

OUTLINE OF THE PHYSICAL CHEMISTRY OF COLLOIDS

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In the short time at our disposal it will be possible only to discuss some of the outstanding features of the physical chemistry of colloids. Since the first use of the term "colloid" by Thomas Graham in 1861 the subject has advanced so rapidly that no one but a specialist could hope to read all the literature connected with it. There are at present two journals devoted to colloids; the "Kolloide Zeitschrift" and the "Kolloide Beiheft," both edited by Wolfgang Ostwald. Extended treatises on the subject have been written by Ostwald, Zsigmondy, Hatschek and others, and scientific journals of the most diverse character will be found to contain articles pertaining to colloids at least a few times a year.

In order to get a rough idea of the place colloids occupy in nature let us make the experiment of shaking up some soil in water. There will be a certain portion that will settle out almost as soon as the shaking ceases. Another portion will remain suspended in the water for a short time, but will be separated if the mixture is run through a filter paper. This is usually termed a "coarse suspension." The turbid fluid that has gone through the filter is a colloidal solution. The solid it contains differs from the portion that remained on the filter paper chiefly in the fineness of division of its particles, or in terms more usual in this branch of science, the degree of dispersion of the particles. We may then, following Wo. Ostwald, take the size of the largest particle that will go through a filter paper as the upper limit of the size of colloidal particles. The arbitrary nature of this division will be evident to everyone, but it is in accord with the general usage of chemists. If a precipitate is not stopped by a filter paper a chemist makes expressive remarks concerning colloids. The lower limit of the degree of dispersion of colloids we may also take from Ostwald. This may be given as the size of the smallest particle that will be briefly described later. Now the diameter of the particles that an ordinary filter paper will pass is about $100 \mu\mu$, or 1-1000 millimeter, and the ultramicroscope can make evident to the eye particles of a diameter of $6\mu\mu$, or six millionths of a millimeter in diameter. We can then agree for the present to consider solutions containing particles of sizes that come within this range as colloidal solutions.

The first investigators in the subject thought that but few substances can be obtained in the colloidal condition. Later, and as the result of an enormous number of researches, it has become evident that practically any solid or liquid substance may, by proper manoeuvring, be obtained in colloidal solution in some solvent. The method of preparing colloidal solutions are quite diverse as a consideration of the following typical examples will show.

(a) A colloidal solution of silver chloride may be prepared by mixing a very dilute solution of silver nitrate with a very dilute solution of common salt. The use of very dilute solutions is a method of producing colloidal solutions of many slightly soluble substances.

(b) An interesting series of colloidal solutions of gold may be prepared by treating gold chloride solutions with reducing agents. These vary from the translucent blue to the transparent orange red solutions. In the latter the gold is in such a fine state of division that the separate particles are scarcely visible in the ultramicroscope.

(c) A colloidal solution of ferric hydroxide may be prepared by simply pouring a few drops of ferric chloride into boiling water.

(d) Bredig's method, which is applicable to a number of metals, consists in causing an electric arc to strike, under water, between electrodes made of the metal of which a colloidal solution is desired. With the use of high frequency alternating currents this method has recently been used in the preparation of colloidal solutions of a number of metals in a great range of degrees of dispersion.

(e) Colloidal tungsten and chromium may be made by treating the finely ground metals alternately with acid and alkali. This is known as the etching method. Colloidal tungsten prepared in this way was used in the manufacture of the early fragile tungsten filaments.

(f) It has also been found possible to prepare colloidal solutions of a number of metals simply by keeping them for a long time in boiling water in the absence of oxygen.

The question now arises; what properties in common have solutions prepared by such different methods and involving such different substances? The size of the particles has already been mentioned, some other properties will be considered in the following paragraphs.

One very interesting and important property of colloidal solutions can be observed only with the ultramicroscope, an instrument which renders the separate particles visible. Under this instrument the particles are observed to be in motion, the more rapid the smaller they are. This phenomenon is known after its discoverer as the Brownian movement. A study of this motion has led in the last few years to a virtual proof of the molecular theory of matter. A review of the work in this field as carried out by Perran and others will not, of course, be possible here. Briefly, however, the basis of it is as follows: In order to account for the observed properties of gases the kinetic theory has postulated that at a given temperature the kinetic energy of all gas molecules is the same. Since the kinetic energy is the product of the mass of the molecule and the square of its velocity, the speed with which a large molecule moves must be smaller than that of a small molecule. On the assumption that the colloidal particle is a very large molecule, it is found that the directly observed velocity of the particles has exactly the value predicted by the kinetic theory of gases.

The optical principle of the ultramicroscope, which has made this and many other investigations on colloids possible, is shown in figure 1. The cell *E*, which holds the colloidal

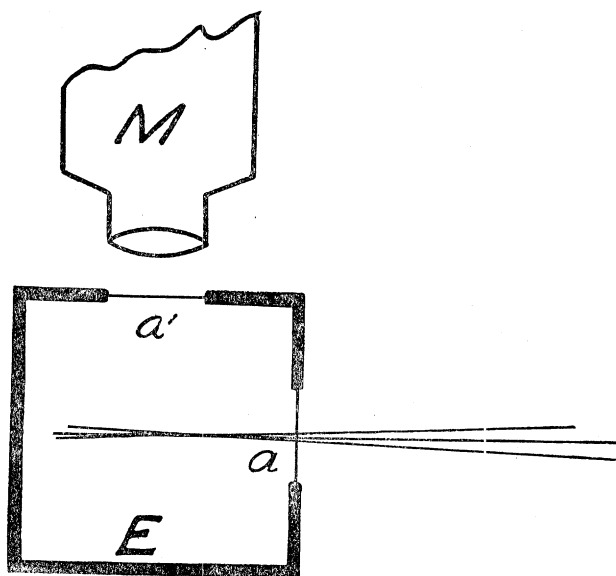


Figure 1. Principle of the Ultra Microscope

solution, has two thin quartz windows, a and a' . By means of a slit and a series of lenses, rays of light from an arc light enter window a in a plane a few thousandths of a millimeter thick. This light impinges on a few of the colloidal particles in the solution and causes them to be centers of light emission. The effect can then be observed by means of an ordinary microscope, M against a black background through window a' . The same principle is, of course, involved when a ray of sunlight enters a darkened room and makes brilliant spots of light of the motes in the beam.

A property common to colloidal solutions is the slow diffusion of the particles through gelatinous substances and through membranes. Upon this property is based the easiest method of determining whether a solution is colloidal or not. A test of this kind can be made by pouring some gelatin in the bottom of test tubes, and on top of the gelatin solutions of, say, colloidal gold and of potassium dichromate. After an hour or so it will be observed that the dichromate has diffused several millimeters down into the gelatin, whereas the boundary between the gelatin and the colloidal solution is just as sharp as at the beginning of the experiment.

The surface exposed by the colloidal particles to the solvent is, as a simple calculation will show, enormous, so that surface effects that are very slight with ordinary solids may be greatly increased by getting the solids into the colloidal condition. One such surface effect is *adsorption*. Willard Gibbs's reasoning led him to the conclusion that any substance the addition of which lowers the surface tension at a solid-liquid or gas-liquid surface is in greater concentration at that surface than in the bulk of the liquid, in other words, the substance is *adsorbed* at the surface. This has been amply verified by experiment. Adsorption phenomena play a large role in the theory of colloids. It can readily be shown that adsorption has a large part in the catalytic effect of colloidal platinum on the decomposition of hydrogen peroxide.

Under most conditions the colloidal particles are found to be charged electrically and will migrate to one pole or the other when an electric current is passed through the solution. The origin of this charge is not entirely clear, and its magnitude and even its sign may be changed by the addition of small quantities of electrolytes. If by some means the electric charge is neutralized the colloidal material is rendered unstable and may be readily coagulated or precipitated.

Of the three general types of colloids only one, the *sol*, has been mentioned in the preceding discussion. A *sol* may be defined as a solid dispersed in a liquid medium. Discussion of the *emulsoids*, or liquids dispersed in liquid media, and of *gels*, or liquids dispersed in solid or semi-solid media, must be omitted both because of their complexity and because of lack of time.

In conclusion, it may be said that the scientific and practical results of the study of colloids have amply repaid for the arduous researches made upon them and we may look for similar if not greater results from the researches to be made in the near future.
