THE PREPARATION AND PROPERTIES OF COLLOIDAL MIXTURES.[1]

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It was by the well-known investigations of the English physicist Graham, published in the seventh decade of the last century, that the general attention of scientists was first drawn to the existence of a class of homogeneous mixtures, differing materially in their properties from ordinary solutions, such as those of salt and sugar. Impressed by the fact that the dissolved substance as a rule separates from the one class of solutions in the amorphous and often gelatinous state, and from the other in the form of crystals, he designated the former substances colloids and the latter crystalloids, and their solutions have since been commonly known respectively as colloidal and as crystalloidal or ordinary solutions. During the period immediately following Graham's classical researches, the subject of colloidal solutions received comparatively little attention. Within the last fifteen years, however, this field has become a favorite hunting ground of both physical chemists and physiologists in their searches after new truths, and greatly has the store of our knowledge in regard to this important state of aggregation been thereby increased. Yet the difficulty in reaching

[1] Presidential address delivered at the Philadelphia meeting of the American Chemical Society, December 29, 1904.

general conclusions as to the properties of these solutions has proved to be a very great one, owing to the complexity of the phenomena and to the apparent contradictions between many of the results obtained with different colloids and by different investigators. Moreover, the original literature of the subject has become so extensive and so detailed as to be almost overwhelming to one who, with limited time to devote to it, desires to obtain a general survey of this field of work. Therefore, although recently, several German monographs[1] upon the subject have appeared, it has seemed to me that a brief review of some of the more important principles thus far established might be of general interest to the members of this Society. I have had, however, not a little hesitation in undertaking to present to you even such an elementary account of the results attained as is here contemplated, for I have not myself been an investigator in this field and cannot claim even an intimate acquaintance with the original literature. I was led to make the attempt by the cordial assurances of assistance, which have been most amply fulfilled, from my colleague, Dr. J. C. Blake, who has been engaged in researches upon colloids for a number of years. I am greatly indebted also to Mr. Charles Field, 3rd, for his able and freely proffered assistance in the preparation of the experiments which I am to have the privilege of presenting to you as illustrations.

THE TWO CLASSES OF COLLOIDAL MIXTURES.

It seems appropriate to begin the consideration of the subject with a definition of the class of substances to which our attention is to be devoted. In accordance with the general use of the term, colloidal mixtures are most simply defined as liquid (or solid) mixtures of two (or more) substances which are not separated

[1] A. Lottermoser : "Anorganische Colloide," 1901, Ahrens Sammlung chemischer und chemisch-technischer Vorträge, 80 pages.—A Müller : " Die Theorie der Kolloide : Übersicht über die Forschungen, betreffend die Natur des Kolloidalzustandes," 1903, 56 pages. Fr. Deuticke, Leipzig und Wien.—G. Bredig : "Anorganische Fermente : Darstellung kolloidaler Mettalle auf electrische Wege und Untersuchung ihrer katalytischen Eigenschaften," 1901, 99 pages, W. Engelmann, Leipzig.—H. J. Hamburger : "Osmotischer Druck und Ionenlehre in der medicinischen Wissenschaften," 1904, Vol. III, pp. 58-106. J. F. Bergmann, Wiesbaden.—W. Pauli : "Der kolloidale Zustand und die Vorgänge in der lebendigen Substanz," 1902, Vieweg und Sohn, Braunschweig.

from one another by the action of gravity however long continued nor by filtration through paper, but which are so separated when the liquid is forced through animal membranes, the substance then remaining behind being designated the colloid. This distinguishes them on the one hand from suspensions of fine visible particles, and on the other from ordinary solutions, and it implies that the colloidal particles are intermediate in size between the particles of such suspensions and the molecules which are present in ordinary solutions. It is obvious, however, that this definition is not based upon a really fundamental dstinction either in the properties exhibited by the various mixtures or in the character of their particles. It would, therefore, not be surprising to discover that the so-defined group of colloids include substances having very different properties in other respects than that just considered. The first result of the researches upon colloids which I wish especially to emphasize is that there are in fact at least two kinds of dissolved or suspended substances retained by animal membranes, which differ so radically in their other properties that their inclusion in the same class is sure to lead to serious confuslon, unless special pains be taken to discriminate between them. I shall therefore distinguish two sub-classes of colloidal mixtures. As types of these I would draw your attention to these aqueous solutions of gelatine and of colloidal arsenious sulphide. The former class possesses a much greater viscosity than that of water; the latter does not appreciably differ from it in this respect (Expt.).[1] The former gelatinizes upon cooling or upon evaporation, and passes again into solution upon heating or addition of the solvent; the latter does not gelatinize upon cooling, and if gelatinized by other means it does not redissolve upon heating (Expt).[2] The former is not coagulated by the addition of salts (unless in excessive amount);[3] the latter immediately

[1] A large test-tube containing a 1 per cent. solution of gelatine in water and one containing a colloidal suspension of arsenious sulphide were shown, each being shaken to indicate the viscosity.

[2] Two tubes with the same contents as before, but previously brought to 0° by immersion in ice water, were shown.

[3] A very large quantity of any salt may, by reason of its osmotic or dehydrating action, cause a precipitation of the colloid, but this effect is quite distinct from the coagulation of colloidal suspensions, which is produced by a relatively small quantity of a salt and by a quantity varying greatly with the valence of its ions.

gives an abundant precipitate (Expt.).[1] We have therefore to distinguish the viscous, gelatinizing, colloidal mixtures, not coagulated by salts, from the non-viscous, non-gelatinizing, but readily coagulable mixtures. The former class I shall designate *colloidal solutions*, the latter, *colloidal suspensions*. This nomenclature[2] is adopted in the belief, held also by others,[3] that a more fundamental distinction between the two classes of mixtures is the possession by the former of the characteristic properties of true solutions—osmotic pressure, diffusibility, and usually a limited solubility of the colloid at some temperature, and the absence of these properties in those in the latter class, and the manifestation by them of many similarities to macroscopic and microscopic suspensions. Even though this may not be a sharp line of division, it is highly probable that typical members of two classes exhibit these properties of true solutions in such a different degree as to make the differentiation an important one. Unfortunately, however, colloidal mixtures have not yet been satisfactorily enough investigated with respect to these properties to enable a classification to be based exclusively upon them.

COLLOIDAL SOLUTIONS.

I will now proceed to discuss the characteristics of the two classes as manifested by typical representatives, first briefly considering the colloidal solutions. These substances are, for the most part, obtained directly from animal or vegetable sources and are purified by dialysis. Among the most important are gelatine, agar-agar, unheated albumen, caramel, starch, dextrine, and many natural gums.

A number of the important properties of these colloidal solu-

[1] To a tube half-filled with a 1 per cent. gelatine solution and to one half-filled with a colloidal suspension of arsenious sulphide 10 cc. normal magnesium chloride solution were added. No effect was observed in the first tube; a voluminous yellow precipitate resulted in the second.

[2] As Dr. Blake suggests to me, it might be better to confine the term colloid to the mixtures of the first class, since Graham applied it only to these and since it literally signifies glue-like or gelatinous, and to designate mixtures of the second class by a new term which will not suggest any relationship to those of the first class. The universal application of the term colloid to both classes and the difficulty of finding a new descriptive term for the latter class seem to make the compromise here proposed more practicable.

[3] Müller : *Ztschr. anorg. Chem.*, **36**, 344 (1903); Bechhold : *Ztschr. phys. Chem.*, **48**, 393 (1904).

tions have already been alluded to, but some of them deserve further consideration. The contrasts and similarities between them and ordinary solutions may first be mentioned. Such colloids possess a much slower rate of diffusion, a much smaller osmotic pressure, and a much slighter influence on the vapor-pressure, freezing-point, and boiling-point of the solvent than do corresponding weights of crystalline substances. So small are these effects that whether they exist at all is a question to which much investigation and discussion has been devoted. The now existing experimental data seem to show, however, that the gel-atinizing non-coagulable colloids do possess these properties and influences in an appreciable degree. The results of the osmotic pressure determinations in the cases where it has been measured against a parchment or animal membrane, which would not re-tain the mineral impurities, are especially significant. Thus by this method it was found by Pfeffer[1] that a 6 per cent. glue solu-tion and by Linebarger[2] that a 2.5 per cent. tungstic acid solu-tion exerted a pressure of about one-third of an atmosphere, and by Starling[3] that a 10 per cent. solution of the colloids of blood-serum produced one of 40 mm. of mercury. Further investiga-tions in this direction would be of great value. The results of Graham,[4] too, seem to leave no doubt as to the existence of diffu-sion; he found, for example, that albumen diffused one-seventh as fast, and caramel one-fourteenth as fast as cane-sugar. Thus, these colloids exhibit the same properties as ordinary dissolved substances, but in a lesser degree—a fact which is explained in accordance with the modern theory of solutions by the simple assumption that they are true solutions, but that their molecules consist of aggregates of the ultimate chemical molecules and are therefore of much greater weight and complexity than those of non-colloidal substances.

This assumption seems, however, of itself alone, scarcely suf-ficient to account for the abnormal viscosity of these colloids, their power of gelatinization, and their property of permitting the free passage through them of non-colloidal substances but preventing entirely that of other colloids of either of the two classes. This last property is the same one that is involved in the permeability

[1] " Osmotische Untersuchungen," 1877.

[2] *Am. J. Sci.*, **143**, 218 (1902).

[3] *J. Physiol.*, **24**, 320 (1899).

[4] *Phil. Trans.*, **151**, 185 (1861).

of animal membranes for crystalloids and their impermeability
for colloids, since such membranes are themselves nothing more
than gelatinized colloids.   Yet it deserves, on account of its great
importance, a somewhat fuller consideration.   This difference in
behavior towards crystalloids and colloids may be readily illus-
trated by immersing sticks of gelatine or agar jelly in one experi-
ment in a colored salt solution and in another in a colored
colloidal suspension, and allowing them to remain for a day
or more.   Such experiments are in progress in these vessels,
one of which contains a solution of copper sulphate and am-
monia and the other a colloidal suspension of ferric ferrocyanide
or Prussian blue.   Sticks of agar jelly were placed in each of these
two days ago.   Upon removing the sticks and cutting them in
two (Expt.),[1] it will be noticed that the ammoniated copper sul-
phate has permeated the stick uniformly to its center while the
Prussian blue has not entered it at all.

Not only are gelatinized colloids permeable to salts, but, re-
markably enough, they offer only a very slight, often scarcely
appreciable, hindrance to the passage of these substances through
them.   Thus, the accurate experiments of Voigtländer[2] have
shown that the rate of diffusion of salts and mineral acids is the
same, at any rate within 1 per cent., in a solid jelly containing 3
to 5 per cent. of agar-agar as it is in one containing only 1 per
cent. of agar-agar, and it is therefore presumably the same as in
water itself, though the accuracy with which this latter conclusion
has yet been directly tested is much less.   It has also been shown
by the measurements of Arrhenius that the electrical conductivity
of salts in a gelatine jelly is only a few per cent. different from
that in pure water, and that there is no sudden change in its value
when the jelly sets.   This property is, however, dependent on
the rate of motion of the ionized molecules of the salt through
the medium between the electrodes, and the slight variation in

[1] Two cylindrical sticks, 5 cm. in diameter and 15 cm. in height, of a
4 per cent. agar jelly had been prepared by pouring the hot liquid solution
into large glass tubes corked at one end, allowing the mass to cool, and
pushing out the solid sticks.   One of these had been placed in a nearly
saturated copper sulphate solution to which enough ammonium hydroxide
was added to redissolve the precipitate first formed.   The other had been
placed in a colloidal suspension of Prussian blue made by mixing equal
volumes of 0.02 molal solutions of ferric chloride and potassium ferrocyanide.
[2] *Ztschr. phys. Chem.*, **3**, 329-331 (1889).

it caused by the presence of colloids, even in quantity sufficient to produce gelatinization, proves that the flow of such molecules is but little impeded by the colloid.

Returning now for a moment to the other side of the phenomenon—the impermeability of one colloid by another, attention may be called to an apparently related fact of much importance, namely, to the fact that the presence of a gelatinizing colloid in a liquid in fairly small quantity prevents the coagulation of colloidal suspensions by salts, and therefore usually prevents the formation of a coagulated precipitate when the solutions of two chemical substances are mixed which, under ordinary conditions, give rise to such a precipitate. Thus when aqueous solutions of silver nitrate and sodium chloride are mixed, an abundant curdy precipitate is produced, but, if a little gelatine solution be first added to one of the salt solutions, only an opalescence results, and the silver chloride formed by the metathesis remains indefinitely in the state of a colloidal suspension (Expt.).[1] Glycerol, sugar, and even ether in some cases have a similar influence. This result may arise from the fact that in the presence of the gelatine the particles of silver chloride after attaining a certain size are not capable of diffusing, and hence of coming into contact with one another. Bechhold,[2] however, has made it probable that, at any rate in many cases, the gelatine prevents the coagulation in another way, namely, by forming an envelope around the solid particle. Whatever may be the explanation of the phenomenon, it is one of great technical importance, especially in relation to photography, for upon it is based the preparation of the so-called emulsions of silver salts in gelatine, collodion, or albumen with which dry plates, films, and printing-out paper are coated.

Recent investigations, especially those of Bütschli,[3] van Bem-

[1] 200 cc. of a 0.05 molal silver nitrate solution containing 2.5 per cent. nitric acid (sp. gr. 1.42) were mixed in a lecture jar with 200 cc. of a 0.05 molal sodium chloride solution; a curdy white precipitate separated immediately. The experiment was then repeated with solutions of the two salts of the same concentration as before in each of which 1 per cent. of gelatine had been dissolved; the mixture became opalescent at once, and the milkiness had greatly increased in fifteen minutes, but no coagulation of the precipitate occurred even on long standing.

[2] *Ztschr. phys. Chem.*, **48**, 396 (1904).

[3] "Untersuchungen über microscopische Schäume und das Protoplasma," Leipzig, 1892; "Ueber den Bau quellbarer Körper und die Bedeutung der Quellung, Göttingen," 1896; "Untersuchung über Structuren," Leipzig, 1898. These references are cited from Müller's "Theorie der Colloide."

melen,[1] and Hardy[2] have proved that the gelatinization of
these colloidal solutions arises from the separation of a portion of
the colloid in the solid state in more or less continuous masses.
The resulting jelly, or gel, as it is technically called, has been
shown to have an irregular sponge-like structure, the web consist-
ing of a solid solution of the two substances and the interstices
being filled with a liquid solution of them. This has been proved
in some cases by direct microscopic observation, and in
others, by separating the liquid from the solid portion by pressure
and by analyzing these portions, which were thus shown to have
a very different composition with respect to the proportions of the
two constituents. Thus Hardy[1] states that when a solution of
13.5 grams of gelatine in a mixture of 50 cc. of alcohol and 50 cc.
of water is gradually cooled, it remains homogeneous until a tem-
perature of 17° is reached. Then it separates into two liquid
phases, and is seen to consist of small microscopic droplets sus-
pended in a fluid matrix. As the temperature falls, these drop-
lets cohere to one another and at 12° they have become solid, form-
ing a framework built up of little spherical masses. The mixture
as a whole has then become a jelly. At 14° the droplets were sep-
arated and found to contain 18 per cent. of gelatine while the
matrix contained only 5.5 per cent. The important statement is
also made that the first appearance of the droplets is attended
by a great increase in viscosity, while the subsequent increase
is a continuous one. The abnormal viscosity of such colloidal
mixtures is therefore probably always due to a physical hetero-
geneity of this kind. The investigations made with other gelati-
nizing colloids, such as agar, albumen, starch, and even silicic
acid, have led to a similar conclusion in regard to the structure of
the jelly.

COLLOIDAL SUSPENSIONS.

Methods of Preparation.—The mixtures of this class have been,
for the most part, prepared artificially. I will therefore first
describe the principles of some of the methods which have been
employed for this purpose.

Of these principles the most important one is, that when an in-
soluble substance is produced *in the absence of electrolytes* by a re-
action between two chemical compounds, it almost invariably

[1] *Ztschr. anorg. Chem.*, **18**, 14 (1898).

[2] *J. Physiol.*, **24**, 176 (1899).

separates in the state of a colloidal suspension. Electrolytes must not be present in considerable quantity for the reason that ions coagulate these suspensions. Thus, when I add a solution of hydrogen sulphide, a slightly ionized substance, to one of arsenious oxide, also slightly ionized, no coagulated precipitate of arsenious sulphide results, but only a turbid yellow liquid, which, when poured through filter-paper, leaves nothing behind (Expt.).[1] It will be noted that in this case the other product of the reaction is water, an un-ionized compound. If this reaction had been carried out with a solution of arsenious chloride, instead of with that of the oxide, the ordinary precipitate of arsenious sulphide would, of course, have been obtained, for, in this case, the hydrochloric acid produced by the reaction, being largely dissociated into hydrogen and chlorine ions, coagulates the colloidal suspension. Thus, upon adding some hydrochloric acid to this mixture, a large precipitate is immediately produced (Expt.).[2] As a second illustration of this method, I will add hydrogen sulphide water to a solution of mercuric cyanide (Expt.).[3] In this case also a colloidal suspension of the sulphide results, for the three substances involved in the reaction, hydrogen sulphide, mercuric cyanide, and hydrocyanic acid, are non-electrolytes; but, upon the addition of hydrochloric acid, or still better of magnesium chloride, to this solution, the precipitate immediately coagulates (Expt.).[4] It is not necessary, of course, that electrolytes be entirely excluded, but only that they be not present at any point at such a concentration as will produce coagulation. The method is, therefore, of fairly general applicability. Thus a colloidal suspension of Prussian blue can be prepared by mixing dilute solutions of nearly equivalent quantities of ferric chloride and potassium ferrocyanide, for the product of

[1] To 200 cc. of a 1 per cent. solution of arsenious oxide (prepared by boiling 12 grams of the solid with water for fifteen minutes, cooling, and filtering), 200 cc. of saturated hydrogen sulphide water were added. The mixture was then poured through a ribbed filter.

[2] To the arsenious sulphide suspension just prepared, 10 cc. HCl (sp. gr. 1.12) were added.

[3] 200 cc. $\frac{1}{8}$ molal $Hg(CN)_2$ solution and an equal volume of saturated hydrogen sulphide water were poured simultaneously into a lecture jar ; a black liquid resulted. The resulting colloidal mixture was poured through a ribbed filter ; scarcely any precipitate remained on the filter.

[4] To the suspension just prepared, 10 cc. normal $MgCl_2$ solution was added.

the reaction, potassium chloride, has a coagulating effect only at higher concentrations (Expt.).[1]

A second method which has, at any rate until recently, been even more commonly employed than that just described, consists in the dialysis of a salt solution in which a colloidal base or acid is present, either owing to natural hydrolysis or to the previous addition of an alkali or acid. Thus colloidal silicic acid may be prepared by dialyzing either a solution of sodium silicate alone, or one to which hydrochloric acid has been previously added. Colloidal ferric hydroxide is obtained by the dialysis of a ferric chloride solution which has been treated with ammonium carbonate until a permanent precipitate begins to form. Here is a suspension of this substance which has been prepared in this way (Expt.).[2] This process of dialysis is commonly resorted to also for freeing colloidal solutions or suspensions prepared in other ways, from mineral impurities. It is most conveniently carried out in parchment tubes, which are now an article of commerce. As the surface exposed by these is large, the process is a comparatively rapid one. The solution to be dialyzed is placed within such tubes, and these are immersed first in running tap water and afterwards in distilled water which is frequently renewed (Expt.).[3]

There is one other method of sufficient importance to deserve mention, and this is the process described by Bredig of preparing colloidal suspensions of metals by producing an electric arc under water between electrodes of the metal in question. This is most readily carried out with the non-oxidizable metals, such

[1] 200 cc. of a 0.02 molal ferric chloride solution and 200 cc. of a 0.02 molal of potassium ferrocyanide solution were simultaneously poured into a lecture jar : a dark blue liquid resulted. Of this mixture, 50 cc. were added to 300 cc. water : the liquid was then seen to be perfectly clear.

[2] A dark red but perfectly clear colloidal suspension of ferric hydroxide was exhibited. This had been prepared by adding to a molal ferric chloride solution a molal ammonium carbonate solution until the precipitate forming on each addition would barely dissolve. The mixture was next dialyzed, first against running tap water, then against distilled water, and finally against conductivity water. It was then filtered and diluted with an equal volume of conductivity water. The solution, which now contained 2.40 grams Fe_2O_3 per liter, had a specific conductance of only 35×10^{-6}. This solution was used in all the subsequent experiments with this colloid.

[3] Such a dialyzing arrangement as is here described was exhibited.

as gold or platinum, in the manner here illustrated (Expt.).[1] The method depends on the fact that the metal is volatilized into the arc or spattered into it in an extremely finely divided form, and is then condensed or absorbed by the water, which, owing to the absence of electrolytes, has little tendency to cause aggregation of the particles.

Besides these colloidal suspensions artificially prepared from mineral substances, others can be obtained by dialysis and other treatments from animal and vegetable sources. Among the most fully investigated of these are heated albumen and gum mastic.

Properties Indicating Heterogeneity.—Turning now to the properties of such colloidal suspensions, it seems appropriate first to refer to those which indicate that these mixtures really are suspensions of minute particles and not true solutions, or, in the language of modern physical chemistry, that they are heterogeneous, two-phase systems. The fact that the components of the mixture are separated by filtration through animal membranes or close-grained porcelain filters is not of itself an evidence of physical heterogeneity, for by copper ferrocyanide membranes, such as Pfeffer first prepared, which differ from these presumably only in the size of their pores, sugar and even salts can be separated from true solutions. In some cases, the presence of particles in suspension in so-called colloidal mixtures has been proved directly by microscopic observation;[2] thus this is the case with the colloidal mercuric sulphide and with colloidal arsenious sulphide when prepared under certain conditions, but not under others; the same is true of blue colloidal gold, which can be produced in a variety of ways, for example, by the reduction of gold chloride solution by hydrazine. In most cases, however, the colloidal

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[1] Each of two gold wires 1.5 mm. in diameter and 8 cm. long was inserted in a binding post screwed into a wooden handle. The wires both dipped about 2 cm. below the surface of a 1/2000 normal hydrochloric acid solution contained in a 12 cm. crystallizing dish. One wire was held firmly in position by a clamp upon its handle; the other was held loosely by a clamp, but was also grasped by the hand, whereby its end could be kept at such a distance from the end of the other wire as to form and maintain an arc. The gold wires were connected through a coil of nickel steel wire of 12 ohms resistance with the terminals of a 110-volt direct-current circuit. Red clouds of colloidal gold were formed near the arc, and in half a minute the whole liquid had assumed a red color.

[2] It would seem best to designate such mixtures microscopic suspensions, and to confine the term colloidal suspensions to those whose particles have a size beyond the limit of microscopic visibility, it being, of course, understood that there is no fundamental distinction between them.

particles can not be seen even under the best conditions; they are, therefore, smaller than one-seventh of a micron (1/7000 mm.), which is about the limit of microscopic visibility. It will be of great interest to determine whether they can not be detected in many other cases with the help of the new Zeiss microscope, which, by employing quartz lenses and ultraviolet light (having a much shorter wave-length than ordinary light) and obtaining the image photographically, extends the limit of visible diameters to about one-half of its present value. With such an "ultramicroscope" Raehlmann[1] has already observed the suspended particles in an albumen solution. By the optical method of Siedentopf and Zsigmondy,[2] in which the colloidal mixture is intensely illuminated by a thin beam of light, and the diffused light reflected from the suspended particles at right angles to the beam is viewed with a powerful microscope, the presence of still smaller particles having a diameter of 1/100 micron, has been detected in red-gold suspensions and in other colloidal mixtures.

A strong indication of the heterogeneity of colloidal suspensions is furnished also by the familiar optical phenomenon which is often called the Tyndall effect; namely, when a beam of light is passed through any medium containing particles in suspension, the beam becomes visible, as does a sunbeam in dusty air, owing to a diffuse reflection of light from the particles. This can readily be shown to occur with colloidal suspensions of gold and of arsenious sulphide, such as were prepared a few minutes ago (Expt.).[3] Moreover, in every case where reflection takes place from nonmetallic surfaces the reflected light is polarized, and this is found, in fact, to be true of the rays diffusely reflected from a colloidal suspension by examining them with a Nicol prism (Expt.).[4] It has been shown by Lobry de Bruyn,[5] to be sure, that not only colloidal solutions (colloidal mixtures of the first class), but also

[1] *Berl. klinische Wochenschrift*, 1904, p. 186.

[2] *Ztschr. Elektrochem.*, **8**, 864 (1902).

[3] A beam of light from a projection-lantern, made smaller by covering the lens with a diaphragm with a circular aperture 1 cm. in diameter, was thrown into a colloidal gold suspension in a rectangular jar placed 15 cm. in front of the lens; the path of the beam in the liquid was strongly luminous.

[4] A Nicol prism was inserted between the lantern and the colloidal suspension, and the Nicol was slowly rotated; the light in the liquid was seen to be much brighter in some positions of the Nicol than in those at right angles to them.

[5] See Hamburger's " Osmotischer Druck und Ionenlehre," Vol. 3, p. 63.

ordinary solutions of some substances with complex molecules like sugar exhibit this phenomenon, so that it is not a decisive criterion of a suspension. They do so, however, in an incomparably less degree than do typical colloidal suspensions, so that it at least furnishes evidence that the particles in the latter mixtures are of much larger size than are those in the former.

Whether the well-defined colloidal suspensions possess in appreciable degree what may well be regarded as the best single criterion of a true solution—a measurable osmotic pressure—does not, in spite of its importance, seem to have been the subject of investigation by the direct osmotic method. Nor is there conclusive evidence that they show the closely related phenomenon of diffusion.[1] If the existence of these properties to an extent corresponding at all to the size and number of the particles should be demonstrated, it would, of course, prove that the distinction between colloidal solutions and suspensions is not one of quality, but only one of degree.

Properties Related to the Electrification of the Particles.—I will next consider a quite distinct class of properties, which depend not on the size of the colloidal particles, but apparently upon the presence of electric charges upon them.

The most direct evidence of this electrification is furnished by the migration of the colloidal particles through the liquid under the influence of an applied electromotive force—a phenomenon that was first extensively studied by Picton and Linder[2] in 1897, but which has since been further investigated by several other workers.[3] This effect I will illustrate with the colloidal suspensions of arsenious sulphide and ferric hydroxide with which these two U-tubes are filled. The upper ends of the U-tubes are covered with goldbeaters' skin and are surrounded by wider tubes containing pure water in which platinum electrodes are

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[1] It is true that Whitney and Blake (this Journal, **26**, 1361 (1904)) have shown that red colloidal gold which had been migrated under a potential-gradient to the foot of a vertical tube covered with goldbeaters' skin immediately began to diffuse upward when the electric field was destroyed and did so at a rate comparable with that of salts, but it seems possible that the phenomenon was due to some counter-electrical effect.

[2] *J. Chem. Soc.*, **71**, 568 (1897).

[3] For a review of the preceding investigations upon the migration of colloids and for a description of the most accurate work thus far executed see the recent article of W. R. Whitney and J. C. Blake : This Journal, **26**, 1339–1387 (1904).

placed, so that the products of electrolysis collecting around them may not influence the colloid. I will connect these tubes in parallel with the terminals of a 110-volt circuit in such a way that the current will flow through each of them in the direction from left to right, as will be shown by the copper coulometer in series with them. (Expt.)[1] It will be some minutes before any result will be observed. Then it will be seen that the ferric hydroxide has moved down with a sharp surface of demarkation on the side where the current enters, leaving a clear layer of water above, and that the arsenious sulphide has done the same but on the opposite side of the tube. In other words, the ferric hydroxide particles are migrating with the positive current towards the cathode, the arsenious sulphide with the negative current towards the anode. The former are therefore positively, and the latter negatively charged. These results are typical ones—the same behavior is exhibited by all colloidal suspensions, and, it may be added, also by fine microscopic suspensions, such as those of quartz, kaolin, and lampblack. Other basic hydroxides, like those of aluminum, chromium, and thorium, and certain dyestuffs migrate to the cathode just as does that of iron. The suspended particles of almost all other substances, whether colloidal or microscopic, migrate to the anode. This is true, for example, of silicic acid, stannic acid, metallic sulphides, salts like silver

[1] The U-tubes employed were 15 cm. in total height and had a bore of 3 cm. Over the tops of the tubes goldbeaters' skin was tied. At the bottom of the bend was a hole 1 cm. in diameter. The tubes had been completely filled before the lecture by inverting them and pouring the colloidal mixtures in through this hole, which was then closed by slipping a rubber band over it. Over each arm of each tube a straight tube of only slightly greater diameter was placed. These extended downwards nearly to the top of the bend of the U-tube and were there united to the latter by a rubber band. They also extended 5 cm. above the goldbeaters' skin at the top of the U-tubes. These outside tubes were filled with conductivity water. The colloidal suspensions had been prepared as described above, and had been dialyzed for a week, first against distilled water and finally against conductivity water. This must be done in order to remove electrolytes as completely as possible, since otherwise the heat produced by the current causes convection and disturbance of the migrating surface. The electrical connections were made with large wires, so as to be readily seen, in the way stated above. A 220-volt circuit, if available, is to be preferred. The copper coulometer referred to consisted of a thick copper wire as anode, and a strip of platinum foil as cathode, placed in a beaker containing a very dilute copper sulphate solution.

iodide and Prussian blue, and metals like gold and platinum. Of special interest with reference to the explanation of the phenomenon is the fact discovered by Hardy[1] that an egg-albumen suspension migrates towards the cathode in an acid liquid and towards the anode in an alkaline one.

In regard to the cause and character of the electrification two assumptions deserve consideration: one is that it is simply an example of contact electricity, the colloid particle assuming a charge of one sign and the surrounding water one of the other. This correlates this phenomenon of migration with that of electrical endosmose; for the motion of suspended kaolin, for example, through water against the positive current is obviously the converse of the flow of water through a porous clay diaphragm with the current. It does not, however, give an obvious explanation of the facts that the basic colloidal particles become positively charged and the acidic and neutral ones negatively charged, or of the peculiar behavior of albumen. The other assumption accounts for these facts. According to it the phenomenon is a simple case of ionization, the character of which may be best illustrated by specific examples. Thus, each aggregate of ferric hydroxide molecules may dissociate into one or more ordinary hydroxyl ions and a residual positively charged colloidal particle, and each aggregate of silicic or stannic acid molecules into one or more hydrogen ions and a residual negatively charged colloidal particle. Albumen, which is known to be capable of forming salts with both acids and bases, would, acting as a salt, dissociate into an ordinary positive ion and a colloidal negative one in alkaline solution, and into an ordinary negative ion and a colloidal positive one in acid solution. To explain the behavior of neutral substances like gold or quartz by this hypothesis, it is necessary to supplement it by the assumption that in these cases it is the water or other electrolyte combined with or adsorbed by the colloidal particles which undergoes ionization. It seems not improbable that there may be truth in each of these hypotheses, contact electrification occurring in the case of the coarser suspensions, and ionization in the case of those which approximate more nearly to colloidal solutions. It should be noticed that these hypotheses do not differ as to the charge on the colloidal particle itself, the existence of which is in fact experimentally demon-

[1] *J. Physiol.*, **24**, 292 (1899); *Ztschr. phys. Chem.*, **33**, 387 (1900).

strated, but only as to the location of the accompanying charge of opposite sign, namely, as to whether it is on the water itself or on ordinary ions dissolved in it. This matter is not essential to our further considerations.

The migration of colloids under a potential-gradient is not only of great theoretical importance in showing that the particles are electrified, but it is also of much experimental value from the standpoint of the exact investigation of these substances, since, as Whitney and Blake[1] have shown, it furnishes the most perfect method we have of obtaining colloidal suspensions free not merely from dissolved but from adsorbed electrolytes. This method may therefore be briefly described, using red colloidal gold as an example. If a suspension of this colloid, purified as far as possible by dialysis, be migrated downwards in a vertical tube whose ends are covered with goldbeaters' skin and are surrounded by larger tubes containing pure running water in which the electrodes are placed, the gold finally collects as a thick mud on the goldbeaters' skin at the bottom, while the electrolytes pass out in large part into the liquid around the electrodes (Expt.).[2] If now the liquid in the tube be drawn off and the mud be added to pure water, it immediately passes again into the state of colloidal suspension (Expt.),[3] and the migration can then be repeated if desired. In this way a gold suspension has been prepared which had an electrical conductivity only about twice as great as that of the double-distilled water ordinarily used in conductivity work. Moreover, it is evident that a colloidal solution of any concentration can be prepared by this method. Many other colloids also, such as colloidal silver or Prussian blue, which can be obtained in the solid state either by this method or by filtration, evaporation, or coagulation, immediately form again a colloidal suspension on the addition of pure water (Expt.).[4]

[1] This Journal, **26**, 1345 (1904).

[2] The apparatus, as here described, containing a red gold suspension which had been migrated down, leaving a colorless liquid above the gold mud collected on the goldbeaters' skin, was exhibited.

[3] The tube was quickly inverted, whereupon the gold mud disseminated itself through the colorless liquid beneath, yielding an apparently homogeneous red solution.

[4] A few centigrams of dry colloidal silver were added to 500 cc. of water; a turbid brown liquid resulted. The colloidal silver had been prepared by mixing a silver nitrate solution with a solution of tannic acid in ammonia, filtering the mixture with the help of suction through a porous cup, scraping off the mud from the wall, and drying it in the air.

Passing over, because of lack of time, some interesting facts in regard to the conductivity and rate of migration of pure colloids, I will turn now to the extremely important phenomenon of their coagulation. It will be seen that this phenomenon is certainly closely related to the electric charges on the colloidal particles. Indeed, it seems highly probable that they remain in suspension because of their electrification. Thus Hardy[1] found that egg-albumen, whose particles are shown by their migration to be positively charged in acid solution and negatively in alkaline solution, immediately coagulate when the solution is made neutral. I would also call your attention to another interesting fact having, apparently, the same significance, namely, to the fact that when two colloidal suspensions, whose particles have an electric charge of the same sign, are mixed, they have no influence upon each other, but when two suspensions, with particles oppositely electrified, are brought together, the two colloids combine with each other, and with proper proportions a complete coagulation results. Thus, upon mixing these suspensions of colloidal gold and of arsenious sulphide, no coagulation occurs (Expt.),[2] but when the suspensions of ferric hydroxide and arsenious sulphide, which we have seen from their behavior on migration have opposite electric charges, are poured together, there is immediate coagulation, and in a few minutes the precipitate settles, leaving the liquid clear above (Expt).[3]

Ordinary dissolved substances are also to be divided into two classes with respect to their effect in coagulating colloids. Non-electrolytes, whether organic or inorganic, have no tendency to produce coagulation; indeed, organic substances, like ether, glycerol, or sugar, often increase the stability of the suspension. On the other hand, strong electrolytes, that is, substances, which

[1] *J. Physiol.*, **24**, 292 (1899).

[2] 200 cc. of a colloidal gold suspension (previously made by adding an ethereal solution of dry auric chloride to an aqueous solution of acetylene and dialyzing) were mixed with 200 cc. of a colloidal arsenious sulphide suspension.

[3] 150 cc. of the dialyzed ferric hydroxide suspension, prepared as described in a preceding foot-note, and 200 cc. of the dialyzed arsenious sulphide suspension were poured simultaneously into a lecture jar; a large flocculent precipitate of a color intermediate between that of ferric hydroxide and arsenious sulphide formed at once and soon settled, leaving the liquid nearly clear above. The right proportions of the two colloids to give rise to complete precipitation must be determined by trial for any pair of preparations.

are themselves largely dissociated into electrically charged particles
or ions, cause coagulation, when their concentration in the solu-
tion becomes sufficiently great. Although complete coagula-
tion does not occur suddenly as the quantity of electrolyte is in-
creased, yet the interval between the concentration at which, in
a given time, the particles become visibly larger and that at which
they have become large enough to settle out or to be retained by a
filter is usually so small that a fairly definite concentration can
be specified at which each electrolyte causes a certain, experi-
mentally determinable, degree of coagulation in a definite time.[1]
Now recent investigations have demonstrated the remarkable
fact that this coagulation-concentration is nearly the same for
different ions having the same electric charge (or valence), but
that it diminishes enormously with increase of the electric charge
of the ion of unlike sign to that of the colloid, while it is not
affected by a change in the electric charge on the ion of like sign.

These principles are well illustrated by the results given in
the table, which were obtained by Freundlich,[2] on the one hand
with the negative colloid, arsenious sulphide, and on the other
with the positive colloid, ferric hydroxide, by determining the
concentration which in two hours caused such coagulation as
would prevent any of the colloid from passing through a hard-
ened filter.

Coagulation-concentration in milli-equivalents per liter.

of As_2S_5, a negative colloid, by			of FeO_3H_3, a positive colloid, by	
NaCl... 71	$MgCl_2$...... 2.0	$AlCl_3$........ 0.39	NaCl... 9.3	K_2SO_4... 0.41
KNO_3. 70	$Ba(NO_3)_2$. 1.9	$Al(NO_3)_3$.. 0.41	KNO_3.. 11.9	$K_2Cr_2O_7$. 0.39
K_2SO_4. 91	$MgSO_4$..... 2.3	$Ce_2(SO_4)_3$. 0.40	$BaCl_2$... 9.6	$MgSO_4$ .. 0.43

I can also roughly illustrate these principles by experiments
with these two colloids.[3]

[1] That the phenomenon really consists in a different *rate* of coagulation
at different concentrations, and not in an equilibrium established at any defi-
nite concentration, has been emphasized by Freundlich (*Ztschr. phys. Chem.*,
44, 143 (1903)). Unfortunately, there has been no systematic investigation of
the matter in this direction in spite of its great importance as a help in ex-
plaining the mechanism of the coagulation.

[2] *Ztschr. phys. Chem.*, **44**, 135, 151 (1903).

[3] Separate 50 cc. portions of an arsenious sulphide suspension (made by
mixing equal volumes of a 1 per cent. As_2O_3 solution and of a saturated
hydrogen sulphide solution and filtering) were poured into a row of conical
lecture jars each of which contained already 200 cc. of a solution of one of

It is evident from these facts that it is the ion with a charge opposite to that of the colloid particles that is mainly responsible for their coagulation, but what the mechanism of this coagulation is, is not yet understood, though it has been the subject of much discussion. Interesting though they are, I shall not try to describe the explanations that have been suggested; for, in my opinion, mere speculative hypotheses, that is, hypotheses which have not been shown to facilitate to an important extent a knowledge of the actual phenomena, are of little value except to the investigators of them, and to them only because of the possibility of their future development into really useful conceptions. The recent literature of colloids furnishes a striking example of the unfortunate tendency even of our modern investigators and text-book writers to attach greater importance to hypothetical interpretations of imperfectly known phenomena than to a determination and presentation of the laws in regard to them.

Even an elementary consideration of the properties of colloids should include a discussion of the absorption or co-precipitation of other substances with them when they are gelatinized or coagulated—a phenomenon which is of great importance in analytical chemistry, as well as in other directions. But, as I fear this lecture has already exceeded its normal length, I shall have to omit entirely this side of the subject.

I shall, too, have to content myself with a mere reference to the importance of a knowledge of the properties of colloids not only in the industrial applications of chemistry, but also in many other sciences and arts. Mention can only be made of the facts that the industries of dyeing, of tanning, and of glass-making and

the following substances having the concentration in milli-equivalents per liter shown by the numbers preceding the symbols : (1) 0.6, $AlCl_3$*; (2) 1.5, $MgCl_2$; (3) 20, $MgCl_2$*; (4) 60, NaCl; (5) 400, NaCl*; (6) 60, Na_2SO_4; (7) 400, Na_2SO_4*. Separate 50 cc. portions of a ferric hydroxide suspension, prepared as described in a preceding foot-note, were also added to 200 cc. portions of the following solutions having the indicated concentrations in milli-equivalents per liter : (1) 0.02, $K_3Fe(CN)_6$; (2) 0.1, $K_3Fe(CN)_6$*; (3) 0.1, Na_2SO_4; (4) 1.6, Na_2SO_4*; (5) 5, NaCl; (6) 50, NaCl*; (7) 5, $MgCl_2$; (8) 50, $MgCl_2$*. Coagulation and flocculation took place almost immediately in the solution to whose symbols an asterisk is attached, but nothing (or at most only a slight increase in turbidity) occurred in the other cases. These results were discussed in detail by the speaker with reference to the principles involved.

coloring, and of the manufacture of photographic materials and of modern explosives have to deal primarily with substances in this peculiar state of aggregation; that the clarification of syrups and other liquors and that of water and sewage by pre-cipitation are based on the phenomena of absorption by colloidal substances; that it is with these substances as constituents of living bodies that physiology is mainly concerned; that they constitute the culture-media of the bacteriologist, to the employ-ment of which the development of his science is largely due; and that to the geologist the phenomenon of the sedimentation of mud and slimes, which is closely related to that of the coagula-tion of colloidal suspensions, is one of much interest.

With these brief indications of the importance of the subject, I must now conclude this very inadequate survey of it. It re-mains only for me to express to you my thanks for your kind at-tention.

NOTE ON THE EFFICIENCY OF CENTRIFUGAL PURIFICA-TION.

BY THEODORE WILLIAM RICHARDS.

For many years the advantages of centrifugal separation of mother liquor from crystals have been realized by technical chem-ists in the preparation and drying of sugar and many other sub-stances. Probably also the washing of these substances during rapid rotation has been practiced by many. Certainly both these operations have frequently been used in this laboratory for the preparation of the pure substances necessary in precise work. Nevertheless, there is known to me no quantitative study of the efficiency of these processes; hence a short note concerning a brief series of experiments (made in the first place merely to determine the grade of purity which was probably being attained in a special series of consecutive recrystallizations) may be of service.

In the following tests, sodium nitrate was selected as a typical substance, and to it was added an impurity (nitric acid) whose quantity could easily be estimated. Sodium nitrate was chosen