

Colloid



 [Milk](#) is an [emulsified](#) colloid of liquid [butterfat](#) globules dispersed within a [water](#)-based solution.

A **colloid** is a substance microscopically dispersed throughout another substance.^[1]

The dispersed-phase particles have a diameter of between approximately 2 and 500 [nanometers](#).^[2] Such particles are normally invisible in an optical [microscope](#), though their presence can be confirmed with the use of an [ultramicroscope](#) or an [electron microscope](#). [Homogeneous](#) mixtures with a dispersed phase in this size range may be called *colloidal aerosols*, *colloidal emulsions*, *colloidal foams*, *colloidal dispersions*, or *hydrosols*. The dispersed-phase particles or droplets are affected largely by the [surface chemistry](#) present in the colloid.

Some colloids are translucent because of the [Tyndall effect](#), which is the scattering of light by particles in the colloid. Other colloids may be opaque or have a slight color.

Colloidal solutions (also called colloidal suspensions) are the subject of [interface and colloid science](#). This field of study was introduced in 1861 by [Scottish](#) scientist [Thomas Graham](#).

IUPAC definition

Colloidal: State of subdivision such that the molecules or polymolecular particles dispersed in a medium have at least one dimension between approximately 1 nm and 1 μm , or that in a system discontinuities are found at distances of that order.^[5]

Colloids

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Introduction

There should be a more exciting name for the phenomena to be discussed here. The dull term *colloid* that reminds us of glue is, nevertheless, the accepted word. It was coined in the early 19th century by the Father of Physical Chemistry, Thomas Graham (1805-1869), to distinguish those materials in aqueous solution that would not pass through a parchment membrane from those that would. Glue was indeed a material that would not, and the Greek for glue is *kolla*, from which we also get "protocol" and "collagen." Those that would pass through were things like salt, and other soluble crystalline substances, which Graham called *crystalloids*. As we shall see, the field is much, much richer than this.

Colloids received little attention until the end of the century, when van't Hoff, Oswald and Nernst founded modern physical chemistry and they, and others, became fascinated by colloid phenomena. There had been famous observations by Tyndall and others in the meantime, but chemists could not get excited over glue. Then, in the 1920's and 1930's, the importance of colloids to industrial processes and biochemistry changed everything. Colloids became a hot field, and soon every elementary textbook said something about them. In writing some of the other articles on the site recently, I became gradually aware of the fascination of colloids, and recognized that my knowledge of them was very deficient. This article is the result, and I hope it will serve as an introduction to what colloids are all about, and demonstrate how interesting and useful they are.

An interesting philosophical point was suggested by this study. Colloids are often called a "fourth state of matter," and I wondered just how meaningful this concept is. We shall find that it is very difficult to encapsulate any concept concerning colloids in a word, though heaven knows chemists have tried, and many words have been coined. It is necessary to name things to think about them efficiently, and one thing scientists have done assiduously is to assign names. Biology comes to mind, with endless terms and names based only on surface appearances, at least until recently. Naming gives the appearance of knowledge, where there is no real

knowledge at all. The antithesis to mere naming is mathematical analysis, which gives real conclusions and effective knowledge. The danger of names comes when they are regarded as real things and are used to delimit instead of simply to denote and describe.

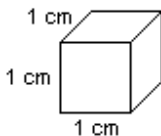
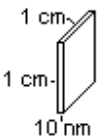


It is easy to recognize the three conventional states of matter in ice, water and steam. The names solid, liquid and gas can be attached to certain suites of properties, and makes a useful distinction. In a gas, particles of the substance move freely and have to be stopped by walls. In a liquid, the particles are sometimes associated, sometimes not, but always occupy a certain volume. In a solid, the particles cannot move far relatively, and can only vibrate. Many substances can be classified by these properties, but the terms do not separate matter into three mutually exclusive boxes, and may not be descriptive enough. Where is tar, for example, or jelly, or a substance above its critical point? Colloids will give many examples of substances for which the simple classification into three states is wholly inadequate.

The properties of matter depend almost completely on its structure. All metals are alike, to a good approximation. They are shiny, soft, tough substances that conduct electricity. All ionic crystals are alike (granted differences in crystal symmetry). They are hard, transparent and do not conduct electricity in the solid state. They can usually be crushed into white powders. The variations between metals, or between ionic crystals, are very much less important than their similarities. Saying that a substance is a metal, or an ionic crystal, says much more than simply that it is a solid. Solidity is only a macroscopic appearance, of no fundamental significance, like being green.

I have seen the definition of matter as "that which occupies space." But what about gases? They occupy space, of course, but two or more gases can occupy the *same* space, as far as appearances go. The important thing is to use terms like solid, liquid, gas only as far as they are useful descriptions, and not consider them as exclusive classifications into which everything must fit. To see that this is not trivial, consider the many sciences (not generally chemistry or physics) in which there are bitter controversies about which named category to assign to some object or process. We should not be limited by the arbitrary names we give our concepts.

Properties of Colloids

I recalled that colloids were particles larger than molecules, but smaller than grains of sand. This is true, and colloidal dimensions can be considered to be from about 10 nm up to 1000 nm, or 1 μm , but mere size is not the important thing about colloids. The overwhelmingly important property of colloids is that they have very large surface area. To some degree, they are *all surface* and their properties are those of their surfaces. I do not remember appreciating this properly before, but I can assure you of its significance. Incidentally, 1 μm is about the size of a bacterium. I shall use the word "colloid" to refer to a substance of colloidal dimensions, or to a colloidal system, indifferently.

State of Subdivision				
mass	laminated	fibrillar	corpuscular	
				
1 cm 1 cm 1 cm	1 cm 10 nm	1 cm 10 nm 10 nm	10 nm 10 nm 10 nm	
N	1	10^6	10^{12}	10^{18}
A_1, m^2	6×10^{-4}	2×10^{-4}	4×10^{-10}	6×10^{-16}
A_2, m^2	6×10^{-4}	200	400	600
State of Subdivision and Total Area				

To see the significance of this observation, consider the cubic centimeter in the diagram at the right. In this form, it has an area of 0.0006 m^2 . We could say that it is almost all

volume. Most of its molecules are safely resident behind its surface, secure from disturbance or attack. Let us now divide it into thin laminae, 10 nm thick, a colloidal distance. The cube becomes a million laminae, with a total surface area of 200 m^2 . Every molecule is now only a short distance from the cold outdoors, and the material is all surface. We have turned the mass cube into a *laminated colloid* by this delicate slicing alone.

Continuing, we now slice each of the million laminae into a million fibers, and the surface area doubles. We still have a colloid, of course, with two dimensions colloidal, but have not increased the area greatly, not as we did in the first slicing. We can expect *fibrillar* colloids as well as laminar ones. Finally, each fiber is chopped into a million bits, giving a *corpuscular* colloid. This increases the surface area only by 50%, to 600 m^2 . From the mass to the corpuscle, the surface area has been increased by a factor of a million, which is typical of a colloid. Note that most of this increase came with the first dimension to "go colloidal," so we can call anything with any least dimension of colloidal size to be a colloid. This was another thing that I did not appreciate in my ignorance.

The large area emphasizes surface effects relative to volume effects, giving colloids different properties than those of bulk matter. The surface tension of a liquid is the free energy required per unit area to create new surface. For water against air, its value at 20°C is 72.75 dyne/cm. For mercury against air, it is 450 dyne/cm. For mercury against water, it is 375 dyne/cm, not surprisingly close to the difference of the other two values. The ratio of surface to volume for a sphere of diameter d , or a cube of side d , is $6/d$. The surface energy of small drops will strongly affect their properties. If a cubic centimeter of water were divided into 10 nm cubes as above, the coalescence of the cubes would release enough surface energy to heat the water by about 10°C . A cubic centimeter of mercury would be warmed by 143°C by the same procedure.

It is better to define a colloid as a system in which the surface area is large and in which surface effects are predominant, rather than simply in terms of particle size. Indeed, in foams there are no colloidal particles at all—it is the thinness of the films that creates the colloidal behavior. Similarly, in a gel the fibrous structure is what is colloidal. In any colloidal system, there must be at least one structural dimension of colloidal size in order for the large surface area to exist in a limited volume, however. This broadened definition of colloid is not only reasonable, it is useful. A colloid is a material system that is mainly surface.

The next important characteristic is that a colloid is a *two-phase* (at least) system. A *phase* is a homogeneous component of a system, in the sense of the Phase Rule. The Gibbs Phase Rule applies to systems in which the phases have negligible surface energy, which is perfectly applicable to phases that are "all volume" as our centimeter cube was, or even to phases of microscopic dimensions (larger than $1 \mu\text{m}$). It does not apply to the system of colloid phases, in which surface energy predominates. Therefore, be careful when applying the Phase Rule to colloidal systems.

A colloidal system consists of an *internal phase*, which is the material of colloidal dimensions, and an *external phase*, which is the material in which the colloid is dispersed. These designations are analagous to the terms *solute* and *solvent* used for simple solutions (which form a single Gibbs phase). As the particles of a corpuscular colloid become smaller and smaller, we go over

imperceptibly from a two-phase colloid to a single-phase solution, and there is no definite boundary. This gives a hint as to why I discussed names and their significance in the introductory paragraph.

The colloidal system that is most similar to a simple solution is a dispersion of corpuscles, or particles, in a liquid. This is called a *sol*, and the liquid is the external phase. This is the classical colloid as described by Graham. If the external phase is a solid instead of a liquid, the system is called a *solid sol*. The only difference is the mobility of the molecules. In a solid sol, they can move only by diffusion. If the external phase is a gas, usually air, instead of a liquid, we have an *aerosol*. There is no definite boundary between a sol and a solution, but still they are significantly different. There is also no definite boundary between a sol and a coarse suspension. A coarse suspension will settle out rapidly, while a sol may be permanent.

The particles that appear in a sol may be wetted by the liquid, or may not. Wetting is a typical surface effect, and so is of paramount importance in a colloid system. In the first case, the liquid is *adsorbed* on the surface of the particle. The terms *adsorb* and *absorb* sound alike, but are quite different. A substance that is absorbed is taken into the volume of the absorbing substance, like water into sand. If it is adsorbed, it attaches itself only to the surface. Since colloids are all surface, as we have pointed out, adsorption is what is important with them. If the particle adsorbs the external phase, it is called *lyophilic*, or *hydrophilic*, if the external phase is water. The Greek verb "luo" means to dissolve or destroy, and philic is from "philos," love. A lyophilic colloid "loves the external phase." On the other hand, if the particle does not adsorb the external phase, it is said to be *lyophobic*, or "fears the external phase."

Sols that contain inorganic particles, such as metals, are mostly lyophobic, as are most aerosols and solid sols. Lyophobic hydrosols are a very common kind of colloid, and deserve detailed description. For example, consider the hydrosol of gold with particles about 4 nm in size. This was one of the first sols studied extensively, and has interesting properties. With about 0.1% gold, the sol is a rich ruby red. The similar solid sol in glass makes ruby glass. The gold particles absorb strongly in the green and blue, so the transmitted light is red. There is a little yellow-green scattered light, but mostly it is a case of absorption by the gold metal. If the gold particles clump together, which they may do as time passes, the color of the solution changes. When the particles are about 40 nm in diameter, the solution is blue, with considerable scattered light. If the particles agglomerate further, the color disappears and gold flakes settle out.

Bacteria, which are about 1 μm in diameter, can be suspended in water to form a sol, which has all the classic properties. The Brownian motion, the Tyndall effect (turbidity), and even electrophoresis are seen. The bacteria act as a hydrophobic sol, peptized by their electrostatic charge. The properties of a sol are largely independent of the nature of the internal phase.

There are two interesting questions here about the stability of the sol. First, what keeps the gold suspended in the red solution so that the tiny particles do not settle out? Second, how are the particles kept from agglomerating? Let's take the first question first. The gold particles fall under gravity through the water. The terminal velocity v of their fall is given by Stokes's equation, $(mg - m'g) = 6\pi\eta av$, where m is the mass of the particle, a its radius, m' the mass of the water displaced, and η is the viscosity of water (1.002 centipoise at 20°C). A correction factor $(1 +$

$K\lambda/a$) must be applied for the small particles, where K is a constant, λ is the mean free path of the liquid molecules (this factor really applies better to aerosols), and a is the radius of the particle. On the other hand, the particles are subject to the bombardment of the molecules of the liquid, which produces the Brownian movement. For a sufficiently small particle, the upward diffusion produced by the Brownian movement overcomes the gravitational fall, and an equilibrium is reached, much like the equilibrium of gases in the atmosphere. Perrin first verified this effect, although it is quite complicated in this case, the gas-like effect only occurring close to the upper surface of the sol. There is a *critical size* for a particle, below which it will not settle out. At any rate, this is why colloidal-size particles do not settle out of a sol.

Now for the second question. Generally, if two colloidal particles collide, they will stick together and make a bigger particle, because it is usually favored by energy. Eventually, the particles get larger than the critical size to be suspended by the Brownian movement, and they settle out. There must be some good reason if this is not to happen. In most lyophobic colloids, the particles are electrically charged with the same sign, and this keeps them apart, since they repel one another. The particles are charged mainly because they adsorb certain ions in the environment. In water, they may be OH^- ions, which are generally present, and give the particles a negative charge. The H^+ ions are hydrated, so are not as easy to adsorb, but apparently some particles like them, and become positively charged. If you try to make a hydrosol with particles of opposite charges, they neutralize each other and the sol collapses. Since lyophobic sols are stabilized by electric charge, adding electrolytes generally destroys the sol. When rivers reach the sea with their loads of colloidal sediment, the ions in sea water coagulate the sol, and the load is deposited in the delta. There are other ways for a particle to become charged. A zinc particle, for example, may become negative when some zinc dissolves according to $\text{Zn} \rightarrow \text{Zn}^{++} + 2\text{e}^-$, and the electrons remain on the particle.

How the charges are distributed is an interesting question. The sol appears electrically neutral on the large scale. The particle with its adsorbed charges is called a *granule*. The charges are in a thin layer on the surface. They attract an atmosphere of opposite charges from the external phase, just as an electron in a plasma surrounds itself with a shielding positive charge by attracting positive ions and repelling electrons. The whole neutral structure, granule plus mobile external charge, is called a *micelle*. This, then, is what moves around, the charged particle and its cloud of opposite charge. When we apply an electric field to the sol, the cloud of charge is moved in one direction, and the granule moves in the other. There is a local viscous flow about the granule, and the micelle moves toward the anode, if the granule is positive, or toward the cathode, if it is negative. This movement is called *electrophoresis*, and can be practically useful. The particles of a sol do not repel one another until they come quite close, and their micelles overlap, because of the shielding.

The *mobility* of the colloidal particle is its velocity in a unit field. Helmholtz developed a formula for the mobility, $M = \zeta\kappa/4\pi\eta$. Here, κ is the dielectric constant of the external phase, η its viscosity, and ζ is the potential difference across the micelle from the outside to the adsorbed charges on the particle, that is, through the fluid that is sliding around the granule. From measurements of M , it is possible to find ζ , which becomes a kind of "fudge factor" since it is hard to calculate. For the small gold particles in the red sol, $M = 4 \times 10^{-4} \text{ cm}^2/\text{s-V}$, and $\zeta = -0.058 \text{ V}$. The negative sign indicates that the gold migrates to the anode, and so has a negative charge.

The Helmholtz equation gives $M = 4.15 \times 10^{-4}$, which doesn't prove much except that we know how to use the equation. Since the equation is written in esu, we must divide by $(300)^2$ to convert volt to statvolt.

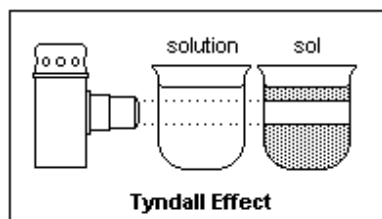
In order to create a lyophobic sol, we must either reduce a mass to colloidal size, called *dispersion*, or we must build the colloidal particles from molecules, called *condensation*. In either case, a third substance, a *peptizing* agent, may have to be added to stabilize the sol. This agent can supply ions that will be adsorbed on the particles resulting from dispersion or condensation to give them a stabilizing charge. For clays, the OH^- ion is a peptizing agent, which can be supplied by alkalis. Dispersion can be done mechanically, in a *colloid mill* that grinds the substance into small, equal particles. Another method is with an electric arc. Metal electrodes are used, at a current of 5-10A and voltage of 30-40V. Bredig made particles of about 40 nm by this method, and it was improved by Svedburg to obtain sols of many metals down to 5 nm particle size. Ultrasonics can also be used to disperse sols.

When a sol is created in a nonpolar solvent, the particles may not be charged (and must be stabilized by some other means). They do not then exhibit electrophoresis or other electrical phenomena depending on granule charges.

Colloids and Light

A homogeneous phase or solution does not disturb the propagation of light, except to change its phase velocity to $v = c/n$, where c is the speed of light in vacuum and n is the index of refraction. In a gas, density fluctuations that are a natural result of the free movement of the molecules can scatter light. *Scattering* is the emission of light in all directions, which decreases the intensity of the ordered beam. This Rayleigh scattering is proportional to the inverse fourth power of the wavelength, so blue light is scattered more than red, giving the blue color of the clear sky. Scattering should be distinguished from *absorption*, which is the conversion of the energy of the light to other forms. Both scattering and absorption cause *attenuation* of the light beam. The transmitted beam and the scattered light may be colored if the scattering or absorption is not constant with wavelength. The blue sky and the orange sunset colors have the same cause, Rayleigh scattering by density fluctuations.

A colloidal system contains particles that affect a light beam by scattering and absorption. If the particles are of a size comparable to the wavelength of light or larger, they scatter or absorb light independently. The same thing happens if they are separated by distances comparable to or greater than the wavelength of light. The wavelength of visible light is 400-700 nm, with the maximum sensitivity at 555 nm. This is in the middle of the range of colloidal dimensions, so colloids can be expected to have significant effects on a light beam.



One common effect of colloids is *turbidity*, an effect like that of stirring up mud in water. Slight turbidity may not be noticed until a beam of light passes through the colloid. Colloidal systems need not be turbid: a gel may be quite transparent when the particles are small. Solutions, as homogeneous phases, are not turbid. The turbidity causes scattering so that the path of the

light beam can be clearly seen. This is called the *Tyndall effect*, and the observed scattered light is called the *Tyndall cone*. John Tyndall (1820-1893) was Faraday's successor at the Royal Institution. He suggested that the blue sky was caused by scattering by dust particles, but Rayleigh later found the true cause, showing that the sky would be blue even if the air were pure. The scattered light is polarized perpendicularly to the direction of the beam if the particles are approximately spherical and small. If the particles are nonspherical, or larger than a wavelength, the scattered light will be partially polarized.

The Tyndall effect is a common atmospheric phenomenon. Searchlights produce Tyndall cones in slightly hazy air. Smoke is often blue when seen in scattered light, orange in transmitted light. This was quite clear in the summer of 2002, when forest fires near Denver put smoke in the air, and the sunlight became a strange reddish color. The crepuscular rays seen at sunset, which seem to radiate from the position of the sun, are parallel Tyndall cones. A laser beam may make a distinct Tyndall cone in dusty air. If you have a piece of polarizing filter, try to determine the polarization of any Tyndall cones you may observe. All the Tyndall cones that you see are evidence of lyophobic sols.

If the sol is composed of transparent particles with an index of refraction considerably different from that of the external phase, and they are present in sufficient concentration, the sol will become opaque and white, the limit of turbidity. If the particles have the same index of refraction, the Tyndall effect will be small. This property is used in enamels, which are opaque glasses fused onto a metal substrate, and in pottery glazes. Stannic oxide, for example, gives a white enamel or glaze.

A beam of bright sunlight entering through a window may be marked with moving bright specks that are light scattered from colloidal dust grains that are always present in the air. The grains themselves, which may be submicroscopic, are not seen, only the light they scatter. This principle is used in the *ultramicroscope* that allows individual, submicroscopic particles to be observed. Only the light from them is detected against a dark background, so that they can be counted and their motion observed; no image of the particles can be formed. The instrument consists of a bright light source, a slit and optics to focus the slit on the sample, and a microscope. A thin slice of the sample is illuminated by the slit. By turning the slit 90° the depth of the area viewed can be determined. The direction of viewing is at right angles to the illumination. Some ultramicroscopes are coaxial and use a different illumination method. If the number of particles per unit volume is found in this way, by counting using a squared graticule, and the weight of colloid per unit volume is known, then the size of the particles can be determined.

Colloids can produce color. The red of a gold sol or ruby glass has already been mentioned, where the color is due to the wavelength dependence of scattering and absorption. Color can also be produced by the interference of white light, especially if there are thin films or a periodic regularity in the density. The colors in thin oil films are familiar, and the films are, of course, colloidal in thickness. Color produced by such means is called *structural*. Color produced by absorption by colored pigments is called *pigmental*. The blue color seen in blue eyes and birds' feathers is structural, caused by scattering by fibers. Brown pigments in the iris modify the blue color to green, then overwhelm it to make brown eyes. Much color in the insect world is

structural, such as the colors of a butterfly's wings, often combined with pigmental color to produce a great variety. The greenish colors of crude oil and its products are a result of colloidal suspensions.

Aerosols

An aerosol of colloidal solid particles may be called a *smoke*, while if the particles are liquid, it is a *fog*. Sometimes the two are combined, in a suspension of solid particles with an adsorbed liquid film on the surface. The original *smog* was a smoke with a liquid film of sulphuric acid, which made it excessively unpleasant to breathe. The Great Smog occurred in London on 5 December 1952, killing nearly 4000 people who had respiratory problems, and stimulating clean air legislation. Now it usually lacks the smoke, and is a fog of some unpleasant liquid coming from motorcars instead. Aerosols have the usual characteristics of lyophobic sols: a strong Brownian movement, the scattered blue light of the Tyndall effect, and stabilization with particle charges.

Clouds are aerosols of water particles, supported by the Brownian motion like any sol. The droplets are produced by condensation of water vapor on *condensation nuclei*, which are usually hygroscopic particles of dust, or positive ions. The mist above splashing water is positively charged, with compensating negative charge in the form of unhydrated negative ions. For condensation to occur, the air must be supersaturated for water vapor. The radius of the droplets is large for colloidal particles, and they are often supported by updrafts more than by Brownian motion. The radius of cirrus cloud droplets may be 2 μm . When they reach a radius of about 0.04 mm, the droplets fall as rain, often coalescing with others. The largest raindrops have a radius of about 3.6 mm, and such large drops are rare.

Raindrops can be blown upwards into freezing air by updrafts, gathering water by coalescence with others, and freezing to a solid ball. This can happen repeatedly, forming large hailstones that eventually fall. The largest hail reported may be the 3" diameter hail that fell in Bloomington, Ind. in 1917. A farmer was killed by hail near Lubbock, Texas in the 1930's, but this is the only reported fatality.

Saturated air can be expanded adiabatically to cool it and achieve supersaturation. This can be done in the laboratory with the Wilson cloud chamber with an adiabatic expansion against a piston or the equivalent, which does work that cools the air. The cooling is given by $T_2/T_1 = (V_1/V_2)^{k-1}$, where k is the ratio of the specific heat at constant pressure to the specific heat at constant volume (1.4 for air). In clean air, condensation occurs for a volume ratio greater than 1.25. From 1.25 to 1.34, the condensation falls as fine rain. For 1.25 to 1.28 the condensation is on negative ions, and the particle radius is 200 μm . For 1.28 to 1.34 the condensation is on the positive ions, and the particle radius is 20 μm . For larger expansion ratios, the mists can be colored: 1.408 gives green, 1.422 purple, and 1.429 red.

At the lower expansion ratios, condensation is difficult enough that it may occur along the tracks of alpha particles, which ionize strongly, making the tracks visible. The condensation soon settles out, since the droplets are large. The chamber can work with alcohol vapor as well as water vapor.

The vapor pressure p' of a small drop of radius r is greater than the vapor pressure p of a plane surface of the liquid. The vapor pressure p' is given by $\ln(p'/p) = (1/RTd)(2\gamma/r - q^2/8\pi r^4)$, if q is the charge density on the surface. γ is the surface tension of the liquid. This shows that a charge of either sign will stabilize a small droplet against evaporation. In the absence of a charge, small droplets will evaporate in favor of large drops. Electric charges may explain the stability of clouds, and the fact that rain may not fall from them.

An aerosol of starch grains, with a density of 100g/m^3 , has a very large surface area, and adsorbs O_2 from the atmosphere. Starch grains in flour are from 5 nm to 200 nm in diameter. It is no wonder that it is a violent explosive. Coal ground to pass through a 200-300 mesh sieve can be blown directly into a fire as a convenient fuel. It can also make a sol with fuel oil to form a *colloidal fuel* that can be used exactly like fuel oil. Coal dust is reputed to be a fire hazard, but it is not as dangerous as starch dust. Many "coal dust" explosions may have another cause.

Smudge pots are used to protect agricultural plants from frost. They are small fires producing dense smoke. The heat produced by the fires is probably one of the most important effects. The smoke may provide condensation nuclei for the dews of evening, increasing the heat by the latent heat of the condensed vapor. The aerosol blanket slows loss of heat by radiation, which can be very important into a clear night sky.

Smoke is also used for military purposes, for concealment or signalling. White phosphorus burns to hygroscopic P_2O_5 , which forms a dense white fog in humid air. Silicon tetrachloride mixed with ammonium hydroxide gives a dense white smoke of ammonium chloride and metasilicic acid. This smoke is used in skywriting, since it is easily made from liquids when needed. The navy's smoke for concealment was made by restricting the air supply to the boilers, producing thick black smoke from the funnels. Radar and the end of gunnery has rendered smoke screens useless. Colored smoke may be used for signalling.

Emulsions

An *emulsion* is a colloidal system in which both phases are liquid. If the liquids were miscible, they would form a solution, so emulsions are lyophobic colloids. The typical example is water and oil. The internal phase is determined by which component has the higher surface tension. This component will form spherical bubbles immersed in the other, which will be a continuous phase. The granules of an emulsion may be large, even microscopic. An emulsifying agent is usually required to form a stable emulsion. The emulsifying agent, or *protective colloid*, is *surface-active*, meaning that it reduces the surface tension of the liquid, and so tends to concentrate in boundary films. In the case of water and oil, sodium oleate, a *soap* reduces the water surface tension and raises that of the oil, so that the emulsion will be oil droplets in water, and quite stable. There are many other *detergents*, but sodium oleate will serve as a good example.

Oleic acid is a fatty acid with the formula $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$, a monounsaturated carboxylic acid with a long hydrocarbon chain. Fats are glyceryl esters of this acid. Glycerol has three OH groups, each of which can take the H off the end of the oleic acid and stick the rest to the glycerol framework, making a *triglyceride*. Boiling the fat with NaOH makes three

molecules of sodium oleate, a liquid soap. The hydrocarbon chain nestles up to the oil, the sodium to the water, and peptizes the oil. The emulsion can be made by simply shaking oil, water and soap together, but this will not make droplets of a uniform size. The larger droplets may "cream off" in this case, and float to the surface of the emulsion. The emulsion may be *homogenized* by blowing it through small orifices under a pressure of 4000 to 5000 psi. The small, uniform drops that result will make a stable, long-lasting emulsion.

Milk is an emulsion of oil ("butterfat") in a watery sol of the hydrophilic protein casein in which the external phase is a solution of lactose and various salts. Milk will "cream" unless homogenized, since the fat globules range from 100 nm to 22 μm in diameter. Cream can contain from 29% to 56% fat, in packed globules stabilized by casein. Human milk contains albumin in addition to casein. Mayonnaise is an emulsion of oil in water, using egg yolks as an emulsifying agent. Hollandaise sauce is another emulsion, of butter in lemon juice, again using egg yolks as an emulsifying agent. Butter itself is an emulsion, this time of water droplets in oil. The cosmetic "vanishing cream" is an oil-in-water emulsion. If this is reversed, "nourishing cream" is a water-in-oil emulsion. Crude oil as it comes from the well is often emulsified with water. In this case, heating is sufficient to "break" the emulsion, and separate the oil from the salt water. Many insecticides are oil-in-water emulsions for spraying. The oil wets the oily leaf surfaces and sticks, while the water carrying the poison evaporates. Lubricating grease is a water-in-oil emulsion. The emulsifying agent, calcium oleate, is soluble in oil, not in water, and so makes the water the internal phase. The idea here is to make the lubricant stiff, so it will not drip off.

Whether a component of an emulsion is the internal or external phase is determined by the relative surface tensions, not by the amounts of the components. Equal-sized globules can close-pack like spheres to occupy 74% of the volume. The internal phase can be even higher in concentration if the globules are not all the same size, so the smaller can huddle in the voids left by the larger. Because of the presence of an emulsifying agent, emulsions are very stable, and "breaking" them when required can be difficult.

To find out whether an emulsion is oil-in-water or water-in-oil, the effect of adding a small amount of either oil or water to a sample of the emulsion on a microscope slide is observed. If you add the external phase, it will mix easily and quickly, but the internal phase will not mix and remain a drop. This is called the *dilution test*.

Foams

A foam may be an internal phase of gas in an external phase of liquid or solid. In a liquid foam, a colloidal adsorptive agent forms a film that bounds the gas bubble. Bubbles blown with soap solution are related to foams, but are quite large and have an independent existence. Smaller bubbles in a mass form the more usual foam. People washing dishes or clothes are reassured by a thick layer of soap foam on the water, showing that there is still detergent left to emulsify additional oil. Such foams are mainly air, with very little liquid. The colloidal dimension in a foam is the thickness of the film, not the size of the bubble. The bubble is lighter than its surroundings, and will rise to the top, where it joins the foam. In beer, the foam is stabilized by albumin and by the hop resins added to the beer. When carbon dioxide is released, it uses the adsorptive agent it finds to make the foam. This "head" on Guinness stout is famous and creamy-

-and carefully engineered. Meringue is a dried foam using egg albumin. Marshmallows use sugared gelatin for the same purpose.

Ore flotation depends on the property of the adsorptive agent to wet the valuable metallic sulphides or other ore, but not the silicates, which are preferentially wetted by water. Note again the central role played by surface chemistry. A froth is made with water and the adsorptive agent, and mixed with the ore to be beneficiated. The froth floats to the surface, where it is skimmed off, together with the enriched ore. In a few special cases, the valuable mineral is wetted by the water, while the gangue sticks to the oil. We use the buoyancy of the bubbles to effect the separation.

A fire-fighting foam is made from mixing water, aluminium sulphate and sodium bicarbonate with an adsorptive agent. The carbon dioxide that is released makes a dry foam, while the other ingredients form a kind of gel. This foam can be used on all kinds of fires, including burning oils.

Examples of solid foams are pumice, meerschaum, and Ivory® soap. The white soap has colloidal air beaten into it so that it will float. Meerschaum, "sea foam" in German, is a light-colored metamorphic rock associated with serpentine, and is a magnesium silicate, also known as *sepiolite* from its resemblance to light cuttlefish (*sepia*) bone. It is soft, smooth, light and translucent, used mainly for carving smoking pipes. It is fibrous and porous, with gaseous inclusions, apparently a dried gel. It is so porous that it floats on water, in spite of its mass density of 2.0 g/cc. Pumice, an extrusive igneous rock, is a solidified foam of volcanic glass, usually obsidian. It also floats on water, and makes a good gentle abrasive. Diatomaceous earth consists of the microscopic shells of diatoms, very common marine plants, made of opaline silica and very porous. It adsorbs nitroglycerine to make dynamite, rendering it much less sensitive and much safer to handle. Bread is, of course, a dried foam as well. The protein *gluten* makes the film that surrounds the CO₂ bubbles produced by the enzyme zymase secreted by the yeast. Zymase acts on the sugars (hexose) produced from starch by other enzymes, and also makes ethyl alcohol at the same time as the carbon dioxide. The alcohol is often the desired product! Hydrophilic gluten and water make a good gel in "strong" flours that include as much CO₂ as possible and hold the starch granules. Rye flour has little gluten, and will not make light bread by itself. Foams aid digestion by providing as large a surface area as possible.

Gels

So far we have looked at lyophobic colloids, which will have nothing to do with the other phase. A lyophilic colloid, by contrast, actively seeks out the other phase and adsorbs it strongly. In most cases, the other phase is water, so we are dealing with hydrophilic colloids. Aluminum hydroxide and orthosilicic acid are inorganic examples. Most organic colloids are hydrophilic. Gelatin is of animal origin, derived from protein, made by boiling bones and horny parts. Gums are of vegetable origin. Gums are branching polysaccharides, soluble in water. They include the *mucilages* carrageenan (from Irish moss, a seaweed) and agar-agar (also from seaweed), which are sulphate esters. Gum arabic is from the acacia tree, and gum mastic is from the *Pistacia lentiscus*. Gums are secreted by trees to protect and seal wounds. When you find any of these in a

list of food ingredients, they are for the purpose of making a gel. Ice cream may contain guar gum, cellulose gum, locust bean gum and carrageenan. These gums are not digestible.

A *resin* is similar to a gum in purpose, but is insoluble in water. Resins are notably secreted by evergreens, and are terpene derivatives, soluble in turpentine and similar solvents. Rosin is the residue when turpentine is distilled. Amber and copal are other natural resins, while alkyd and phenolic resins are artificial, used in plastics and paint.

Gelatin or gums dissolve in hot water. As the clear colloidal system cools, its viscosity increases steadily. The viscosity of the external phase is not affected in hydrophobic sols, by distinction. At some point, the system *gels*, forming a wobbly but definitely solid body. This is really an extraordinary thing to happen. If you heat the gel, it will melt and form a viscous liquid. On cooling, it will gel again. If you dry it out, it will shrink and look horrible. On adding water, it will plump up again into a wiggly gel. These colloids are called *reversible* or *elastic*. The gels formed from inorganic hydroxides will not reform a gel once they have dried out, and the dry form will be brittle. The pore spaces will still be there, however, and will absorb moisture and other substances. Silica gel is a widely used substance. Though it can be renewed by heating and live to absorb again, it will never again be wobbly and gelatinous. I say absorb, since it will appear to be this, but on a microscopic scale it is still adsorption, of course.

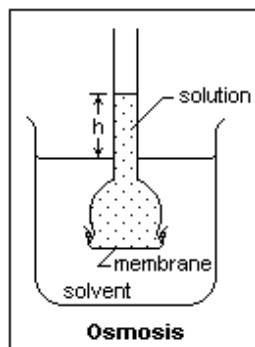
Gels are used as culture media for microorganisms. Gelatin was originally used, but it melts at 37°C, and so cannot be used to study microorganisms at body temperature. Agar-agar makes a gel that can stand higher temperatures, so it is used in preference as a culture medium, poured into the familiar Petri dish. It was first used by Robert Koch.

The colloidal phase in a gelatin is fibrillar, composed of fibers of colloidal cross-section. When a gel sets, these fibers form a tangled mass like a pile of brush, that holds the system together. Droplets in a gel are lens-shaped, showing the packing. There has been quite a bit of controversy over the structure of gels, but the fibrillar structure seems correct. The original idea of a cellular structure is untenable. The fibers adsorb large quantities of water, and there are also droplets of water, so that the gel is mainly water, given a doubtful rigidity by the stacks of fibers.

Pectin is a gelatin-like protein substance found in the rind of citrus fruit, in apples and generally in fruits. If a slightly acid solution of pectin is made 65% or 70% sucrose, it will gel. This is the reaction used to make jams. The verb *pectize* is used to describe the creation of a gel, as *peptize* is to create a sol.

Gels have some curious properties. As they age, *syneresis* may occur, which is the loss of liquid. This is a result of the closer agglomeration of the colloid. The reduced active area requires less water, so the excess water is eliminated. It does not mean that the gel is deteriorating. Another property is *thixotropy*. On agitation, the gel becomes fluid, but reverts to the gel when left alone. Fresh gelatin gels are quite thixotropic, and advantage can be taken of this to add ingredients to a jelly. The "thixo-" comes from the future of the Greek verb for "touch," *thixomai*, and a thixotropic substance would be one whose state changes with touching.

Colloids and Membranes



Let's review the phenomenon of *osmosis*. In the diagram, we have put some solution into a container closed off by a *semipermeable membrane*, and put the container into a vessel containing the pure solvent. Consider the dots as representing the dissolved substance. This applies to a sol, as well as to a solution, but there will be more "solute" particles in the solution. The membrane can be cellophane, but ordinary wrapping cellophane cannot be used, since it has been lacquered to close the pores. The pores must be small enough to prevent the solute from passing through. The solvent is found to cross the membrane and enter the solution, making it more dilute. The level of the solution rises to some

height h in equilibrium. If d is the density, then $\pi = dgh$ is the *osmotic pressure*. This is the pressure required on the solution side to make the rate of movement of the solvent the same in both directions across the membrane. If the solution is dilute, van't Hoff's equation gives the osmotic pressure: $\pi V = nRT$, where the volume V of the solution contains n moles of solute.

The osmotic pressure of a solution containing 1 mole of solute per 1 kg of solvent, called a 1 molal solution, is quite large, about 25 atmospheres (as we can estimate from van't Hoff's equation). Not only is this hard on cellophane membranes, but would require a liquid column 825 feet high, which is inconvenient. Nevertheless, osmotic pressures are high enough to push fluids to the tops of high trees (this is actually a complex subject about which there is controversy). Strong semipermeable membranes can be made by precipitating insoluble salts in the pores of unglazed porcelain. Sols will exert quite modest osmotic pressures, since there are many fewer particles per unit volume. In fact, the pressures are so low that they cannot be used in most cases to find the number of particles per unit volume. However, the molecular weight of haemoglobin was determined in this way. Cell walls are semipermeable membranes. If an erythrocyte (red blood cell) is put into pure water, it will swell and burst because it contains a solution of electrolytes in a semipermeable membrane. If put into strong salt solution, it will become dehydrated and shrivel. Solutions of the same osmotic pressure are called *isotonic*. Isotonic solutions are used to prevent damage to biological systems. Erythrocytes are about $8.6 \mu\text{m}$ in diameter and $2.6 \mu\text{m}$ thick, and slightly concave on the faces. They are a bit large for colloidal particles, though the blood plasma is a colloid that can gel under certain circumstances. Like platelets, which are definitely colloidal, they are not living cells like the leucocytes that accompany them.

The separation of colloids and crystalloids is called *dialysis*, and can be carried out with a suitable semipermeable membrane, just as in osmosis. Chemists actually distinguish dialysis, in which the components diffuse at different rates across a membrane, from *ultrafiltration*, in which larger particles are mechanically stopped while smaller ones are allowed to pass. Ultrafiltration can occur through gels, while dialysis uses dialytic membranes. There is no fundamental difference between the processes, however.

Dialysis is carried out in the body by the kidneys, which separate the crystalloids urea, uric acid, hippuric acid and ammonia compounds from the colloidal albumin and other proteins of the blood. The crystalloids diffuse more rapidly across the interface than the larger particles. In the laboratory, we can put the sample to be dialyzed into a container like that used for osmosis, and change the solvent as it becomes concentrated in the crystalloids. Parchment paper can be used

for the dialytic membrane. A bag of parchment paper can be filled with the sample to be dialyzed, and it can be suspended in a bath of moving warm water for rapid dialysis. Membranes can also be prepared from other animal membranes, or collodion (nitrocellulose dissolved in alcohol and ether), or artificial sheet polymers. Electrodialysis can also be used, taking advantage of ion migration in an electric field.

Dialysis has many industrial applications. Sugar is extracted from sugar beets by using the cell walls as dialytic membranes, washing cut beets in warm water. Dialysis is used in the artificial fiber industry to separate alkali from the colloidal fiber material, and in the pharmaceutical industry for the purification of colloidal medicines. Dialysis is used in artificial kidney machines to simulate the action of the kidneys.

Colloids and Adsorbents

As has been pointed out, absorption is a volume effect, while adsorption is a surface effect. Colloids, having large surface areas for a given volume, are excellent at adsorption. A cubic centimeter of charcoal can have a surface area of 1000 m^2 , so a little charcoal can do a lot of adsorbing. Adsorption may be specific. For example, Ni, Pt and Pd in colloidal form adsorb H_2 up to 1000 or 3000 times their volume. Palladium is the best at this. At red heat, palladium metal will absorb hydrogen readily, and release it at even higher temperature. Black palladium powder can be made by reducing PdCl_2 in solution. Because of the adsorption, these metals, in colloidal form, make excellent catalysts for hydrogenation.

Usually, adsorption is not very specific, and a wide variety of substances can be adsorbed on a certain medium. Adsorption is temperature-sensitive, being much more effective at low temperatures, and evolving the adsorbed substances at higher temperatures. Carbon at room temperature does not adsorb oxygen and nitrogen, but does so at liquid-nitrogen temperatures. Adsorption is generally accompanied by a negative change in enthalpy, so it is *exothermic*. The temperature dependence is a consequence of LeChatelier's Principle.

The three most commonly used adsorbents are carbon as charcoal, alumina and silica. When specially prepared as adsorbents, they are called *activated*. Activation is usually a matter mainly of heating, and perhaps some chemical cleaning. A saturated adsorbent may be re-activated by heating, say at 175°C for 6-8 hours in air. Charcoal may be prepared from wood, bone, blood and sugar. The charcoal from different sources has different impurities and therefore somewhat different characteristics. Charcoal is a *nonpolar* adsorbent that is good for organic vapors and nonpolar substances in general. Alumina and Silica are *polar* adsorbents and are best for polar substances, like water.

Charcoal is used in gas masks, since it readily adsorbs toxic organic vapors rather indiscriminately. It does not adsorb carbon monoxide or ammonia well, so special adsorbents for these must be included. Carbon monoxide is usually oxidized to the dioxide, and ammonia by silica gel. Therefore, a complete gas mask canister contains a mechanical filter, charcoal, silica gel, and an oxidant for CO. Charcoal can be used to produce ultra-high vacuum by cooling it to liquid nitrogen temperatures. If charcoal in a stout glass tube in a U-shape is saturated with chlorine or sulphur dioxide, and then sealed off, the gas is liquefied when the charcoal end of the

tube is heated, and the other end is cooled. Natural gas may be filtered through charcoal to remove higher alkanes. Pentane and hexane are more strongly adsorbed than the lighter methane and ethane. Charcoal is, in general, used when organic substances are to be removed from a gas.

Alumina gel and silica gel are produced by drying the gel produced by precipitating the hydroxides in water. Alumina gel is good for water vapor, carbon dioxide and alcohol. It makes an excellent laboratory dessicant. A small amount of colorimetric indicator is added that is blue when the alumina is dry, but turns pink when it has adsorbed water and is alkaline. The dessicant can then be regenerated by heating in an oven. Alumina gel is generally used for drying organic liquids, which it also decolorizes, and for removing acids from oils. It also removes oil vapor from compressed air. Alumina gel is a good example of the nonspecificity of adsorption.

Silica gel is the most generally useful adsorbent. It is especially good at adsorbing benzene, for example from coke-oven gas. Silica gel is used to dry carbon dioxide, hydrogen and oxygen before they are liquefied or solidified. It is often found in small bags in sealed packages that must be protected from humidity. These bags are easily re-activated by heating. Silica gel can be used to dry natural gas for pipeline transport, to prevent the formation of ice clathrates at low temperatures. These clathrates can form above the freezing point and easily clog pipelines.

Other colloidal adsorbents found naturally are *diatomite*, also known as diatomaceous earth or kieselguhr, which is composed of diatom shells made from opaline silica, and *bentonite*, a strongly hydrophilic colloidal clay consisting mainly of montmorillonite. Bentonite can clarify and deodorize petroleum, purify and soften water, make drilling mud, plug leaks as a grout, improve cleaning powders, and destroy building foundations by swelling. Diatomite has perhaps even more uses than bentonite. Both are valuable colloidal minerals.

Adsorbents are important in dyeing fabrics. Often the fabric will not adsorb the dye directly, since the dye may be polar and the fiber nonpolar. However, gels like amphoteric metal hydroxides, especially aluminium hydroxide, may cling to the fibers while strongly adsorbing the dyes. Such intermediates are called *mordants*, which are usually colloids. The dye and the mordant together, without the fiber, is called a *lake* (from the same word that gave "lacquer"). Purple of Cassius is a famous lake, formed on stannic hydroxide gel by colloidal gold.

References

Most textbooks of Elementary Chemistry will include a chapter on colloids that makes a good introduction to the subject.

R. J. Hartman, *Colloid Chemistry* (London: Pitman & Sons, 1949). A classic reference with a great deal of description of colloid phenomena of all types.

Classification[

Because the size of the dispersed phase may be difficult to measure, and because colloids have the appearance of [solutions](#), colloids are sometimes identified and characterized by their physico-chemical and transport properties. For example, if a colloid consists of a solid phase dispersed in a liquid, the solid particles will not [diffuse](#) through a membrane, whereas with a true solution the dissolved ions or molecules will diffuse through a membrane. Because of the size exclusion, the colloidal particles are unable to pass through the pores of an ultrafiltration membrane with a size smaller than their own dimension. The smaller the size of the pore of the ultrafiltration membrane, the lower the concentration of the dispersed colloidal particles remaining in the ultrafiltered liquid. The exact value of the concentration of a truly dissolved species will thus depend on the experimental conditions applied to separate it from the colloidal particles also dispersed in the liquid. This is particularly important for [solubility](#) studies of readily [hydrolysed](#) species such as Al, Eu, Am, Cm, or [organic matter complexing](#) these species. Colloids can be classified as follows:

Medium / Phases		Dispersed phase		
		Gas	Liquid	Solid
Dispersion medium	Gas	NONE (All gases are mutually miscible)	Liquid aerosol Examples: fog , hair sprays	Solid aerosol Examples: smoke , ice cloud , air particulates
	Liquid	Foam Example: whipped cream , shaving cream	Emulsion Examples: milk , mayonnaise , hand cream	Sol Examples: pigmented ink , blood
	Solid	Solid foam Examples: aerogel , styrofoam , pumice	Gel Examples: agar , gelatin , jelly	Solid sol Example: cranberry glass

Based on the nature of interaction between the dispersed phase and the dispersion medium, colloids can be classified as: Hydrophilic colloids: These are water-loving colloids. The colloid particles are attracted toward water. They are also called reversible sols. Hydrophobic colloids: These are opposite in nature to hydrophilic colloids. The colloid particles are repelled by water. They are also called irreversible sols.

In some cases, a colloid can be considered a homogeneous mixture. This is because the distinction between "dissolved" and "particulate" matter can be sometimes a matter of approach, which affects whether or not it is homogeneous or heterogeneous.

Hydrocolloids

A **hydrocolloid** is defined as a colloid system wherein the colloid particles are hydrophilic polymers dispersed in [water](#). A hydrocolloid has colloid particles spread throughout water, and depending on the quantity of water available that can take place in different states, e.g., [gel](#) or [sol](#)

(liquid). Hydrocolloids can be either [irreversible](#) (single-state) or [reversible](#). For example, [agar](#), a reversible hydrocolloid of [seaweed](#) extract, can exist in a gel and solid state, and alternate between states with the addition or elimination of heat.

Many hydrocolloids are derived from natural sources. For example, [agar-agar](#) and [carrageenan](#) are extracted from seaweed, [gelatin](#) is produced by hydrolysis of proteins of [bovine](#) and fish origins, and [pectin](#) is extracted from [citrus](#) peel and apple [pomace](#).

[Gelatin desserts](#) like jelly or [Jell-O](#) are made from gelatin powder, another effective hydrocolloid. Hydrocolloids are employed in food mainly to influence [texture](#) or [viscosity](#) (e.g., a sauce). [Hydrocolloid-based medical dressings](#) are used for [skin](#) and [wound](#) treatment.

Other main hydrocolloids are [xanthan gum](#), [gum arabic](#), [guar gum](#), [locust bean gum](#), cellulose derivatives as [carboxymethyl cellulose](#), [alginate](#) and [starch](#).

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Interaction between particles

The following forces play an important role in the interaction of colloid particles:

- [Excluded volume repulsion](#): This refers to the impossibility of any overlap between hard particles.
- [Electrostatic interaction](#): Colloidal particles often carry an electrical charge and therefore attract or repel each other. The charge of both the continuous and the dispersed phase, as well as the mobility of the phases are factors affecting this interaction.
- [van der Waals forces](#): This is due to interaction between two dipoles that are either permanent or induced. Even if the particles do not have a permanent dipole, fluctuations of the electron density gives rise to a temporary dipole in a particle. This temporary dipole induces a dipole in particles nearby. The temporary dipole and the induced dipoles are then attracted to each other. This is known as van der Waals force, and is always present (unless the refractive indexes of the dispersed and continuous phases are matched), is short-range, and is attractive.
- [Entropic forces](#): According to the second law of thermodynamics, a system progresses to a state in which entropy is maximized. This can result in effective forces even between hard spheres.
- [Steric forces](#) between polymer-covered surfaces or in solutions containing non-adsorbing polymer can modulate interparticle forces, producing an additional steric repulsive force (which is predominantly entropic in origin) or an attractive [depletion force](#) between them. Such an effect is specifically searched for with tailor-made [superplasticizers](#) developed to increase the workability of concrete and to reduce its [water content](#).

Preparation

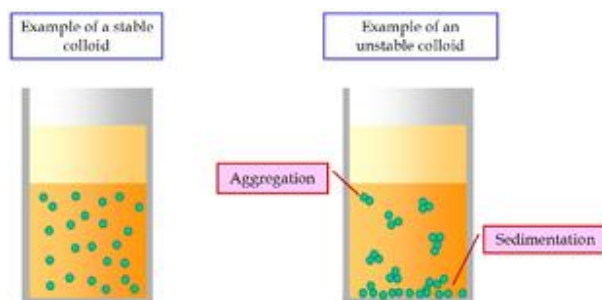
There are two principal ways of preparation of colloids:^[6]

- Dispersion of large particles or droplets to the colloidal dimensions by milling, [spraying](#), or application of shear (e.g., shaking, mixing, or [high shear mixing](#)).
- Condensation of small dissolved molecules into larger colloidal particles by precipitation, condensation, or redox reactions. Such processes are used in the preparation of colloidal [silica](#) or [gold](#).

Stabilization (peptization)[

The stability of a colloidal system is the capability of the system to remain as it is.

Stability is hindered by aggregation and sedimentation phenomena, which are driven by the colloids tendency to reduce surface energy. Reducing the interfacial tension will stabilize the colloidal system by reducing this driving force.



Examples of a stable and of an unstable colloidal dispersion.

Aggregation is due to the sum of the interaction forces between particles.^{[7][8]} If attractive forces (such as van der Waals forces) prevail over the repulsive ones (such as the electrostatic ones) particles aggregate in clusters.

Electrostatic stabilization and steric stabilization are the two main mechanisms for stabilization against aggregation.

- **Electrostatic stabilization** is based on the mutual repulsion of like electrical charges. In general, different phases have different charge affinities, so that an electrical double layer forms at any interface. Small particle sizes lead to enormous surface areas, and this effect is greatly amplified in colloids. In a stable colloid, mass of a dispersed phase is so low that its buoyancy or kinetic energy is too weak to overcome the electrostatic repulsion between charged layers of the dispersing phase.
- **Steric stabilization** consists in covering the particles in polymers which prevents the particle to get close in the range of attractive forces.

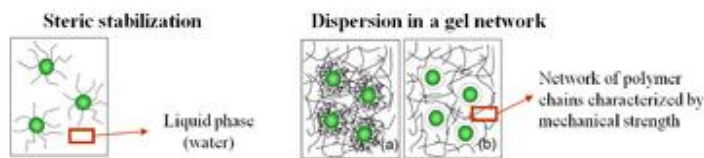
A combination of the two mechanisms is also possible (electrosteric stabilization). All the above mentioned mechanisms for minimizing [particle aggregation](#) rely on the enhancement of the repulsive interaction forces.

Electrostatic and steric stabilization do not directly address the sedimentation/floating problem.

Particle sedimentation (and also floating, although this phenomenon is less common) arises from a difference in the density of the dispersed and of the continuous phase. The higher the difference in densities, the faster the particle settling.

- The **gel network stabilization** represents the principal way to produce colloids stable to both aggregation and sedimentation.^{[9][10]}

The method consists in adding to the colloidal suspension a polymer able to form a gel network and characterized by shear thinning properties. Examples of such substances are xanthan and guar gum.



Steric and Gel network stabilization.

Particle settling is hindered by the stiffness of the polymeric matrix where particles are trapped.^[9] In addition, the long polymeric chains can provide a steric or electrosteric stabilization to dispersed particles.

The rheological shear thinning properties find beneficial in the preparation of the suspensions and in their use, as the reduced viscosity at high shear rates facilitates deagglomeration, mixing and in general the flow of the suspensions.

Destabilization (flocculation)

Unstable colloidal dispersions can form [flocs](#) as the particles aggregate due to interparticle attractions. In this way photonic glasses can be grown. This can be accomplished by a number of different methods:

- Removal of the electrostatic barrier that prevents aggregation of the particles. This can be accomplished by the addition of salt to a suspension or changing the pH of a suspension to effectively neutralize or "screen" the surface charge of the particles in suspension. This removes the repulsive forces that keep colloidal particles separate and allows for coagulation due to van der Waals forces.
- Addition of a charged polymer flocculant. Polymer flocculants can bridge individual colloidal particles by attractive electrostatic interactions. For example, negatively-

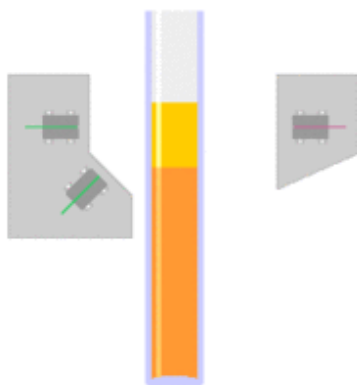
charged colloidal silica or clay particles can be flocculated by the addition of a positively-charged polymer.

- Addition of non-adsorbed polymers called depletants that cause aggregation due to entropic effects.
- Physical deformation of the particle (e.g., stretching) may increase the van der Waals forces more than stabilization forces (such as electrostatic), resulting coagulation of colloids at certain orientations.

Unstable colloidal suspensions of low-volume fraction form clustered liquid suspensions, wherein individual clusters of particles fall to the bottom of the suspension (or float to the top if the particles are less dense than the suspending medium) once the clusters are of sufficient size for the [Brownian forces](#) that work to keep the particles in suspension to be overcome by gravitational forces. However, colloidal suspensions of higher-volume fraction form colloidal gels with viscoelastic properties. Viscoelastic colloidal gels, such as [bentonite](#) and [toothpaste](#), flow like liquids under shear, but maintain their shape when shear is removed. It is for this reason that toothpaste can be squeezed from a toothpaste tube, but stays on the toothbrush after it is applied.

Monitoring stability[

1/ Positionning
Positionnement



Measurement principle of multiple light scattering coupled with vertical scanning

Multiple light scattering coupled with vertical scanning is the most widely used technique to monitor the dispersion state of a product, hence identifying and quantifying destabilisation phenomena.^{[11][12][13][14]} It works on concentrated dispersions without dilution. When light is sent through the sample, it is backscattered by the particles / droplets. The backscattering intensity is directly proportional to the size and volume fraction of the dispersed phase. Therefore, local changes in concentration (e.g. [Creaming](#) and [Sedimentation](#)) and global changes in size (e.g. [flocculation](#), [coalescence](#)) are detected and monitored.

Accelerating methods for shelf life prediction

The kinetic process of destabilisation can be rather long (up to several months or even years for some products) and it is often required for the formulator to use further accelerating methods in order to reach reasonable development time for new product design. Thermal methods are the most commonly used and consists in increasing temperature to accelerate destabilisation (below critical temperatures of phase inversion or chemical degradation). Temperature affects not only the viscosity, but also interfacial tension in the case of non-ionic surfactants or more generally interactions forces inside the system. Storing a dispersion at high temperatures enables to simulate real life conditions for a product (e.g. tube of sunscreen cream in a car in the summer), but also to accelerate destabilisation processes up to 200 times. Mechanical acceleration including vibration, [centrifugation](#) and agitation are sometimes used. They subject the product to different forces that pushes the particles / droplets against one another, hence helping in the film drainage. However, some emulsions would never coalesce in normal gravity, while they do under artificial gravity.^[15] Moreover segregation of different populations of particles have been highlighted when using centrifugation and vibration.^[16]

As a model system for atoms]

In [physics](#), colloids are an interesting model system for [atoms](#). Micrometre-scale colloidal particles are large enough to be observed by optical techniques such as [confocal microscopy](#). Many of the forces that govern the structure and behavior of matter, such as excluded volume interactions or electrostatic forces, govern the structure and behavior of colloidal suspensions. For example, the same techniques used to model ideal gases can be applied to [model](#) the behavior of a hard sphere colloidal suspension. In addition, phase transitions in colloidal suspensions can be studied in real time using optical techniques, and are analogous to phase transitions in liquids.

Crystals]

Main article: [Colloidal crystal](#)

A colloidal crystal is a highly [ordered](#) array of particles that can be formed over a very long range (typically on the order of a few millimeters to one centimeter) and that appear [analogous](#) to their atomic or molecular counterparts.^[17] One of the finest [natural](#) examples of this ordering phenomenon can be found in precious [opal](#), in which brilliant regions of pure [spectral color](#) result from [close-packed](#) domains of [amorphous](#) colloidal spheres of [silicon dioxide](#) (or [silica](#), SiO₂).^{[18][19]} These spherical particles [precipitate](#) in highly [siliceous](#) pools in [Australia](#) and elsewhere, and form these highly ordered arrays after years of [sedimentation](#) and [compression](#) under [hydrostatic](#) and gravitational forces. The periodic arrays of submicrometre spherical particles provide similar arrays of [interstitial voids](#), which act as a natural [diffraction grating](#) for [visible light waves](#), particularly when the interstitial spacing is of the same [order of magnitude](#) as the [incident](#) lightwave.^{[20][21]}

Thus, it has been known for many years that, due to [repulsive Coulombic](#) interactions, [electrically charged macromolecules](#) in an [aqueous](#) environment can exhibit long-range [crystal](#)-like correlations with interparticle separation distances, often being considerably greater than the individual particle diameter. In all of these cases in nature, the same brilliant [iridescence](#) (or play of colors) can be attributed to the diffraction and [constructive interference](#) of visible lightwaves that satisfy [Bragg's law](#), in a matter analogous to the [scattering](#) of [X-rays](#) in crystalline solids.

The large number of experiments exploring the [physics](#) and [chemistry](#) of these so-called "colloidal crystals" has emerged as a result of the relatively simple methods that have evolved in the last 20 years for preparing synthetic monodisperse colloids (both polymer and mineral) and, through various mechanisms, implementing and preserving their long-range order formation.

In biology]

In the early 20th century, before [enzymology](#) was well understood, colloids were thought to be the key to the operation of [enzymes](#); i.e., the addition of small quantities of an enzyme to a quantity of water would, in some fashion yet to be specified, subtly alter the properties of the water so that it would break down the enzyme's specific [substrate](#), ^[citation needed] such as a solution of [ATPase](#) breaking down [ATP](#). Furthermore, [life](#) itself was explainable in terms of the aggregate properties of all the colloidal substances that make up an [organism](#). As more detailed knowledge of [biology](#) and [biochemistry](#) developed, the colloidal theory was replaced by the [macromolecular](#) theory, which explains an enzyme as a collection of identical huge [molecules](#) that act as very tiny [machines](#), freely moving about between the water molecules of the solution and individually operating on the substrate, no more mysterious than a [factory](#) full of machinery. The properties of the water in the solution are not altered, other than the simple [osmotic](#) changes that would be caused by the presence of any [solute](#). In humans, both the [thyroid gland](#) and the [intermediate lobe](#) (*pars intermedia*) of the [pituitary gland](#) contain colloid follicles.

In the environment]

Colloidal particles can also serve as transport vector^[22] of diverse contaminants in the surface water (sea water, lakes, rivers, fresh water bodies) and in underground water circulating in fissured rocks^[23] ([limestone](#), [sandstone](#), [granite](#), ...). Radionuclides and heavy metals easily [sorb](#) onto colloids suspended in water. Various types of colloids are recognised: inorganic colloids ([clay](#) particles, silicates, [iron oxy-hydroxides](#), ...), organic colloids ([humic](#) and [fulvic](#) substances). When heavy metals or radionuclides form their own pure colloids, the term "[Eigencolloid](#)" is used to designate pure phases, e.g., $\text{Tc}(\text{OH})_4$, $\text{U}(\text{OH})_4$, $\text{Am}(\text{OH})_3$. Colloids have been suspected for the long-range transport of plutonium on the [Nevada Nuclear Test Site](#). They have been the subject of detailed studies for many years. However, the mobility of inorganic colloids is very low in compacted [bentonites](#) and in deep clay formations^[24] because of the process of [ultrafiltration](#) occurring in dense clay membrane.^[25] The question is less clear for small organic colloids often mixed in porewater with truly dissolved organic molecules.^[26]

In intravenous therapy]

Colloid solutions used in [intravenous therapy](#) belong to a major group of [volume expanders](#), and can be used for intravenous [fluid replacement](#). Colloids preserve a high [colloid osmotic pressure](#) in the blood,^[27] and therefore, they should theoretically preferentially increase the [intravascular volume](#), whereas other types of volume expanders called [crystalloids](#) also increase the [interstitial volume](#) and [intracellular volume](#). However, there is still controversy to the actual difference in efficacy by this difference.^[27] Another difference is that crystalloids generally are much cheaper than colloids.^[27] Recently, however, it has been determined that the use of colloids was bolstered by faked research studies.^[28]^[clarification needed]

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Further reading]

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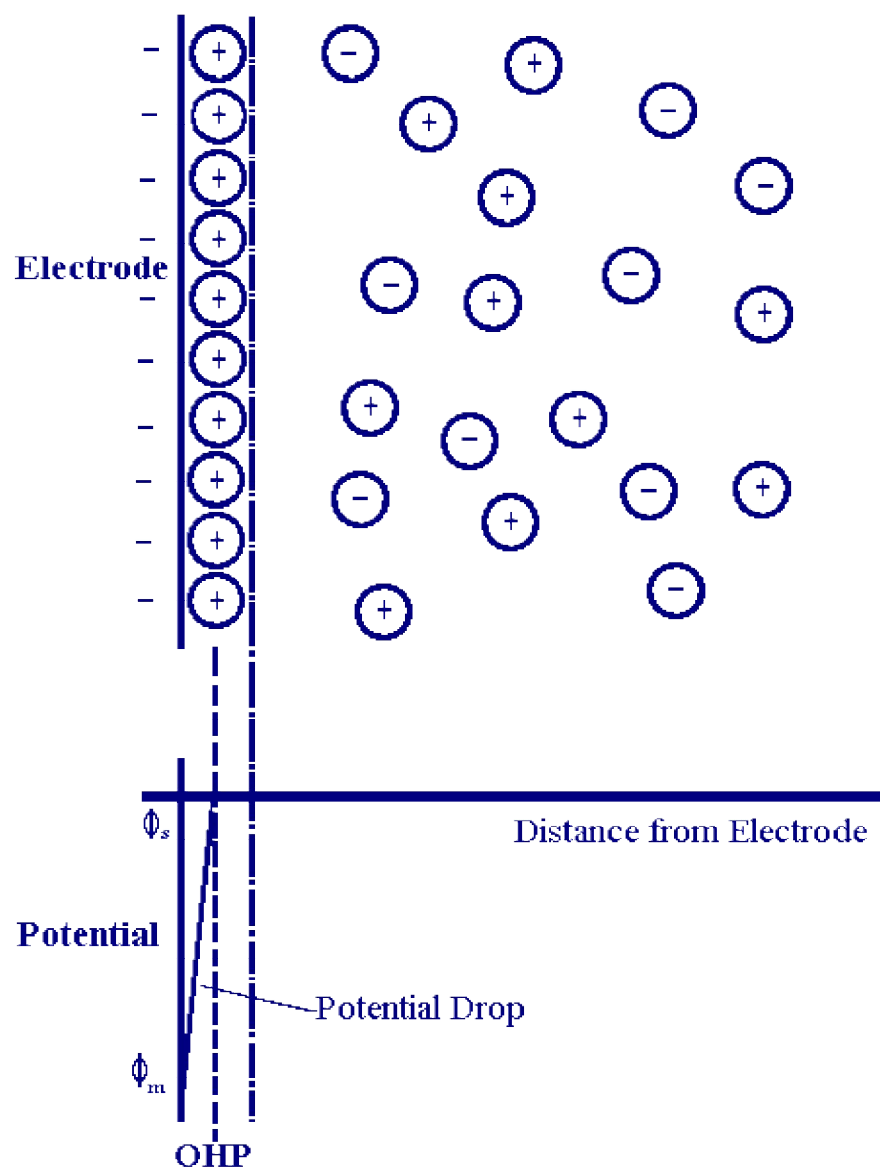
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The Electrical Double Layer

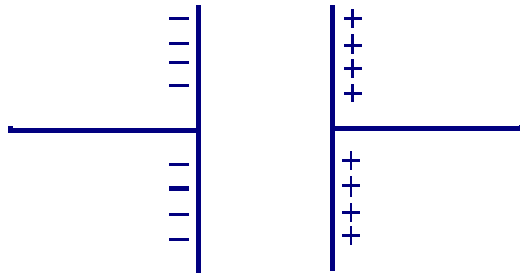
In the discussion of electron transfer reactions so far there has been no mention of the nature of the electrode/electrolyte interface. It is clear that any interface will disrupt the electrolyte solution since the interactions between the solid and the electrolyte will be considerably different to those in solution. For electrodes which are under potentiostatic control there will also be the additional influence of the charge held at the electrode. These different factors result in strong interactions occurring between the ions/molecules in solution and the electrode surface. This gives rise to a region called the electrical double layer. Many models have been put forward to explain the behaviour observed when electrochemical measurements are performed in electrolyte solutions. Below we introduce two of the models which have been used to explain the effects occurring in this region.

The Electrical Double Layer

The model which gave rise to the term 'electrical double layer' was first put forward in the 1850's by Helmholtz. In this model he assumed that no electron transfer reactions occur at the electrode and the solution is composed only of electrolyte. The interactions between the ions in solution and the electrode surface were assumed to be electrostatic in nature and resulted from the fact that the electrode holds a charge density (q^m) which arises from either an excess or deficiency of electrons at the electrode surface. In order for the interface to remain neutral the charge held on the electrode is balanced by the redistribution of ions close to the electrode surface. Helmholtz's view of this region is shown in the figure below

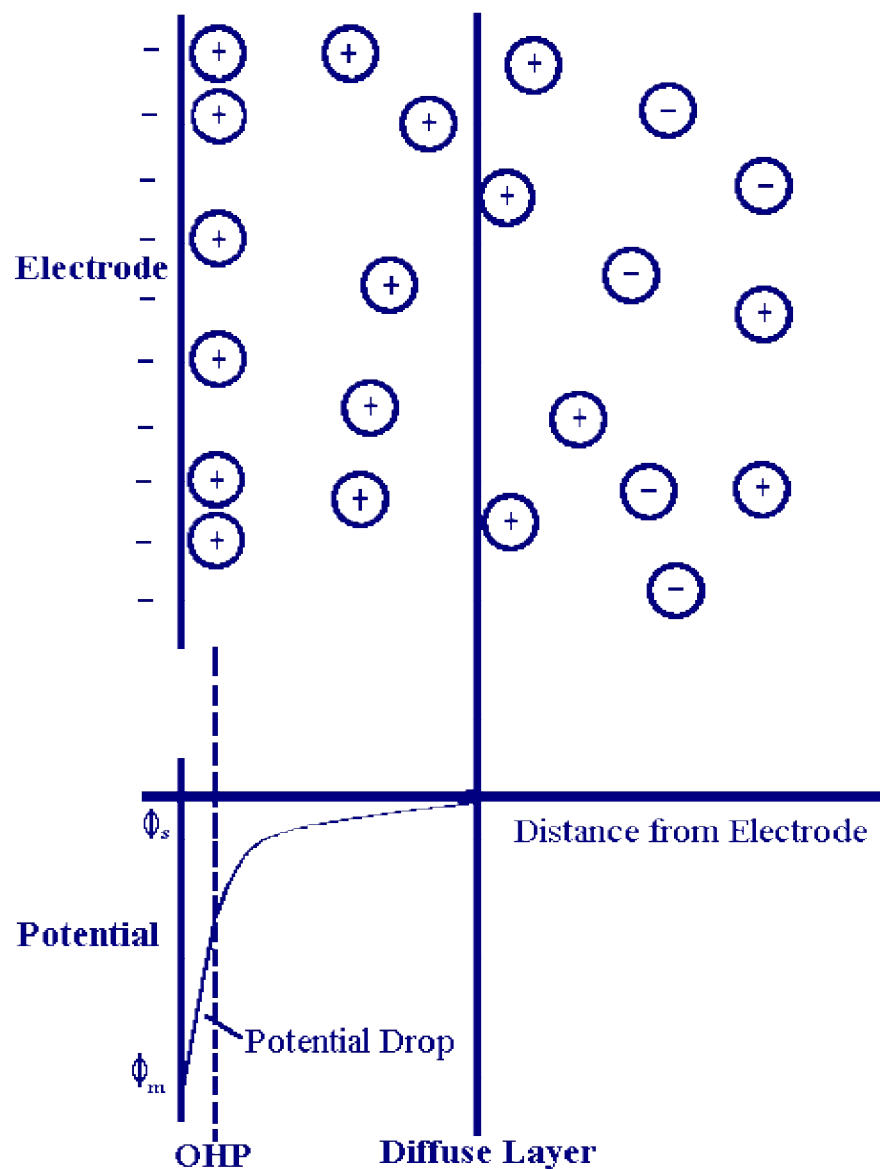


The attracted ions are assumed to approach the electrode surface and form a layer balancing the electrode charge, the distance of approach is assumed to be limited to the radius of the ion and a single sphere of solvation round each ion. The overall result is two layers of charge (the double layer) and a potential drop which is confined to only this region (termed the outer Helmholtz Plane, OHP) in solution. The result is absolutely analogous to an electrical capacitor which has two plates of charge separated by some distance (d)



with the potential drop occurring in a linear manner between the two plates. It is perhaps no surprise that when impedance analysis is performed on electrochemical systems the response due to the electrolyte redistribution is modelled in terms of capacitative elements.

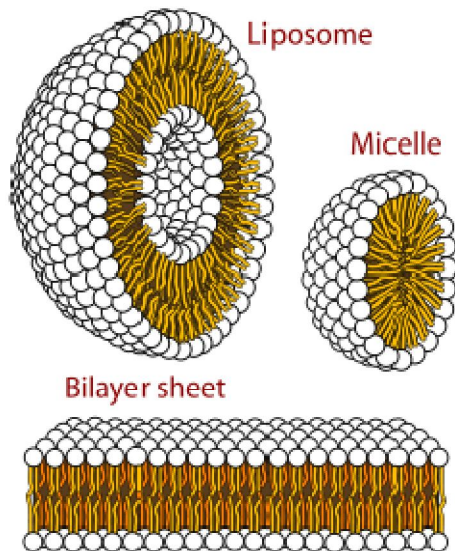
The model of Helmholtz while providing a basis for rationalising the behaviour of this region does not account for many factors such as, diffusion/mixing in solution, the possibility of absorption on to the surface and the interaction between solvent dipole moments and the electrode. A later model put forward by Stern begins to address some of these limitations



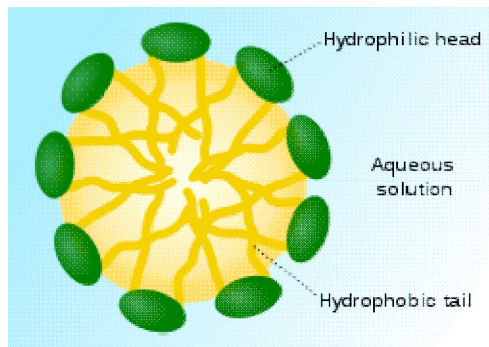
now the ions are assumed to be able to move in solution and so the electrostatic interactions are in competition with Brownian motion. The result is still a region close to the electrode surface (100×10^{-10} m) containing an excess of one type of ion but now the potential drop occurs over the region called the diffuse layer.

Many modifications and improvements have been made to these early models with the latest approaches using numerical modelling to follow the redistribution effects as the electrode potential is varied.

Micelle



Cross section view of the structures that can be formed by phospholipids in aqueous solutions (Note that, unlike this illustration micelles are usually formed by single chain lipids since it is tough to fit two chains into this shape)



Scheme of a micelle formed by [phospholipids](#) in an [aqueous](#) solution

IUPAC definition

Micelle: Particle of colloidal dimensions that exists in equilibrium with the molecules or ions in solution from which it is formed.

Note: Based on definition in ref. [\[1\]](#)

[\[2\]](#)

Micelle (polymers): Organized auto-assembly formed in a liquid and composed of amphiphilic *macromolecules*, generally amphiphilic di- or tri-block copolymers made of solvophilic and solvophobic blocks.

Note 1: An amphiphilic behavior can be observed for water and an organic solvent or between two organic solvents.

Note 2: Polymeric micelles have a much lower critical micellar concentration (CMC) than soap or surfactant micelles, but are nevertheless at equilibrium with isolated macromolecules called unimers. Therefore, micelle formation and stability are concentration-dependent.^{[\[3\]](#)}

A **micelle** (pronounced /mar'sel/ or /mar'si:l/, plural **micelles**, **micella**, or **micellae**) is an aggregate of [surfactant](#) molecules dispersed in a liquid [colloid](#). A typical micelle in [aqueous solution](#) forms an aggregate with the [hydrophilic](#) "head" regions in contact with surrounding [solvent](#), sequestering the [hydrophobic](#) single-tail regions in the micelle centre. This phase is caused by the [packing behavior](#) of single-tailed [lipids](#) in a [bilayer](#). The difficulty filling all the volume of the interior of a bilayer, while accommodating the area per head group forced on the molecule by the hydration of the lipid head group, leads to the formation of the micelle. This type of micelle is known as a normal phase micelle (oil-in-water micelle). Inverse micelles have the head groups at the centre with the tails extending out (water-in-oil micelle). Micelles are approximately spherical in shape. Other [phases](#), including shapes such as ellipsoids, cylinders, and [bilayers](#), are also possible. The shape and size of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, [temperature](#), [pH](#), and [ionic strength](#). The process of forming micelles is known as micellisation and forms part of the [Phase behaviour](#) of many lipids according to their [polymorphism](#).

History

The ability of a soapy solution to act as a [detergent](#) has been recognized for centuries. However, it was only at the beginning of the twentieth century that the constitution of such solutions was scientifically studied. Pioneering work in this area was carried out by [James William McBain](#) at the [University of Bristol](#). As early as 1913, he postulated the existence of "colloidal ions" to explain the good electrolytic conductivity of [sodium palmitate](#) solutions.^{[\[4\]](#)} These highly mobile, spontaneously formed clusters came to be called micelles, a term borrowed from biology and popularized by G.S. Hartley in his classic book *Paraffin Chain Salts: A Study in Micelle Formation*.^{[\[5\]](#)}

Solvation[

Individual surfactant molecules that are in the system but are not part of a micelle are called "monomers". Lipid micelles represent a molecular assembly, in which the individual components are thermodynamically in equilibrium with monomers of the same species in the surrounding medium.

In water, the hydrophilic "heads" of surfactant molecules are always in contact with the solvent, regardless of whether the surfactants exist as monomers or as part of a micelle. However, the lipophilic "tails" of surfactant molecules have less contact with water when they are part of a micelle—this being the basis for the energetic drive for micelle formation. In a micelle, the hydrophobic tails of several surfactant molecules assemble into an oil-like core the most stable form of which has no contact with water. By contrast, surfactant monomers are surrounded by water molecules that create a "cage" of molecules connected by [hydrogen bonds](#). This water cage is similar to a [clathrate](#) and has an [ice](#)-like [crystal](#) structure and can be characterized according to the hydrophobic effect. The extent of lipid solubility is determined by the unfavorable entropy contribution due to the ordering of the water structure according to the hydrophobic effect.

Micelles composed of ionic surfactants have an electrostatic attraction to the ions that surround them in solution, the latter known as [counterions](#). Although the closest counterions partially mask a charged micelle (by up to 90%), the effects of micelle charge affect the structure of the surrounding solvent at appreciable distances from the micelle. Ionic micelles influence many properties of the mixture, including its electrical conductivity. Adding salts to a colloid containing micelles can decrease the strength of electrostatic interactions and lead to the formation of larger ionic micelles.^[6] This is more accurately seen from the point of view of an effective charge in hydration of the system.

Energy of formation

Micelles only form when the concentration of surfactant is greater than the [critical micelle concentration](#) (CMC), and the temperature of the system is greater than the critical micelle temperature, or [Krafft temperature](#). The formation of micelles can be understood using [thermodynamics](#): micelles can form [spontaneously](#) because of a balance between [entropy](#) and [enthalpy](#). In water, the [hydrophobic effect](#) is the driving force for micelle formation, despite the fact that assembling surfactant molecules together reduces their entropy. At very low concentrations of the lipid, only monomers are present in true solution. As the concentration of the lipid is increased, a point is reached at which the unfavorable entropy considerations, derived from the hydrophobic end of the molecule, become dominant. At this point, the lipid hydrocarbon chains of a portion of the lipids must be sequestered away from the water. Therefore, the lipid starts to form micelles. Broadly speaking, above the CMC, the entropic penalty of assembling the surfactant molecules is less than the entropic penalty of caging the surfactant monomers with water molecules. Also important are enthalpic considerations, such as the electrostatic interactions that occur between the charged parts of surfactants.

Micelle Packing Parameter

The micelle packing parameter equation is utilized to help "predict molecular self-assembly in surfactant solutions".^[7]

$$\frac{v_o}{a_E \cdot l_o}$$

Where, v_o is the surfactant tail volume, l_o is the tail length and a_E is the equilibrium area per molecule at the aggregate surface.

Inverse/reverse micelles

In a [non-polar](#) solvent, it is the exposure of the hydrophilic head groups to the surrounding solvent that is energetically unfavourable, giving rise to a water-in-oil system. In this case the hydrophilic groups are sequestered in the micelle core and the hydrophobic groups extend away from the centre. These inverse micelles are proportionally less likely to form on increasing headgroup charge, since hydrophilic sequestration would create highly unfavorable electrostatic interactions.

Uses

When surfactants are present above the CMC ([Critical micelle concentration](#)), they can act as [emulsifiers](#) that will allow a compound that is normally insoluble (in the solvent being used) to dissolve. This occurs because the insoluble species can be incorporated into the micelle core, which is itself solubilized in the bulk solvent by virtue of the head groups' favorable interactions with solvent species. The most common example of this phenomenon is [detergents](#), which clean poorly soluble lipophilic material (such as oils and waxes) that cannot be removed by water alone. Detergents also clean by lowering the [surface tension](#) of water, making it easier to remove material from a surface. The emulsifying property of surfactants is also the basis for [emulsion polymerization](#).

Micelle formation is essential for the absorption of fat-soluble vitamins and complicated lipids within the human body. [Bile salts](#) formed in the liver and secreted by the gall bladder allow micelles of fatty acids to form. This allows the absorption of complicated lipids (e.g., lecithin) and lipid soluble vitamins (A, D, E and K) within the micelle by the small intestine.

Micelles are used for [targeted drug delivery](#).

Notes[

[^] Alan D. MacNaught, Andrew R. Wilkinson (ed.). *Compendium of Chemical Terminology: IUPAC Recommendations* (2nd ed.). Oxford: Blackwell Science. [ISBN 0865426848](#).

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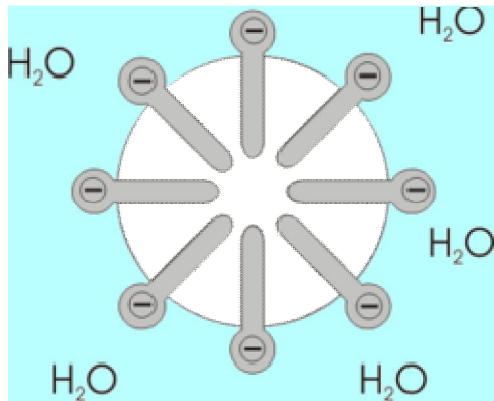
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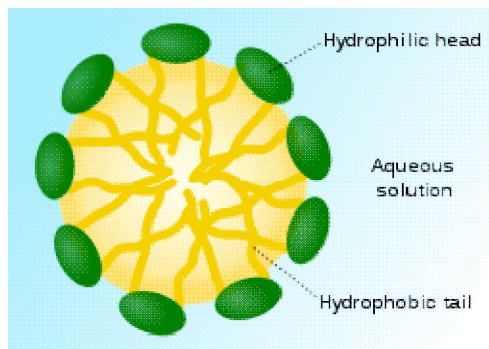
Structural Biochemistry/Lipids/Micelles

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Structure



An example of micelles in polar solvent (Water, in this case)



Some micelles have two hydrocarbon chains

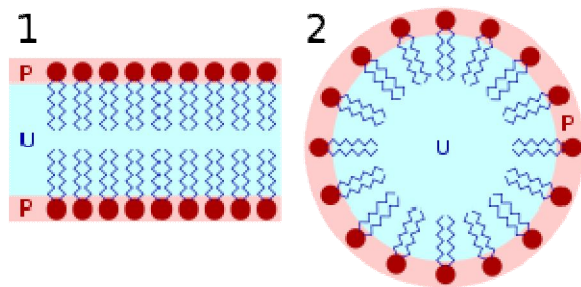
Micelles are lipid molecules that arrange themselves in a spherical form in aqueous solutions. The formation of a micelle is a response to the amphipathic nature of fatty acids, meaning that they contain both hydrophilic regions (polar head groups) as well as hydrophobic regions (the long hydrophobic chain). Micelles contain polar head groups that usually form the outside as the surface of micelles. They face to the water because they are polar. The hydrophobic tails are inside and away from the water since they are nonpolar. Fatty acids from micelles usually have a single hydrocarbon chain as opposed to two hydrocarbon tails. This allows them to conform into a spherical shape for lesser steric hindrance within a fatty acid. Fatty acids from Glycolipids and phospholipids, on the other hand, have two hydrophobic chains that are too bulky to fit into the a spherical shape as micelles do. Thus, they preferred to form glycolipids and phospholipids as "lipid bilayers", which are discussed in the next section.

Micelles form spontaneously in water, as stated above this spontaneous arrangement is due to the amphipathic nature of the molecule. The driving force for this arrangement is the hydrophobic interactions the molecules experience. When the hydrophobic tails are not sequestered from water this results in in the water forming an organized cage around the hydrophobic tail and this

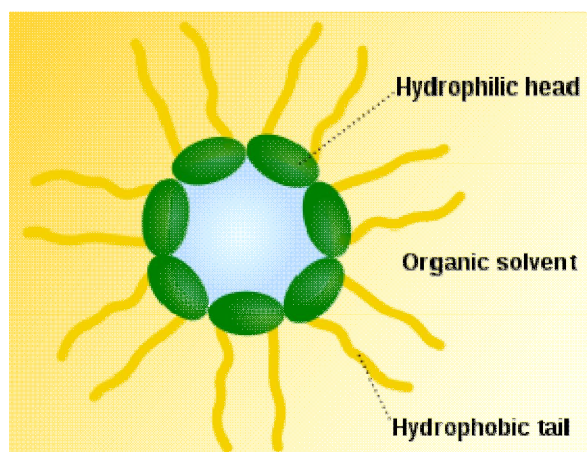
entropy is unfavorable. However, when the lipids form micelles the hydrophobic tails interact with each other, and this interaction releases water from the hydrophobic tail and this increases the disorder of the system, and this increase in entropy is favorable.

Bilayer sheet

The preferred structure of lipids in aqueous solutions are usually a bilayer sheet of lipids rather than spherical micelles. This is because the two fatty acid chains are too big and bulky to fit into the interior of a micelle. Therefore, micelles usually have one hydrocarbon chain instead of two. Lipid bilayers form rapidly and spontaneously in an aqueous media and are stabilized by hydrophobic interactions, Van der Waals attractive forces, electrostatic interactions and hydrogen-bonding. The function of the lipid bilayer is to form a barrier between the two sides of the membrane. Due to the fact that the lipid bilayer consists of hydrophobic fatty acid chains, ions and most polar molecules have trouble passing through the bilayer. The one exception to this rule is water because water has a high concentration, small size, and a lack of a complete charge. In order for a molecule to pass through the lipid bilayer it must move from an aqueous environment to a hydrophobic environment and then back into an aqueous environment. Therefore the permeability of small molecules is related to the solubility of said molecule in a nonpolar solvent versus the solubility of the molecule in water.



Micelles can also have a structure that is inside out of its normal structure. Instead of having the hydrocarbon chains inside, they can face outside and while the polar heads are arranged inside the sphere. This happens in a "water in oil" situation because there is so much oil surrounding the drop of water that the hydrocarbon chains face outside instead of inside.



Size

Sizes of micelles range from 2 nm (20 Å) to 20 nm (200 Å), depending on composition and concentration. The size of a micelle is more limited than that of a lipid bilayer. A lipid bilayer can span up to 10^7 Å or 10^6 nm.

The lipid bilayer is not a rigid structures, rather they are quite fluid. The individual lipid molecules are able to move or diffuse laterally across the membrane quite easily, this process is called lateral diffusion. However, lipids have much more trouble flipping from one side of the membrane to the other, this process is called traverse diffusion or flip, because this would involve the polar head traveling through the hydrophobic core, and this interaction between polar and hydrophobic regions is unfavorable. So the lipid can move around laterally at a rate of about 2 micrometers per second, while it takes a much longer amount of time to flip flop.

the fluidity of a lipid bilayer also depends on both the temperature and the hydrocarbon chain. As the temperature is increased the fluidity of the lipid bilayer increases as well. Also the more cis double bonds the hydrocarbon tail has the more fluid the structure becomes. This is because when the hydrocarbon tail has cis double bonds it can no longer pack as well as the saturated hydrocarbon tail, so it becomes more fluid. Also the longer the hydrocarbon tail, the higher the transition temperature, which is the temperature at which the bilayer goes from rigid to fluid, this is because longer hydrocarbon tails can interact more strongly than shorter chains.

Formation

Micelles form when the polar head and the non polar tails arrange in a special way. They are usually driven to arrange either with the polar heads out (oil in water) or with the polar head in (water in oil). Micelles only form when the concentration of surfactant is greater than the critical micelle concentration (CMC). The surfactant is any surface active material that can part the surface upon entering. The CMC is the concentration above surfactant when micelles will form spontaneously. The higher the concentration, the more micelles there are. Micelle formation also depend on the Krafft temperature. This temperature is when surfactants will form micelles. If the temperature if below the Krafft temperature, then there is no spontaneous formation of micelles.

As the temperature increases, the surfactant will turn into a soluble form and be able to form micelles from a crystalline state. The hydrophobic effect is also a driving force that needs to be taken into account. This effect is characterized by the fact that like to form intermolecular aggregates in aqueous substances and in intramolecular molecules. Micelle formation can be summed up by thermodynamics, driven by entropy and enthalpy.

Function and Usage[

Micelles usually form in soap molecules. Soap often form as micelles because they contain only one hydrocarbon chain instead of two. Therefore they make up the soap property. Micelles act as emulsifiers that allows a compound that is usually insoluble in water to dissolve. Detergents and soap work by insert the long hydrophobic tails from soap into the insoluble dirt (such as oil) while the hydrophilic head face outside and surround the nonpolar dirt. Then, this micelle can be washed away since the outside of the micelle is soluble with the solvent, which is usually polar. This is the reason why soap helps clean oily and waxy substances off from dishes since water alone cannot pull the oil off.



Micelles are also at work in the human body. Micelles help the body absorb lipid and fat soluble vitamins. They help the small intestine to absorb essential lipids and vitamins from the liver and gall bladder. They also carry complex lipids such as lecithin and lipid soluble vitamins (A, D, E and K) to the small intestine. Without micelles, these vitamins will not be able to be absorbed into the body which will lead to serious complications. Micelles also help clean the skin. Many facial washes use micelles to perform this task. They clean the skin by removing oil and other substances without the need of being washed afterward.

Reference[[edit](#)]

Biochemistry, Berg

1. [↑ The Journal of Biological Chemistry, Detergents as Tools in Membrane Biochemistry, November 21, 2012](#)

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["http://en.wikibooks.org/w/index.php?title=Structural Biochemistry/Lipids/Micelles&oldid=2545529"](http://en.wikibooks.org/w/index.php?title=Structural_Biochemistry/Lipids/Micelles&oldid=2545529)

Category:

dialysis

Process of removing blood from a patient with **KIDNEY FAILURE**, purifying it with a hemodialyzer (artificial kidney), and returning it to the bloodstream. Many substances (including **UREA** and inorganic **SALTS**) in the blood pass through a porous membrane in the machine into a sterile solution; particles such as blood cells and **PROTEINS** are too large to pass. This process controls the acid-base balance of the blood and its content of water and dissolved materials

Ultrafiltration

Ultrafiltration (UF) is a variety of [membrane filtration](#) in which [hydrostatic pressure](#) forces a liquid against a [semipermeable membrane](#). [Suspended solids](#) and [solutes](#) of high [molecular weight](#) are retained, while water and low molecular weight solutes pass through the membrane. This [separation process](#) is used in industry and research for purifying and concentrating macromolecular (10^3 - 10^6 [Da](#)) solutions, especially [protein](#) solutions. Ultrafiltration is not fundamentally different from [microfiltration](#), [nanofiltration](#) or [gas separation](#), except in terms of the size of the molecules it retains. Ultrafiltration is applied in cross-flow or dead-end mode and separation in ultrafiltration undergoes [concentration polarization](#).

Process]

Ultrafiltration systems eliminate the need for clarifiers and multimedia filters for waste streams to meet critical discharge criteria or to be further processed by wastewater recovery systems for water recovery. Efficient ultrafiltration systems utilize membranes which can be submerged, back-flushable, air scoured, spiral wound UF/MF membrane that offers superior performance for the clarification of wastewater and process water.

Membrane geometries

Spiral wound module:

Consists of large consecutive layers of membrane and support material rolled up around a tube. Maximizes surface area.

Less expensive, however, more sensitive to pollution.

Tubular membrane:

The feed solution flows through the membrane core and the permeate is collected in the tubular housing.

Generally used for viscous or bad quality fluids.

System is not very compact and has a high cost per unit area installed

Hollow fiber membrane:

The modules contain several small (0.6 to 2 mm diameter) tubes or fibers.

The feed solution flows through the open cores of the fibers and the permeate is collected in the cartridge area surrounding the fibers.

The filtration can be carried out either “inside-out” or “outside-in”

Ultrafiltration module configurations[

Pressurized system or pressure-vessel configuration:

TMP (transmembrane pressure) is generated in the feed by a pump, while the permeate stays at atmospheric pressure.

Pressure-vessels are generally standardized, allowing the design of membrane systems to proceed independently of the characteristics of specific membrane elements.

Immersed system:

Membranes are suspended in basins containing the feed and open to the atmosphere.

Pressure on the influent side is limited to the pressure provided by the feed column.

TMP is generated by a pump that develops suction on the permeate side.

Ultrafiltration, like other filtration methods can be run as a continuous or batch process

Applications[

- [Dialysis](#) and other [blood](#) treatments
- Concentration of [milk](#) before making [cheese](#)
- Downstream processing (e.g., concentration) of biotechnology-derived proteins (e.g., therapeutic antibodies)
- Desalting and solvent-exchange of proteins (via diafiltration)
- Fractionation of [proteins](#)
- Clarification of [fruit juice](#)
- Recovery of [vaccines](#) and [antibiotics](#) from [fermentation](#) broth
- Laboratory grade [water purification](#)
- [Industrial wastewater treatment](#)
- [Drinking water disinfection](#) (including removal of [viruses](#))
- Removal of [endocrines](#) and [pesticides](#) combined with Suspended [Activated Carbon](#) pretreatment

Gold Number

is a term used in [colloidal chemistry](#). It is defined as the minimum amount of [lyophilic colloid](#) in milligrams which prevents the [flocculation](#) of 10ml [gold sol](#) by the addition of 1 ml of 10% NaCl solution.

Coagulation of gold sol is indicated by colour change from red to blue when [particle size](#) just increases. **More is the gold number less is the protective power** of the lyophilic colloid since it means that the amount required is more. It was first used by [Zsigmondy](#). The amount is taken in terms of weight in milligrams.

The gold number of some [colloids](#) is given below.

Protective Colloids	Gold Number
Gelatin	0.005-.01
Haemoglobin	0.03-0.07
Egg Albumin	0.15-0.25
Potato Starch	25
Gum arabic	0.15-0.25
Caseinate	0.01
Sodium Oleate	1-5
Dextrin	6-20

Synthetic protective colloids

The *protective value* we propose gives the number of grams of a red gold sol which are just protected by 1 g. of the protective agent against flocculation by 1% NaCl solution. Gelatine has a protective value of 90, i.e., 1 g. of gelatine protects 90 g. of gold sol. Amphions are good protecting colloids. One of the ionic groups attaches the protecting agent to the colloidal particle, the other supplies the electrical charge.

Synthetic protective colloids were prepared by introducing acidic groups into the basic polyethylenimine molecule, and by introducing basic groups into the polyacrylic acid molecule.

With some synthetic protective colloids, the protective value can be increased as much as one hundred times by the action of heat and time. The interaction between the protecting agent and the sol to be protected requires a longer time than the 3 minutes previously recommended. We recommend that the reaction be allowed to go to completion.

Good protecting colloids form stable complexes with the coagulating metal ions.

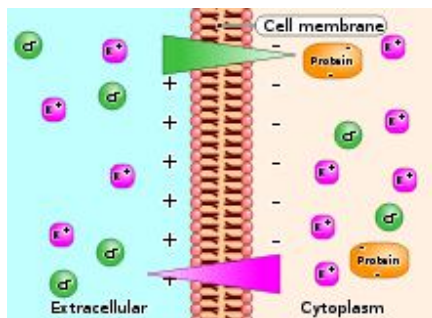
The protective value changes strongly as the pH of the sol is varied within a narrow range. With some polyamphions the protective value, at a given sol pH, can be increased by shifting the isoelectric point (IEP). The protective values and gold numbers of some protecting agents are compared. A synthetic polyacrylic hydrazide had the highest protective value of 400.

The protecting action of natural gelatine is at a minimum at the IEP, but that of the synthetic hydrazide of polyacrylic acid is greatest at this point. In this context the VW theory of Heller is discussed, and the distance between the ionic groups on the polymer chain is postulated as a further important factor contributing to the formation of the stabilizing layers

Gibbs–Donnan effect

From Wikipedia, the free encyclopedia

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Donnan equilibrium across a [cell membrane](#) (schematic)

The **Gibbs–Donnan effect** (also known as the **Donnan effect**, **Donnan law**, **Donnan equilibrium**, or **Gibbs–Donnan equilibrium**) is a name for the behavior of [charged particles](#) near a [semi-permeable membrane](#) that sometimes fail to distribute evenly across the two sides of the membrane.^[1] The usual cause is the presence of a different charged substance that is unable to pass through the membrane and thus creates an uneven [electrical charge](#).^[2] For example, the large [anionic](#) proteins in [blood plasma](#) are not permeable to [capillary](#) walls. Because small [cations](#) are attracted, but are not bound to the proteins, small anions will cross capillary walls away from the anionic proteins more readily than small cations.

Some ionic species can pass through the barrier while others cannot. The solutions may be [gels](#) or [colloids](#) as well as solutions of electrolytes, and as such the phase boundary between gels, or a gel and a liquid, can also act as a selective barrier. The [electric potential](#) arising between two such solutions is called the [Donnan potential](#).

The effect is named after the American [physicist Josiah Willard Gibbs](#) and the British [chemist Frederick G. Donnan](#).^[3]

The Donnan equilibrium is prominent in the triphasic model for articular [cartilage](#) proposed by Mow and Lai, as well as in electrochemical [fuel cells](#) and [dialysis](#).

The Donnan effect is extra osmotic pressure attributable to cations (Na^+ and K^+) attached to dissolved plasma proteins.

Contents

-

Example[

The presence of a charged impermeant ion (for example, a protein) on one side of a membrane will result in an asymmetric distribution of permeant charged ions. The Gibbs–Donnan equation at equilibrium states (assuming permeant ions are Na^+ and Cl^-):

$$[\text{Na}_{\text{Side 1}}] \times [\text{Cl}_{\text{Side 1}}] = [\text{Na}_{\text{Side 2}}] \times [\text{Cl}_{\text{Side 2}}]$$

Example:

Start	Equilibrium
Side 1: 9 Na, 9 Cl	Side 1: 6 Na, 6 Cl
Side 2: 9 Na, 9 Protein	Side 2: 12 Na, 3 Cl, 9 Protein

thixotropy,

reversible behaviour of certain gels that liquefy when they are shaken, stirred, or otherwise disturbed and reset after being allowed to stand. Thixotropy occurs in [paint](#), such as lithopone in oil, which flows freely when stirred and reverts to a gel-like state on standing. Quicksand, a [mixture](#) of [sand](#) and water, is rendered thixotropic by the presence of certain clays. [Drilling mud](#), made thixotropic by the

inclusion of bentonite, forms a cake on the wall of the drill hole to keep drilling [fluid](#) in the hole and to prevent outside water from entering

Thixotropy

is a property exhibited by some fluids which have a gel-like consistency when they are stationary, but which thin when they are subjected to shear stress. One of the classic examples of a thixotropic fluid is quicksand. As long as it is undisturbed, the sand will be relatively thick. Once something falls in and begins thrashing around, putting stress on the quicksand, it becomes more liquid. In addition to being of concern to people who happen to fall into pits of quicksand, thixotropy is a property which can be utilized in a number of interesting ways.

thixotropic

fluid will become increasingly less viscous as it is subjected to strain such as agitation, shaking, or stirring. As soon as the strain stops, the fluid will recover its viscosity, slowly setting up into a semisolid state again. This is in contrast with a rheopectic fluid, which will experience increasing viscosity as it is agitated; a mixture of cornstarch and water, for example, will be gelatinous at rest but will firm up when subjected to pressure. Cornstarch and water “gloop” is sometimes used in science classes to introduce students to the concept with a fluid they can feel and manipulate.

Engineers who study [fluid mechanics](#) have a number of explanations for how thixotropy works, depending on the fluid involved and the types of forces it is subjected to. Understanding this property can be important for people who work with thixotropic fluids, as it will allow them to predict fluid behavior and to explore ways in which this property can be harnessed

Liesegang rings



Some Liesegang Rings

Liesegang rings are a phenomenon seen in many, if not most, chemical systems undergoing a [precipitation reaction](#), under certain conditions of concentration and in the absence of convection.

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History

The phenomenon was first noticed over one hundred years ago (in 1896) by the German chemist [Raphael E. Liesegang](#), and has aroused the curiosity of chemists for many years. It was first noted when he dropped a solution of [silver nitrate](#) on to a thin layer of gel containing [potassium dichromate](#). After a few hours, sharp concentric rings of insoluble silver dichromate formed.

When formed in a test tube by diffusing one component from the top, layers or bands of precipitate form, rather than rings.

Silver nitrate potassium dichromate reaction[

The reactions are most usually carried out in test-tubes into which a [gel](#) is formed that contains a dilute solution of one of the reactants.

If a hot solution of agar gel, also containing a dilute solution of [potassium dichromate](#) is poured in a test-tube, and after the gel solidifies, a more concentrated solution of [silver nitrate](#) is poured on top of the gel, the silver nitrate will begin to diffuse into the gel. It will then encounter the potassium dichromate and will form a continuous region of precipitate at the top of the tube.

After some hours, the continuous region of precipitation is followed by a clear region with no sensible precipitate, followed by a short region of precipitate further down the tube. This process continues down the tube forming several, perhaps a couple of dozen regions of clearing, then precipitation rings.

Some general observations[

Over the decades huge number of precipitation reactions have been used to study the phenomenon, and it seems quite general. Chromates, metal hydroxides, carbonates, and sulfides, formed with lead, copper, silver, mercury and cobalt salts are sometimes favored by investigators, perhaps because of the pretty, colored precipitates formed.

The gels used are usually [gelatin](#), [agar](#) or [silicic acid](#) gel.

The concentration ranges over which the rings form in a given gel for a precipitating system can usually be found for any system by a little systematic empirical experimentation in a few hours. Often the concentration of the component in the agar gel should be substantially less concentrated (perhaps an order of magnitude or more) than the one placed on top of the gel.

The first feature usually noted is that the bands which form farther away from the liquid-gel interface are generally farther apart. Some investigators measure this distance and report in some systems, at least, a systematic formula for the distance that they form at. The most frequent observation is that the distance apart that the rings form is proportional to the distance from the liquid-gel interface. This is by no means universal, however, and sometimes they form at essentially random, irreproducible distances.

Another feature often noted is that the bands themselves do not move with time, but rather form in place and stay there.

For very many systems the precipitate that forms is not the fine coagulant or flocs seen on mixing the two solutions in the absence of the gel, but rather coarse, crystalline dispersions. Sometimes the crystals are well separated from one another, and only a few form in each band.

The precipitate that forms a band is not always a binary insoluble compound, but may be even a pure metal. Water glass of density 1.06 made acidic by sufficient acetic acid to make it gel, with 0.05 N copper sulfate in it, covered by a 1 percent solution of hydroxylamine hydrochloride produces large tetrahedrons of metallic copper in the bands.

It is not possible to make any general statement of the effect of the composition of the gel. A system that forms nicely for one set of components, might fail altogether and require a different set of conditions if the gel is switched, say, from agar to gelatin. The essential feature of the gel required is that thermal convection in the tube be prevented altogether.

Most systems will form rings in the absence of the gelling system if the experiment is carried out in a capillary, where convection does not disturb their formation. In fact, the system does not have to even be liquid. A tube plugged with cotton with a little ammonium hydroxide at one end, and a solution of hydrochloric acid at the other will show rings of deposited [ammonium chloride](#) where the two gases meet, if the conditions are chosen correctly. Ring formation has also been observed in solid glasses containing a reducible species. For example, bands of silver have been generated by immersing silicate glass in molten AgNO_3 for extended periods of time (Pask and Parmelee, 1943).

Theories

Several different theories have been proposed to explain the formation of Liesegang rings. The chemist [Wilhelm Ostwald](#) in 1897 proposed a theory based on the idea that a precipitate is not formed immediately upon the concentration of the ions exceeding a solubility product, but a region of [supersaturation](#) occurs first. When the limit of stability of the supersaturation is reached, the precipitate forms, and a clear region forms ahead of the diffusion front because the precipitate that is below the solubility limit diffuses onto the precipitate. This was argued to be a critically flawed theory when it was shown that seeding the gel with a colloidal dispersion of the precipitate (which would arguably prevent any significant region of supersaturation) did not prevent the formation of the rings.

Another theory focuses on the [adsorption](#) of one or the other of the precipitating ions onto the colloidal particles of the precipitate which forms. If the particles are small, the absorption is large, diffusion is "hindered" and this somehow results in the formation of the rings.

Still another proposal, the "[coagulation](#) theory" states that the precipitate first forms as a fine colloidal dispersion, which then undergoes coagulation by an excess of the diffusing electrolyte and this somehow results in the formation of the rings.

Some more recent theories invoke an [auto-catalytic](#) step in the reaction that results in the formation of the precipitate. This would seem to contradict the notion that auto-catalytic reactions are, actually, quite rare in nature.

The solution of the [diffusion equation](#) with proper boundary conditions, and a set of good assumptions on supersaturation, adsorption, auto-catalysis, and coagulation alone, or in some

combination, has not been done yet, it appears, at least in a way that makes a quantitative comparison with experiment possible.

A general theory based on Ostwald's 1897 theory has recently been proposed [\[1\]](#). It can account for several important features sometimes seen, such as revert and helical banding.

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