

COLLOIDS

by

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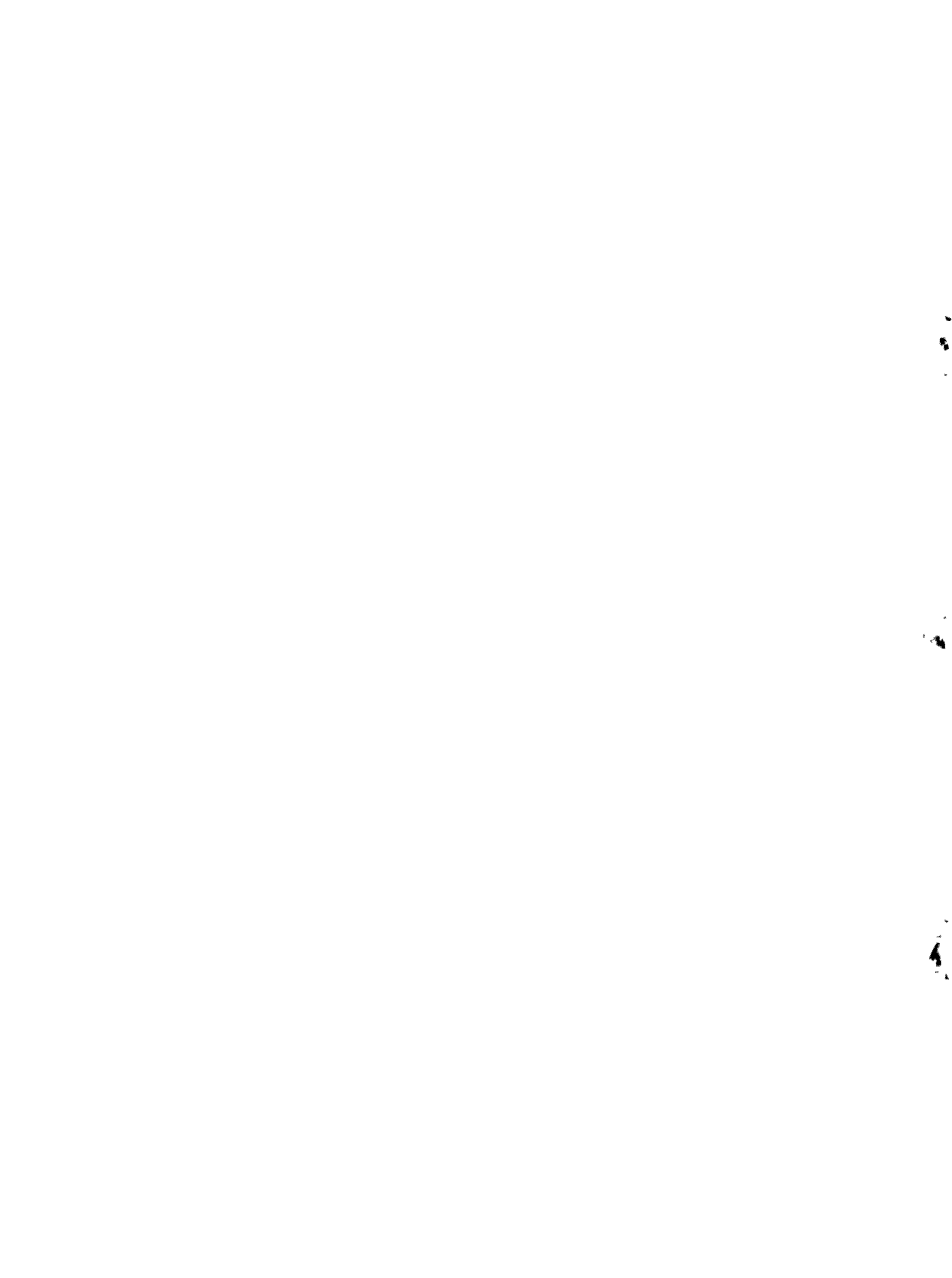
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The most sensitive and difficult control problem occurs at the moment of the first precipitating incident and during the stage of transformation in an active crowd. A show of weakness—or maybe even unnecessary repression—will escalate the crowd into the Roman-holiday stage. It is essential to identify spokesmen who command a hearing with the crowd—often not the established group leaders—and open serious negotiations with them. Poorly arranged negotiating sessions before television cameras are easily turned into occasions for incitement of the crowd. If the provocations of excessive policing are avoided and one or two dramatic concessions of great symbolic importance made, a cooling-off period may be secured in which more comprehensive measures to relieve tensions in the situation can be undertaken.

Once collective behaviour is fully escalated there is seldom any technique available except massive suppression, and some experts believe that crowd behaviour will spring up again if crushed before it has substantially run its course. Interference with an expressive crowd, and even with many fads, crazes, and instances of hysterical contagion, often turns it into a hostile, active one. As the intensity of feeling begins to decline, the time is then ripe to quicken the end of crowd behaviour by intensifying negotiations with spokesmen respected by the crowd.

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(R.H.T.)

Colloids

A colloid is any substance composed of fine particles whose dimensions are much larger than those of atoms or ordinary molecules but much smaller than those of particles visible to the unaided eye; colloids cannot be detected by optical microscopes in transmitted light. Usually colloidal particles exist as a dispersion in some medium, but they may exist purely—*i.e.*, without a medium. Some colloids are vital to everyday life—cheese, dough, paints, silk, rubber, proteins, plastics, clay, foam, smoke, and gelatin, for example. The presence or absence of colloids may be harmful or useful. They can be generated and also eliminated by nature as well as by industrial or technological processes. Because colloidal systems have certain properties in common and because their existence is limited by a range of factors, such as temperature, they were once classified as another state of matter (liquid, solids, and gas being the three classical states, or phases). This classification is no longer adequate. A classification according to the particular states of matter involved—*e.g.*, solid in liquid, liquid in liquid, solid in gas—although not exhaustive is still useful.

To understand the behaviour of colloids, a knowledge of molecular structure is necessary, but only a brief generalization can be given here (for a full account, see CHEMISTRY; ATOMIC STRUCTURE; MOLECULAR STRUCTURE; CHEMICAL BONDING). Every atom, the smallest particle of an element, consists of a positively charged nucleus surrounded by negative electrons (equal in number to the positive charges) arranged in a characteristic structure for each element. These electron structures tend to be unstable, and the neutral atoms either gain or lose electrons to become charged negatively or positively; or atoms share electrons in order to achieve stable configurations. Charged atoms are called ions. Oppositely charged particles attract one another, and ions may thus bond to form compounds that are termed electrovalent, or ionic. Shared electrons, on the other hand, do not produce ions but directly bond the sharing atoms into molecules, or other kinds of aggregates, and such bonds and compounds are called covalent. Other kinds of bonding between molecules and atoms result in the various states of matter and in special kinds of association, especially among organic molecules. Organic compounds all have in common the fact that they are built around open or closed chains of covalently bonded carbon atoms and that these structures can be classified and named according to their characteristics. Furthermore, types of organic compounds can be linked together in various ways, a fact of primary importance in the study of colloids. Various groups of atoms, called functional groups, which are not compounds and cannot exist free, may also be linked in endless variation to the carbon chains and cycles; functional groups always give the parent molecule their own characteristic properties, and therefore an organic molecule may have many properties that react to the environment in recognizable ways, no matter how complex it may be. Chemical reactions always involve changes in the electron structures of atoms and, therefore, in the bonds between atoms or the molecules involved.

Colloidal particles consist of aggregates of molecules, sometimes only of atoms, linked or bonded together in a variety of ways. The production of colloidal particles or their elimination, either by further clotting or by breaking them up into molecules, is based on standard principles of chemical and physical bonding, but still contains elements of empiricism, especially in obtaining the desired size range (between 10^{-7} and 10^{-3} cm). It is safe to say that the colloids prepared in living organisms by biological processes are absolutely vital to the existence of the organism and that the colloids generated with inorganic compounds in the earth, waters, atmosphere, and in technological processes, though not nearly so important at first examination, are just as vital to the existence of life-forms.

The general structure of matter

This article is divided into the following sections and subsections:

History of colloid studies

Irreversible systems

Lyophobic sols (dilute suspensions)

Emulsions

Foams

Pastes (concentrated suspensions)

Gel structures

Reversible systems

Polymers

Proteins

Gels

Association colloids

HISTORY OF COLLOID STUDIES

The art of preparing and processing colloidal materials goes back as far as civilization itself. The scientific study of colloids, however, dates only from the beginning of the 19th century, one of the first important experiments being with a lump of clay in a U-tube filled with water. When an electric potential difference was applied to the two ends of the tube, the water was seen to move toward the negative electrode, while particles of clay moved toward the positive electrode. Such a movement to either positive or negative electrode of suspended, now called colloidal, particles under an applied electrical field is termed electrophoresis. Another early discovery was that particles in suspension when viewed under a microscope are in ceaseless, irregular, or random motion, called Brownian movement in honour of a British botanist, Robert Brown, who in 1827 first recorded the phenomenon using aqueous suspensions of pollen. Brownian movement is now known to result from the irregular bombardment of colloidal particles by molecules of the surrounding liquid.

Francesco Selmi, an Italian chemist, published (1845–50) the first systematic study of inorganic colloids, in particular silver chloride, Prussian blue, and sulfur. Selmi showed that these colloidal bodies would coagulate (group together into large aggregates that separated from the liquid, a process similar to the precipitation of a substance from solution into solid particles that then settle out) if salts were added to the system and that the salts differed in their coagulating or precipitating power. From the absence of temperature changes upon coagulation, or upon another process called peptization (see below), he concluded that the particles were not simple molecules distributed as molecules throughout the medium but some kind of combination of molecules.

Thomas Graham, a Scottish chemist, is usually regarded as the founder of modern colloid science. During the 1860s, Graham clearly recognized those properties regarded as characteristic of the colloidal state, such as absence of crystallinity and of ordinary chemical relations and an exceedingly low rate of diffusion, which arises from the large size of colloidal particles (about 10^{-7} to about 10^{-3} centimetre). He also recognized the biological significance of colloids.

The term colloid (from the Greek word for "glue") was coined by Graham in 1861 and applied by him to such substances as gelatin, albumin, and gums, which are retained by membranes such as parchment paper when subjected to dialysis (a technique of separating substances by their different rates of diffusion through semipermeable membranes). Such substances as salts and sugars, which readily pass through the membrane, he termed crystalloids, because of the comparative ease with which they could be obtained in crystalline form from their solutions. Of Graham's other contributions to the nomenclature of colloids, those still in use are the terms sol, gel, peptization, and syneresis. A sol is a dispersion of a solid in discrete units (*i.e.*, a solid broken up into independent particles and distributed through a liquid or gaseous medium), the type of dispersion medium being shown by a prefix—*e.g.*, hydrosol (for dispersions in water), aerosol (for dispersions in air). A gel is a dispersion of the solid particles linked together to form a structure with some mechanical strength. Peptization, from analogy with peptic digestion, referred to the spontaneous dispersion

of a precipitate to form a colloid as, for example, the dispersion of a precipitate of Prussian blue when an attempt is made to wash it. The term syneresis (from a Greek word meaning "to contract") was suggested by the study of silicic acid (obtained from water glass and dilute acids) for the phenomenon of spontaneous shrinkage of a gel with the exudation of the dispersion medium.

An interesting example is provided by gold sols, colloids that are prepared by reducing (freeing the elemental metal from its compound) dilute solutions of gold chloride and that are usually strikingly coloured (ruby red, blue, green, and other colours). Although gold sols had been known to the alchemists of the 17th century, the English physicist and chemist Michael Faraday, in 1857, was the first to make a scientific study of their preparation and properties. He showed that addition of salts turned the ruby-red sols blue and then coagulated them and that these effects could be prevented by the addition of gelatin and other hydrophilic (easily dissolved in water as compared with hydrophobic, difficult to dissolve in water) colloids. The ruby sols, which had all the appearances of solutions, were shown by him to contain particles of gold because, unlike true solutions, a cone of light passing through them became visible to an observer situated at right angles to the beam. This phenomenon, later studied in more detail by John Tyndall, a British physicist, is usually referred to as the Tyndall effect. Of the other metal sols, those of silver were much studied, particularly in the United States, in connection with the photographic process. The preparation and purification of sols were facilitated by electro dialysis (separation by applying an electrical field, and allowing the dissolved impurities to diffuse through a membrane) and by ultrafiltration—*i.e.*, filtration through filters of very fine pore size.

The stability of hydrophobic sols to salts that were added to the system was quantitatively examined after electrophoresis had shown that all colloids carry an electric charge, the same kind of charge on each particle in the system, and that it is to this charge that hydrophobic colloids owe their stability; because like charges repel one another, the particles cannot come into collision and, therefore, cannot coagulate and group together into larger than colloidal size. Coagulation is brought about, however, by the addition of an ion carrying the charge opposite to that on the colloidal particle, and the coagulating power of an ion increases rapidly with its charge (*e.g.*, to coagulate negatively charged sols such as gold or arsenic sulfide, the requisite concentration of sodium, calcium, and aluminum ions, with single, double, and triple positive charges, respectively, are approximately in the ratio 1:1/70:1/900). Addition of a hydrophilic colloid to a hydrophobic one protects the latter from the coagulating action of salts, a phenomenon termed protection. Hydrophilic colloids such as the proteins, the condensation products of amino acids that are the essential constituents of all living cells, are only precipitated by high concentrations of a salt. For a series of salts, the comparative efficacy runs approximately parallel to their solubility in water, indicating that precipitation of the colloid is caused by dehydration, or removal of water molecules, from the colloid particle.

In 1903 the invention of the ultramicroscope brought a notable advance in techniques for examining colloidal systems. The chief difference from the usual method of microscopic examination was the mounting of the microscope at right angles to the incident light beam, which strikes the object to be examined; the colloidal particles, because of the light they scatter laterally, then stand out as bright points of light on a dark ground. This apparatus can detect particles down to about 100 angstroms (Å) in size (one angstrom is 10^{-8} centimetre, or 3.9370079×10^{-9} inch), compared with about 2000 Å for the ordinary microscope.

In 1905 the terms hydrophilic and hydrophobic were introduced to differentiate aqueous suspensions of markedly differing properties, as typified by gelatin and the colloidal dispersion of metals, respectively. These types differ in many ways, the most striking being in their sta-

Stability
of sols

Graham's
definitions

Hydrophilic and hydrophobic suspensions

bility to salts added to their systems and their reversibility after precipitation. A gelatin solution, for example, is only precipitated by high concentrations of salts and, after drying, will readily take up water again. It "likes" water; it is hydrophilic. A sol of a metal, or of an insoluble salt, is precipitated readily by traces of salts and does not return to the colloidal state, even if the salts are eliminated by washing the precipitate. It "abhors" water; it is hydrophobic. These phenomena reveal the reversible property of hydrophilic systems and the irreversible property of hydrophobic ones. For dispersion media other than water, the parallel terms lyophilic and lyophobic (*lyo-* from a Greek word meaning "to loosen, to dissolve") were proposed.

Many striking developments in physics and chemistry in the early years of the 20th century were relevant to colloids, including, for example, the increase in knowledge of the electronic structure of the atom, of molecular size and shape, and of the nature of solutions. In addition, powerful new methods for studying the size and shape of colloidal particles were developed, such as ultracentrifugation, electrophoresis, diffusion, and the scattering of light and of X-rays. The study of interfaces (surfaces of discontinuity between substances or states of matter), clearly of great relevance to colloids, developed as a major field, surface chemistry. The investigation of colloids in industry and biology also led to major developments in the knowledge of detergents, dyes, proteins, polymers, and other substances.

IRREVERSIBLE SYSTEMS

Classes of colloids

The main classification of colloids is into reversible and irreversible systems. (Any system is irreversible if, after its components have been induced to interact, the products of their reaction are so stable, or are removed so effectively from the system, that no manipulation of the system will bring about a reaction to reproduce the original components. In a reversible system the products of a reaction may be induced to react in a way that will reproduce the original components. The reactions may be physical or chemical.) In the irreversible systems, to which belong sols (dilute suspensions), emulsions, foams, pastes (concentrated suspensions), and certain types of gels, the size of the particles is greatly dependent upon the method of preparation. In the reversible systems particle size is either determined by the molecular size of the colloidal material, as in polymers, polyelectrolytes, and proteins, or the particles are formed from small molecules by a reversible association, as in soaps, detergents, and certain dyes. The most important aspects of these diverse systems are outlined below.

Lyophobic sols (dilute suspensions). Lyophobic sols are dilute systems, some typical examples of which are colloidal metals, silver chloride, and Prussian blue, which already have been mentioned. Of suspensions in gaseous media (aerosols), some, such as fogs, mists, and smokes, are well-known; others, such as airborne suspensions of bacteria, viruses, and molds, are less obvious but of equal importance. Various kinds of smoke have found considerable use in war for camouflage and antipersonnel purposes, and peacetime uses of aerosols include insecticidal sprays and frost prevention in orchards by means of smudge pots. The removal of smokes still presents a major industrial problem. In an electrostatic precipitator, the smoke passes between oppositely charged wires (charged to a high potential difference); because of the charges that smoke particles carry or that are induced upon them by the electrical field, the particles are attracted to one or other of the wires, which then neutralizes them and thereby enables the particles to cluster into aggregates too large to be carried upward by the rising gases; these larger masses can then be collected by mechanical means from the precipitators.

Electrostatic precipitators

Dilute suspensions are known in all three dispersion media, gas, liquid, and solid. Only those in air and in aqueous solutions will be considered here. The dispersed particles are almost invariably composed of a large number of atoms or molecules and are usually visible in the ordinary microscopes or ultramicroscopes (about

$\frac{1}{1,000,000}$ to about $\frac{1}{1,000}$ centimetre). The amount of particles in the dispersed phase is always small, usually much less than 1 percent. Suspensions can be prepared by breaking down particles of macroscopic (large-scale) dimensions, a process called dispersion, or by growth from molecular or atomic units, a process called aggregation, until particles of the requisite colloidal dimensions are obtained.

Dispersion is usually carried out in the laboratory by grinding the substance in an agate mortar and, commercially, by means of a colloid mill in which the mixture of coarse particles and dispersion medium is subjected to intense shearing forces; a protective colloid is frequently added to prevent the colloidal particles produced by the mill from reaggregating. Metals can be dispersed in liquids by striking an electric arc between them, usually in the presence of a trace of sodium hydroxide to stabilize (*i.e.*, prevent from forming agglomerates) the sol formed. In some cases dispersion can be brought about by adding a small amount of a third substance called a peptizing agent; clays, for example, are peptized by alkalies, and many finely divided precipitates are peptized by soaps or other hydrophilic colloids.

In aggregation processes the first step is to form a supersaturated solution (in which more solute is dissolved than the solvent can contain normally, and any disturbance of the system will force the excess of dissolved solute out of solution) by chemical or physical means. This supersaturation leads to formation of solute nuclei that grow to colloidal size and then have to be stabilized in order to prevent flocculation—*i.e.*, coagulation of the particles into large flakes. An example of such a chemical process is the reaction between arsenic oxide and hydrogen sulfide in very dilute solution; in this reaction the insoluble arsenic sulfide appears in the form of minute particles dispersed in the aqueous solution. A common physical method is typified by the formation of sulfur sols by pouring a solution of sulfur in alcohol into water. Mist, fog, and clouds are aerosols formed by physical means in the atmosphere—the rapid cooling of air that is saturated with water vapour to a temperature at which the vapour condenses into minute droplets of water.

The size of the particles formed in aggregation processes is determined by the rates of nucleation (formation of nuclei) and by the growth of the nuclei into crystals or crystal-like growths. A high rate of nucleation is imperative for the formation of small particles, because the fewer the nuclei are, the larger they will grow, the total mass of substance precipitating being the same whatever the number of nuclei.

Importance of large numbers of nuclei

Liesegang rings. Another phenomenon in which nucleation plays an important role, the Liesegang rings (named after the German physicist and chemist R.E. Liesegang), is observed if an insoluble precipitate is formed during the diffusion of one reactant into the other. If, for example, a thin layer of dilute potassium dichromate in a gelatin gel is placed on a glass plate and a crystal of silver nitrate is placed at the centre, a precipitate of insoluble silver chromate is eventually produced in the form of concentric rings as shown in Figure 1. Each band is formed when a certain supersaturation has been reached locally, so that nucleation occurs. By subsequent growth of the nuclei, the concentration is lowered in the neighbourhood of the bands, and the diffusion of silver nitrate can proceed a certain distance before a sufficient degree of supersaturation is again reached and the next band precipitates. These bands are very similar to the banding in some minerals, such as agate, and are believed to explain such formations.

Stability. The stability of sols arises chiefly from the electrical charges carried by the particles (all being negative or all being positive), thus preventing contact under conditions such that without charges collisions would occur. The charges are usually obtained by the preferential adsorption of one type of ion, often a negative ion, because most sols are negatively charged. When the sol particles are close together, however, attractive forces (of the same nature as those between gas molecules, which cause gases to condense into liquids) make themselves

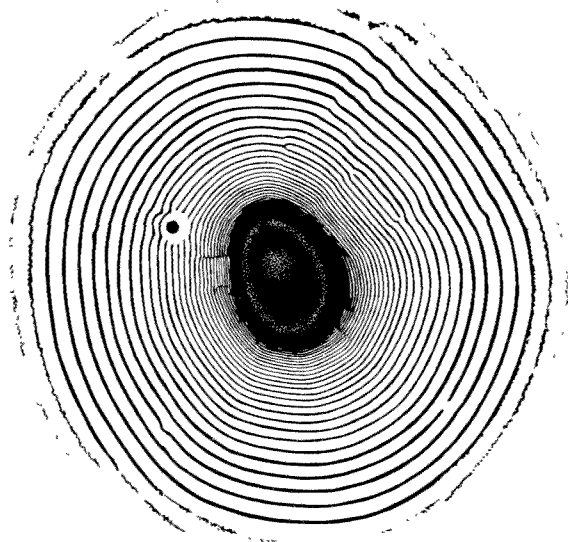


Figure 1: Liesegang rings of silver chromate. These resemble the banding in many minerals and are believed to explain the mineral formation (see text).

felt. The addition of inorganic salts, which effectively screen the charges on the colloidal particles, leads to a reduction of the range of the electrical repulsive forces, so that the attraction becomes predominant and coagulation follows.

Emulsions. The term emulsion is used to denote any colloidal dispersion of one liquid in another, but in practice only oil and water (aqueous) solutions need to be considered, because biological emulsions, as well as those of most domestic and industrial importance, contain an oil and an aqueous solution as the two immiscible phases. In order to attain the requisite degree of stability, a third component, called the emulsifying agent, is necessary and is usually present in amounts of about 1 to 5 percent. Emulsions can exist in two types, oil-in-water (indicated by O/W) and water-in-oil (W/O), depending upon whether the aqueous or the oil phase is the continuous one (*i.e.*, one in which the other exists in dispersed form). Two fundamental problems arise: the origin of the stability induced by the emulsifying agent and the reason some agents promote oil-in-water and others water-in-oil.

Importance of emulsions

The technical and biological aspects of emulsions are vast. The principal technical uses are in pharmacy and cosmetics (creams and ointments are usually emulsions), in food preparations (*e.g.*, salad dressings, mayonnaise, margarine), and in many industries, particularly leather, textiles, and paper. Margarine, for example, is a water-in-oil emulsion stabilized by about 1 percent of oxidized soybean oil; mayonnaise and other salad dressings are emulsions of edible vegetable oils in aqueous solutions of edible acids stabilized by egg yolk.

Commercially, oils are often emulsified with water to achieve three main goals: dilution of the oil, increase in area of interface or overall surface contact between the components, and modification of physical properties. Dilution effects economy by spreading the oil over a larger surface, as, for example, in polishes and oil-soluble insecticides. An increase in area of interface may accelerate some chemical reactions (*e.g.*, polymerization of vinyl compounds, hydrolysis of fats in soap manufacture). The modification of physical properties includes the removal of objectionable characteristics, as, for example, emulsification diminishes the taste or smell of pharmaceutical preparations such as cod-liver oil and increases the fluidity of heavy oils such as tar. On the other hand, crude petroleum is frequently produced as a water-in-oil emulsion. Breaking up this emulsion is often difficult, but it is a necessary step before further processing of the petroleum can take place.

In evaluating the stability of emulsions, creaming, coagulation, and coalescence should be distinguished. Cream-

ing is the accumulation of the droplets, usually at the top of the emulsion, under the influence of gravity. Small drops cream much more slowly than large ones. In coagulation the droplets come together to form aggregates in which the original drops are still separated. Coagulation enhances creaming. Coalescence means that the drops unite to form a continuous phase; fresh milk creams markedly in a few hours, and by acidification it can be made to coagulate, after which coalescence is strongly increased by churning.

Creaming, coagulation, and coalescence

Emulsification is achieved by intense agitation of the mixture. On a small scale this can sometimes be achieved merely by shaking the mixture by hand, but it is more usual to force the coarse emulsion under pressure through some type of valve, as in the farmer's "cream machine." Industrially, various types of colloid mills are used in which the emulsion is subjected to intense shearing forces, finally passing through a homogenizer. These treatments decrease the particle size and so increase the stability. (Milk is frequently homogenized in order to diminish creaming.)

The principal emulsifying agents for oil-in-water emulsions are: proteins, gums, carbohydrates, natural and synthetic soaps, clays, and certain hydrated oxides, particularly of silicon or aluminum; for water-in-oil emulsions: heavy metal salts (*e.g.*, zinc stearate, nickel oleate), long-chain alcohols such as cetyl alcohol, long-chain esters such as glyceryl monooleate, oxidized oils, soot, lampblack, graphite, and other substances.

Various theories have been advanced to explain emulsifiers, the most simple being that originally suggested for solid powders. As Figure 2 shows, for idealized spherical particles, if the solid is preferentially wetted by one component or phase, then more particles can be accommodated if the interface between the two components is convex to the wetting phase; and, in an encounter between two droplets, actual contact between the liquid in the droplets is prevented by the particles clinging to them, so that coalescence of the droplets cannot occur. In other words, preferential wetting by water should tend to give oil-in-water emulsions as in Figure 2B, while preferential wetting by oil should give the inverse type, as in Figure 2A. This difference is in agreement with the above list of emulsifiers, those promoting oil-in-water emulsions being all hydrophilic, whereas those that favour water-in-oil are more oleophilic (readily soluble in oil). Other conditions are also involved, however, in particular the relative amounts of oil and water and even the order in which the phases are mixed.

Natural and synthetic soaps soluble in water are among the most widely used oil-in-water emulsifying agents. Certain synthetic soaps (see below *Association colloids*) are often preferable to ordinary (fatty acid) soaps, because they are not precipitated by calcium ions (which do form a precipitate with ordinary soaps), and so the synthetic soaps can be used with hard water (high in calcium ion). The electrical charge acquired by the oil drops when they adsorb the soap ions is one factor in stability; the mechanical properties of the adsorbed film seem to be another one. The strong reduction of the interfacial tension facilitates emulsification greatly.

As mentioned before, the salts of divalent and trivalent metals with fatty acids (*e.g.*, nickel oleate) are efficient emulsifiers for the water-in-oil type. In these systems, the

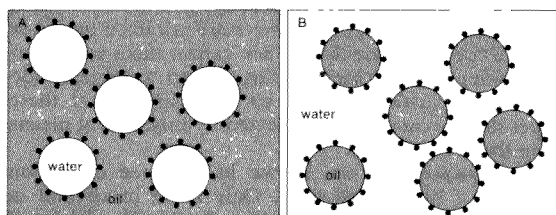


Figure 2: Solid powder at an oil-water interface, showing (A) how preferential wetting by oil tends to give water-oil emulsions and (B) how preferential wetting by water tends to give oil-water emulsions.

Phase
inversion

interfacial film consists of solid particles or of a polymeric skin rather than a film one molecule deep, a monolayer. A simple experiment to illustrate phase inversion (reversal of the roles components play in a system) is to prepare an oil-in-water emulsion stabilized by sodium oleate (soluble in water) and to add a few drops of saturated magnesium chloride; on being shaken, the system inverts to the water-in-oil type because of the magnesium oleate that is formed. Proteins and gums as emulsifiers normally promote only the oil-in-water type of emulsion. A great variety of proteins are used commercially, such as egg albumin, dried blood, casein (from milk); and proteins are wholly or partly responsible for the stability of many natural emulsions such as milk and rubber latex. Food emulsions are frequently stabilized by proteins, gelatin, and other substances. The stabilizing action of these arises from the mechanical protection given by the protein monolayers, or films, that form spontaneously and that are relatively impenetrable for oil.

Foams. A foam is a gaseous dispersion, usually of air, in a liquid. Pure liquids do not give stable foams, and, for any reasonable stability, a third component, the foaming agent, is essential. Of the great variety of substances that act as foam promoters, the best known are the natural and synthetic soaps, proteins including gelatin and other compounds obtained from proteins, certain finely divided solid powders, certain polymers (large molecules formed from smaller ones), and the saponins (naturally occurring substances that produce a soapy lather).

Household soap, which consists chiefly of a mixture of sodium stearate and sodium palmitate, is well-known for its bubble-blowing capacity. This property is greatly improved by the addition of glycerol, which probably acts by increasing the viscosity of the film. Many synthetic soaps, sodium cetyl sulfate, for example, are equally effective and have an added advantage in that their lathering power is not readily diminished by hard water (see below *Association colloids*).

Stabilization of foams arises mainly from the same factors that govern the stability of emulsions. Indeed, a suspension of air bubbles in water (a foam) is very similar to a suspension of oil droplets in water. In both cases the same types of stabilizers are used. Proteins as in whipped cream, marshmallow (made from gelatin and sugar), and meringue (from egg white) find a wide use as foaming agents in foodstuffs, because of their edible or non-toxic nature. The fire foam used to combat oil fires consists of bubbles of carbon dioxide (liberated from sodium bicarbonate and aluminum sulfate) stabilized by dried blood, glue, or any other cheap protein-containing materials. Beer froth is believed to be stabilized by the colloidal constituents present in the brew, which include proteins and carbohydrates. Saponins, noted for their foaming capacity, are obtained commercially from various plants and are complex mixtures. They form rather solid surface films with a mechanical strength to which their foams owe their stability, just as in the case of proteins. Of the polymers with foaming power for aqueous solutions, the most important are methyl cellulose (water-soluble type) and polyvinyl alcohol (see below *Polymers*). Certain finely divided solids, particularly if they have a waxy or hydrophobic (not soluble in water) surface, such as aluminum stearate or heavy metal soaps insoluble in water, remain at the air-water interface on agitation and stabilize the foam so formed. By suitable treatment many other materials can be made to behave similarly, and this behaviour forms the basis of what is called the froth-flotation method for separating minerals. The structure of a single bubble in a foam stabilized by a fine powder is quite similar to that of the emulsion droplet represented in Figure 2B.

Foaming may often be an undesirable property, as in lubricating oils, and its prevention is not always easy. Aqueous foams can usually be broken by spraying with small amounts of certain alcohols (e.g., amyl, octyl) or fatty acids.

Pastes (concentrated suspensions). Pastes are concentrated dispersions of fine solid particles in a liquid con-

tinuum. From the practical point of view they are of extreme importance, covering such diverse materials as paints, putty, clays, dough, drilling muds, toothpaste, and others. These materials are all noted for their peculiar and characteristic mechanical properties, as is indicated by such terms applied to them as plasticity, ductility, and moldability. The study of the flow and deformation properties of pastes, which are so vital in their practical uses, belongs to the science called *rheology*.

The flow behaviour of a paste is determined not only by the volume concentration of the solid particles but also by their size and shape, by their size distribution, and by the colloidal stability of the suspended particles. At a given solid concentration, a flocculated paste (one in which particles are held together loosely in amorphous, cloudy flakes) may be stiff and plastic, whereas a stable, or deflocculated, one may be easily pourable. Examples of flocculated systems are very polar compounds (in a polar molecule the distribution of electrons is not symmetrical and causes the molecule to behave as though it had a positive end and a negative end, or pole) in organic media (e.g., silica, calcium carbonate, and other inorganic salts in such oils as benzene) or nonpolar substances such as carbon black in polar media such as water. Such systems can be rendered deflocculated by suitable additives, a practical example being the addition of aluminum stearate to the oil vehicle of inorganic paints. By such means a higher concentration of the disperse phase can be obtained without increasing the consistency of the material; or, alternatively, an increase in pourability can be obtained at the same solid concentration. It is for higher concentration that materials such as sodium silicate are added to potter's clay, because the water present, which ultimately will have to be removed, should be kept to a minimum. Putty, another example of a paste, consists of finely ground whiting (natural calcium carbonate) in a medium of linseed oil.

Pastes, particularly those with the higher concentrations of disperse phase, usually show some sort of yield value (give) upon deformation (alteration of form). This property is clearly essential if the material is to exhibit plastic properties (e.g., potter's clay), because it has to retain its shape against the forces of gravity. Certain pastes exhibit the phenomenon known as thixotropy; i.e., after stirring or shaking they become much thinner in consistency, returning to their original state on being allowed to stand. A well-known example is quicksand, which consists of a paste of sand and water made thixotropic by the presence of certain clays. Paint should be thixotropic in order to flow easily under the brush and to allow the brush streaks to disappear. After a short time the applied paint should solidify to prevent the paint from flowing away from vertical planes. The reverse phenomenon, termed dilatancy, in which a suspension that flows freely under a small force turns rigid when larger forces are applied, is shown by very concentrated, highly stabilized suspensions—e.g., by pastes of pure silica in water.

Gel structures. A flocculated paste, or suspension of very fine particles, often behaves as a gel—i.e., a quasi-homogeneous solid-like system, but rich in liquid. During the flocculation a scaffolding structure is formed by the molecules, preventing sedimentation of the floc in the structure and enmeshing the dispersion medium. Such structures are preferentially formed by long or flat particles. The systems are often thixotropic; the bonds between the particles can be broken by mechanical action. They show syneresis; i.e., in the long run the scaffolding retracts by further flocculation, and liquid is exuded. Examples of gels are: certain clays, particularly bentonite (flat particles), iron hydroxide (flat), and vanadium pentoxide (needles). Those gels formed from ferric hydroxide are reddish brown and become more transparent when liquefied. Fatty-acid salts such as aluminum, calcium, and zinc oleates are the thickening agents in many greases, which are examples of gels with a nonaqueous liquid phase.

In some cases gels are formed directly by chemical reaction. Substances that tend to separate as amorphous precipitates frequently give colloids that are gels when

Importance
of pastesThixotropic
pastes

first formed, the hydroxides of aluminum, chromium, and silicon being good examples. Of these, the formation of silica gel by reaction between sodium silicate (water glass) and acids or between silicon tetrachloride and water has been much studied. The colloid, a sol, first formed slowly transforms spontaneously into another type of colloid, a translucent gel, that shows bluish opalescence, and this gel may later shrink, exuding the aqueous medium (syneresis). The changes are believed to arise from polymerization (the process of linking together small molecules, called monomers, into chains to form large molecules—the polymer—consisting of as many as hundreds of thousands of monomers) of the monosilicic acid first formed. The process can be repeated in one, two, or three dimensions, leading to a colloid composed of silicic acids with high molecular weight that form a rather rigid three-dimensional gel.

Ion-exchange
in clays

A property of clays of great agricultural importance is called base exchange or, more correctly, ion or cation exchange (ions are atoms or groups of atoms with electric charges; cations have positive, anions have negative charge). If, for example, a salt solution such as potassium sulfate percolates through a soil, the potassium ions (with a single positive charge) are removed and replaced by an equivalent amount of calcium ions (with two positive charges) originally present in the clay. The percentages and types of clay in soil determine its physical structure as well as its chemistry, both of which are of primary importance to the growth and health of plants. Such ion-exchange processes form the basis of the zeolite process and of similar processes. In the above case, calcium ions in the water are replaced by sodium ions, which have one less positive charge, and the water is thus softened because sodium salts are soluble whereas calcium salts are not.

Clays, the finest mineral constituents of the soil, consist of layer structures of aluminosilicates (compounds of aluminum, silicon, and an alkali or alkaline-earth metal) in which some cations are easily accessible and exchangeable. The nature of these ions is not critical for maintaining the clay structure; only their total electric charge is important.

Zeolites are essentially infinite three-dimensional frameworks, potentially infinite in size, as in the various forms of silica (silicon dioxide), except that some of the silicon atoms (often about one-half) are replaced by aluminum atoms. This replacement makes the framework of the colloid negative (silicon has four positive while aluminum has three positive charges), and equivalent cations are taken up in the interstices to maintain electrical neutrality. Synthetic zeolites have been manufactured in various ways, such as by fusing a mixture of sodium carbonate, china clay or alumina, and silica (sand, quartz, etc.), the resulting glassy (vitreous) mass being then washed out (leached) with water.

REVERSIBLE SYSTEMS

Reversible colloids are characterized by the fact that colloidal solutions or gels can be formed spontaneously when the dry colloid and the dispersion medium are brought together. The size of the particles in reversible colloids is determined by the molecular weight of the colloidal material in the case of polymers or by reversible association (as explained below) in the case of detergents, certain dyes, and a few other substances.

Polymers. Polymers are high-molecular-weight substances built up of a large number of identical (or practically identical) repeating units (generally, simple molecules), the single conglomerate molecule being of colloidal dimensions. Familiar polymeric materials that are colloids are cellulose in wood and plants and proteins in horn, hair, and wool. In nature, three different functions of polymers can be distinguished: they serve as building materials (cellulose, proteins of skin and muscle); they are storage substances (starch, glycogen); and they play a fundamental role in biochemical reactions (enzymes, nucleic acids, genes). These functions are related to the high molecular weight of the substances. The bonds between atoms holding them together in organic molecules

(called primary bonds) are quite strong, not inferior to the bond strength between atoms in inorganic molecules. The bonds, however, between organic molecules (called secondary bonds) are weak and can be easily disrupted. Crystals of organic substances of low molecular weight, as a rule, are soft, indicating weak intermolecular bonds. Consequently, a structure built of organic materials in order to be strong should contain a high proportion of primary bonds, a condition that can be achieved by building the structure with polymers. Another important property of organic materials is that they can be processed at much lower temperatures than are needed to process inorganic materials, such as metals or ceramics. The intricate functions necessary to regulate biochemical reactions including reproduction can, of course, be more easily incorporated in large than in small molecules, because the large molecules allow more diversification. The commercial synthesis of polymers—broadly speaking, of plastics—seeks to mimic nature in many respects. Strong, tough, and insoluble materials are manufactured at much lower temperatures than metals or glass for an almost endless list of purposes.

Most polymers, both natural and synthetic, are linearly built; *i.e.*, they are long chains. In solution, and often even in the dry state, the colloid composed of this long chain is folded or coiled. In proteins and nucleic acids the coiling is regular. In synthetic polymers and in many natural ones such as rubber and gums, the coiling is irregular and determined by chance rather than by some building principle, so that the term statistical coils is used. The large extension in solution of polymer molecules is the cause of a high viscosity (sluggish flow), which can be used for determining the molecular weight of the polymer. When linear polymers are interconnected locally, a cross-linked polymer network is obtained. Such a network, when deformed, tends to return to its original shape because that was the situation of most probable coiling. A network, therefore, cannot flow at all but behaves as a gel. The behaviour of coils cross-linked in such networks also explains both the elasticity of rubber and the swelling of dried polymer gels.

Polymer
chains

Polymers are usually subdivided, according to their origin, into natural and synthetic, although an intermediate class, man-made derivatives from natural polymers, is also a convenient classification. Some of the more important members of these three subgroups are as follows:

1. Natural polymers: cellulose, starch, rubber, proteins, nucleic acids, and the products from linseed and other drying oils.
2. Derivatives from natural polymers: nitrocellulose, cellulose acetate, regenerated cellulose (viscose, cellophane), and vulcanized rubber.
3. Purely synthetic polymers: nylon, polystyrene, polythene, synthetic rubbers, silicones, phenol-formaldehyde and urea-formaldehyde resins.

Natural polymers. Cellulose is a colloid that is the principal building constituent of the plant kingdom. Paper is derived from wood pulp. Cotton and flax, widely used in the textile industries, are almost wholly cellulose. The cellulose molecule consists of a linear array of many thousands of molecules of glucose, linked end to end in a process that eliminates one water molecule (a reaction called condensation) at each link. The chain length, or degree of polymerization, depends upon the source and the method of extraction of the cellulose.

Starch is another colloid of great importance in the plant world, not as a building material but as a convenient means of storing glucose and, hence, energy and food; wheat, maize (corn), and other grains consist largely of it. It resembles cellulose in being a product of glucose but differs in having a branched-chain structure rather than a straight-chain one. Starch can be dispersed in hot water and is then used for various purposes.

Natural rubber is a linear polymer built up from units of the compound isoprene and is a colloid with characteristic properties. The rubber is obtained in the form of a milky suspension called latex from a wide variety of plants and trees. After the latex has been coagulated by adding acetic acid, or in other ways, the resulting so-

Structure
of rubber

called crepe rubber is usually compounded with other materials to make it suitable for industrial use. For example, in the manufacture of tires it is compounded with carbon black and certain inorganic fillers such as zinc oxide and sulfur, and then subjected to heat treatment. The action of sulfur leads to vulcanization, as it is termed, which is the formation of cross-links between the chains through one or more sulfur atoms. Vulcanization makes the product colloid more resilient and less liable to plastic flow.

Paints usually consist of a colloidal dispersion of an inorganic coloured powder (*e.g.*, lead chromate, zinc oxide) in an oily medium containing unsaturated compounds, such as linseed oil, which, when exposed as a thin film to the action of air, rapidly oxidize and polymerize, forming a protective skin for the underlying material and the pigment. In modern paints the linseed oil is often replaced by rubber or synthetic polymers.

Derivatives from natural polymers. Cellulose forms the basis from which several important colloidal substances are derived. A group of compounds called nitrocellulose, or cellulose nitrate, made by treating cotton or other cellulose materials with a mixture of nitric acid and sulfuric acid, have properties that vary considerably, the members with high nitrate content being used as propellants (*e.g.*, cordite), the ones with less nitrate as lacquers, etc. Celluloid, the oldest commercially made plastic, consists of a mixture of cellulose nitrate with camphor. Cellulose acetate, obtained from cellulose and acetic acid, is manufactured for artificial silk, for lacquers, for safety film, and for water-desalting membranes. Cellulose can also be dissolved and reprecipitated to form the colloids cellophane and rayon.

Purely synthetic polymers. The science and the production of purely synthetic polymers were greatly developed during World War II. Synthetic rubber was and is still made on a large scale by copolymerizing a mixture of butadiene and styrene, both of synthetic origin, to give a linear polymer resembling in many ways natural rubber. Nylon is made by condensing diamines with dibasic acids, the resulting structure having a close resemblance to that of natural silks and other fibrous proteins.

Many other types of colloidal polymers are made by polymerization of vinyl compounds, for example, polythene, polyvinyl chloride, polymethyl methacrylate (Perspex or Plexiglas), and polyacrylonitrile (Orlon).

The silicones are more recently developed polymers based upon a silicon-oxygen chain. They are much more stable to heat, organic solvents, and chemical reaction than are the older plastics and thus find many uses.

Bakelite

Another well-known type of colloid, the polymer Bakelite, is made by heating phenols with formaldehyde. These are cross-linked polymers, termed thermosetting, because once formed they do not soften when warmed, in contrast with the linear polymers noted above that are thermoplastic; *i.e.*, they soften upon warming and harden again upon cooling.

Polyelectrolytes. Polymers carrying a large number of ionizable groups deserve special attention. An example of these so-called polyelectrolytes is polyacrylic acid, a long-chain polymer with a carboxylic acid group on every other carbon atom of the chain. Many natural polymers, such as gum arabic, agar, proteins, and nucleic acids, are also polyelectrolytes. Because of the mutual repulsion between the ionized groups linked to the polymer chain, the form of the coil of a linear polyelectrolyte depends greatly upon its degree of ionization. Viscosity and swelling increase strongly with ionization.

Proteins and nucleic acids. The most important classes of hydrophilic colloids in living organisms are the proteins and the nucleic acids. The complete genetic information of the cell is laid down in the molecular structure of the nucleic acids, in particular that of deoxyribonucleic acid (DNA). This information is transported from the cell nucleus to the rest of the cell in the form of ribonucleic acid (RNA), which in its turn directs the synthesis of the proteins. Simple viruses are nucleoproteins (combinations of nucleic acids and proteins) that have the ability to reproduce themselves when injected into an

uninfected host organism. Enzymes are proteins that regulate and catalyze all of the complex chemical reactions that occur in the cell and are essential for life. Nature uses proteins also as protective colloids, for example for fat particles in milk or rubber particles in latex, and as a means of building rigid structures in which mechanical strength is required. Materials such as horn, hair, skin, cuticle, connective tissue, and muscle are largely protein in nature. Gelatin and glue are breakdown products from proteins such as collagen. Biological membranes are colloidal and consist of lipids (fatty material) associated with proteins and nucleic acids.

The nucleic acid molecules are very long chains, consisting of alternating phosphate and sugar groups, each sugar group carrying one of four organic bases as a side group. The sugar in RNA is ribose, in DNA it is deoxyribose, containing one oxygen atom less than ribose. The great variety necessary for carrying all the genetic information is obtained by variations in the order in which the four different bases are arranged along the chain. The molecular weight of the DNAs is in the many millions, that of the RNAs varies with their specific role in the cell and ranges from about 25,000 to a few millions.

Protein molecules are chains called polypeptides, built up by condensing a long series of α -amino acids, the simplest of which are glycine and alanine.

Proteins can be classified in various ways—for example, according to their degree of complexity, their size and shape, their solubility, their origin, and in other ways. Classified on the basis of complexity, proteins are divided into those that contain only α -amino acids (*e.g.*, egg albumin, the chief constituent of egg white) and those that contain additional groups (*e.g.*, hemoglobin, the red pigment of blood responsible for oxygen transport, in which the protein part of the molecule is linked to a substance called heme, which is one of a group of compounds called the porphyrins). On the basis of shape, proteins are frequently classed as globular or fibrous, the former having a corpuscular shape (*e.g.*, hemoglobin, egg albumin), sometimes approximately spherical, the latter being very much more elongated (*e.g.*, myosin, an important constituent of muscle). Two other important fibrous proteins—both insoluble—are keratin, of which hair and wool are largely composed, and fibroin, the chief constituent of natural silk. Under some conditions (*e.g.*, strong urea solutions), globular proteins can be unrolled, or denatured, forming fibrous proteins that are much less soluble than the native proteins.

In the early days, proteins were largely separated by means of repeated (fractional) precipitation with salts—those precipitated by half-saturated ammonium sulfate being termed globulins, and those that required fully saturated ammonium sulfate being called albumins. Alcohol can also precipitate proteins; added in less than precipitating amounts, it renders them more readily coagulated by salts. In all cases precipitation occurs most readily at the isoelectric point (see below).

The size and shape of soluble proteins (and of other polymers in solution) have been found chiefly by measuring rates of diffusion and their rates of movement in very strong centrifugal fields. In the ultracentrifuge, the protein molecules are subjected to intense forces up to 1,000,000 times that of gravity. By such means it has been determined that the molecular weight of many proteins lies in the range from about 10,000 to several million. The single molecules are thus of sufficient size to bring them into the colloidal range. For example, hemoglobin has a molecular weight of about 68,000; hemocyanin, the respiratory pigment of certain snails, has a molecular weight of about 5×10^6 . In both these cases, the molecules are approximately spherical in shape, showing that in the colloidal particle the polypeptide chain must be folded in some way, whereas others, such as myosin, are quite elongated, with the polypeptide chain more or less fully extended.

Because of the presence of ionizable groups, protein molecules in solution normally carry a charge. In very acid solutions they are positively charged; in very alkaline ones, negatively charged. At some value of acidity the

Classification of proteins

Size and shape of proteins

net charge is zero. This value is termed the isoelectric point and is of considerable importance. It can be determined in various ways, usually by applying the process of electrophoresis.

Gels. Several lyophilic colloids can form gels, which can be considered as network structures with enmeshed liquid. The jelling component may be gelatin, agar, starch, pectin, or some other substance, which is usually present in concentrations of less than 10 percent. Table jellies are usually made from gelatin, a protein; jams are jelled by pectin, a carbohydrate derivative. Agar plates, widely employed in bacteriological work, consist of a suitable nutrient medium jelled by the addition of 1–2 percent agar, a polymer of carbohydrate prepared from certain seaweeds. Some materials such as gelatin and agar set to a gel on cooling, whereas in other cases gelation is brought about by heating as in egg white and blancmange. In both cases, however, gelation arises from a process akin to a diminution of the solubility of the jelling agent leading to the formation of interconnections between the individual molecules.

Association colloids. Soaps and other detergents and a number of dyes constitute by far the most important substances classed as association colloids—*i.e.*, substances of relatively small molecular weight that associate spontaneously to form particles of a type called micelle (defined below) of colloidal size in certain concentration ranges.

Soaps. Soaps were originally limited to colloidal substances of natural occurrence, but a great number of compounds have been prepared synthetically in view of their importance as wetting agents, emulsifiers, and detergents. A few typical soaps, classified as anionic (negative), cationic (positive), and neutral according to the charge carried by the organic part of the molecule, are: sodium palmitate, anionic; sodium dodecyl sulfate, anionic; cetyltrimethylammonium bromide, cationic; polyethylene oxide derivatives, neutral. In addition, there are naturally occurring colloids that act as soaps, such as the bile salts and lecithin, substances of great biological importance.

All these colloids, as well as the colloids that are dyes, despite their diverse chemical types, have as common features a large hydrocarbon portion (also called paraffin or alkane) and a small polar (charge-carrying) group. These two parts of the molecule differ radically in their affinity for water, and it is this two-sided contradictory, or amphipathic, nature that leads to the formation of colloidal aggregates.

With aqueous solutions of the sodium and potassium salts of the long chain fatty acids, certain physical properties such as a high electrical conductivity suggest that the ions on the paraffin chain are aggregated, forming a colloidal particle—*i.e.*, an ionic micelle (defined below), as shown in Figure 3. In the case of sodium palmitate,

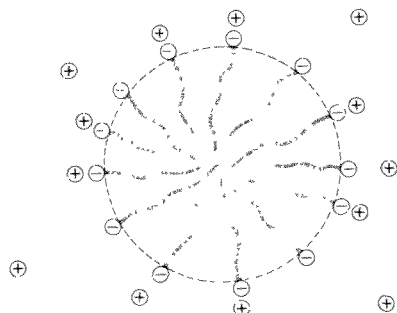


Figure 3: Structure of a micelle formed by the aggregation of paraffin-chain ions in a soap solution.

for example, the diameter of the micelle, as determined from diffusion measurements, is about 40 angstroms and thus contains about 50 molecules, the molecular weight being about 14,000. In relatively dilute solutions the shape of micelles is spherical or slightly elongated. In

concentrated solutions they may be spherical, elongated rods or threads, or flat structures.

Aggregation to micelles is caused by the tendency of the water to squeeze out the paraffin chains, the same factor that is largely responsible for the marked surface activity of soap solutions. The characteristic features of soap solutions arise from the combination of surface activity and the peculiar properties of micelles in solution. The power of soap solutions to dissolve organic compounds that are insoluble or only slightly soluble in water arises directly from the presence of micelles. Micelles, as shown in Figure 3, have an interior closely resembling a droplet of liquid hydrocarbon, in which hydrocarbons and other compounds can dissolve. One important application of this phenomenon is in connection with synthetic polymers, for it enables polymerization of relatively insoluble monomers such as styrene (see above *Polymer*) to be carried out in aqueous solution or emulsion.

The characteristic and most widely used colloidal property of soap solutions is, of course, their detergent action. What is generally called dirt consists either of greasy materials or of particles with a greasy surface. Its removal involves three separate stages—access of the detergent to the dirty surface, the loosening or peptizing of the dirt, and finally its removal into the bulk of the solution. Because of its greasy surface, dirt is hydrophobic and not wetted by water, but adsorption of the surface-active soap molecules makes its outer surface hydrophilic and therefore greatly increases its affinity for water. In addition, the detergent, because of its powerful tendency to adsorb on, or cling to, all surfaces, will tend to displace the grease from the surface. The dirt thus loosened is detached by mechanical agitation and carried away into the solution as an emulsion or suspension, or solubilized in the interior of the micelles.

The chief drawback of fatty-acid soaps (ordinary household soaps) arises from their property of having insoluble calcium or magnesium salts. This characteristic explains the impossibility of getting a lather in seawater with ordinary soap and the necessity to soften hard water; *i.e.*, the calcium and magnesium ions must be removed in order to keep the soap in solution. Many of the synthetic detergents do not suffer from this disadvantage and thus are used in seawater soaps.

Ordinary household soap is prepared by boiling natural fats (compounds that are glycerides of the higher fatty acids) with strong caustic soda solution. After hydrolysis is complete, the soap is salted out by addition of common salt. The potassium salts, which make soft soap, are preferable to sodium salts for some purposes, because the potassium soaps have a higher solubility in cold water.

Dyes. Dye molecules, although resembling the soaps in possessing a hydrophobic part and one or more polar groups, lack their comparative uniformity as regards the relative disposition of these constituent parts. This situation results in the aggregation being much more specific and hence in a more varied colloidal behaviour. Dye-stuffs are usually classed as acidic or basic (corresponding to anionic or cationic soaps) according to whether the organic ion carries a negative or a positive charge. The question of aggregation is of considerable importance in connection with the colloidal aspect of the dyeing process. The size of the aggregates, or micelles, can be determined by the same methods as for soaps, diffusion being regarded as the best. The degree of association is increased by increasing salt content, which explains the influence of salts in dyeing.

The dyeing process has naturally excited considerable interest throughout history, although it is by no means fully understood. The materials to be dyed are usually colloids of a fibrous nature, consisting of macromolecules of vegetable, animal, or purely synthetic origin. Most vegetable fibres, such as linen and cotton, have the colloidal structure of cellulose as the fundamental constituent; wool and silk are the principal animal fibres, and, of the purely synthetic materials, nylon is without doubt the best known. In dyeing a fibre, the coloured molecules have to diffuse into the interior, in which they are held in position by precipitation or by some other reaction.

The
soaping
process

The
dyeing
process

Micelles

The behaviour of wool and silk is probably the simplest, for the major factor in bringing about combination is believed to be salt formation between the dye anions on the fibre. With cellulose (cotton and rayon) the affinity of the dye for the fibre is probably caused by van der Waals forces and hydrogen bonding.

Dyes also find an important use in the identification of biological materials (*e.g.*, bacteria) by staining methods. These depend upon the different affinities of the enveloping constituents for various dyes, the principles involved being closely related to those in ordinary dyeing. Dye-stuffs of the basic type (*e.g.*, Gentian Violet) find use as antiseptics, resembling the cationic soaps in their bactericidal powers.

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(J.T.G.O.)

Cologne

A river port on the Rhine, Cologne (German Köln) is the fourth largest city in the Federal Republic of Germany, or West Germany, the largest city in the *Land* (state) of Nordrhein-Westfalen (North Rhine-Westphalia), and the historic, cultural, and economic capital of the Rhineland. Cologne's historic importance is due to its location at the crossing of the route from England, France, Belgium, and The Netherlands to eastern Europe with that route between Italy and northwestern Europe, a great traffic artery of the Rhine. The medieval commercial centre that grew up there was also a centre of learning and the arts.

Despite the destruction of 90 percent of the central city during World War II, Cologne's appearance still reflects its history; religious and secular buildings and monuments of all periods remain standing. It is the see of a Roman Catholic archbishop, and its cathedral is the largest Gothic church in northern Europe. It is an important banking and insurance centre, and its manufactures include the famous eau de Cologne toilet water.

History. After Julius Caesar destroyed the Eburones in 53 BC, the Roman general Agrippa colonized the area with the Ubii, who came from the right (east) bank of the Rhine. In AD 50, at the request of Agrippina the Younger, the wife of the emperor Claudius, the title of Roman colony was conferred upon the town that was her birthplace. It was named Colonia Claudia Ara Agrippinensium, which was shortened to Colonia; later it was made the headquarters of the governor of Lower Germany. The excavated remnants of the Praetorium, the governor's residence, are located beneath the present city hall. After AD 258, Postumus ruled as emperor from Cologne a separate empire comprising Gall, Britain, and Spain. The emperor Constantine the Great built a castle (310) and a permanent bridge to it across the Rhine. Ceramics and glass were manufactured in Cologne in Roman times. About 456 it was conquered by the Franks, and it soon became the residence of the kings of the Ripuarian part of the Frankish kingdom.

A Christian community existed in the town probably as early as the 2nd century, the first-known mention of a bishop having been in 313. Charlemagne made it an archbishopric, and, by the 10th century, the archbishop dominated the city, receiving a wide range of tolls, customs

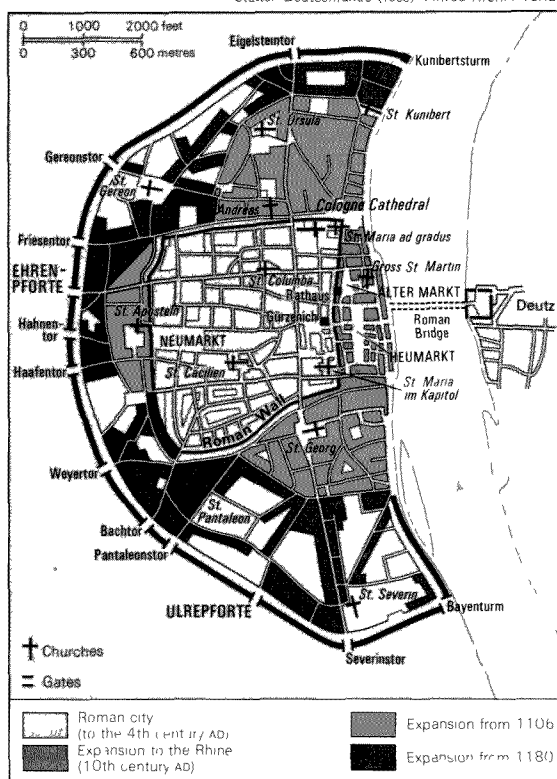
duties, and other payments. The city's industry and trade grew during the Middle Ages, especially from about the 10th century, and increasingly bitter conflicts developed between the wealthy merchants and the archbishop. The former sought commercial and political freedom, the latter the preservation of his temporal power, which was augmented from the 13th century when the archbishop became one of the electors privileged to choose the German king. It was not until the battle of Worringen, in 1288, that the Archbishop was finally defeated, and the city of Cologne secured full self-government. From that time, Cologne was, in fact, a free imperial city, although it was only officially recognized as such in 1475.

Until the end of the 14th century, the government of the city of Cologne was in the hands of the wealthy patricians, but, in 1396, after a bloodless revolution, a new municipal constitution was established under which the 22 branches of the guilds became the basis of the government, for they elected a council that had power over all internal and external affairs.

This medieval period was a splendid one for Cologne. It was a prominent member of the mercantile Hanseatic League, and its merchants had probably the widest connections and the most varied trade of all the German towns. Crafts included the manufacture of textiles and books and leather, enamel, and metalworking, the work of Cologne's goldsmiths being particularly fine. The wine industry was well established, the arts flourished, and the city had many beautiful churches. The three greatest of the later Catholic scholars and theologians known as the Scholastics—Albertus Magnus, St. Thomas Aquinas, and John Duns Scotus—all taught in its schools. After the Thirty Years' War (1618-48), involving all western Europe in a struggle for balance of power, the city declined. As late as 1794, when the French occupied Cologne, public Protestant services were still banned, and the city has remained predominantly Roman Catholic ever since. The Jewish community, which had existed from the time of Constantine the Great, was expelled in 1424, and until 1794 no Jew was allowed to remain overnight in the city.

In 1798 Cologne was taken by France, and, when the Archbishop Elector died in 1801, the see was left vacant and was to be so for 20 years until the archbishopric was

Adapted from J. von Reinhardt, *Handbuch der historischen Stätten Deutschlands* (1963) Alfred Kroner Verlag



Cologne in 1752.

restored in 1821. In 1815 Cologne passed to Prussia, and from that time a new era of prosperity began. Its industry showed as wide a variety as in medieval days, and, when railways were introduced, its geographical position made it a great railway centre. The interest in organization, shown in the days of the guilds, contributed in 1797 and 1803 to the formation of a chamber of commerce, the oldest of its kind in Germany. The arrest of the Archbishop in 1837 created a sensation that became known as the Cologne Incident. Liberal points of view were represented in the 19th century by the *Rheinische Zeitung*, edited (1842–43) by Karl Marx and Moses Hess, while the *Neue Rheinische Zeitung*, edited (1848–49) by Marx, Friedrich Engels, and Ferdinand Freiligrath, was a Socialist newspaper. After German defeat in World War I, Cologne was garrisoned by the British army until 1926. The population grew from 41,685 in 1801 to 372,529 in 1900 and reached 768,352 in 1939.

World
War II
damage

In World War II, Cologne sustained 262 air raids, there were 20,000 casualties, and the city was left in ruins, with nearly all the dwellings in the old town damaged and 91 out of 150 churches destroyed. In March 1945, the war's end for Cologne, the population had sunk to 40,000. By December, however, there were 447,000 in the city, and the population continued to rise rapidly while a vast work of clearance and reconstruction was undertaken. Most new industries located in new business districts, and much of the growing population settled in satellite suburbs.

The modern city. *Location and boundaries.* Cologne, which is situated about 44 miles northeast of Aachen, 21 miles northwest of Bonn, and 25 miles southeast of Düsseldorf, lies 210 feet above sea level. Most of the city is on the left bank of the Rhine in a fertile lowland plain. The area of the modern city region is about 97 square miles (251 square kilometres), the greatest distance west to east being about 13 miles and, north to south, 15 miles. Cologne has 52 suburbs administered in eight city areas. The heavily industrialized districts of Rodenkirchen, Hürth, Frechen, and Dormagen and the rural residential areas of Lövenich, Widdersdorf, Pulheim, Sinnersdorf, and Stommeln surround the city on the left bank of the Rhine. On the right bank are the districts of Deutz, Mülheim, and Kalk and the adjacent towns of Porz, Bensberg, Bergisch Gladbach, and Leverkusen.

Layout of the city. Cologne is laid out in the semicircle that it assumed in 1180, when the city wall was built, with 12 fortified gates and 83 towers. With the several new parishes brought within the town boundaries, it became, at the time, larger than the city of Paris. The flat side of the semicircle lies athwart the Rhine, 440 yards (400 metres) across, which is spanned by eight bridges, of which five were rebuilt after World War II and three are new constructions. The perimeter of the semicircle is defined by great ring roads, the Ringstrassen, which in the 1880s replaced the medieval fortifications. Since 1920, greenbelts have been laid out along the 19th-century fortifications. Modern suburbs have grown beyond the Ringstrassen, but the main shopping and business streets, such as the Hohe Strasse (north–south) and Schildergasse (west–east), as well as the city's historic buildings, lie within it.

Transportation. Cologne's geographical position and commercial importance have combined to make it a focal point for communications. The city is a great rail junction, with 800 to 1,000 trains passing through daily. The headquarters of the West German airline, it shares its airport with Bonn, to the southeast, and, in the 1970s, on the edge of the central city, a helicopter landing ground had services to fly patrons to Brussels, Liège, Maastricht, and Bonn. The *Autobahn* "expressway" connected Cologne with Aachen, the Rhine–Ruhr industrial district, Frankfurt, and the south. The Rhine harbour, important since Roman days, had become, by the 1970s, one of the larger inland ports in Germany, handling over 10,000,000 tons of merchandise annually. Small seagoing craft used the river, and there were four passenger-ship lines with a fleet of 38 river steamers. Further, the city was served by 15 streetcar and 30 bus routes.

Population. Of the population of more than 862,000 in 1970, 63 percent were Roman Catholic, 28 percent were Protestant, 17 percent were refugees from the lost eastern territories and the German Democratic Republic (East Germany) after 1961 or from elsewhere in eastern Europe, and about 7 percent were foreigners. The population density was about 8,800 per square mile.

Architectural features. The Cologne Cathedral (Dom) dominates all other historic buildings in the city. It stands on the site of a church completed in 873. After a fire in 1248, rebuilding was begun: the choir was completed in 1322, and work on the cathedral went on until 1510, when Renaissance contempt for the Gothic style is said to have brought building to a halt. Work was resumed in 1842, and the building was completed according to the original design in 1880. It was badly damaged during air raids in 1944, but by 1948 the choir was again in regular use, as was the rest of the interior by 1956. Recent excavations supplied proof that the bishop's church was located on this site during the Merovingian period, and it is probable that the Roman bishop's seat was located here also.

The cathedral, 470 feet long and 175 feet wide, is impressive in its vastness. Its great twin towers rise 515 feet above the centre of the city. The 14th-century stained-glass windows in the choir are considered especially beautiful, and the cathedral is also notable for its other art treasures. On the high altar are relics attributed to the Magi, sent to Cologne from Mailand (1164) and preserved in a gold shrine (begun by Nikolaus von Verdun in the 1180s) that is one of the finest medieval examples of the goldsmith's art. The painting above a secondary altar is a triptych by Stefan Lochner, the outstanding painter of the Cologne school of the early 15th century. In clear, bright colours it depicts the adoration of the kings. A reminder of Cologne's more ancient past lies at the south side of the cathedral—a mosaic floor of a banquet hall of a great Roman villa discovered during excavations near the cathedral in 1941. Other Roman remains in Cologne are a 1st-century tower of the earliest city wall, Roman–Frankish catacombs, and a Roman mausoleum in Weiden, on the outskirts. The Ubier Monument, discovered in the 1960s, dates from the period of Ubii occupation of the area. Remains of the medieval walls may still be seen, and there are three surviving gates, the Eigelsteintor, Hahnentor, and Severintor. The Bayenturm, a medieval tower, stands near the Rhine.

The cathedral itself is ringed with noble churches, largely built in the prosperous Middle Ages. St. Gereon, St. Severin, and St. Ursula are of late Roman origin, although the buildings are 11th–13th century. The Romanesque St. Maria im Kapitol and St. Kunibert were severely damaged in World War II. Both date from the 7th century, although the actual buildings are 11th and 13th century, respectively. Famous also are the Romanesque churches of St. Pantaleon, St. Aposteln, and Gross St. Martin. Numerous other churches date from as early as the 11th century. The 14th-century Antoniterkirche, a secularized monastery church, was made over to the Protestants in 1802 and became the first public Lutheran church in Cologne. It contains a war memorial, the "Angel of Death," by the contemporary sculptor Ernst Barlach.

Among Cologne's secular medieval buildings that suffered in World War II and have undergone reconstruction are the Overstolzenhaus and the Gothic Rathaus (Town Hall), with its 16th-century porch. The Gürzenich, or Festhaus (banqueting hall), of the merchants of the city (1441–47), reconstructed as a concert and festival hall, and the 16th-century Zeughaus, or arsenal, which contains a historical museum, were only outwardly restored in medieval form.

These ancient buildings share the crowded city centre with modern banking and insurance houses, shops and offices, a new theatre and opera house (opened 1957), and, immediately north of the cathedral, the great railway station. Near the perimeter of the city is the new town hall.

Cologne
Cathedral's
history
and art

Medieval
churches