCULATION VALUES

$(Fe(OH)_3$ Sol (+ve)		As_2S_3 Sol (–ve)	
Electrolyte	Concentration (millimoles/litre)	Electrolyte	Concentration (millimoles/litre)
NaCl, (Cl^-)	9.3	NaCl, (Na^+)	51
KCl, (Cl^-)	9.0	KCl, (K^+)	50
K_2SO_4, (SO_4^{2-})	0.20	$BaCl_2$, (Ba^{2+})	0.69
$K_3Fe(CN)_6$, $[Fe(CN)_6]^{3-}$	0.096	$AlCl_3$, (Al^{3+})	0.093

It may be noted how rapidly the precipitation power increases with the increases of valence. The ratio for the mono-, di-, and trivalent anion or cation are approximately 1 : 40 : 90 for $Fe(OH)_3$ sol and 1 : 70 : 500 for the As_2S_3 sol.

(*b*) **By Electrophoresis.** In electrophoresis the charged sol particles migrate to the electrode of opposite 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 opposite charge can be effected by mixing them. The positive particles of one sol are attracted by the negative particles 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 adsorbed electrolyte. This takes away the charge from the particles which settle down.

(5) Protective action of sols

Lyophobic sols are readily precipitated by small amounts of electrolytes. However these sols are often 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 **Protective colloid.**

Example. If a little gelatin (hydrophilic colloid) is added to a gold sol (hydrophobic sol), the latter is 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. Thus the 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 of different colloids is measured in terms of the **'Gold number'** introduced by Zsigmondy. The gold number 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 when the particle size just increases.

The gold numbers of hydrophilic colloids are given in Table 22.3. The smaller the gold number of 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 ineffective protective colloid.

TABLE 22.3. GOLD NUMBERS OF SOME HYDROPHILIC COLLOIDS

Lyophilic colloid	Gold number
Gelatin	0.005 – 0.01
Egg albumen	0.08 – 0.10
Gum arabic	0.10 – 0.15
Potato starch	25

The use of protective colloids to stabilize colloidal systems is widespread. In the preparation of ice cream, gelatin is added to act as a protecting agent to the colloidal particles of ice. If the ice particles coagulate, the smooth texture of ice cream is lost. *Argyrol*, used in eye drops, is a sol of silver protected by organic material.

Origin of charge on sol particles

All the dispersed particles of a particular sol carry a positive or a negative charge. They acquire this charge by

(*a*) Adsorption of ions from the aqueous medium

(*b*) Ionisation of surface groups

(1) By Adsorption of ions

In most cases **the charge on the sol particles originates by the selective adsorption of ions common to the particles from the dispersion medium.**

Examples. (*i*) Ferric hydroxide sol particles are positive because they adsorb the common ion Fe^{3+} from the aqueous medium.

$$Fe(OH)_3 + Fe^{3+} \longrightarrow \underset{\text{Positive ferric hydroxide sol particle}}{Fe(OH)_3/Fe^{3+}}$$

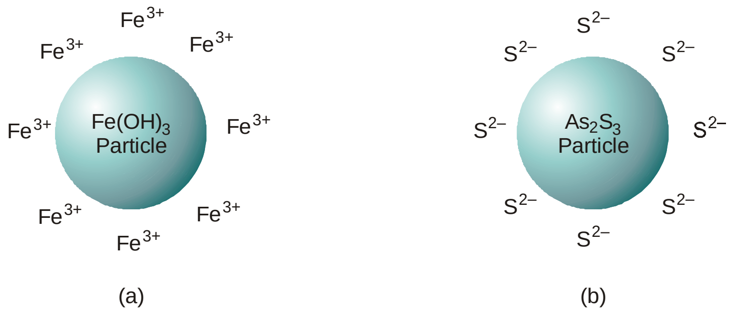


Figure 22.22
(*a*) $Fe(OH)_3$, sol particles adsorb Fe^{3+} ions and become positive ;
(*b*) As_2S_3 sol particles adsorb S^{2-} ions and acquire negative charge.

(*ii*) Arsenic sulphide sol particles acquire a negative charge since they adsorb the common ion S^{2-} from the medium.

$$As_2S_3 + S^{2-} \longrightarrow \underset{\text{Negative arsenic sulphide sol particle}}{As_2S_3/S^{2-}}$$

It is not necessary that a particular sol particles always adsorb the same kind of ions. In fact, **the particles may adsorb the anions or cations whichever are in excess and acquire the corresponding charge.** For example, AgCl sol produced by the addition of $AgNO_3$ solution to sodium chloride solution, bears a positive charge if Ag^+ ions are in excess. On the other hand, if Cl^- ions are in excess, the AgCl sol particles acquire a negative charge.

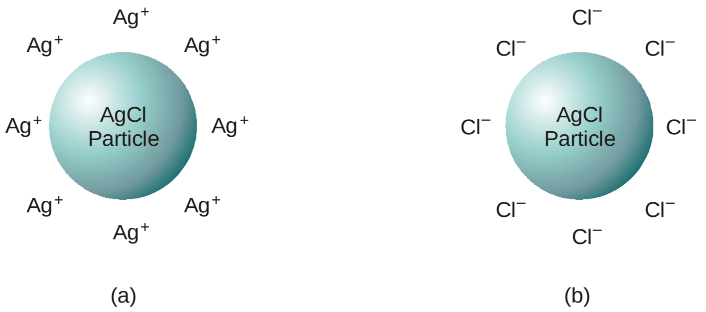


Figure 22.23
(*a*) When Ag^+ ions are in excess, AgCl sol particle adsorbs these ions and becomes positive; (*b*) when Cl^- ions are in excess, the AgCl particle adsorbs these and acquires a negative charge.

(2) Ionization of Surface groups

(*a*) **Charge on Soaps and Detergent sols.** Soaps and detergent sol particles are aggregates of many molecules. The hydrocarbons tails of the molecules are directed to the centre, while the groups $-COO^-Na^+$ (or $-OSO_3^-Na^+$) constitute the surface in contact with water. As a result of ionization of the surface groups, the particle surface is now made of the anionic heads $-COO^-$ (or $-OSO_3^-$). This makes the sol particle negative.

(*b*) **Charge on Protein sols.** Protein sol particles possess both acidic and basic functional groups. In aqueous solution at low pH, the $-NH_2$ group (basic) acquires a proton to give $-NH_3^+$ while at high pH the —COOH group (acidic) transfers a proton to OH^- to give $—COO^-$. Thus the protein sol particle has positive charge at low pH and negative charge at high pH. At an intermediate pH called the **isoelectric point,** the particles will be electrically neutral. The changes in the charge of the protein sol are shown by the direction of movement of the dispersed phase in electrophoresis.

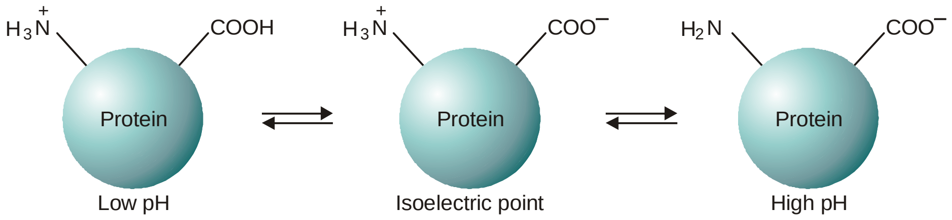


Figure 22.24
Charge on protein sol changes with pH.

STABILITY OF SOLS

A true colloidal solution is stable. Its particles do not ever coalesce and separate out. The stability of sols is mainly due to two factors :

(1) Presence of like charge on sol particles

The dispersed particles of a hydrophobic sol posses a like electrical charge (all positive or all negative) on their surface. Since like charges repel one another, the particles push away from one another and resist joining together. However, when an electrolyte is added to a hydrophobic sol, the particles are discharged and precipitated.

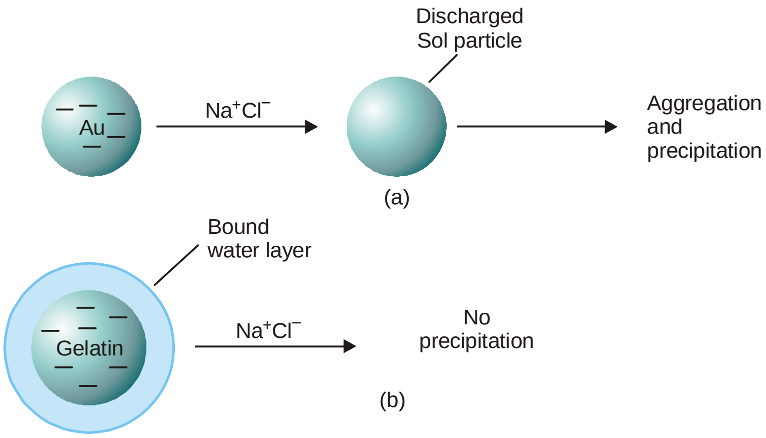


Figure 22.25

(*a*) A negatively charged gold particle is precipitated by Na^+ ions; (*b*) The water layer around gelatin particle does not allow Na^+ ions to penetrate and discharge the particle.

(2) Presence of Solvent layer around sol particle

The lyophilic sols are stable for two reasons. Their particles possess a charge and in addition have a layer of the solvent bound on the surface. For example, a sol particle of gelatin has a negative charge and a water layer envelopes it. When sodium chloride is added to colloidal solution of gelatin, its particles are not precipitated. The water layer around the gelatin particle does not allow the Na^+ ions to penetrate it and discharge the particle. The gelatin sol is not precipitated by addition of sodium chloride solution. Evidently, **lyophilic sols are more stable than lyophobic sols.**

ASSOCIATED COLLOIDS

The molecules of substances as soaps and artificial detergents are smaller than the colloidal particles. However in concentrated solutions these molecules form aggregates of colloidal size. **Substances whose molecules aggregate spontaneously in a given solvent to form particles of colloidal dimensions are called Associated or Association Colloids.**

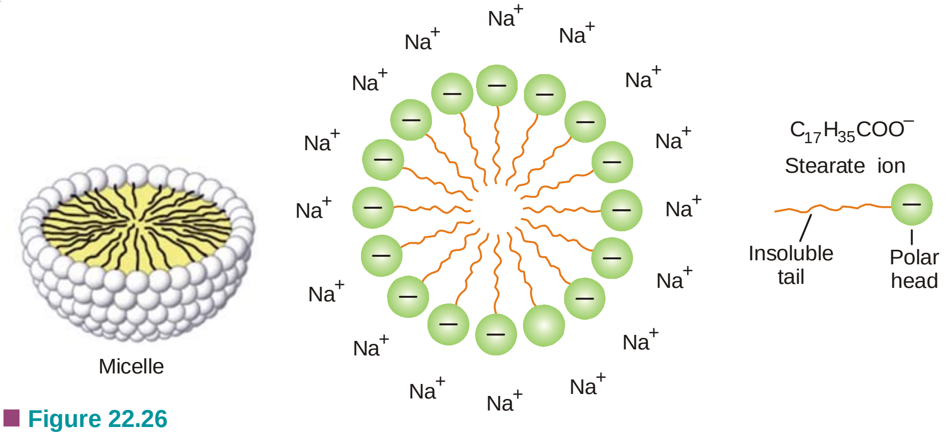
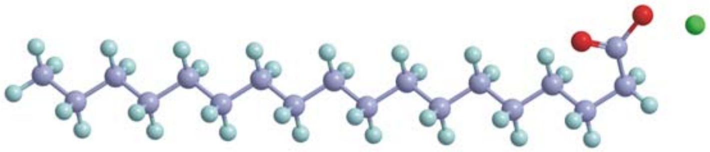


Figure 22.26

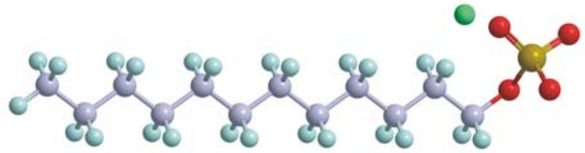
A soap micelle.

The colloidal aggregates of soap or detergent molecules formed in the solvent are referred to as **micelles.** Some examples of associated colloids are :

$C_{17}H_{35}—CO\bar{O}Na^+$
Sodium stearate



$C_{12}H_{25}—SO_2\bar{O}Na^+$
Sodium dodecyl sulphate



Explanation. Soap or detergent molecule ionises in water to form an anion and sodium ion. Thus sodium stearate (a typical soap) furnishes stearate anion and sodium ion in aqueous solution.

$$\underset{\text{Sodium stearate}}{C_{17}H_{35}COO^- \, Na^+} \longrightarrow \underset{\text{Stearate ion}}{C_{17}H_{35}COO^-} + Na^+$$

As many as 70 stearate ions aggregate to form a micelle of colloidal size. The stearate ion has a long hydrocarbon chain (17 carbons) with a polar —COO^- group at one end. The zig zag hydrocarbon tail is shown by a wavy line and the polar head by a hollow circle. In the micelle formation, the tails being insoluble in water are directed toward the centre, while the soluble polar heads are on the surface in contact with water (Fig. 22.26). The charge on the micelle due to the polar heads accounts for the stability of the particle.

Cleansing Action of Soaps and Detergents

The cleansing action of soap is due to

(1) Solubilisation of grease into the micelle
(2) Emulsification of grease

Solubilisation. In relatively strong solution the soap (or detergent) anions spontaneously form a micelle. The hydrocarbon tails are in the interior of the micelle and COO^- ions on the surface. The grease stain is thus absorbed into the interior of the micelle which behaves like liquid hydrocarbons. As the stain is detached from the fabric, the dirt particles sticking to the stain are also removed.

Emulsification. As already discussed the soap or detergent molecules are ionised in water. The anions are made of oil-soluble hydrocarbon tails and water-soluble polar heads. Thus soap anion has a long hydrocarbon tail with a polar head, —COO^-. When soap solution is added to a fabric, the tails of the soap anions are pegged into the grease stain. The polar heads protrude from the grease surface and form a charged layer around it. Thus by mutual repulsions the grease droplets are suspended in water. The emulsified grease stains are washed away with soap solution.

EMULSIONS

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

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

Types of Emulsions

There are two types of emulsions.

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

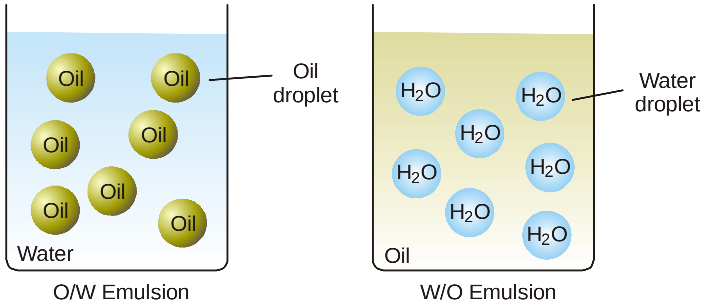


Figure 22.27
Two types of Emulsions.

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 an emulsion is called **emulsification.** This can be done by agitating a small proportion of one liquid with the bulk of the other. It is better accomplished by passing a mixture of the two liquid through a colloid mill known as **homogenizer.**

The emulsions obtained simply by shaking the two liquids are unstable. The droplets of the dispersed phase coalesce and form a separate layer. To have a stable emulsion, small amount of a third substance called the **Emulsifier** or **Emulsifying agent** is added during the preparation. This is usually a soap, synthetic detergent, or a hydrophilic colloid.

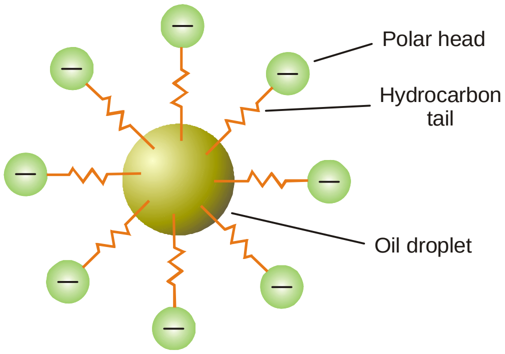


Figure 22.28
Role of emulsifier (Soap).

Role of Emulsifier

The emulsifier concentrates at the interface and reduces surface tension on the side of one liquid 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 oil droplet, while the head extends into water. Thus the soap acts as go-between and the emulsified droplets are not allowed to coalesce.

Properties of Emulsions

(1) **Demulsification.** Emulsions can be broken or 'demulsified' to get the constituent liquids by heating, freezing, centrifuging, or by addition of appreciable amounts of electrolytes. They are also broken by destroying the emulsifying agent. For example, an oil-water emulsion stabilized by soap is broken 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 other hand the dispersed liquid when mixed with it will at once form a separate layer. This property of emulsions is used to detect the type of a given emulsion.

WHAT ARE 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. The process of a gel formation is known as **Gelation.**

Explanation. Gelation may be thought of as partial coagulation of a sol. The coagulating sol particles first unite to form long thread-like chains. These chains are then interlocked to form a solid framework. The liquid dispersion medium gets trapped in the cavities of this framework. The resulting semisolid porous mass has a gel structure. A sponge soaked in water is an illustration of gel structure.

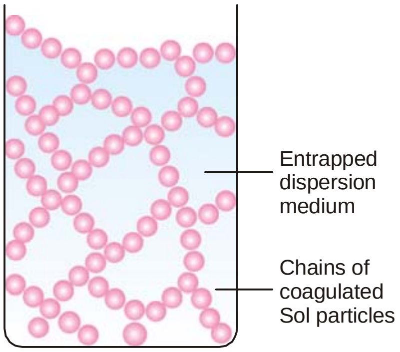


Figure 22.29
The network of the coagulated sol particles enclosing liquid, forming a gel.

Two types of Gels

Gels may be classified into two types :

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

Elastic gels are obtained by cooling fairly concentrated lyophilic sols. The linkages between the molecules (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 appropriate chemical action. Thus silica gel is produced by adding concentrated hydrochloric acid to sodium silicate solution of the correct concentration. The resulting molecules of silicic acid polymerise to form 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. But once 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. This causes increase in the volume of the gel and process is called **Swelling.**

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

(4) **Thixotropy.** Some gels are semisolid when at rest but revert to liquid sol on agitation. This reversible sol-gel transformation is referred to as **Thixotropy.** Iron oxide and silver oxide gels exhibit this 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 is essential 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 by a 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 our system. Halibut-liver oil and cod-liver that we take are, in fact, the emulsions of the respective oils in water. Many ointments for application to skin consist of physiologically active components dissolved in oil and made into an emulsion with water. Antibiotics such as penicillin and streptomycin are produced 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 or thixotropic paints* also contain long-chain polymers. At rest, the chains of molecules are coiled and entrap much dispersion medium. Thus the paint is a semisolid gel structure. When shearing stress is applied with a paint brush, the coiled molecules straighten and the entrapped medium is released. As soon as the brush is removed, the liquid paint reverts to the semisolid form. This renders the paint 'non-drip'.

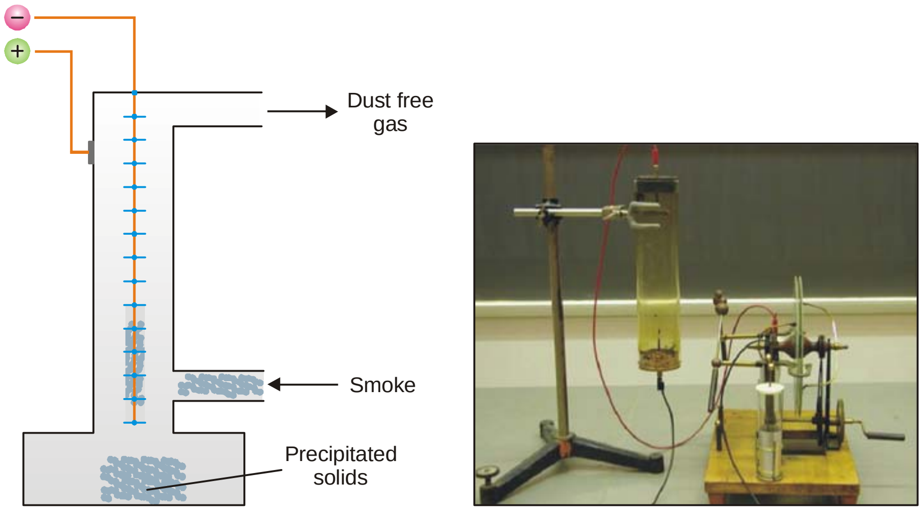


Figure 22.30
Cottrell Smoke precipitator.

(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** (See Fig. 22.30). The smoke is let past a series of sharp points charged to a high potential (20,000 to 70,000 V). The points discharge high velocity electrons that ionise molecules in air. Smoke particles adsorb these positive ions and become charged. The charged particles are attracted to the oppositely charged electrodes and get precipitated. The gases that leave the *Cottrell precipitator* are thus freed from smoke. 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 process of coagulation is used to remove these. The sol particles carry a negative charge. When aluminium sulphate (*alum*) is added to water, a gelatinous precipitate of hydrated aluminium hydroxide (*floc*) is formed,

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

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

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.

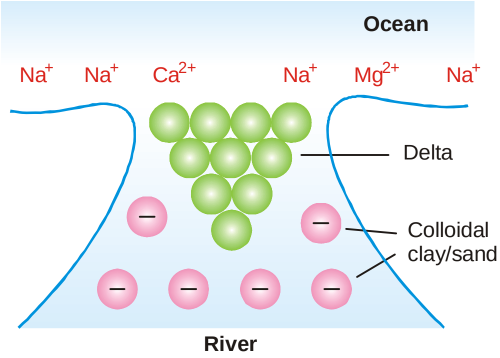


Figure 22.31
Formation of Delta.

(6) Formation of Delta

The river water contains colloidal particles of sand and clay which carry negative charge. The sea water, on the other hand, contains positive ions such as Na^+, Mg^{2+}, Ca^{2+}. As the river water meets sea 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 waste products such as urea and uric acid pass through the membranes, while colloidal-sized particles of blood proteins (haemoglobin) are retained. Kidney failure, therefore, leads to death due to accumulation of poisonous waste products in blood . Now-a-days, the patient's blood can be cleansed by shunting it 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, uric acid) diffuse across the tube walls into the washing solution. The purified blood is returned to the patient. The use of artificial kidney machine saves the life of thousands of persons each year.

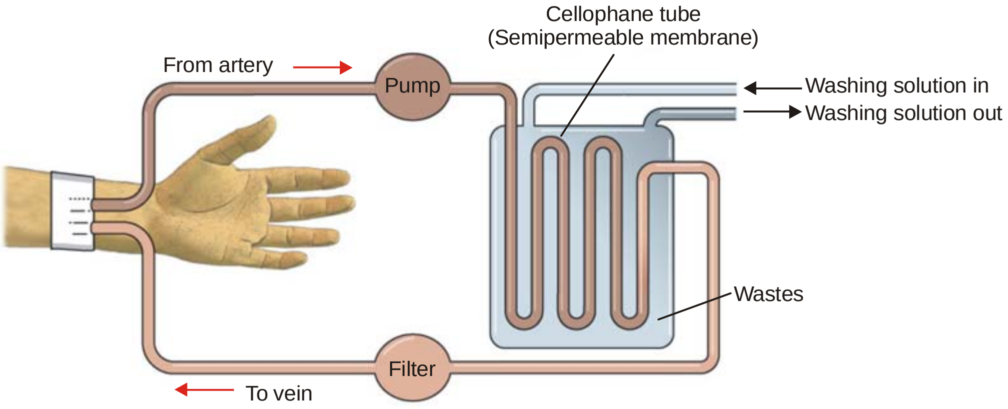


Figure 22.32
An artificial kidney machine for purification of blood by dialysis.

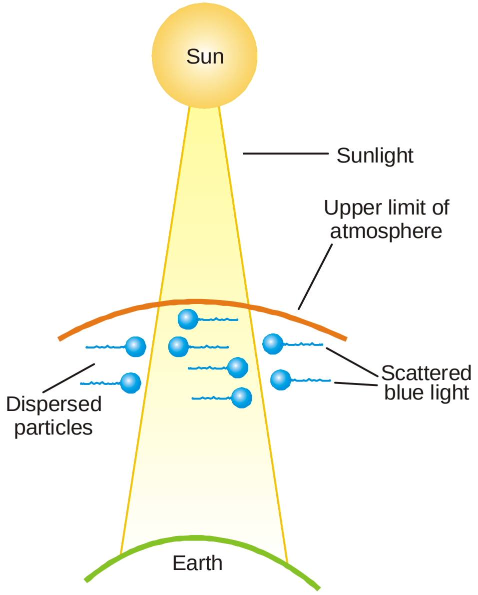
(8) Adsorption indicators

These indicators function by preferential adsorption of ions onto sol particles. Fluorescein (Na^+Fl) is an example of adsorption indicator which is used for the titration of sodium chloride solution against silver nitrate solution.

When silver nitrate solution is run into a solution of sodium chloride containing a little fluorescein, a white precipitate of silver chloride is first formed. At the end-point, the white precipitate turns sharply pink.

Explanation. The indicator fluorescein is a dye (Na^+Fl^-) which gives coloured anion Fl^- in aqueous solution. The white precipitate of silver chloride formed by running $AgNO_3$ solution into NaCl solution is partially colloidal in nature.

(*a*) *Before the end-point,* Cl^- ions are in excess. The AgCl sol particles adsorb these ions and become negatively charged. The negative $AgCl/Cl^-$ particles cannot adsorb the coloured fluorescein anions (Fl^-) due to electrostatic repulsion. Thus the precipitate remains white.



■ **Figure 22.33**
Blue colour of sky (illustration).

(*b*) *After the end-point,* Ag^+ ions become in excess. AgCl sol particles adsorb these and acquire 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 ice particles dispersed in air. As the sun rays enter the atmosphere (Fig. 22.33) these strike the colloidal particles. The particles absorb sunlight and scatter light of blue colour (4600–5100Å). The light that is incident at earth's surface is considerably reddened due to the removal of most of the blue light in the upper atmosphere.

WHAT ARE MACROMOLECULES ?

Colloidal solutions are formed by aggregation of atoms or molecules to give particles of colloidal size. Yet there are **substances which are themselves composed of giant molecules and dissolve in a solvent to yield colloidal solutions directly.** These giant molecules are termed **macromolecules.** The dimensions of the macromolecules fall in a range between 10Å and 10,000Å. Proteins (gelatin), synthetic polymers (plastics), synthetic rubber, cellulose and starch all possess macromolecules.

Solutions of macromolecules behave like reversible colloids or lyophilic sols. They show a weak *Tyndall effect* and possess high viscosity. **Macromolecules in solution do not carry an electric charge and do not show electrophoresis.**

Molecular weight of Macromolecules

The molecular weight is an important property of polymeric substances such as proteins, polymers (plastics, starch) and other macromolecules. **Generally, molecules of a protein or a polymer may not be of the same size.** Therefore all the experimental methods of molecular weight determination will give some kind of an average value. Two types of average molecular weights have been defined.

(1) **Number average molecular weight.** It is defined as :

$$\overline{M}_n = \frac{\text{Total weight, } W}{\text{Total number of particles}}$$

$$\overline{M}_n = \frac{n_1 M_1 + n_2 M_2 + ...}{n_1 + n_2 + ...}$$

$$\overline{M}_n = \frac{\Sigma n_i M_i}{\Sigma n_i}$$

$n_i M_i$ stands for the weight of macromolecules numbering n_i and having molecular weight M_i. The experimental methods based on properties which depend on the number of particles present *e.g.*, *osmotic pressure, yield number average molecular weight.*

(2) **Weight average molecular weight.** It is defined as :

$$\overline{M}_w = \frac{m_1 M_1 + m_2 M_2 + ...}{m_1 + m_2 + ...}$$

$$= \frac{\Sigma m_i M_i}{\Sigma m_i}$$

where m_1, m_2, etc. represent mass of macromolecules having molecular weights M_1, M_2, etc. respectively.

Since $W_i = n_i M_i$

$$\overline{M}_v = \frac{n_1 M_1^2 + n_2 M_2^2 + ...}{n_1 M_1 + n_2 M_2 + ...}$$

$$\overline{M}_v = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i}$$

Molecular weights determined by methods based on properties dependent on the mass of the particles are *the weight average molecular weights.*

According to the definitions set out here, $\overline{M}_w > \overline{M}_n$. The two are equal only when all particles are identical in weight.

SOLVED PROBLEM. A polymer mixture contains two polymers, one having molecular weight 100,000 and the other having molecular weight 60,000. The two components are present in equimolar concentration. Calculate the number average and the weight average molecular weights.

SOLUTION

$$\overline{M}_n = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2}$$

$$= \frac{1 \times 100,000 + 1 \times 60,000}{1 + 1} = \frac{160,000}{2}$$

$$= 80,000$$

This is the number average molecular weight of the polymer mixture.

$$\overline{M}_w = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i}$$

$$= \frac{1 \times (100,000)^2 + 1 \times (60,000)^2}{1 \times 100,000 + 1 \times 60,000}$$

$$= \frac{100 \times 10^8 + 36 \times 10^8}{160,000} = \frac{136 \times 10^8}{16 \times 10^4}$$

$$= \frac{136}{16} \times 10^4$$

$$= 85{,}000$$

Thus the weight average molecular weight is **85,000**.

DETERMINATION OF MOLECULAR WEIGHTS OF MACROMOLECULES

There are a number of methods available for the determination of molecular weight of macromolecules. Here, we will discuss the more important ones.

(1) Osmotic Pressure Method

The van't Hoff equation for dilute solutions may be written as :

$$p = \frac{c}{M} RT$$

or $$\frac{p}{c} = \frac{RT}{M}$$

where p = osmotic pressure, atm ; c = concentration of solution gl^{-1}; R = gas constant, 0.08205 l atm deg^{-1} mol^{-1}; T = kelvin temperature ; M = molecular weight of the solute (polymer).

In actual determination of molecular weight of a high polymer, osmotic pressure (p) of a series of small concentrations (c) is measured with the help of a special Osmometer shown in Fig. 22.35. The plot of p/c against c is a straight line (Fig. 22.34).

It is extrapolated to zero concentration. This gives RT/M as the intercept from which the molecular weight can be calculated .

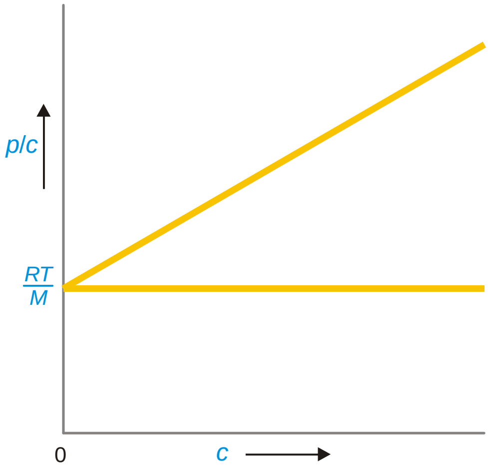


Figure 22.34
Plot p/c versus c : giving intercept = $\frac{RT}{M}$

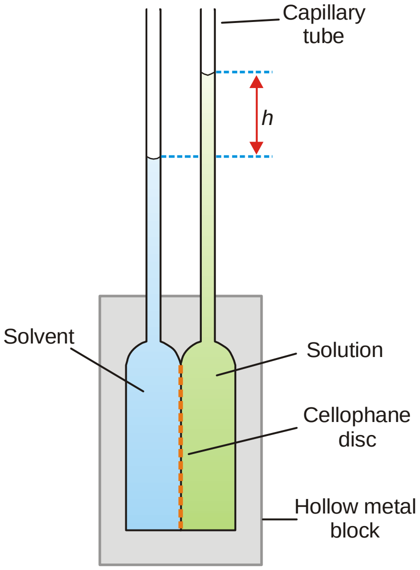


Figure 22.35
Fuos-Mead Osmometer for measuring osmotic pressure of polymer solution.

Fuos-Mead Osmometer. It is a modern device for measuring the osmotic pressure of polymer solutions (Fig. 22.35). It consists of two hollow metal blocks holding a cellophane disc in between.

Each block carries a capillary tube. The hollow metal compartments are charged with solvent and solution through the side-tubes (not shown). Osmosis occurs across the semipermeable membrane (cellophane disc). The height of the solution in the capillary (*h*) is read off differentially to eliminate surface tension effect.

(2) Viscosity method

It is a very convenient method for determining the molecular weights of macromolecules in solution. The addition of macromolecules to a solvent increases its viscosity over that of pure solvent.

The **relative viscosity** of a solution of a polymer, denoted by η_r, is given by the expression

$$\eta_r = \frac{\eta}{\eta_0} \qquad \text{...(1)}$$

where η is viscosity of solution and η_0 that of the solvent at the same temperature.

The **specific viscosity,** denoted by η_{sp}, is given by

$$\eta_{sp} = \eta_r - 1 \qquad \text{...(2)}$$

In terms of (1) and (2), the intrinsic viscosity is defined as

$$[\eta] = \lim_{C \to 0} \left(\frac{\eta_{sp}}{c} \right)$$

where c is the concentration of the solute. The plot η_{sp}/c against η gives a straight line. Extrapolation to $c = 0$ yields the intrinsic viscosity.

It was shown by staudinger that an empirical relationship exists between intrinsic viscosity $[\eta]$ and the molecular weight $[M]$ of the high polymer.

$$[\eta] = kM^a$$

where k and a are constants for a specific polymer in a specific solvent. Once k and a are known for a polymer-solvent combination, M may be calculated from a determination of the value of intrinsic viscosity.

The viscosity measurements yield the weight average molecular weight of a macromolecular substance.

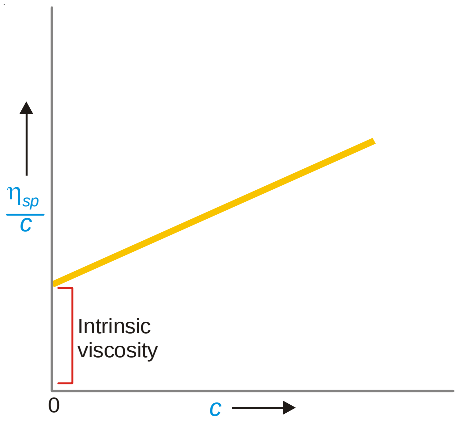


Figure 22.36
Plot of η_{sp}/c versus c.

(3) Svedberg's Sedimentation method

The rate of selling or sedimentation of polymer particles under the influence of gravitation force is very slow. Svedberg devised a centrifugal machine with the help of which macromolecules could be sedimented with speed. As a result, the particles move down in the containing tube. This causes a concentration gradient in the tube. The rate, dx/dt, at which the macromolecules sediment, is given in terms of the sedimentation constant S by the following expression :

$$S = \frac{dx}{dt} / \omega^2 x$$

where x is the distance of the solute species from the centre of rotation and ω is the angular velocity.

The sedimentation constant, S, is related to the molecular weight of the polymer by the expression :

$$M = \frac{S\,RT}{D\,(1 - \rho / \rho')}$$

where ρ and ρ' are the densities of the solvent and solute respectively. The rate at which sedimentation occurs, determined experimentally, can thus be used for finding the molecular weight of macromolecules. Since the rate of sedimentation depends on the mass of the particle undergoing sedimentation, the molecular weight obtained by this method is the *weight average molecular weight*, $\overline{M}_w$.

(4) Sedimentation Equilibrium method

This method for determining molecular weight of a high polymer is quicker and convenient compared to method (3).

If a sol is whirled sufficiently long in an ultracentrifuge, a stage is reached at which the sol no longer settles. At this stage an equilibrium is reached between the centrifugal force and diffusion of the material in a direction opposite to the centrifugal force. If c_1 and c_2 be the concentrations of the particles at points x_1 and x_2 cm from the centre of rotation, the molecular weight, M, of the high polymer is given by the relation

$$\text{In}\,\frac{c_2}{c_1} = \frac{M\omega^2(\rho - \rho')\,(x_2^2 + x_1^2)}{2RT\rho}$$

or

$$M = \frac{2RT\rho \ln c_2 / c_1}{\omega^2(\rho - \rho')\,(x_1^2 - x_2^2)}$$

By determining the concentrations c_1 and c_2 at the two levels x_1 and x_2 in the settling cell at sedimentation equilibrium, M can be calculated.

EXAMINATION QUESTIONS

1. Define or explain the following terms :

(*a*) Catalyst
(*b*) Homogeneous catalysis
(*c*) Heterogeneous catalysis
(*d*) Activation energy
(*e*) Catalysis
(*f*) Arrhenius equation

2. What are colloids? How are they classified? How would you prepare the colloidal solution of

(*a*) gold;
(*b*) arsenious sulphide; and
(*c*) sulphur.

3. What is electrophoresis? How does this phenomenon provide information about the sign of charge on particles.

4. (*a*) What is meant by peptization? Give a suitable example.
(*b*) Describe a method for purifying colloidal solutions.
(*c*) Discuss the function of a protective colloid.

5. What are emulsions? How are they classified? How are they prepared?

6. (*a*) What are lyophillic colloids? Why are they called reversible colloids?
(*b*) Why $MgCl_2$ is a better coagulant than KCl for As_2S_3 sol.

7. Discuss the origin of charge on colloidal particles. What is meant by electrical double layers? What is meant by Zeta potential?

8. (*a*) Explain the stability of colloids.
(*b*) Write the difference between gels and emulsions.
(*c*) Explain the Schulze-Hardy rule for coagulation.

9. State different methods of preparation of colloidal dispersions. Describe Bredig's arc method in detail.

10. (*a*) Explain Relative, Specific, and Intrinsic viscosities. How are they related to each other?
(*b*) Describe the viscosity method for determining the molecular weight of a polymer.

11. What are emulsions and gels? What distinguishes between elastic and non-elastic gels?

12. (*a*) What do you understand by the number average and the weight average molecular weight of macromolecules?

(*b*) Discuss in detail the sedimentation equilibrium method for determining the molar masses of polymers.

13. (*a*) Define number average and weight average molecular weights.

(*b*) Describe osmometric method for the determination of molecular masses of polymers.

(*c*) Write intrinsic viscosity-molecular weight relationship. Define the values of two constants appearing in the above relation when fractions of polymer of molecular weights 34000, 61000 and 130000 dissolved in an organic solvent gave the intrinsic viscosities 1.02, 1.60 and 2.75 respectively at 25°C.

14. (*a*) What are emulsions and what is emulsifying agent?

(*b*) What are Micelles? Give examples.

15. (*a*) How is weight average and number average molecular weight ratio is used to predict the polydispersity in polymer systems?

(*b*) "Even the 95% purity of chemicals is not sufficient for the synthesis of polymer chains containing more than 20 molecules". Justify the statement.

16. (*a*) What is a colloid? Discuss the essential difference between lyophillic and lyophobic colloids.

(*b*) Write short notes on :

(*i*) Tyndall effect and Brownian movement

(*ii*) Electrophoresis and its applications (*Nagpur BSc, 2000*)

17. (*a*) Describe condensation polymerisation and addition polymerisation. Point out the type of polymerisation process involved in the following :

(*i*) Polystyrene (*ii*) Nylon

(*iii*) Polyester (*iv*) Polyethylene

(*b*) Explain with examples the number average and weight average molecular weights of polymers. Which type of molecular weight is determined by the following techniques :

(*i*) Osmotic pressure method

(*ii*) Sedimentation equilibrium method (*Punjabi BSc, 2000*)

18. Discuss briefly the viscosity method for the determination of molecular weight of a polymer. (*Guru Nanak Dev BSc, 2000*)

19. For the determination of molecular weight of polymers how can the viscosity measurement be helpful? (*Panjab BSc, 2000*)

20. (*a*) What is a protective colloid? How does a hydrophilic colloid stabilise a hydrophobic one? Give an account of Gold number in this context.

(*b*) What do you understand by the coagulation value of an electrolyte?

(*c*) What are gels? Give examples. (*Lucknow BSc, 2001*)

21. (*a*) What is the size range of colloidal particles? Distinguish between a molecular solution and a colloidal dispersion.

(*b*) Describe one method for the preparation of colloidal solutions. (*Mizoram BSc, 2002*)

22. Write a short note on 'origin of charge on colloidal particles'. (*Arunachal BSc, 2002*)

23. Give in details the methods of preparation of colloids. (*Sri Venkateswara BSc, 2002*)

24. Give three points of difference between lyophobic and lyophillic colloids. (*Arunachal BSc, 2003*)

25. Explain why :

(*a*) Alum is used in town water supply

(*b*) Alum is used in shaving

(*c*) Tyndall cone is formed when a beam of light is concentrated on a colloidal solution

(*Agra BSc, 2004*)

26. Define gold number. The gold numbers of A, B, C and D are 0.005, 0.05, 0.5 and 5 respectively. Which of these has the greatest protective action. Explain your answer. (*Mysore BSc, 2004*)

27. Calculate the number average molecular weight of a sample of nylon having 1000 molecules of 5000 ; 2000 molecules of 6000 and 4000 molecules of 1000 molecular weight.

Answer. 3000 (*Sri Venkateswara BSc, 2005*)

28. Calculate the weight average molecular weight of a polymer containing equal number of particles with molecular weights 5000 and 10000.

Answer. 8333 (*Madurai BSc, 2005*)

29. Calculate weight average molecular weight of a sample containing equal number of particles with molecular weight 10,000 and 20,000.

Answer. 16667 (*Baroda BSc, 2006*)

30. Calculate number average molecular weight of a given sample of a polymer having 1000 molecules of 5000, 500 molecules of 4000 and 200 molecules of 3000 molecular weights.

Answer. 4470 (*Punjabi BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. In true solutions, the diameter of the dispersed particles is in the range from

(*a*) 1 Å to 10 Å
(*b*) 10 Å to 100 Å
(*c*) 100 Å to 200 Å
(*d*) 200 Å to 500 Å

Answer. (*a*)

2. In a suspension the diameter of the dispersed particles is of the order

(*a*) 10 Å
(*b*) 100 Å
(*c*) 1000 Å
(*d*) 2000 Å

Answer. (*d*)

3. In a colloidal solution, the diameter of dispersed particle is in the range

(*a*) 10 Å to 100 Å
(*b*) 10 Å to 500 Å
(*c*) 10 Å to 1000 Å
(*d*) 10 Å to 2000 Å

Answer. (*d*)

4. A colloidal solution consists of

(*a*) a dispersed phase
(*b*) a dispersion medium
(*c*) a dispersed phase in a dispersion medium
(*d*) a dispersion medium in a dispersed phase

Answer. (*c*)

5. The sols in which the dispersed phase exhibits a definite affinity for the medium or the solvent is called

(*a*) lyophillic sols
(*b*) lyophobic sols
(*c*) emulsions
(*d*) hydrosols

Answer. (*a*)

6. The scattering of light by the dispersed phase is called

(*a*) Brownian movement
(*b*) Tyndall effect
(*c*) adsorption
(*d*) electrophoresis

Answer. (*b*)

7. In lyophobic sols, the dispersed phase has no ________ for the medium or solvent

(*a*) repulsion (*b*) attraction
(*c*) solvation (*d*) hydration

Answer. (*b*)

8. The lyophillic sols are
(*a*) reversible in nature
(*b*) irreversible in nature
(*c*) sometimes reversible sometimes nonreversible
(*d*) none of the above

Answer. (*a*)

9. The dispersal of a precipitated material into colloidal solution by the action of an electrolyte in solution is called
(*a*) coagulation (*b*) dialysis
(*c*) peptization (*d*) ultra-filtration

Answer. (*c*)

10. An arsenic sulphide sol (AS_2S_3) is prepared by the reaction

$$AS_2O_3 + H_2S \longrightarrow AS_2S_3(sol) + 3H_2O$$

This method of preparing colloidal solution is
(*a*) reduction (*b*) oxidation
(*c*) hydrolysis (*d*) double decomposition

Answer. (*d*)

11. A sol of sulphur is produced by passing hydrogen sulphide into solution of sulphur dioxide

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

This method is known as
(*a*) reduction (*b*) oxidation
(*c*) hydrolysis (*d*) double decomposition

Answer. (*a*)

12. The process of removing ions (or molecules) from a sol by diffusion through a permeable membrane is called
(*a*) ultra-filtration (*b*) dialysis
(*c*) electrophoresis (*d*) osmosis

Answer. (*b*)

13. ________ do not show Tyndall effect
(*a*) true solution (*b*) colloidal solutions
(*c*) suspensions (*d*) none of these

Answer. (*a*)

14. The continuous rapid zig-zag movement executed by a colloidal particle in the dispersion medium is called
(*a*) Tyndall effect (*b*) Brownian movement
(*c*) electrophoresis (*d*) peptization

Answer. (*b*)

15. The explanation of Brownian movement was given by
(*a*) Robert Brown (*b*) Robert Boyle
(*c*) Albert Einstien (*d*) Tyndall

Answer. (*c*)

16. The movement of sol particles under an applied electric potential is called

(*a*) electrophoresis (*b*) electro-osmosis
(*c*) electrofiltration (*d*) none of these

Answer. (*a*)

17. The presence of the double layer in colloids accounts for

(*a*) kinetic properties (*b*) electrical properties
(*c*) optical properties (*d*) stability of colloids

Answer. (*b*)

18. If the sol particles in a given colloid moves towards the anode, they carry

(*a*) positive charge (*b*) negative charge
(*c*) no charge (*d*) sometimes positive sometimes negative charge

Answer. (*b*)

19. A sol of Ferric chloride moves to the negative electrode. The colloidal particles carry

(*a*) no charge (*b*) positive charge
(*c*) negative charge (*d*) none of these

Answer. (*b*)

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

(*a*) osmosis (*b*) diffusion
(*c*) electro-osmosis (*d*) electrophoresis

Answer. (*c*)

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

(*a*) peptization (*b*) coagulation
(*c*) osmosis (*d*) diffusion

Answer. (*b*)

22. The precipitating effect of an ion in dispersed phase of opposite charge ________ with the valence of the ion

(*a*) decreases (*b*) increases
(*c*) no effect (*d*) none of these

Answer. (*b*)

23. The precipitating power of Al^{3+}, Na^+, Ba^{2+} is in the order

(*a*) $Na^+ > Ba^{2+} > Al^{3+}$ (*b*) $Ba^{2+} > Na^+ > Al^{3+}$
(*c*) $Al^{3+} > Na^+ > Ba^{2+}$ (*d*) $Al^{3+} > Ba^{2+} > Na^+$

Answer. (*d*)

24. The effectiveness of SO_4^{2-}, Cl^- and $[Fe(CN)_6]^{3-}$ ions for precipitating $Fe(OH)_3$ positive sol decreases in the order

(*a*) $[Fe(CN)_6]^{3-} > SO_4^{2-} > Cl^-$ (*b*) $Cl^- > SO_4^{2-} > [Fe(CN)_6]^{3-}$
(*c*) $SO_4^{2-} > Cl^- > [Fe(CN)_6]^{3-}$ (*d*) $[Fe(CN)_6]^{3-} > Cl^- > SO_4^{2-}$

Answer. (*a*)

25. The precipitating effect of an ion on dispersed phase increases with the valence of the precipitating ions. This rule is known as

(*a*) flocculation value rule (*b*) Hardy-Schulze rule
(*c*) Brownian rule (*d*) gold number rule

Answer. (*b*)

26. The charge on AS_2S_3 sol is due to

(*a*) absorption of H^+ ions (*b*) adsorption of H^+ ions
(*c*) adsorption of S^{2-} ions (*d*) absorption of S^{2-} ions

Answer. (*c*)

27. The number of milligrams of a hydrophilic colloid that will just prevent the precipitation of 10 ml of gold sol on addition of 1 ml of 10 per cent sodium chloride solution is called

(*a*) gold number	(*b*) charge number
(*c*) absorption number	(*d*) silver number

Answer. (*a*)

28. The _______ the gold number of a hydrophilic colloid, the greater is its protective power

(*a*) higher	(*b*) lower
(*c*) constant	(*d*) none of these

Answer. (*b*)

29. The charge on the sol particles is due to _______ of ions common to the particles from the dispersion medium

(*a*) selective adsorption	(*b*) selective coagulation
(*c*) selective peptisation	(*d*) selective absorption

Answer. (*a*)

30. An emulsion is a colloidal solution of a _______ dispersed in another liquid

(*a*) solid	(*b*) liquid
(*c*) gas	(*d*) medium

Answer. (*b*)

31. A gel is a colloidal system in which a _______ is dispersed in a _______ medium.

(*a*) solid, liquid	(*b*) liquid, solid
(*c*) liquid, liquid	(*d*) liquid, gas

Answer. (*b*)

32. The human kidneys purify the blood by _______ through natural membranes

(*a*) osmosis	(*b*) diffusion
(*c*) dialysis	(*d*) emulsification

Answer. (*c*)

33. Milk is an example of

(*a*) sol	(*b*) gel
(*c*) emulsion	(*d*) true solution

Answer. (*c*)

34. The function of an emulsifier is to

(*a*) coagulate a colloidal solution	(*b*) stabilise an emulsion
(*c*) stabilise a sol	(*d*) electrify a colloidal solution

Answer. (*b*)

35. Ice cream is a dispersion of _______ in cream

(*a*) water	(*b*) water vapour
(*c*) ice	(*d*) cooling agent

Answer. (*c*)

36. The function of alum used for the purification of water is to

(*a*) coagulate the sol particles	(*b*) disperse the sol particles
(*c*) emulsify the sol particles	(*d*) absorb the sol particles

Answer. (*a*)

37. The macromolecules possess

(*a*) high viscosity	(*b*) high molecular weights
(*c*) show a weak Tyndall effect	(*d*) all of these

Answer. (*d*)

38. The blue colour of the sky is due to

(*a*) Brownian movement
(*b*) Tyndall effect
(*c*) the presence of macromolecules
(*d*) electrophoresis

Answer. (*b*)

39. The weight average molecular mass of macromolecules is ________ than the number average molecular mass

(*a*) greater
(*b*) lesser
(*c*) equal
(*d*) none of these

Answer. (*a*)

40. Macromolecules in solutions do not show

(*a*) electrophoresis
(*b*) osmosis
(*c*) Tyndall effect
(*d*) Brownian movement

Answer. (*a*)

41. In osmosis pressure method for determination of molecular weight of macromolecules, a plot of p/c versus $\frac{RT}{M}$ is a ________

(*a*) straight line
(*b*) curved line
(*c*) sine curve
(*d*) none of these

Answer. (*a*)

42. Fog is an example of colloidal system of

(*a*) liquid dispersed in a liquid
(*b*) solid dispersed in a solid
(*c*) gas dispersed in a liquid
(*d*) liquid dispersed in a gas

Answer. (*d*)

43. Gold number gives

(*a*) the number of gold atoms present is one gram of gold
(*b*) the number of gold atoms required to coagulate one g of the colloidal solution
(*c*) the number of gold atoms present in one gram of gold alloy
(*d*) none of the above

Answer. (*d*)

44. Which of the following does not show Tyndall effect?

(*a*) colloidal solution
(*b*) isotonic solution
(*c*) both of these
(*d*) none of these

Answer. (*b*)

45. Which of the following has minimum flocculating power?

$$Pb^{4+},\ Al^{3+},\ Ba^{2+},\ Na^{+}$$

(*a*) Na^+
(*b*) Ba^{2+}
(*c*) Al^{3+}
(*d*) Pb^{4+}

Answer. (*a*)

46. Smoke is an example of

(*a*) solid dispersed in solid
(*b*) solid dispersed in liquid
(*c*) solid dispersed in gas
(*d*) gas dispersed in solid

Answer. (*c*)

47. Which of the following is not a colloidal solution?

(*a*) brine solution
(*b*) fog
(*c*) smoke
(*d*) butter

Answer. (*a*)

48. Which of the following is the most effective in causing the coagulation of ferric hydroxide sol?

(*a*) NaCl
(*b*) Na_2SO_4
(*c*) $K_2 SO_4$
(*d*) $K_3 [Fe (CN)_6]$

Answer. (*d*)

49. Peptization involves

(*a*) digestion of food
(*b*) precipitation of colloidal solution
(*c*) hydrolysis of proteins
(*d*) breaking of a precipitate to colloidal state

Answer. (*d*)

50. The cleansing action of soap is due to

(*a*) hydrolysis of salt present in soap
(*b*) ionisation of salt present in soap
(*c*) high molecular mass of soap
(*d*) emulsification properties of soap

Answer. (*d*)

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