

# Colloid Chemistry\*

## A Comparatively New But Exceedingly Promising Field

By John Waddell

AMONG the Greeks *ηκωλλα* denoted glue, and *τα κωλλωδη* (whence the word *colloid*) were substances similar to glue. But to the Greeks, the phrase colloidal gold or colloidal silver would have sounded strange, nor did they dream of quartz in a colloidal form. And not to the Greeks alone were these terms unfamiliar—they were not used till comparatively lately; but of recent years great progress has been made in the study of colloids and now this branch of chemistry has attained remarkable prominence. Not only are there manuals on the subject, but journals are devoted to the recording of its development.

Nearly twenty-five years ago a great impetus was given to physical chemistry when Wilhelm Ostwald issued the first number of the *Zeitschrift für physikalische Chemie*, which has now reached its seventy-eighth volume. In 1906 Wolfgang Ostwald, a son of Wilhelm, issued the first number of the *Zeitschrift für die Chemie und Industrie der Kolloide*, and not only is it already in its ninth volume but, owing to the superabundance of the material provided, Beihefte are from time to time sent out.

As physical chemistry, with its theories of osmotic pressure, electrolytic dissociation, and the phase rule, has found application not only in industrial and analytical chemistry, but in a field whose breadth may be recognized from the fact that it takes in geology and metallurgy, on the one hand, and biology and physiology on the other; so colloid chemistry has in its domain the color of glass and precious stones, a matter which has been of interest from time immemorial, the coagulation of gelatine by tannin, long made use of in the leather manufacture, and the art of photography, a comparatively late by-product of scientific research.

Colloid chemistry may be considered a subdivision of physical chemistry just as electro-chemistry may be, but it is so large a subdivision that like electro-chemistry it takes a place of its own. Colloid chemistry may be said to have begun with Thomas Graham, who in 1861 published a paper in the Transactions of the Royal Society of London upon the separation of substances by diffusion. He found that some substances when dissolved in water and placed in a vessel of parchment paper floating in pure water pass readily through the parchment to the water outside. Sugar and salt and crystalline substances of that kind are among the number. On the other hand, albumen and gelatine and substances that do not crystallize, pass through parchment to a very slight extent. Graham divided soluble substances in this regard into two classes, crystalloids and colloids.

In 1870, Prof. John Tyndall delivered one of his brilliant lectures at the Royal Institution on "Dust and Disease." In the course of his investigations upon the subject it was necessary for him to obtain air perfectly free from dust particles. For this purpose he bubbled air through a solution of caustic potash and through strong sulphuric acid, expecting that these very powerful chemicals would destroy all of the dust, but to his surprise he found that this severe treatment was not effective. He found, however, that by passing air through a red-hot tube containing platinum gauze the dust could be burned and so removed.

How was the presence or absence of dust particles in the air detected? Just by making use of a phenomenon which we observe every time the sun shines into a room, and we watch the moles dancing in the sunbeam. By means of a converging lens an intense beam of light was made to pass through the air under examination. If dust was present it was made luminous and so visible, thus tracing out the course of the light; if dust was not present the path of the beam through the air was blank and could not be seen. This method Tyndall exhibited not only in the lecture mentioned but on many other occasions.

In 1903 Siedentopf and Zsigmondy constructed an apparatus depending upon the same principle by which particles far smaller than can be seen with the ordinary microscope may be made visible. It is an arrangement by which an intense illumination is obtained in the field of a powerful microscope. A very minute particle so illuminated disperses the light and is thus visible against a dark background. Particles of gold can thus be detected whose size is such that on the scale of magnification which would enlarge a red corpuscle of the blood to the diameter of 3 inches the gold particles would be only as large as the full stop at the end of this sentence. The apparatus by which particles of this size are made manifest is called an ultra microscope, and the title of Zsigmondy's book, "Colloids and the Ultra Microscope," indicates that there is a connection

between the work of Graham and the work of Tyndall.

Let us again turn back to work done many years ago by Faraday. In 1857 he made experiments with gold chloride. Gold chloride in concentrated solution is yellow, but a sufficiently dilute solution is practically colorless. Chlorine and gold have not a very strong affinity and the chlorine can be removed in a number of ways and the gold obtained as a dark substance looking like a very fine black powder. If this black powder is collected and rubbed on a hard surface it can be made to show the ordinary color of gold. Faraday added to a very dilute solution of gold chloride a few drops of ether in which phosphorus was dissolved. It gave a ruby colored liquid without any metallic appearance and quite clear. Slight variations may be made in the experiment producing marked differences in the result. If calcium chloride is added to the gold chloride solution the addition of phosphorus in ether gives, instead of ruby, a violet or blue color. Addition of many different substances to the ruby solution change its shade in the same way. So also does boiling. The dark colored solutions give a sediment within a shorter or longer time seldom reaching as much as a week; the ruby-colored liquid may remain clear for years. In time, however, all of the liquids yield a dark sediment and the fluid above it becomes colorless. The ruby color is transparent, so also is frequently the violet, but before sedimentation takes place the liquid becomes cloudy. Faraday was of the opinion that the color in all cases was due to very fine particles floating in the liquid. It is well known that on account of interference of light, substances with no inherent color may acquire various tints, as is seen in mother of pearl where very fine markings produce the effect. Very fine particles produce a color in the same way. If the color is due to the presence of fine particles, those producing ruby would naturally be considered the smallest, for they remain longest in suspension. Faraday found that even the ruby liquid may present a slightly hazy appearance in an intense beam of sunlight, thus indicating the presence of very small particles.

Within recent years not only gold but nearly all other metals have been made to color water or some appropriate liquid, producing what appears to be a solution. For this purpose, an electric arc is formed or electric sparks passed between wires of the metal placed in the liquid. The metal is volatilized, part of it collects and forms a sediment and part remains in the liquid producing a color. In no case does the color thus produced equal in beauty the brilliant ruby shade produced in Faraday's experiment with gold.

It does not appear that Graham, when working with colloidal solutions a few years after Faraday's experiments with gold, considered that there was any connection between the two. His theory of colloid solutions was that they were like crystalloid solutions except that the colloid material dissolved consisted of large molecules, too large to readily pass through parchment paper. For thirty years, work more or less desultory was carried on; a number of colloid solutions were prepared, ferric hydroxide, a modification of iron rust, and aluminium hydroxide closely akin to corundum, were obtained in soluble form. But though new preparations were made, very little attention was paid to theoretical considerations. It was found that while sugar, salt, and similar substances in solution exert osmotic pressure and lower the freezing point of water, colloids had but little effect. It is commonly known that the water of the ocean requires a lower temperature to freeze it than does the fresh water of rivers and lakes, and crystalloid substances have to a greater or less extent the same effect as sea salt. Other things being equal, the greater the molecular weights of the crystalloid the less the effect of a given amount of it. Hence if colloid substances have a molecular weight very large as compared with crystalloid, the very small effect in lowering the freezing point would be explained.

Sulphide of arsenic and some other sulphides were obtainable in a colloidal state and when Carey Lea, in 1888, produced a water soluble substance containing over ninety-five per cent of silver, it was called colloidal silver and was considered to be an allotropic modification of the metal. In 1891 Barus and Schneider carried out investigations which in their view indicated that colloidal silver was not an allotropic form, but that it was ordinary silver in a very fine state of division. Set over against each other were then the two theories, the solution theory and the suspension theory. Most investigators had adopted the former, though Berzelius, Richter, and Faraday before the term colloid had come into use, had dealt with liquids of that class and had attributed the phenomenon to finely divided particles. However, the contest went on until in 1903 the ultra-

microscope of Siedentopf and Zsigmondy made visible, in many colloid solutions, distinct particles and thus obtained a triumph for the suspension theory or, as it is sometimes called, the theory of heterogeneity.

As geologists distinguish, according to the size of the particles, between pebbles, gravel, and sand, so Zsigmondy distinguishes in a similar manner between suspensions and colloidal solutions. Suspensions may roughly be taken to include particles of all sizes from microscopic up, which will float in the liquid; colloidal solutions include all particles of smaller size. The boundary between the two is about 1/10,000 of a millimeter (1/250,000 of an inch), the limit of visibility with a microscope. With the ultramicroscope particles of 1/20 this size may be detected and colloidal solutions contain not only these particles but some so small that we are not able to detect them in any way.

It is not possible by simple grinding to make any insoluble substance so fine that it will act like colloidal solution; it would merely form a suspension. But by the action of chemicals upon each other particles so fine may be produced that a colloidal substance will appear. The more insoluble the substance produced, the more likely is it that such a substance will be formed. Every analytical chemist meets a phenomenon like this frequently. When barium chloride is added to a soluble sulphate a very insoluble substance is produced and some of the particles are so small that they are liable to run through the filter. If both solutions are very dilute no precipitate may be formed for some seconds. Probably during part of that time, at least, the greater portion of the barium sulphate may be in a colloidal state, and some of it may continue in that form. At all events, the addition of electrolytes such as hydrochloric acid or ammonium chloride assists in the coagulation of the barium sulphate just as electrolytes cause the coagulation of colloidal gold. So also nitric acid is added to aid the precipitation of silver chloride. Less insoluble substances form larger crystals which are not liable to run through the filter.

Hydrosols, as colloidal solutions in water are called, when evaporated change to a jelly or solid residue. In some cases this residue can again be dissolved by addition of water. This is the case with glue, gum arabic and similar substances. They are reversible hydrosols. Irreversible hydrosols, like colloidal metals after precipitation, and completely dried silica, cannot be redissolved. Reversible hydrosols are not usually affected by electrolytes; irreversible hydrosols are for the most part extremely sensitive, tending to coagulate. A solution of a reversible hydrosol added to an irreversible one tends to make the latter reversible. Thus a colloidal solution of gold mixed with glue when dried up has a blue color, but addition of water brings it back to its original condition. The reversible colloid acts as a protection to the irreversible.

Colloidal solutions are poor conductors of electricity, but if two electrodes differing by 120 volts or more are placed in the liquid, the colloid will collect mainly at one or other of the poles. This seems to indicate an electric charge upon the particles, though it may be due to the presence of a very small quantity of an electrolyte. In any case, where the particles seem to be negative since they collect round the positive pole, they appear to be more readily coagulated by the positive ions and conversely positive particles are coagulated by negative ions.

One of the most notable hydrosols is that of gold already mentioned, an irreversible hydrosol, not forming a jelly like silicic acid, but a more compact material which settles into a small bulk under the influence of the proper electrolytes. In the ruby-colored hydrosol no doubt some of the particles are too small to be detected even with the aid of the ultra microscope, whose limit is reached when the particle is so minute that, using the standard already employed, fifty or sixty thousand of them could lie side by side on the diameter of the following full stop. The average particles are a little larger than this; twenty or thirty thousand only could lie together across the dot, their diameter being fifteen millionths of a millimeter. The number of them required to make a weight of one gramme, or fifteen grains, is approximately represented by the figure one followed by sixteen naughts. It is only when these particles join to form larger ones that they settle, and the particles thus produced have about twenty times the diameter of the smallest that can be detected by the ultramicroscope, and are almost if not quite visible with a powerful microscope of the ordinary kind.

Zsigmondy discovered that the finest particles have a very remarkable motion. It has been long known that microscopic particles like the globules of fat in milk have a more or less vibrating motion, the so-called

\* Republished from *Queen's Quarterly*.

Brownian motion, but the motion of the gold particles is of a very different order. Zsigmondy, who describes these motions in his book on colloids, was so surprised when first he saw them that for some time he hesitated to publish his discovery. He expected that the gold particles in colloid solutions would be as quiet as those in real suspensions. After making this statement he adds:

"How entirely erroneous was this idea! The small gold particles no longer float, they move—and that with astonishing rapidity. A swarm of dancing gnats in a sunbeam will give one an idea of the motion of the gold particles in the hydrosol of gold. They hop, dance, jump, dash together, and fly away from each other, so that it is difficult in the whirl to get one's bearings. The motion gives an indication of the continuous mixing up of the fluid, and it lasts hours, weeks, months, and, if the fluid is stable, even years. Sluggish and slow in comparison is the analogous Brownian movement of the larger gold particles in the fluid, which are the transition forms to ordinary gold that settles. The smallest particles which can be seen in the hydrosol of gold show a combined motion, consisting of a motion of translation, by which the particle moves from one hundred to one thousand times its own diameter in 1/6 to 1/8 of a second, and a motion of oscillation of a considerably shorter period, because of which the possibility of the presence of a motion of oscillation of a higher frequency and smaller amplitude could not be determined but is probable."

Allied to the ruby-colored colloidal solution of gold is ruby glass. It is made by adding chloride of gold in small quantity to molten glass. The molten glass does not become colored. When quickly cooled it remains colorless and even when slowly cooled no color may appear. The ruby color is nearly always brought out by heating the colorless glass to the softening point, which is several hundred degrees below the temperature at which the glass is made. Poorly made or spoiled ruby glass, as it is called, has a blue or violet shade.

The process of coloring can be illustrated by heating a strip of colorless ruby glass at one end while the other is kept cold. At the spot where the heating takes place the red color develops and grows fainter toward the cold end where no change takes place. Where the red color is fully developed particles may be detected by means of the ultramicroscope; where it is faint particles are no longer visible but probably exist, though very minute. In the colorless portion there are probably few if any particles, the gold being in the form of a compound in the glass and not in the metallic condition, or, if metallic, dissolved in the same way that sugar is dissolved in water. Spoiled ruby glass acts in a somewhat similar manner to good ruby glass, but the particles are much brighter and larger, are much farther apart, and can be detected farther from the heated end.

The formation of gold particles in softening glass is in many respects similar to the growth of crystals. In a solution, crystals grow round nuclei. If a supersaturated solution is cooled far below its supersaturation

point crystallization does not take place even though nuclei are present. The case of the glass is similar. When the glass is cooled, nuclei are formed, but the gold in solution does not deposit on these nuclei. There is no freedom of motion of the molecules of gold in the hard glass. When, however, the glass is heated to the softening point the molecules move more freely, the nuclei grow and the particles become sufficiently large to give a ruby color. Under ordinary circumstances only about half of the gold separates out; the balance remains in homogeneous solution. When the glass is heated to a very high temperature the solubility of the gold increases, the particles disappear, and the glass again becomes colorless.

A very important recent application of colloid chemistry is in the preparation of filaments of tungsten for electric incandescent lamps. In the construction of a lamp the object aimed at is light efficiency, the production of as great illuminating power as possible for a given expenditure of electric energy or, conversely, the use of as little energy as possible for a given illumination. It is readily seen that the higher the temperature of the filament the greater the efficiency. The light obtained from a filament heated till it becomes just faintly red is practically useless, but to produce it very considerable energy is required and much less than double the energy would increase the illuminating power more than twenty-fold.

The metal tungsten is very infusible and can be heated to about 2,800 deg. Cent. without melting or deteriorating to any considerable extent, whereas carbon filaments, which have been used almost universally until very lately, should not be heated beyond a temperature of 1,800 deg. Cent. The extra thousand degrees of temperature makes a very great difference in the luminosity. To attain the high temperature it is necessary that the filament should be made very thin; a diameter of 0.03 mm. is suitable. Nine hundred of these threads could lie side by side in an inch, five of them together have approximately the diameter of No. 40 cotton thread. It is easy to draw out gold and silver wire to this degree of thinness, but tungsten is a very brittle metal which could be obtained only in the form of a powder until the high temperature got by use of electricity made it possible to melt the powder into a compact mass which, however, as just stated, cannot be drawn out into wire. But when the metal is changed into the colloidal state it becomes plastic and can be forced by pressure through a very fine hole, thus producing a thread.

Grinding the metallic powder for months does not serve to produce the fine state of division of a colloid, but the very fine powder after being treated alternately with alkalis and acids becomes colloidal and when precipitated is of such consistence that if pressed through minute holes bored through ruby, threads of the required thickness may be obtained. Wire prepared in this way has little coherence, but when a suitable electric current is passed through it the fine particles unite at the higher temperature produced to form

a solid metal thread of good electric conductivity.

The application of colloid chemistry to dyeing depends upon the phenomenon called *adsorption*. Many substances have the power to condense gases upon their surface and to hold firmly, liquids and finely divided solids. Glass, for instance, is covered with a very thin invisible but often not negligible coating of water and gas which can be got rid of only by heating for some hours in a vacuum. The adsorptive power increases with the surface and depends upon the nature of the adsorbing and of the adsorbed substance. Certain colloids are especially readily adsorbed by certain other colloids. Hence filters in which the pores are far wider than the diameter of the particles in a colloid solution can often be used for separating the colloid from the liquid. Were it not for this adsorptive power of colloids the obtaining of a clear liquid by filtration would often be impossible, and so the chemist in the laboratory as well as the municipal engineer sometimes depends for the success of his operations upon this phenomenon. On the other hand, adsorption makes it more difficult than it otherwise would be, to wash precipitates obtained in the course of analysis from the surrounding liquid, and so acts as a hindrance. This is particularly the case when the solid forming the precipitate is a colloidal jelly, as when ferric hydroxide is precipitated by a solution of caustic potash. It is almost impossible to wash out the potash.

Colloids have a selective power of adsorption. Some colloids are not only not adsorbed by certain others, but act as a protection to colloids which otherwise would be adsorbed. Filters which prevent colloidal gold from passing through them under ordinary circumstances, cannot keep back the particles if the liquid contains some egg albumen as well.

In a number of dyes the ultramicroscope shows the solution to be colloidal, and even where the particles are too small to be individually detected the colloid character is frequently observable. While the theory of dyeing is not complete, it appears that in many cases the material of the fabric acts as a colloidal jelly which adsorbs the colloidal dye stuff as ferric hydroxide adsorbs potash. Sometimes the fabric itself does not adsorb the dye stuff but can take up a colloidal mordant which is capable of adsorbing the dye. When cotton is soaked in alum solution and then treated with soda, aluminium hydroxide is formed as a colloidal jelly which permeates the material and can adsorb many of the colloidal dyes and thus the dyeing is effected. It is not the object of this review to go into details; it is evident that a large domain is here opened up.

Nature works on a large scale as well as on a small. In streams, lakes, and rivers processes go on by which from hard and massive rocks colloidal solutions are made. When these reach the sea the salts present coagulate the fine particles which settle to form a sediment. This sediment makes an exceedingly fertile soil and may be used to enrich poorer land. Here is one point out of several in which colloid chemistry touches upon agriculture.

## The Early History of Wing Warping Devices

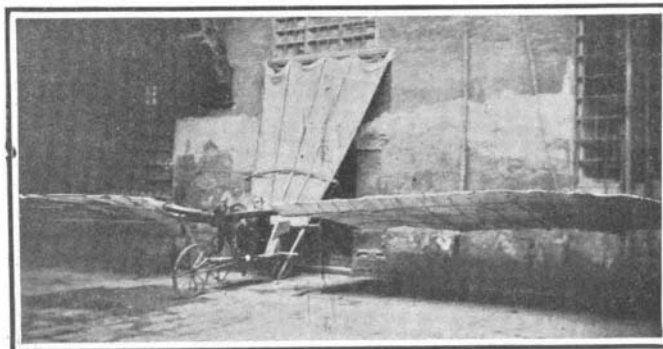
### Who Is the True Inventor?

IN the long extended discussions which have centered around the question of proprietary rights claimed by the Wright Brothers for the use of warping devices for aeroplane wings, and more particularly for the use of these in combination with a vertical rudder, probably the most interesting quotation from the prior art which has been brought to light is that from the work of a Frenchman, Louis Mouillard, a resident of Cairo, where his work was performed and his manuscript book written.

The French paper, *L'Illustration*, once more brings up this subject and gives us some very interesting quotations from Mouillard's work, which it may be mentioned incidentally has been purchased in the name of the French National Aerial League, by Mr. Antoine Bianchi. The book is entitled "Le Vol sans Battement," and has been unearthed thirteen years after the death of its author, from the vaults of the French Consulate of Cairo.

*L'Illustration* takes a patriotic stand in the situation and claims for the French practically the entire glory of the invention of all the essentials of aviation. Whether we follow them entirely in this must depend to some extent on the construction which we lay upon the passages from Mouillard's book that are quoted by A. Henry-Courannier, who writes in *L'Illustration* and to whose charge it has fallen to examine the papers found at Cairo. The writer goes so far as to claim for Mouillard the invention not only of warping but that of the combination of wing warping with the vertical rudder. So far as the warping is concerned, there can be abso-

lutely no question that Mouillard very clearly described and figured the device to effect this. We reproduce here an illustration from an earlier issue of the SCIENTIFIC AMERICAN, showing the Mouillard glider with movable wing tips operated by wires, much in the same way as the modern aeroplane.

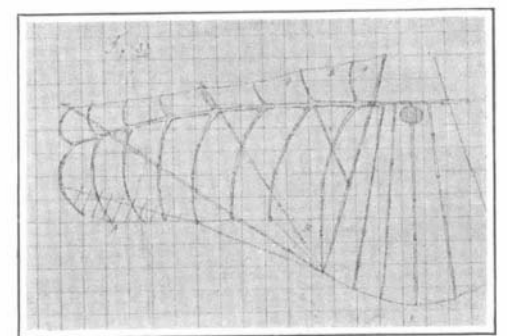


Mouillard Glider of 1895, With Movable Wing-tips.

In support of the contention that Mouillard even anticipated the Wrights in the matter of the combination of warping with vertical rudder, Henry-Courannier quotes the following passage from Mouillard's writings:

"When the aeroplane in its flight attempted to follow

some other direction than that of a head wind, this stiff plane\* followed the air current. . . . This deviation immediately produced a traction upon a cable such as to oppose this new direction of the vertical rudder, the aeroplane being thus caused to offer resistance to the air, and in consequence to bring the machine



Bamboo Skeleton of Wing.

again into the wind." But the matter does not end here. Not only is Mouillard thus shown to be the inventor of warping in combination with vertical rudder, but it is established beyond question that Chanute not only read Mouillard's book but applied for a patent in the name of Mouillard on September 24th, 1892. This patent was issued on May 18th, 1897, and bears

\* A vertical rudder, according to *L'illustration*.