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University of Toronto.
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I hereby certify that the Thesis above mentioned has been accepted by the Senate of the University of Toronto for the Degree of Doctor of Philosophy, in accordance with the terms of the statute in the behalf.

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ON THE PHYSICAL ASPECT OF COLLOIDAL SOLUTION

BY

E. F. BURTON, B.A. (CANTAB.), Ph.D. (TOR.)
DEMONSTRATOR IN PHYSICS IN THE UNIVERSITY OF TORONTO

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PREFACE

The following pages are based on a series of papers published by the author during the past five years. They are:

I. On the Properties of Electrically Prepared Colloidal Solutions. (Phil. Mag., S. 6, Vol. 11, No. 64, April, 1906.)

II. The Action of Electrolytes on Colloidal Solutions. (Phil. Mag., S. 6, Vol. 12, No. 71, Nov., 1906.)

III. The Susceptibility of Iron in Colloidal Solution. (In collaboration with P. Phillips. Proc. Cam. Phil. Soc., Vol. 13, Pt. v, p. 260, Jan., 1906.)

IV. On the Physical Properties of Electrically Prepared Colloidal Solutions. (Thesis upon which the degree of B.A. was granted to the writer by the University of Cambridge.)

V. The Action of Electrolytes on Copper Colloidal Solution. (Phil. Mag., S. 6, Vol. 17, No. 100, April, 1909.)

VI. The Dialysis of Colloidal Ferric Hydrate. (In course of publication in the Transactions of the Canadian Institute.)

In addition to the above experimental work, an attempt has been made to present the general properties of these solutions and to indicate the bearing of the study on various physical questions. It is hoped that the references to original papers will be found sufficient to point out the principal sources of information, apart from the above and certain published treatises on the subject. Among the latter may be cited:

Zsigmondy: Zur Erkenntnis der Kolloide. (Jena, 1905.)

Cotton and Mouton: Les Ultramicroscopes et les Objets Ultramicroscopiques. (Paris, 1906.)

Wo. Ostwald: Grundriss der Kolloidchemie. (Dresden, 1909.)

Svedberg: Herstellung kolloider Lösungen. (Dresden, 1909.)

Freundlich: Kapillarchemie. (Leipzig, 1909.)

The references throughout will show the extent of indebtedness to these works.

The numbers at the end of proper names refer to articles which are listed.

In conclusion, I desire to express my most sincere thanks to Professor J. C. McLennan for his constant interest in the work, and to Professor A. B. Macallum for many helpful suggestions.

E. F. BURTON

Department of Physics,
University of Toronto,
May 4th, 1910

ON THE PHYSICAL ASPECT OF COLLOIDAL SOLUTION

I. INTRODUCTION

Recent advances in many branches of scientific research have tended to emphasize the essential unity of all the sciences in their struggle to unfold the mysteries of the phenomena of life and nature. The biologist, the physiologist, the chemist and the physicist have each come to learn that it will not suffice to view his own particular problems through coloured glasses, and more and more is he impressed with the truth of the dictum that

> " All are needed by each one;
> Nothing is fair or good alone."

Each has been assured of the absolute necessity of taking advantage of every mode of attack offered by his colleagues, while, at the best, our methods seem very meagre when compared to the problems with which we are brought face to face.

Probably few lines of recent advance better illustrate the truth of these words than the study of colloidal solutions. In variety of interests involved, in richness of concrete results obtained in a few short years, in complexity of the enigmas offered for solution, in the importance to the theory of the structure of matter, and in far reaching applications to the phenomena of life and the economy of nature, this study is excelled by perhaps no other.

In respect of practical physical applications resulting from the study one should probably mention first the added power given to the microscopist by the invention of the ultramicroscope. When, as a result of the theoretical work of Rayleigh[1, 2] and the practical developments of the microscope under the Zeiss[3] firm, the advantages of large aperture, of immersion objectives, and of illumination by ultraviolet light were made use of, microscopy had apparently reached a *cul de sac*. Then by an extension of the principles deduced from the Tyndall phenomena,[4] Zsigmondy and Siedentopf[5] produced their ultramicroscope, by which our power of vision has been immensely extended.

In a Bakerian lecture before the Royal Society in 1856, Faraday[6] first draws attention to the important bearing of the optical properties of such solutions on the theory of light. The succeeding work of Rayleigh[7, 8, 9] on the blue colour of the sky has found a new application in the action of colloidal particles on light. The work of Garnett[10] and Ehrenhaft[11] in this connection is deserving of special notice, on account of their attempts to elucidate from theoretical optical reasoning the structure of the particles in various colloidal solutions. The discovery of the existence of the Kerr phenomenon[12] in these liquids, and the work of Cotton and Mouton[13] on the magneto-optical effects in colloidal iron solutions, have led to important results regarding the form of the colloidal particle. An investigation of the effect of the presence of these particles on the dielectric constant of the liquid medium may throw interesting light on the electro-magnetic theory as deduced by Lorentz and others.

However, from the point of view of the physicist the theoretical importance of these solutions is by no means confined to the realm of optics. The particles all possess a very lively vibratory motion, the so called Brownian movement, which has proved of absorbing interest in its relation to the kinetic theory of matter. The work of Smoluchowski[14] and Einstein[15, 16] shows that this motion is theoretically confirmatory of the kinetic view, while the recent results given by Perrin[17] offer a visible proof of the truth of that theory.

When one turns to deal with the electrical properties of these solutions one reaches the borderland between physics and chemistry, over which the physical chemist is supposed to hold sway. However, in these days, when chemists have become physicists, and physicists are adorned with the laurel wreaths of chemists, trespassers on this region from either side need fear no prosecution. Probably the most important, certainly the most enigmatic, property of the colloids is the fact that the particles of the majority of these solutions are electrically charged. The bearing of the possession of this charge on the phenomena of electric endosmose, on the contact difference of potential between solids and liquids, on surface tension effects, together with the action of added electrolytes on the value of the charge on the particle, has furnished work for a host of men, and the ultimate solution of these problems will undoubtedly give us the most valuable knowledge regarding the energies involved in the liquid and solid states. Without dwelling on the light thrown by the study of colloidal solution on some reactions formerly viewed as purely chemical, we might point out the importance of this study in applied chemistry and the economic value of the colloidal state. Dyeing, tanning and glass manufacture afford examples of the way in which the properties of these solutions were made use of before their real constitution had become a subject of theoretically important work. As instances of the rôle these solutions play in nature, attention might be directed to the formation of deltas at river mouths, and to the probability, according to Van Bemmeln,[18] that the retentive property of rich soils for salts necessary to the growth of plants is directly due to the existence of colloidal solutions in the humus of the soil.

Judging by the literature on the subject and considering the structure and action of the constituent parts of the animal body, we may conclude that the study of colloidal solutions is of surpassing interest to the biologist and physiologist. The invention of the ultramicroscope has brought into view bodies, e.g., certain germs, which were theretofore undiscovered. The abundance and ubiquity of natural colloids in the human body brings into prominence the work on semipermeable membranes, surface tension, and the rôle played by the *Schutzkolloid*. Indeed, Perrin[19] has suggested a colloidal explanation of the process of primary cell growth and cell division, ideas which are somewhat supported by the phenomenon of galvanotropism of microscopic animals.[20]

Enough probably has been indicated to show the far reaching importance of this study, while as yet our knowledge of the various actions is very far from being complete, as the closing sentences from two recent works on the subject will show.

"Mit den oben erwähnten Ausführungen soll natürlich keine Theorie der Kolloide gegeben werden, denn die Lehre von den Kolloide wird eine grosse, umfangreiche Wissenschaft werden, anderen Ausbau sich viele beteiligen müssen: erst wenn ein umfangreiches, aus gründlicher physikalisch-chemischer Experimentaluntersuchung hervorgegangenes Tatsachenmaterial systematisch geordnet vorliegt, wird die Theorie der Kolloide sich aus dem Stadium verallgemeinernder Betrachtung von Specialfällen zu dem Range einer exacten Wissenschaft erheben können." (Zsigmondy: Zur Erkenntnis der Kolloide, p. 183.)

"D'un manière générale, nos connaisances sur les objets ultramicroscopiques sont encore bien peu avancées." (Cotton and Mouton: Les Ultramicroscopes et les Objets Ultramicroscopiques, p. 227.)

II. HISTORICAL

Some fifty years ago Graham undertook an elaborate series of experiments on the rates of diffusion, in water and other pure solvents, of various chemical substances soluble in the particular liquid, and was led to the discovery of a very marked division of all compounds into two large groups, the rates of diffusion of materials in one of the groups being of a much higher order than that in the other. He found that such substances as silicic acid, soluble alumina, and certain organic compounds, viz., gum-arabic, tannin, dextrin, caramel, and albumen, possess extremely slow rates of diffusion into pure water, compared with the rates of such compounds as sodium chloride, hydrochloric acid, etc. The former group he called colloids, while the latter he designated crystalloids on account of the fact that they crystallize from saturated solutions. Further examination of the properties of the substances in the two classes showed him that there was a very general line of cleavage between the two groups.

"They appear like different worlds of matter, and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between the material of a mineral and that of an organized mass.

" The colloidal character is not obliterated by liquefaction, and is, therefore, more than a modification of the physical condition of solid. Some colloids are soluble in water, as gelatine and gum-arabic; and some are insoluble, like gum-tragacanth. Some colloids again form solid compounds with water, as gelatine and gum-tragacanth, while others like tannin do not. In such points the colloids exhibit as great a diversity of property as the crystalloids. A certain parallelism is maintained between the two classes notwithstanding their differences.

" The phenomena of the solution of a salt or crystalloid probably all appear in the solution of a colloid, but greatly reduced in degree. The process becomes slow; time, indeed, appearing essential to all colloidal changes. The change of temperature usually occurring in the act of solution becomes barely perceptible. The liquid is always sensibly gummy or viscous when concentrated. The colloid, although often dissolved in a large proportion by its solvent, is held in solution by a singularly feeble force. Hence colloids are generally displaced or precipitated by the addition to their solution of any substance from the other class. Of all the properties of liquid colloids, their slow diffusion in water, and their arrest by colloidal septa, are the most serviceable in distinguishing them from crystalloids. Colloids have feeble chemical reactions, but they exhibit at the same time a very general sensibility to liquid reagents. . . .

" The inquiry suggests itself whether the colloidal molecule may not be constituted by the grouping together of a number of smaller crystalloidal molecules, and whether the basis of colloidality may not really be this composite character of the molecule."[21, 22]

As indicated above, Graham found that the solution of a colloid would not pass through a membrane of a solid colloid, while solutions of crystalloids do so with the utmost ease. This property is of the greatest importance as a practical means of freeing solutions of colloids from crystalloidal impurities, i.e., by so called dialysis.

While Graham gave the name colloid to the solid substance apart from the liquid in which it is dissolved, more recent work by Krafft and Paal[18] has shown that the solvent cannot be neglected, as we now know many substances which are crystalloids as regards solution in water, but colloids when dissolved in other solvents, and conversely. Consequently, we now speak of colloidal solutions, for which we retain the names hydrosol, alcosol, glycerosol, etc., given by Graham to colloidal solutions in water, alcohol, glycerine, etc.

Very little advance in the study of these solutions was made for thirty years after Graham's fundamental discovery. In 1882, Schultze[23] found that the hydrosol of arsenious sulphide agreed, in many of the more essential points, with the hydrosols of iron oxide, etc., described by Graham. Spring[24] and Ebell,[25] in 1883, working with colloidal metal sulphides, noticed the analogy that obtained between those solutions and the finest suspensions of ultramarine in water. This work affords the first suggestion that one might be able to trace a continuous gradation in the size of the particles of a solid in solution, from that of the ordinary crystalloidal molecule, through the dimension of the colloidal particle which appeared to Graham "as a grouping together of a number of smaller crystalloidal molecules," to the grosser complexes in ordinary suspensions, as that of ground porcelain in water. This, in fact, expresses the modern view of the colloidal particle in solution. The idea of a continuous transition from the crystalloidal molecule to the coarse particle had its first proof in the experiments of Linder and Picton,[26] who were able to prepare by various methods four different grades of solution of arsenious sulphide; these different samples they classified according to the size of the aggregate of the sulphide in solution, thus:

As_2S_3 (α) aggregates visible under the microscope.
As_2S_3 (β) aggregates invisible but not diffusible.
As_2S_3 (γ) aggregates diffusible but not filterable.
As_2S_3 (δ) aggregates diffusible and filterable but scattering and polarizing a beam of light.

Previous to the work of Linder and Picton, in 1889, a modification of silver soluble in water had been prepared independently by Loew, Muthmann,[28] and Carey Lea.[29] This was shown by Prange[30] to be a colloidal solution of silver. Hydrosols of other metals have been prepared chemically since then by Lobry de Bruyn,[31] Zsigmondy,[32] Lottermoser,[33,34] and others.

From the fact that the metals of electrodes between which an electric discharge is passing are sputtered off in a finely divided state, Bredig[35] was led to the discovery of a unique method of preparing metallic colloidal solutions in water, merely by sparking electrically between metal electrodes underneath the surface of pure water. In this way he produced solutions of platinum, gold, silver, palladium, and cadmium. Svedberg[36] has extended this method to the production of solutions of sodium, potassium, and rubidium in certain organic liquids. The writer has also prepared solutions of a number of metals in water, the alcohols, and ethyl malonate.[27]

The whole series of colloidal solutions has been divided into two classes, known respectively as reversible and irreversible hydrosols—terms first suggested by Hardy.[37, 38] The determining factor which places a given colloid in one or other of the two classes is the demeanour of the dry residue left after evaporating the solution. If, by the addition of pure water to this residue, the colloidal solution may be reclaimed in its original state, the colloid is called reversible; if the residue is insoluble in pure water, the colloid is known as irreversible. From this point of view, dextrin, gum-arabic, most kinds of albumen, molybdan oxide, gelatine, wolfram acid, etc., are reversible colloids; while the irreversible group consists of the various colloidal oxides, sulphides, stannic acid, as well as the pure metal sols. This is practically the same division as Noyes[39] has made, except that he calls the two classes colloidal solutions and colloidal suspensions respectively.

It remained for the recently invented ultramicroscope to afford optical evidence in unique fulfilment of the forecast suggested by Graham. As is apparent from the work of Linder and Picton referred to above, colloidal solutions contain aggregates graded in size from particles of ordinary mechanical suspensions, visible under the common microscope, down to those which are as small as, or smaller than, the largest molecules of true crystalloidal solutions. Very exhaustive observations, by means of the ultramicroscope, on the sizes of particles in various solutions, have led to the identification of particles much smaller than the former limits of the microscope, leaving a very small gap between the dimensions of the smallest particles actually visible and those usually accepted for the chemical molecule; while, as the Tyndall phenomenon shows, we are not without quite conclusive proof of the existence of particles with dimensions which would bridge that gap. An idea of the size assigned to the various particles is given by Figure 1, in which the different solutions are arranged vertically in order of the sizes of the aggregates in each. (*Vide* Zsigmondy: Zur Erkenntnis der Kolloide, p. 22.)

FIG 1.

III. PREPARATION AND CLASSIFICATION OF COLLOIDAL SOLUTIONS

As the foregoing section illustrates, we have progressed far from Graham's simple classification of all substances into colloids and crystalloids. Graham's work dealt entirely with what happens when two or more chemical individuals are brought together, and the phenomena involved by this union are not at all so simple as one would gather from some of the recent writings on the subject. Although Graham is careful to point out the diversity which really exists in the action of colloids as a class, succeeding writers have tried to include under one comprehensive explanation the workings of all so called colloids.

An important step forward was made in the subdivision, due to Hardy, into reversible and irreversible colloids, and the almost parallel classification first made by Billitzer into hydrophilous and anhydrophilous colloids. As we shall see later, the very marked divergence in the properties of the two classes justifies the discrimination. However, misunderstandings and apparent discrepancies are still being induced by the unnecessary assumption that there is a fixed common action of all colloids of even the irreversible (or anhydrophilous) class. In his recent paper Duclaux,[40] working with colloidal solutions "synthetically prepared by a double decomposition," e.g., ferrocyanide of copper, "assumes, until the contrary is proved, that a property common to such substances of different chemical composition and arrangement can be considered as a general property of colloids." As a result he arrives at conclusions quite contradictory of the formerly published work of Hardy and others, notwithstanding the fact that Hardy[41] had already pointed out that "colloidal solutions differ in their relation to small concentrations of salts, some, such as the hydrosols of metals, of silica and alumina, etc., are precipitated, others appear not to be changed, such as, for instance, hydrosols of albumen or gelatine, others again depend for stability upon the presence of salts."

As a consequence of these facts it seems advisable to insist on a more exact classification which will recognize the experimental divergence exhibited by colloids. The very methods of synthetical preparation of the various solutions suggest a further subdivision; consequently I propose to outline these subclasses and indicate the general types of the methods of preparation of each sub-class.

The unanimity of deportment of the various hydrophilous colloids—agar-agar, gelatine, gum-mastic, etc.—justifies their retention for the present in one class. When we come to the consideration of the anhydrophilous colloids, at least four classes are suggested by the phenomena exhibited.

1. First, we may group together those which have the appearance of very fine suspensions of quite simple uniform particles; they are noticeable in their extreme sensitiveness to added electrolytic solutions, and have usually a very low electrical conductivity. Under this class are included the Bredig metallic solutions, Zsigmondy's gold solutions, tannin, etc. The Bredig solutions are prepared in pure water, contain particles visible in the ultramicroscope, and, usually, the particles shew an electrical charge.

2. Closely allied to those named above, we have a large class which depend for their stability upon a trace of salt absorbed by the colloidal particle. For example, Duclaux prepared his solutions of colloidal copper ferrocyanide by the reaction of potassium ferrocyanide on cupric chloride and found that the colloidal particle (copper ferrocyanide) entangled a certain quantity of potassium; as the percentage of potassium was decreased the stability of the colloid decreased, and the particles tended to coagulate when the potassium content was reduced to zero. The coagulating power of electrolytes appeared to him to be due to the substitution of a new ion for the potassium of the particle, although it is not quite clear how this action results in coagulation. One can see, however, how difficult it would be to compare in a just manner the work of two different men on the action of various samples of this colloidal solution. Although the above may serve as a type of the class, we may mention the following experimental facts which would serve to indicate additional members of this second sub-class of anhydrophilous colloids:

(*a*) Hardy gives the example of acid and alkali globulin as a true example of this class—the acid globulin retaining the negative radical of the acid, etc.

(*b*) The historically important ferric hydrate colloidal solution depends for its stability on a trace of the retained ferric chloride, as dialysis to remove the chloride brings about coagulation.

(*c*) Purified egg-albumen always contains chlorine enough to react on silver nitrate.

(*d*) Salicic acid nearly always contains traces of potassium, sodium and hydrochloric acid; continued dialysis produces coagulation.

(*e*) The metallic sulphides, e.g. As_2S_3 and Sb_2S_3, probably depend for their stability upon a slight trace of entrained H_2S. Of all named in this class, these probably most nearly approach sub-class 1.

(*f*) As additional examples of this action we may refer to the work of Jordis[42] on silicic acid, Lottermoser[43] on silver iodide.

It is important to point out that in some cases, e.g., with copper ferrocyanide, and silver iodide, after the coagulum is formed, addition of the particular stabilizing ion in certain concentration to the moist coagulum reproduces the colloidal solution, and in this way these colloids approach those of the reversible class.

3. Cassius purple affords an example of what may really prove to be a large class; namely those solutions whose particles are really complexes of two different kinds of irreversible colloidal particles. " This purple, an apparently homogeneous, gelatinous precipitate, was looked upon by Berzelius as a chemical compound of stannic acid, gold oxide and tin oxide, on account of its apparent homogeneity and its solubility in ammonia. Other authors called it a mixture of metallic gold and tin oxide. The formula which Berzelius adopted for his compound was in such good agreement with the analysis that there was no way of deciding the question analytically. It was first shewn by synthesis of the gold purple from its components that it was not a chemical union but an intimate mixture of colloidal

gold and colloidal stannic acid."[18] As in the case of salicic acid and stannic acid, which are changed from coagulum to solution by the addition of alkali, so also alkali added to the Cassius purple hydrogel (coagulum) reproduces the hydrosol state.

4. This sub-class owes its existence to the peculiar action of reversible colloids on irreversible solutions. It is noted above that colloids of this latter class are, generally speaking, keenly sensitive to additions of comparatively small traces of electrolytes, while those of the former class remain in solution even in the presence of large quantities of electrolytic solutions. By adding a very slight trace of a reversible colloid, e.g., gelatine, to an irreversible colloid, the former acts as a protector to the particle of the irreversible colloid so that the latter is no longer coagulated by salts. Moreover, if the mixture be evaporated, the colloidal solution may be reproduced by dissolving in pure water. Gelatine added to the solution of sub-class (1) assumes the rôle of a protective colloid (*Schutzkolloid*). Gelatine added to solutions of $AgNO_3$ and KI produces on mixing the two solutions a protected colloid, AgI. Carey Lea's silver, Paal's gold, Mohlau's colloidal indigo belong to this class.[18]

From the foregoing classification, one may expect great variety in the properties of the various colloidal solutions, and still, through it all, the merging of one class into another makes any definite theory of their actions a difficult matter.

IV. GENERAL PROPERTIES OF COLLOIDAL SOLUTIONS

Notwithstanding the differences which separate the various classes of colloidal solutions there are certain properties which are common to the whole series, and other characteristics which, as yet, have not been assigned to every colloidal solution, but which are general in the sense that they are not confined to one group of solutions. A review of these special colloidal characteristics will serve to give a short survey of the field to be covered by the sections which follow.

Historically the fundamental characteristic is that they diffuse into pure water with extreme slowness. They shew hardly measurable effects on the boiling point, freezing point, surface tension (at the air-solution surface), or vapour pressure of the pure solvent. In general they are found to pass readily through the best filter papers, and when viewed with the highest power of the ordinary microscope no particles can be detected in the solution. By means of gelatine filters specially prepared to withstand pressure, Bechhold[44] has shewn that it is possible by filtration under pressure to remove entirely from any solution very small particles of size above any given minimum; he has been able so to grade his filters as to give the sizes of particles in solution by finding which filter of a series holds back the particles from the filtrate. The foregoing properties indicate, in the light of the modern theory of solutions, that the colloids in solution have an extremely large molecular weight.

When a beam of light is passed through a tube containing some of the solution, and viewed at right angles to the direction of the beam, the diffused light is found to be polarized—a phenomenon which indicates, for a small volume of liquid such as we usually employ, the presence of small particles approaching in dimension the wave length of light (Rayleigh[7]). Such particles were first rendered visible by means of a special apparatus, the ultramicroscope designed by Zsigmondy and Siedentopf[5], and afterwards modified by Cotton and Mouton.[13] When viewed by the ultramicroscope the particles are seen to be in constant motion, the Brownian movement, so called after Brown.[45]

Probably the most interesting property of these solutions is the movement of the particles under the influence of an electric field: for nearly every colloidal solution, if two electrodes, between which a difference of potential is maintained, are introduced into a vessel containing the solution, the particles move toward one or other of the electrodes. (*Vide* Burton.[27])

It can hardly be doubted that the stability of colloidal solutions is dependent in a great measure on the charges carried by the particles. If the chief stabilizing effect is due to these charges, an easy explanation of coagulation of solutions by freezing and thawing is at once suggested, as we shall see later.

Intimately connected with the possession of a charge by the particle is the behaviour of irreversible colloids and a few reversible ones towards electrolytes. The addition of small quantities of electrolytes causes the colloid particles to be completely precipitated from the solution. The very weak action of electrolytes on reversible colloids, together with rôle of these solutions as Schutzkolloide towards the irreversible class, has already been referred to in the last section.

Not only do colloids diffuse very slowly through pure water but, also, they cannot diffuse through one another. Consequently, a membrane of reversible colloid will not allow the passage of any colloidal solution through it, but offers no perceptible obstruction to the free transmission of most crystalloidal solutions—a circumstance which leads to the process of dialysis.

Of great interest from a chemical and physiological point of view is the very strong catalytic action that platinum colloidal solution shews in bringing about the decomposition of hydrogen peroxide. This phenomenon, which may be only one phase of the absorptive properties of the colloidal particles, is the basis for Bredig's designation of his electrically prepared solutions as inorganic ferments.

Although the magneto-optical and permeability properties of colloidal solutions containing the ferromagnetic metals would appear very limited in their application to colloidal solutions in general, it is to these solutions that we have to look for any direct evidence on the form and structure of the colloidal particle, and for important indirect evidence as to its constitution.

The succeeding sections will be found to treat of the properties outlined above and will deal more particularly with the action of the Bredig metallic solutions.

V. THE ULTRAMICROSCOPE

Limits of visibility with the ordinary microscope.—Until some five years ago the practical development of the microscope had apparently reached a limit as to the smallness of objects which it could render visible. As far as the pure geometrical theory is concerned, there is really no limit to the magnification possible with a high power microscope. Several grosser reasons, such as convenience of size of instrument, dispersion of light by lenses, absorption and reflection of light passing through a complex lens system, as well as corrections necessary for spherical aberration, coma, astigmatism, curvature of image and distortion, offer practical difficulties to the realization of extremely high magnification. However, the fundamental difficulties in the way of very high magnification are due to the phenomenon of diffraction; the theoretical treatment by which the limit that diffraction sets to the resolving power of the microscope is determined is due chiefly to Helmholtz,[46] Rayleigh,[1, 2] Abbe[3] (see also Porter[47]).

As is well known from the simple diffraction experiments, a point on an object viewed through a system of lenses will not be represented by as fine a point on the image, but will be blurred into a spot of light. If now two points viewed are so close together that these diffraction discs overlap, one would be unable to differentiate the two object points. As has been shown by Rayleigh, the linear separation of two such points, visible as distinct from one another in a microscope, must be at least

$$\frac{\lambda}{2n \sin \alpha}$$

where λ = wave length (*in vacuo*) of light used,
n = refractive index of medium between the object and the objective of microscope,
α = angular aperture of the microscope
($n \sin \alpha$ is called the numerical aperture).

Consequently, other things being equal, in order to decrease the allowable distance between two points, it will suffice to (1) increase α, (2) increase n (i.e., increase the angular aperture of the instrument), or (3) decrease λ.

The Zeiss firm have exerted every effort to take complete advantage of the conditions (1) and (2). By the manufacture of special glasses α has been increased to 73 ° (i.e., $\sin \alpha = .95$), while by the use of immersion objectives, i.e. the introduction of liquids of high refractive indices between the objective and the object, the value of n becomes for water 1.33, for oil of cedar 1.515, for monobromonaphthaline 1.66, etc. The greatest value of the numerical aperture obtainable is virtually 1.53. Taking account of these perfections, the limit of the visibility of small objects by the ordinary microscope is 4×10^{-5} cms., or about the wave length of the light in the middle of the visible spectrum, and experiment has shown that if the size of a small object is below this limit, one can form no idea of its form or size.

The advantage to be gained by decreasing the λ, the wave-length of the light used, has been seized on in the construction of special microscopes for the use of ultraviolet light, but the gain in power is not commensurable with the complexity and expense of the apparatus.

The Ultramicroscope—The foregoing theory applies to the ordinary method of microscopic vision, i.e. by viewing small obstacles in the path of light coming to the eye. The problem is quite different when we are dealing with self-luminous particles, especially if they are on a dark background. For example, we see, as points of light, stars the apparent diameters of which are below the resolving power of the largest telescope: however, we are not able to say anything as to their form or detail. Again, in the case of the spinthariscope of Crookes[48] we see self-luminous points of light which must be much below the resolving power of the microscope used. Fortunately, we are able to take advantage of the diffraction phenomena exhibited by suspended fine particles, and by proper illumination make such particles self-luminous.

A small opaque object intensely illuminated diffracts the light in every direction and acts like a new source of light. We owe to Tyndall the first recognition of this phenomenon. If to a dilute solution of hydrochloric acid some dilute hyposulphite of soda be added, small particles of sulphur form and gradually increase in size; when an intense beam of light is passed through the solution, light is diffused in every direction; it is of blue colour while the particles are small, and is found to be partially polarized. This phenomenon is quite analogous to the very common means by which particles of dust floating in the atmosphere of a darkened room may be made visible by casting a bright beam of light into the room and viewing the light at right angles to its direction. The particles appear as bright moving specks, due to the light diffused by them. These phenomena, first accentuated by Tyndall,[4] formed the basis of very important work by Rayleigh, in which the latter developed the accepted theory of the cause of the blue colour of the sky.[7, 8, 9]

Zsigmondy and Siedentopf[5] used this principle of illumination in the construction of the first ultramicroscope. Figure 2 illustrates the principle of their apparatus, a full description of which can hardly be included in this paper. An intense thin beam of light is focussed in the interior of a solid or liquid containing very fine particles in suspension; the microscope O, of quite ordinary construction, is focussed on the point P, and as the particles come into the path of the incident beam each one diffuses light up the tube of the microscope, and consequently appears as a bright point on a dark background.

FIG. 2.

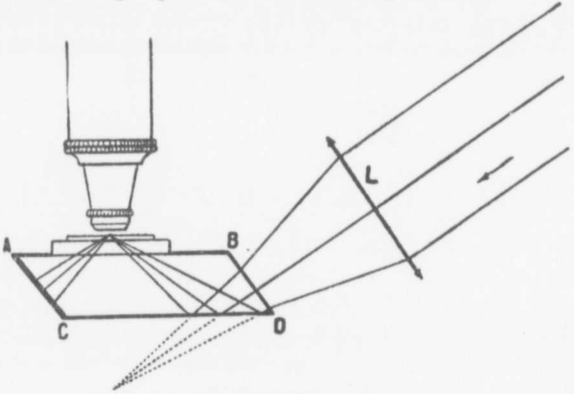

FIG. 3.

Cotton and Mouton[13] have produced an arrangement rather simpler than that of Zsigmondy and Siedentopf, but use the same fundamental principle. The apparatus is shown diagrammatically in Figure 3, which somewhat exaggerates the relative sizes of the smaller parts.

A drop of the solution to be examined is enclosed beneath a thin cover glass on a microscopic slide. The plate is placed on a special block of glass, A B C D, good optical contact being made by an intervening thin layer of liquid, e.g. cedar oil, whose refractive index does not differ much from that of the glass. The block, A B C D (for which a Fresnel rhomb serves very well), allows the direction of a beam of light to be easily adjusted so that, after being internally reflected at the lower surface, C D, the succeeding internal reflection at the upper surface may be made to take place at the critical angle. The proper adjustment of the lens, L, and block allows the beam to

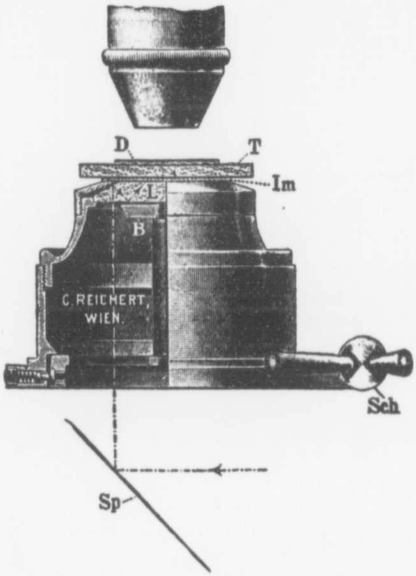

FIG. 4.

come to a focus just at the drop of liquid. As the particles in the solution come into the path of the beam, the light striking them is now no longer totally reflected, but is scattered into the microscope. As the field of view is otherwise dim, the appearance is that of a sky filled with moving stars—the Brownian movement of the particles being at once recognized. No means is afforded of directly comparing the size or shape of the particles as, in general, the better they are in focus, the smaller they appear.

A very convenient and inexpensive form of ultramicroscopic accessory for any microscope is manufactured by Reichert (Vienna).[49] The arrangement which is shown in section in Figure 4 consists of a special condenser, by which the ordinary reflecting mirror of a microscope can be used to transmit light used to illuminate the drop of liquid in a manner quite analogous to that adopted by Cotton and Mouton. The illustration shews the course of the illuminating light with sufficient clearness. This form has the advantage of being adjustable to the stage of any microscope, and is quickly set up for use.

Determination of the size of Ultramicroscopic Particles—As has been noted above, the ultramicroscope reveals to us merely the presence of particles in a transparent solid or liquid, and gives us no direct evidence as to the size, shape or structure of the particles. As applied to colloidal solutions, there are three ways in which the size of the particle may be obtained; namely,

(1) by comparing the brightness of the images,

(2) by observing the mean distance between the suspended particles and weighing the material in unit volume,

(3) by counting the number in a unit volume and weighing the material in that volume.

The first method is one merely for comparing the sizes of particles in solution, and is not of use for exact measurements.

In the second proceeding, if r equals the mean distance in cms. between the particles, and if we consider them to be small spheres, then l, the length of the radius of the sphere, is given by

$$l = r \cdot \sqrt[3]{\frac{3A}{4\pi d}}$$

where A = weight of the particles in unit volume of the liquid and

d = the density of the particle in solution.

The number A may be found by evaporating a given volume of the solution and weighing the residue, while d is taken equal to the density of the particle, e.g. gold, in its ordinary solid state. Of course there is no way of testing the justice of this latter assumption.

The third method was that used by the writer in determining size of colloidal particles.

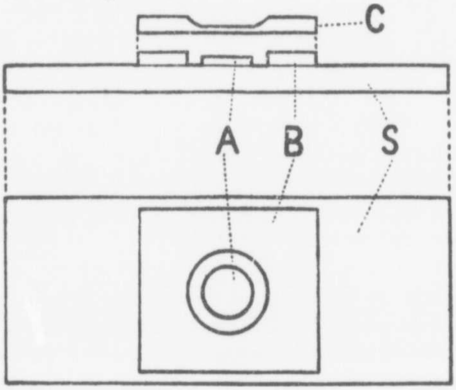

FIG. 5.

The difficulty of determining the volume of liquid viewed was overcome by the use of the special Zeiss slide, used by physiologists in counting the number of blood corpuscles in a unit volume of diluted blood. Figure 5 shews the construction of the slide. At the centre of a circular piece of glass, A, an area of 1 sq. mm. is divided in small squares of 1/20 mm. side by means of fine lines ruled with a diamond point. The plate B surrounds A so as to leave an annular trough about the central disc. The upper surface of B is exactly .1 mm. above that of A, so that when the cover glass C is placed on B a layer .1 mm. thick exists between A and C. The surfaces of A, B, and C are of course ground perfectly plane. When a drop of a sol is placed on A and covered with C, a volume of .00025 cu. mm.

can be discerned through the microscope. By raising and lowering the objective very slightly, it is possible to bring all the particles in a layer .1 mm. thick into view and so, for very dilute solutions, the number of particles per cu. mm. can be very approximately determined. A microscope which magnified about 350 times was used and the slide was moved slightly so that the particles corresponding to 400 of the unit volumes (each .00025 cu. mm.) were counted.

The Brownian movement, at any rate in such a thin layer of liquid, did not shew any constant drift of the particles, and the probability is that as many moved into view a second time as escaped count altogether. It required about one hour to count the number in .1 cu. mm. of solution.

If the amount of metal in 1 cc. of a given colloidal solution can be ascertained, then, assuming that the specific gravity of the metal in this state of fine subdivision retains its ordinary value, an idea of the size of each particle can be obtained from knowing the number of particles in unit volume. Such determinations have been made by the writer for the colloidal solutions of platinum, gold and silver. The weight of metal in a given volume of the solution was obtained by evaporating the liquid in a previously weighed porcelain crucible and finding the weight of the residue; the weight of dissolved impurity remaining after evaporation would be practically infinitesimal. The following is a sample of such determination, typical as regards method and the magnitude of the quantities involved:

A silver solution containing 6.8 milligrams of metal per 100 ccs. was diluted with distilled water to one hundred times its original volume. A drop of the dilute liquid shewed the presence of 300 particles in the volume, .1 cu. mm.

So that in the original solution, per cc., there are 3×10^8 particles which weigh 6.8×10^{-5} grams.

If the specific gravity be taken as 10.5, the mean volume of the particle in solution is 2.2×10^{-14} ccs.

Assuming that the particles are in the form of small spheres, the mean radius being a.

$$\frac{4}{3}\pi a^3 = 22 \times 10^{-15}$$

$$a = 1.7 \times 10^{-5}$$

Repeated determinations of the sizes of the particles in silver solutions gave results quite close to that recorded above. Table I gives the data of the calculation of the sizes in the case of three solutions.

TABLE I

Size of Particles in Silver Hydrosols

Sol.	Weight of silver per 100 ccs.	No. of particles per cc.	Volume of particle.
1	6.8 milligrams	3×10^8	2.2×10^{-14} ccs.
2	6.2 “	2.9×10^8	2.0×10^{-14} “
3	11.2 “	4.2×10^8	2.0×10^{-14} “

Zsigmondy has observed particles in gold colloidal solutions down to the size giving the linear dimension 20 to 80 $\mu\mu$. ($\mu\mu = 10^{-6}$ mms. $= 10^{-7}$ cms.) He found that when they deprived a colloidal solution of all its ultra-microscopically visible particles, the solution had still a faint opalescence and gave chemical reactions unique to the substance in solution.

The kinetic theory gives the following values to the size of the molecules named:

$H_2 = 0.1$ $\mu\mu$.
$CH_3OH = 0.5$ $\mu\mu$.
$CH_3Cl = 0.8$ $\mu\mu$.

The size of Zsigmondy's smallest visible particle is consequently only a small multiple of the size of the largest molecule. There are some colloidal solutions which give indications of large molecular aggregates which are still invisible in the ultramicroscope, e.g. some gold solutions, albumen, etc.

VI. MOTIONS OF PARTICLES IN AN ELECTRIC FIELD

1. *Cationic and Anionic Solutions*—The investigation of this property of the so called colloidal solutions dates from the work of Linder and Picton.[26] Prior to that, experiments on the motion of the particles of ordinary suspensions under an elec-

tric field had been carried out by various workers, and briefly the results obtained were as follows[50]:

In suspension in water the particles of starch, platinum black, finely divided gold, copper, iron, graphite, quartz, feldspar, amber, sulphur, shellac, silk, cotton, lycopodium, paper, porcelain, earth, asbestos, move towards the positive pole.

When the above materials are suspended in a similar manner in turpentine oil, they all move towards the negative pole, with the sole exception of sulphur, which moves in the same direction in turpentine as in water.

Fine gas bubbles of hydrogen, oxygen, air, ethylene, carbon dioxide, and small liquid globules of turpentine and CS_2, when in water, all move toward the positive pole.

Turpentine globules and small gas bubbles in ethyl alcohol move to the positive pole.

Quartz particles and air bubbles in carbon bisulphide move to the negative pole.

These results led Wiedemann to make the statement that "in water all bodies appear, through contact, to become negatively charged, while, through rubbing against different bodies, the water becomes positively charged."

When Linder and Picton tested similar properties of the particles in chemically prepared solutions, they found that such a generalization was inexact. They give the following results:

Suspensions of aniline blue, arsenic sulphide, indigo, iodine, shellac, silicic acid, starch and sulphur in water, and of bromine in alcohol, shew attraction to the positive electrode.

The following materials suspended in water move in the opposite direction: Ferric hydrate, hæmoglobin, Hoffman's violet, Magdala red, methyl violet and rosaniline hydrochloride.

As a conclusion to their work Linder and Picton make the significant statement that experiment seems to shew that, if the solution is basic or tends to break up so as to leave a free base active, the motion is to the negative pole, i.e. the particle is positively charged; if the solution is acidic, motion is to the positive pole, and consequently the particles are negatively charged.

Taking into consideration the recent results of many workers (e.g. Bredig[35] and Burton[27]) we may divide colloidal solutions and suspensions into two classes, anionic and cationic, according as the particles in solution move to the anode, i.e. are negatively charged, or to the cathode, i.e. are positively charged.

Solutions in water:

Anionic.

1. The sulphides of arsenic, antimony and cadmium.
2. Solutions of platinum, silver, gold.
3. Vanadium pentoxide.
4. Stannic acid and silicic acid.
5. Aniline blue, indigo, molybdena blue, soluble Prussian blue, eosin.
6. Iodine, sulphur, shellac, resin.
7. Starch, mastic, caramel, lecithin.

Cationic.

1. The hydrates of iron, chromium, aluminium, copper, zirconium, cerium and thorium.
2. Bredig solutions of bismuth, lead, iron, copper and mercury.
3. Hofmann violet, Magdala red, methyl violet, rosaniline hydrochloride, Bismarck brown.
4. Albumen, hæmoglobin, agar.

The charges on particles of starch, gelatine, agar, and silicic acid are very small and difficult to observe.

Bredig solutions[27] of lead, tin, and zinc in ethyl alcohol are all cationic, while bromine in the same solvent is anionic. Methyl alcohol gives Bredig solutions with lead, bismuth, iron, copper, tin, and zinc which are cationic. The writer has also prepared anionic solutions of platinum, silver, and gold in ethyl malonate by Bredig's method.

2. *Theory of Cataphoresis*—The theory of this motion of finely divided particles in suspension in liquids was long since propounded by Helmholtz[51] and later amplified by Lamb.[32] Without assuming, for the moment, anything with regard to the cause of the formation of the colloidal solutions, we may apply the same theoretical considerations to the movement of these particles.

The fundamental assumption is that when a particle suspended in a liquid becomes charged, there exists about it a double electric layer; when the particle is negatively charged, there is a layer of negative electricity on the surface of the solid particle, while in the liquid immediately surrounding it there is a corresponding layer of positive electricity. "On the whole the algebraic sum of the two equals zero, and the centre of gravity of the complete system, solid particle and surrounding positively charged fluid layer taken together, cannot be moved by the electric forces which arise from the potential fall in the liquid through which the current passes. However, the electric force will tend to bring about a displacement, relatively to each other, of the positively charged fluid layer and the negatively charged particle, whereby the fluid layer follows the flow of positive electricity while the particle moves in the opposite direction. If the liquid were a perfect insulator the new position would still be a condition of equilibrium. Since, however, through the displacement of the layers the equilibrium of the galvanic tension between the solid particle and the liquid is disturbed, and on account of the conductivity of the liquid always seeks to restore itself, the original state of electrical distribution will tend to be continually reproduced and so new displacements of the particle with respect to the surrounding liquid will continually occur."[51]

This theory was put forward by Helmholtz in the course of his mathematical development of the explanation (suggested by Quincke) of the electric transport of conducting liquids through the walls of porous vessels or along capillary tubes; Quincke assumed that there existed a contact difference of potential between the fluid and its solid boundaries. Throughout his treatment of the phenomenon, Helmholtz considers that there is no slipping of the fluid over the surface of the solids with which it is in contact. On this point Lamb disagrees with Helmholtz, holding that the solid offers a very great, but not an infinite resistance to the sliding of the fluid over it, and that, while the effect of this slipping would be entirely insensible in such experiments as those of Poiseuille, it leads to appreciable results in the present case in consequence of the relatively enormous electrical forces acting on the superficial film of the liquid and dragging the fluid, as it were, by the skin through the tube. The practical difference between the views taken by Helmholtz and Lamb respectively may be shewn in a simple case. Using the numerical results found by Wiedemann, Helmholtz infers that for a certain solution of $CuSO_4$ in contact with the material of a porous clay vessel, the contact difference of potential E between the solution and the solid wall is given by

$$\frac{E}{D} = 1.77$$

where D is the E.M.F. of a Daniell's cell. The variation introduced by Lamb would change this equation into

$$\frac{E}{D} \cdot \frac{l}{d} = 1.77 \qquad (1)$$

where $d =$ the distance between the plates of an air condenser equivalent to that virtually formed by the opposed surfaces of solid and liquid, and l is a linear magnitude, measuring the "facility of slipping" and equal to $\frac{\mu}{\beta}$, μ being coefficient of viscosity of the liquid and β the coefficient of sliding friction of fluid in contact with the wall of the tube. Lamb gives reasons for supposing that l and d are of the same order of magnitude (that of 10^{-8} cms). Of course if $l = d$, Helmholtz's formulæ remain unchanged, and it is very probable that the ratio $\frac{l}{d}$ differs very little from unity.

Lamb deduces the following expression for the velocity (v) of a charged particle through a liquid under an electric force, when the motion has become steady:

$$Xe = 4\pi a^2 . \mu . v \frac{1}{l} \qquad (2)$$

where $X =$ gradient of electric potential in the liquid
$e =$ charge on the particle
$d =$ radius of the particle
and μ and l as above.

We may look upon the particle with the double electric layer as a small condenser of two concentric spheres whose distance apart (d the same as before) is small compared with a.

The capacity of such a condenser would then be given by

$$C = \frac{a^2}{d} K \tag{3}$$

where $K =$ specific inductive capacity of the liquid.

If V indicates the contact difference of potential between the solid and the liquid, we have (since $Q = CV$),

$$e = V \frac{a^2}{d} K \tag{4}$$

Substituting this value of e in equation (2) and transposing we get

$$V . \frac{l}{d} = \frac{4\pi}{K} . \frac{\mu v}{X} \tag{5}$$

all electrical measurements being made in electrostatic units.

This equation, which is similar to one given by Perrin,[19] will enable us to find values of $V . \frac{l}{d}$ for any solid and liquid, if for known values of X, and we can observe the corresponding values of v.

We may deduce immediately from this formula that the velocity of a particle of given constitution, in a given liquid medium, is independent of the radius, and the product μv for a given solution must be constant.

3. *Method of Measuring Velocities*—Probably the best method of measuring the velocities of these particles is by means of a U-tube similar to that used by Whetham[53] and Hardy[37, 38] (Figure 6). That used by the writer consisted of a U-tube, each limb of which was about 12 cms. long, and about 1.5 cms. in diameter; the limbs were graduated in mms. throughout their length. Into the bottom of the U-tube is sealed a fine delivery tube provided with a tap (T) and a funnel (F); this tube is bent round so as to run up behind the limbs and to bring the funnel to the same height as the top of the U-tube.

The colloidal solution to be tried is poured into the funnel so as to fill the small tube and funnel to the tap, which is closed; water having a specific conductivity equal to that of the colloid is then poured into the U-tube so as to fill it to a height of about 3 cms. The whole tube may then be placed in a large glass water-bath so as to be almost submerged; this water should be kept at a constant temperature during the course of any experiment. At the end of a few minutes the tap (T) is opened very slightly and the colloidal solution allowed to gently force the water up the limbs of the tube to any required height. If carefully manipulated the surface of separation between the clear water and the solution is very distinct and will remain so for hours. Two electrodes of coiled platinized platinum foil are supported at a convenient level in the two limbs of the tube and the clear water allowed to rise well above them. The electrodes are attached to the terminals of a set of storage cells of constant voltage, and when the current is completed the surface of

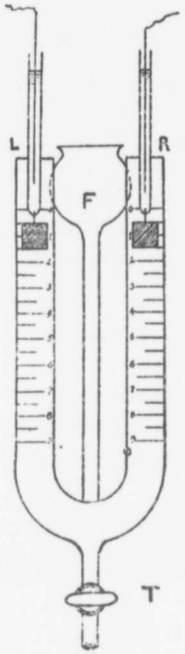

FIG. 6.

separation in one limb will at once begin to rise gradually while that in the other will sink. In practice, the connections may be made through a reversing key and the voltage, usually fixed at about 110 volts, may be left on one way for ten minutes and then reversed for twenty minutes. The velocity is reckoned from the displacement of the surfaces during this final twenty minutes; one-half the sum of the displacements in the two tubes should be taken as the distance travelled by a particle in the given time. A typical set of observations is given in Table II.

Table II.

Time.	Voltage—Sign of Right Electrode.	Temp.	Height of Colloidal Surface.		Observed Velocity in $\frac{\text{cm.}}{\text{sec.}}$
			Left.	Right.	
11.37	+ 118	11°C	54 mms.	55 mms.	
11.47	+ 118		51 "	50 "	
Current	off				
11.48	− 118	11°C	61 "	50 "	
11.58	− 118		55 "	56 "	96×10^{-6}
12.08	− 118	11°C	50 "	62 "	

Electrodes at 15 mms. in each limb.

It will be seen from the Table that there has been an apparent settling of the colloid in the tube while the current was running. This is quite usual but, as the reckoning is made, it could not affect the rate, since this slight lowering of the surface is uniform in both limbs, so that while it is added to the velocity in one limb it is subtracted from the velocity in the other.

In order to find the value of the electric force in the tube, it is of course necessary to know the effective distance between the electrodes A and B. To do this the tube is filled with, say, a .01 normal KCl solution, placed in the water bath, and the resistances are taken with the electrodes placed at the successive centimetre marks down the tube. In this way, for the particular tube used for the above results, it was found that the resistance of the curved part of the tube from 90 in L to 90 in

R was 8.8 times the resistance of each cm. length of the single limbs. So that when, as in the case cited in Table II, the electrodes were placed at 15 in each tube, the effective distance between the electrodes was 23.8 cms., and therefore the strength of the electric field was $\frac{118}{23.8} = 4.9$ volts per cm. Thus the absolute value of the velocity of the silver particles in water at a temperature of 11°C. would be 19.6×10^{-5} cms. per sec. per volt per cm.

4. *Experimental Values of "v"*—In Table III are given the velocities of the particles of various aqueous colloidal solutions prepared by Bredig's method. The temperature in each case is 18°C. The minus sign indicates that the particle bears a negative charge; the positively charged particles have the plus sign before the velocity number.

TABLE III.[27, 54]

Velocities of colloidal particles in cms. per sec. per volt per cm. at 18°C.

Metal in solution.	Specific conductivity of solution 18° C.	Velocity.
Platinum	21.3×10^{-6}	-20.3×10^{-5}
Gold	10.5×10^{-6}	-21.6×10^{-5}
Silver	19.0×10^{-6}	-23.6×10^{-5}
Mercury	3.0×10^{-6}	-25×10^{-5}
Bismuth	7.0×10^{-6}	$+11.0 \times 10^{-5}$
Lead	15.0×10^{-6}	$+12.0 \times 10^{-5}$
Iron	9.4×10^{-6}	$+19.0 \times 10^{-5}$
Copper	6.5×10^{-6}	$+25.4 \times 10^{-5}$

The solutions of platinum, gold, silver, and copper are extremely stable, the metals remaining apparently uniformly in solution for months, while the solutions of bismuth, lead, iron, and mercury are precipitated in the course of a week or so. The bismuth solution is dark brown in colour, not unlike the silver solution in appearance. The lead solution is initially dark brown as well, but if left in contact with the air the particles rapidly turn white, doubtless on account of the formation of a carbonate; but whether in the brown or white state, the particles move to the negative electrode in an electric field. The iron solution always possesses a reddish brown colour, which points to formation of a hydroxide; this quite agrees with the fact given by Linder and Picton that in chemically prepared colloidal solutions of ferric hydrate, the particles move toward the negative electrode. The copper solution is of yellowish brown colour.

If there are particles of varying sizes present in any one solution, no indication of any difference in velocity of the various particles was evident; however, this does not justify the assumption that the particles are all of the same size, because according to the theory given by Lamb, the velocity of similarly constituted particles is independent of the size and shape. This would mean that the potential of each particle in a given solution is constant. If particles of different sizes do exist in these electrically prepared solutions the size would probably depend on the violence of the sparking during the preparation of the solution. Three silver solutions were prepared by using varying currents and voltages for producing the spark, all other conditions being the same except the time of sparking. As shewn in Table IV, the differences in the velocities, which were all determined at 11°C, are all within the limits of error in the experiment.

TABLE IV.

Silver Solutions.

No.	Voltage.	Current.	Time of sparking.	Velocity in $\frac{\text{cm.}}{\text{sec}}$ per $\frac{\text{volt}}{\text{cm.}}$
1	80 volts.	8.5 amperes.	10 mins.	$-19.7 \times 10^{-}$
2	60 "	7.5 "	20 "	-19.6×10^{-5}
3	40 "	6.5 "	30 "	-19.3×10^{-5}

Since there is no *a priori* reason for assuming that all the particles are of a uniform size, these results would confirm Lamb's theory.

It is important to point out that the velocities of these colloidal particles are very little smaller than the velocities of such ions as potassium, sodium, lithium, silver, chlorine, nitrate, etc. (Whetham[53]). Accepting Lamb's conclusion that the velocities with which small particles move under given forces are independent of the size, we see that the velocities of the colloidal particles could be produced if these particles possessed merely a charge equivalent to that of one ion.

As we shall see later, the velocity with which these particles move is greatly affected by the introduction of extremely small traces of electrolytes, and, consequently, one gets some variety in the values of the velocity obtained when the specific conductivity changes. For example, copper solutions, the specific conductivity of which varied from 3.1×10^{-6} to 8.2×10^{-6}, gave velocities varying from 33.0×10^{-5} to 23.4×10^{-5} cms. per sec. It is impossible, therefore, to assign a definite number as the transport number of a particular colloidal particle.

5. *Effect of Viscosity of Solution*—The writer has carried out a series of experiments on the validity of the formula given on page 38, in so far as $\mu v =$ constant, as long as one deals with the same material in the particle and the same liquid medium.

TABLE V

Silver Colloidal Solutions.

No.	Temperature Centigrade.	Velocity (v).	Viscosity of water at given temperature μ	Product μv.
1	3°	15.1×10^{-5}	.016214	24.5×10^{-7}
2	9.9°	18.6×10^{-5}	.013300	24.7×10^{-7}
3	11°	19.6×10^{-5}	.012822	25.1×10^{-7}
4	21°	25.5×10^{-5}	.009922	25.0×10^{-7}
5	31°	30.1×10^{-5}	.007972	24.0×10^{-7}
6	40.5°	37.2×10^{-5}	.006577	24.5×10^{-7}

In Table V are given the velocity determinations for silver colloidal solution in water over a range of temperatures from 3°C to 40.5°C. In performing these experiments the water bath in which the velocity tube was always supported was heated and the water constantly stirred; the temperature was maintained constant at any one time by the use of an ordinary thermostat. The sensibly constant value of μv is in good accord with the requirements of the velocity formula.

These experiments also indicate the primary importance of taking account of the temperature in this work; a neglect of the influence of changing temperature in any form of apparatus for measuring these velocities leads to bewildering results.

A fundamental necessity for the validity of velocity results obtained in the manner indicated in Section 3 is that the specific conductivity of the superincumbent layers of water should be the same as that of the colloidal solution at the lower part of the tube. As those conductivities in each case were made equal at the ordinary temperature of the room before being introduced into the velocity tube, evidently in order that the results may be of any value the temperature coefficients of the two liquids should be the same. These coefficients were compared for a sample of silver colloidal solution and a quantity of water of very nearly the same initial conductivity. The values of the resistances of these liquids at various temperatures are recorded in Table VI, and illustrated by the curves in Figure 7. From these we may safely conclude that the temperature coefficient of the resistance of colloidal silver solution is that of water itself.

TABLE VI

Temperature coefficients of resistance.

Temperature (Cent.)	Resistance of water (Arb. Sc.)	Resistance of Ag. Sol. (Arb. Units).
10	5600	....
15	....	4640
20	4420	4180
25	3910	3720
30	3510	3350
35	3150	3030
40	2900	2790
45	2660	2520

It is quite justifiable to apply these results for silver solutions to the manifestly analogous solutions of the other metals in water, and probably to colloidal solutions in general.

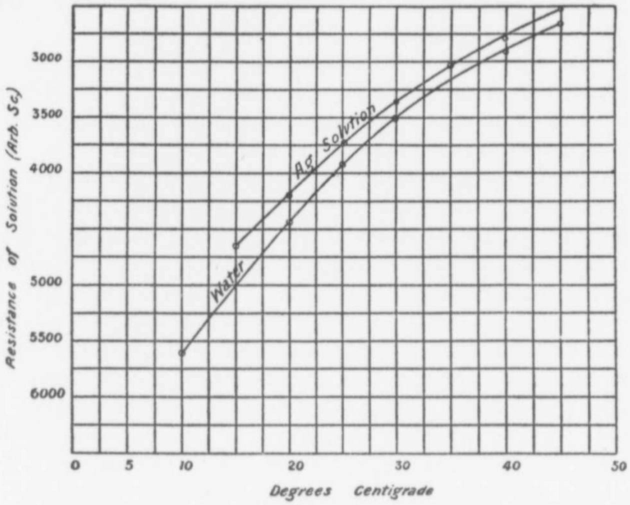

FIG. 7.

VII. THE EFFECT OF THE MEDIUM

1. *Experimental Results*—It has already been pointed out how inadequate was Graham's conception of a solid colloid being such *per se*. We know now that when we deal with colloids we are treating of what happens when two or more chemical individuals are brought together. It is not right therefore to divide chemically simple substances into two classes, colloids and crystalloids. We have many illustrations of the fact that one substance may belong to both classes if we take into consideration different liquid media.

Krafft has shewn that the alkali salts of the higher fatty acids, e.g. sodium stearate, sodium palmitate, sodium oleate, the chief of the soap fats, dissolve in alcohol as crystalloids with normal molecular weights, but that in water they are true colloids. According to Paal sodium chloride, which is *par excellence* a crystalloid in relation to water, easily gives a colloidal solution of sodium chloride in benzol. Tannin, when dissolved in glacial acetic acid, gives a normal molecular weight (322) from the lowering of the freezing point; however, in water, similar determinations indicate a molecular weight of from 2643 to 3700 (i.e. groups of from 8 to 12 molecules), and when a drop of the aqueous solution is examined with the ultramicroscope particles may be seen.

The influence of the medium is also shewn in the preparation of various aqueous solutions. Gum mastic is dissolved in alcohol, and this solution poured into water; the alcohol may be dialysed off, leaving mastic particles suspended in water. White of egg alone appears optically empty, but when dissolved in distilled water gives increasingly marked ultramicroscopic effects. On the other hand, glycogen freshly prepared gives under the ultramicroscope a large number of particles, but on standing the particles gradually disappear.

Not only in the preparation of the colloid is the influence of the medium all important, but variations in the medium often produced changes in the charges in the particles. It will suffice in this connection to recall the work of Hardy[37, 38] on albumen, in which he demonstrated that, if the solution were slightly acidic, the particles are positively charged, whereas if the solution were basic, the particles are negatively charged. It has been shewn by the writer[55] that the addition of certain electrolytes to the metallic hydrosols has the power to change the sign of the charge carried by the particles in solution.

A consideration of the classification of the Bredig metallic hydrosols and alcosols, given in Section VI, sheds light on the influence of the medium. In this connection, interesting phenomena have been observed by the writer[27] in work on the Bredig metallic sols. In the results given in Table III, one is struck with the fact that the particles of the more electro-positive oxidizable metals are all positively charged, while the more electronegative non-oxidizable metals give negatively charged particles. When we recall that the iron in such solutions appears to form the hydrate, and that the particles bear a charge of the same sign as the particles in chemically prepared colloidal solutions of ferric hydrate, one is justified in suspecting that in the cases of iron, bismuth, lead and copper the process of manufacture of these electrically prepared solutions involves the production of a certain amount of the hydrate of the metal. Such an hypothesis at once suggests an analogous action on the part of gold, silver, platinum and mercury, viz. an interaction between the metal and hydrogen—a view to which the already known existence of a hydride of platinum would lend some colour.

The suggestions given by these results for the hydrosols are strengthened by the observations on colloidal solutions in the alcohols, which we may call, after Graham, alcosols. Pure methyl alcohol and pure ethyl alcohol were used in the preparation instead of water.

Although repeated trials were made with the metals gold, silver, and platinum, the writer has never succeeded in getting them to remain suspended in either of these alcohols. On the other hand, the metals lead, tin, and zinc form solutions in both of the alcohols, while with methyl alcohol solutions were also obtained with bismuth, iron and copper. In all these solutions the particles moved to the negative electrode in an electric field, i.e. they are positively charged.

Viewing these results in the light of the chemical nature of the alcohols, the former suggestion as to the interaction between the liquid medium and the metals is strengthened. Although these alcohols have a neutral reaction, they act like weak bases in combining with acids to form salts, or, in other words, they have an easily replaceable OH group. Those easily oxidizable metals would thus be able to form at least a surface coat of hydrate, while the metals gold, platinum, silver, whose existence in a colloidal state we have been led to suspect to depend on a replaceable hydrogen in the liquid, cannot form in the alcohols.

A still further test of this hypothesis is afforded when one uses as the liquid medium a substance which has a replaceable H and not an OH. Anhydrous acids might be used, but there is great difficulty in keeping them free from water, and, as is well known, electrolytes containing acids have extremely strong power of coagulating solutions. Ethyl malonate is a liquid which fulfils the condition of having a replaceable H; the samples used in the experiment were pure from Kahlbaum. When platinum, gold and silver were sparked underneath this liquid, very stable colloidal solutions were obtained; those of the first two metals named are apparently as stable as the corresponding hydrosols, while the gold solution coagulates at the end of a month or so. These particles were all found to bear a negative charge, similar to those of platinum, silver and gold in hydrosols. When the other metals, bismuth, lead, zinc, and iron, were used, a colloidal solution in ethyl malonate could not be obtained.

On sparking with silver electrodes in pure anhydrous ether $(C_2H_5)_2O$, a colloidal solution was obtained, the particles of which possess a negative charge as shewn by a slight motion under the influence of an electric field. Lead electrodes did not give a colloidal solution in ether.

Silver and iron electrodes respectively were sparked under the surface of chloroform. In both cases there was obtained a dense black liquid which easily passed through a filter paper. When the liquids stood undisturbed, that in which iron electrodes were sparked cleared in the course of a day or so, and the transparent liquid on evaporation gave a residue containing ferric chloride in easily recognizable quantities, while that used for silver remained in its original cloudy state for weeks, and shewed no sign of clearing. As a quantitative test, electrodes of iron and silver were sparked in closed vessels in equal volumes of chloroform for equal lengths of time, and with the same currents and voltages; air was drawn over the chloroform during the sparking, so as to carry away the gases given off. This current of air was led through wash bottles containing solutions of potassium iodide by which the chlorine gas produced could be collected and estimated in each case. The sparking with silver gave 50 per cent. more free chlorine gas than did that with the iron.

This deportment of silver and iron with chloroform leads to the conclusion that the iron combines readily with the chlorine of chloroform to form ferric chloride, and leaves free carbon which soon settles, while the silver, in giving off more free chlorine than the iron, reacts in some way so as to keep particles in suspension for a long time. Judging from former experiences, the silver must react with the hydrogen of the chloroform and form its colloidal particles. Doubtless a certain quantity of free chlorine is given off in both cases in consequence of the excessive decomposition of the chloroform which is due to the heat of the spark, although the vessels containing the chloroform were kept imbedded in a freezing mixture.

When similar experiments with silver and iron were tried in carbon tetrachloride, black cloudy liquids resulted, as in the case of chloroform, and chlorine gas was given off, but both liquids cleared after standing undisturbed for a few hours. No quantitative measurement of the chlorine given off in each case was made, but there was a decided difference between the liquid resulting from sparking with silver in chloroform and that from sparking with silver in carbon tetrachloride. We may explain this by saying that the lack of hydrogen in the latter liquid prevents the silver from forming its colloidal solution.

2. *Theoretical Considerations*—There is practically unanimity in the opinion that these particles in colloidal solutions are inclosed by a double electric layer, the electricity of one sign on the surface of the particle being in equilibrium with an equal amount of electricity in the layer of liquid immediately surrounding the particle. It is a matter of doubt as to the means by which this double layer is formed.

Linder and Picton[26] first suggested some interaction between the liquid and the particle: "Experiment seems to shew that if the solution is basic or tends to break up so as to leave a free base active, the motion is to the negative pole. If the solution is acidic (or tends to break up so as to leave a free H active) motion is to the positive pole." This statement is remarkably confirmed by the determinations cited above for solutions in water, the alcohols, and ethyl malonate.

Following the conclusion given by Quincke regarding suspensions of microscopic particles in liquids, many writers have been content to view the phenomena as an effect expressed by the term "contact electrification"; the particles become charged by the rubbing of the moving particles of the liquid itself against the suspended particles.

The recent work of Perrin[19] has produced results which throw considerable light on the phenomena of electrification by contact between liquids and solids. By measurements of the electric osmose of liquids through diaphragms of various materials he is led to announce these two laws:

1. Electric osmose is only appreciable with ionizing liquids; or, in other words, ionizing liquids are the only ones which give strong electrification by contact.

2. In the absence of polyvalent radicals, all non-metallic substances become positive in liquids which are acidic, and negative in basic liquids.

In explaining these results he suggests the hypothesis that a positive electrification of a wall bathed by an acidic liquid is formed by H ions situated in the stationary liquid layer immediately contiguous to the wall. Opposed to it at a small distance there will be a corresponding excess of negative ions forming another layer. If the wall assumes a negative charge it is on account of similar action of the OH ions. It is found that H and OH ions move much more quickly than other ions; if then we explain this high velocity by assuming that they are smaller than other ions, we should expect them to penetrate nearer to the boundary of the liquid and so muster at the limiting layer of a liquid an excess of electric charges of one sign. Although the analogies between this phenomenon of electric osmose and that of the coagulation of colloidal solutions undoubtedly help in explaining the latter, the formation of these solutions can hardly be credited to merely physical diffusion of the H and OH ions. As we have seen from the sign of charges borne by particles in solution, it is those which appear to depend on a replaceable H which are negative, while those depending on a replaceable OH are positive.

The matter is summed up quite clearly in a lecture by Noyes[39]:

" In regard to the cause and character of the electrification two assumptions deserve consideration; one, 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 the phenomena of migration with that of electric endosmose. 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. The other assumption accounts for these facts. According to it the phenomenon is simply one of ionization. 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. . . . To explain the behaviour 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 absorbed 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 coarse suspensions and ionization in the case of those which approximate more nearly to colloidal solutions."

Comparing the results given for the sign of the charges borne by the particles in different solutions we have the following:

1. Water ($H^+.OH^-$) can form two classes of colloids, the particles of which are respectively positively and negatively charged.

2. Replacing the mobile H^+ by the groups C_2H_5 and CH_3, so as to form the alcohols, seems to destroy the power of forming solutions with negatively charged particles.

3. Ethyl malonate $CH_2(COOC_2H_5)_2$, which has the the mobile H, readily forms those solutions containing the negatively charged particles and those only.

It is evident that the formation of the solution depends on the chemical nature of the solvent. This leads to the following theory of the constitution of the solution:

(1) In the case of gold, silver and platinum in water and ethyl malonate, we have an incomplete chemical combination

with the liquid; thus for platinum and water we have the equation:

$$nPt + H^{+}.OH^{-} = (Pt_{n}.H^{+}) + OH$$

In analogy with Nernst's hypothesis of the solution pressure of metals in contact with an electrolyte, we may look upon the platinum-hydrogen aggregate as dissociating slightly so as to form an atmosphere of positively charged hydrogen ions about the negatively charged colloidal particle.

(2) With the other metals in water and the alcohols, we have a corresponding formation of the hydroxide, thus:

$$n.Pb + H^{+}.OH^{-} = (Pb_{n}.OH^{-}) + H\,;$$

and by slight dissociation of the aggregate $(Pb_{n}.OH)$ we obtain a positively charged colloidal particle surrounded by a layer of OH^{-} ions in the liquid.

Strong corroborative evidence for this view is given in the experiments by Mr. P. Phillips and the writer[56] on the magnetic permeability of the iron in a colloidal state in methyl alcohol. These results point to the formation of some compound by the iron particles with the solvent.

In accordance with Helmholtz's explanation we may look upon the motion in an electric field as primarily due to electric endosmose. On this view, in the formula (p. 33) if *l* be put equal to *d*, and *K* is the specific inductive capacity of the liquid medium, the values of *V* for different cases are those recorded in Table VII.

TABLE VII.

Values of V in volts.

Metal	In water K = 80.	In Ethyl Malonate K = 10.6.	In Ethyl Alcohol K = 25.8.	In Methyl Alcohol K = 33.
Platinum	−.031	−.054	....	....
Gold	−.033	−.033	....	...
Silver	−.036	−.040	....	....
Lead	+.018	....	+.023	+.044
Bismuth	+.017	....	....	+.022

This table shews a surprisingly close agreement among the differences of potential between the particles and the liquids. Taking into account the wide differences between the specific inductive capacity, say, for water and ethyl malonate, we can deduce that the charge of electricity on the particle of a given metal must be much greater in water than in ethyl malonate; in other words, the interaction between the particle and the solvent seems to be dependent on what may be defined as the ionizing power of the liquid. It is further interesting to note that these values for the differences of potential between the particles and the liquids are of the same order as the value found by Perrin for the difference of potential between chromium chloride diaphragm and slightly acidulated water (.025 volts), and also agrees in the same way with Helmholtz's values for the difference of potential between very dilute aqueous solutions and the walls of glass tubes in which they were contained, if the corrections are made by introducing the value for the specific inductive capacity of water.

3. *Limiting Concentrations*—In connection with the influence of the medium the possibility of a limiting concentration is important. In his first paper on electrically prepared colloidal solutions, Bredig reports sols of the following concentrations:

Platinum	-	-	-	20 mgs. per 100 ccs.
Gold	-	-	-	14 mgs. per 100 ccs.
Iridium	-	-	-	7 mgs. per 100 ccs.

While with the many platinum, gold, silver and copper solutions which the writer has prepared during the last few years the amount of metal per 100 ccs. has invariably been in the neighbourhood of 10 mgs.

The uniformity of these results points to some cause limiting the amount of metal which a given liquid will retain in the colloidal state. In order to find whether such solutions have a limiting concentration, 800 ccs. of silver hydrosol was prepared and gradually evaporated. At the beginning and at each successive stage at which the volume of the liquid evaporated reached a half value, the amount of metal per 100 ccs., the velocity of the particles, and the size of the particles were determined; the results of these observations are recorded in Table VIII.

TABLE VIII.

Concentrated to	Weight of Ag. per 100 ccs.	Number of particles per cc.	Volume of a single particle.	Velocity constant $v \times 10^{-5}$
Original vol.	6.2 mgs.	2.9×10^8	2.0×10^{-14}	25.2
.5 " "	8.8 "	4.2×10^8	2.0×10^{-14}	23.5
.25 " "	10.2 "	....	....	23.1
.15 " "	12.3 "	....	....	....

It will be seen that the size of the particles and their velocity is apparently not affected by the concentration of the solution. The variation in the amount of metal per 100 ccs. as

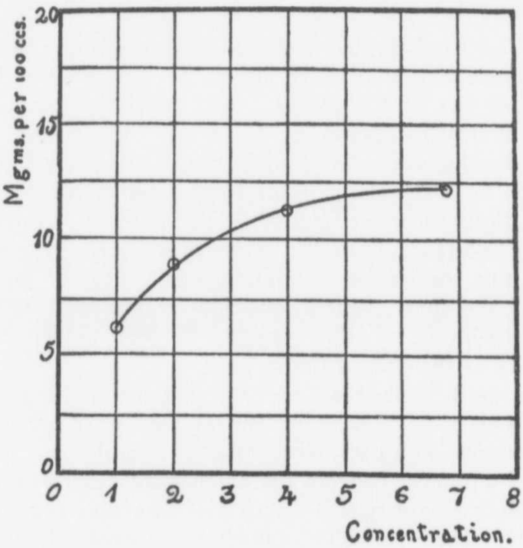

FIG. 8.

the water was extracted from the sol is illustrated in the curve in Figure 8, in which the amount of metal per 100 ccs. at any time is plotted against the reciprocal of the concentration if all the metal had remained in suspension. This indicates strongly that there is a limit to the quantity of colloidal silver possible in water, at about 14 mgs. per 100 ccs.

In order to obviate any irregularity that might be introduced by heating the solution, the evaporation was carried on over sulphuric acid and calcium chloride at very low pressure, an operation extending over about a week.

As this particular solution had been standing undisturbed and unchanged for a month before the evaporation was begun, the apparent settling of the metal is not due merely to the lapse of time. Again, it cannot be due to the concentration of electrolytic impurities in the sol, because these were not sufficient to have any appreciable effect, as is shewn by the velocity determination for the first three samples.

VIII. INFLUENCE OF ADDED ELECTROLYTES

When Graham first discussed his division of materials into crystalloids and colloids, he notes, as one of the important characteristics of the colloids, their relation to added crystalloidal electrolytic solutions. He says: " The colloid, although often dissolved in a large proportion by its solvent, is held in solution by a singularly feeble force. Hence colloids are generally displaced or precipitated by the addition to their solution of any substance from the other class." The mechanism by which this coagulation is brought about is at the present time one of the most debated questions regarding these solutions, and probably in no other respect do they exhibit a greater diversity in their properties.

In the first place we may say that the addition of electrolytes to all colloidal solutions throws the colloid out of solution or produces so called pectization or coagulation. There is a marked difference between the amounts of electrolyte necessary to produce coagulation in the case of reversible and irreversible colloids. The irreversible colloids are exceedingly sensitive to the addition of any electrolyte, while to the reversible colloids it is necessary to add large quantities of some electrolytes before coagulation sets in.

Even among the sub-classes of the irreversible colloids there is a marked difference in this respect. Referring to the two sub-classes of irreversible colloids containing, respectively, the Bredig metal sols and the colloidal sulphides, Zsigmondy differentiates them thus: When those of the former group "suffer coagulation the union of the separate particles is a very intimate one and results, not in the formation of an ordinary jelly, but of a loose powder, or metal sponge; all attempts to change the precipitate directly back into a hydrosol fail. The irreversible hydrosols such as the metallic sulphides may be prepared in solutions a hundred or a thousand times as concentrated as those of the first group. On coagulation the precipitates of this second group have some of the properties of a gel like gelatine. The water is so bound up with the particles in the coagulum, that it is almost impossible to get a complete separation in the dessicator, and, as long as the precipitate is still moist, it is easy to bring it again directly into the state of a hydrosol. When the coagulum is completely dried, the hydrosol cannot be directly reclaimed."[5] (See also Whitney and Blake.[57])

It is a curious fact that many reversible and some irreversible hydrosols are coagulated by the addition of liquids which are non-electrolytes. Reversible hydrosols are precipitated in many cases by ethyl, methyl and propyl alcohol, acetone, formaldehyde, and osmic acid. Among the irreversible sols, ferric hydrate is coagulated by propyl alcohol. However, such cases are rare: for example, the addition of strong sugar solution to gold hydrosol had not the slightest coagulative effect; if anything, it stabilized the colloid.

As very little quantitative work has been done on the action of electrolytes on the reversible colloids, they do not present, in respect of this phenomenon, the interest afforded by the irreversible sols. We shall therefore consider the latter class alone, for the study of the coagulative action of comparatively small quantities of electrolytic solutions on irreversible colloidal solutions, besides being of intrinsic interest, has thrown most important light on the mechanism of such solutions. The suggested theories as to the forces which keep the minute particles in suspension in the liquid media rest to a great extent on the behaviour of these particles on the addition of electrolytes.

The importance of the phenomenon was first emphasized by the quantitative experiments of Linder and Picton.[26] They determined the coagulative power of different salt-solutions on a colloidal solution of arsenious sulphide, and discovered that this property depended directly upon the valency of the metal of the salt. They found that equivalent solutions containing monovalent, divalent, and trivalent metallic ions possess coagulative powers in the ratio of 1 : 35 : 1023. Additional work along the same line has shewn that the valency of the metallic ion is important only in the case in which the colloidal particles are negatively charged. In short, the coagulative power of any electrolytic solution on any colloidal solution depends on the valency of the ion which bears the charge opposite in sign to that on the colloidal particle.

The next fundamentally important step was made by the researches of Hardy.[37, 38] Working with egg albumen, he found that the direction in which its particles move in an electric field, and consequently the sign of the charge on the particles, depends on whether the liquid in which it is suspended is acidic or alkaline. If acidic, the particles are positively charged; if alkaline, the particles are negatively charged. At the point (called the isoelectric point) where the sign of the charge changes, coagulation of the albumen took place. From analogy with this phenomenon, the generally accepted theory of the coagulation of all colloidal particles by electrolytes has been proposed: namely, that the particles have their charges neutralized by the absorption of the oppositely charged ions of an electrolytic solution, and at the isoelectric point, where the charge becomes zero, the colloid coagulates.

Following out this idea, Whetham[58] has given an explanation of the remarkable valency relations of the coagulative powers of electrolytic solutions. On the supposition "that in order to produce the aggregation of colloidal particles which constitutes coagulation, a certain minimum electrostatic charge has to be brought within reach of a colloidal group, and that such conjunctions must occur with a certain minimum frequency throughout the solution," he deduces that the coagulative powers of equivalent solutions containing monovalent, divalent and trivalent ions respectively would be in the ratio of $1:x:x^2$, where x is an arbitrary constant. If x is put equal to 32 this ratio reproduces, in a wonderfully exact way, the experimental numbers of Linder and Picton; the results, calculated and observed, are respectively 1:32:1024 and 1:35:1023. An apparent contradiction of this view is found in the recent work of Linder and Picton, who observe that solutions containing tetravalent metallic ions (Pt and Zr) possess very feeble coagulative power towards colloidal arsenious sulphide; whereas, according to the above theory, solutions of these metals should have a coagulative power 30,000 times that of an equivalent solution of a univalent ion. An explanation of this fact is suggested later in the present paper.

Correlating Hardy's results with the Lippmann phenomenon regarding the connexion between surface tension and potential difference, Bredig[35] suggested a very plausible theory as to the precise causes bringing about coagulation. The surface tension of mercury in contact with an electrolytic solution reaches a maximum when the potential difference between the two phases is zero. If we assume that the colloidal particles are kept in their state of fine subdivision in the liquid medium by the surface tension between the particle and liquid, then anything which tends to decrease the potential difference between the particle and the liquid will increase that surface tension. Such lessening of the potential difference is brought about through the absorption by the particles of ions bearing a charge opposite in sign to that on the particle; now, as the surface tension is increased, the particles tend to decrease the surface exposed to the liquid by uniting with one another and thus bring about coagulation.

As is quite evident, the whole superstructure of the theory of the coagulation of colloids is built up on the results of

Hardy's experiments on egg albumen. According to Noyes,[39] however, the behaviour of the albumen particles may be due to the fact that albumen is an amphoteric substance, capable of acting as a base towards acids and as an acid towards bases. The important question remains then—what effect have the ions of an added electrolyte on the charge of the colloidal particle in general?

In the experiments which follow, the velocities of the particles of gold, silver, and copper solutions respectively are measured both before and after adding varying quantities of an electrolyte. Billitzer,[59] in making similar experiments on colloidal solutions of platinum, mercury, silver, gold, palladium, to which he added gradually increasing amounts of various electrolytes, found that the velocity of the particle gradually decreased and eventually changed its direction, shewing that even the sign of the charge was changed by the addition of the electrolyte. He added gelatine and urea to his solutions in order to prevent coagulation. Whitney and Blake[57] disagree *in toto* with the conclusions of Billitzer, and fail to reproduce his results with colloidal solutions of gold and platinum, free from gelatine. They assign Billitzer's change in the direction of migration to the dissolved gelatine. In the following experiments the addition of traces of various salts to colloidal solutions of gold, silver, and copper (without the addition of either gelatine or urea) brought about in each case a change in the direction of migration of the particles in an electric field.

Since, in the case of gold and silver solutions, the particles are negatively charged, while in copper sol the particles are positively charged, the potent ion in the former solutions should be the metallic (positively charged) ion, whereas the ion coagulating the copper particle should be that from the acid radicle (i.e. negatively charged). The results of experiments on gold and silver will be given separately from those for copper.

The solutions used were prepared in pure water (Sp. Cond. $= 3 \times 10^{-6}$ at 18°C) by Bredig's electrical method, and the velocities were measured as already described.

In each case (silver and gold solutions) the velocity was measured for the pure solution: varying quantities of aluminium sulphate were then added to fresh samples of the stock colloidal solution and the velocity again measured. Aluminium sulphate was used because the metal ions being trivalent have a large coagulative power; if these ions in producing coagulation do diminish the charge on the particles, a very small addition of aluminium ions should have a perceptible effect on the velocity of the particles, while at the same time the specific conductivity, and consequently the current through the colloid, is small. $\frac{N}{1000}$ aluminium sulphate (pure, from Kahlbaum) was added drop by drop to some 40 ccs. of the colloidal solution, the whole well mixed and the velocity measured; each experiment was completed in the course of two hours after adding the electrolyte. In Tables IX and X the velocities corresponding to the various weights of aluminium per 100 ccs. of colloidal solution are given; a gradual decrease in the velocity and final reversal of direction is shewn in each case. The positive sign in the velocity column indicates motion of the particles toward the cathode.

TABLE IX—*Silver Solution.*

Amount of silver per 100 ccs. = 6.5 mgs.

No.	Grms. of Al. per 100 ccs.	Spec. Conductivity of Solution at 18°C.	Velocity at 18°C.
1	0	28.5×10^{-6}	-22.4×10^{-5}
2	14×10^{-6}	29.7×10^{-6}	-7.2×10^{-5}
3	38×10^{-6}	30.3×10^{-6}	$+5.9 \times 10^{-5}$
4	77×10^{-6}	31×10^{-6}	$+13.8 \times 10^{-5}$

TABLE X—*Gold Solution.*

Amount of gold per 100 ccs. = 6.2 mgs.

No.	Grms. of Al. per 100 ccs.	Spec. Conductivity of Solution at 18°C.	Velocity at 18°C.
1	0	3.6×10^{-6}	-33×10^{-5}
2	19×10^{-6}	5.2×10^{-6}	-17.1×10^{-5}
3	38×10^{-6}	6.6×10^{-6}	$+1.7 \times 10^{-5}$
4	63×10^{-6}	11.6×10^{-6}	$+13.5 \times 10^{-5}$

With solutions nos. 2 and 3, both with silver and gold, the velocities given in the Tables are those during the first ten minutes after turning on the current instead of that during the second 20 minutes as in former cases; with these four solutions the motion was gradually interfered with by coagulation which was hastened by the current. But with samples 1 and 4 the motion was quite steady.

Samples of each of the solutions to which the electrolyte had been added were inclosed in test-tubes and the rapidity of coagulation observed. With the silver, solution no. 2 coagulated within a few hours, no. 3 had settled slightly after standing all night, while no. 4 took longer to coagulate than no. 3. With the gold, solutions nos. 2 and 3 both coagulated at the end of a few hours, while no. 4 had not completely coagulated after standing for four days. In each case the pure solution was stable for any length of time.

These results point quite clearly to the existence of an isoelectric point for such solutions, for it is quite apparent that the particle passes through a state of maximum instability at the time when its charge is changing from negative to positive. Figure 9 illustrates the results recorded in Tables IX and X.

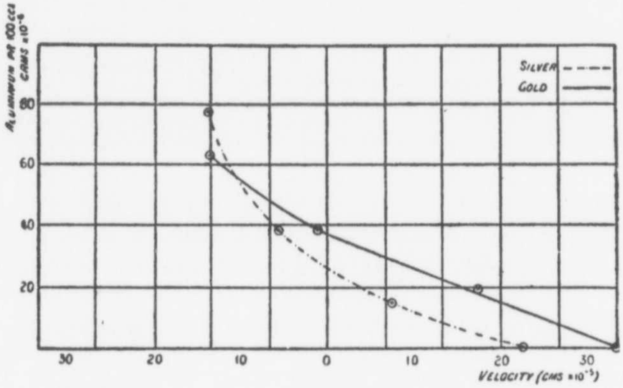

FIG. 9.

The Reversal of the Charge on the Particles—A very striking result of these experiments is the fact that, after passing through the isoelectric point, an increase in the quantity of electrolyte added produces an increase in the stability of the solution. When the minutest traces of aluminium sulphate are added to the colloidal solution, it appears that all of the aluminium ions go to decrease the charge on the particle, and when aluminium is added in quantities just sufficient to neutralize that charge, coagulation of the particles is most rapid. When, however, the electrolyte is added at once in excess of this quantity, the particles act as absorbers of the metallic ions, and the charge on the particle is thus changed at once from a large negative one to a large positive; this positive charge on the particle induces the same surface tension effects as the negative charge, and so maintains the colloidal particles in the state of fine subdivision.

In this action may lie the explanation of Linder and Picton's results on the coagulative power of zirconium and platinum mentioned above. For the experiments detailed above the largest quantity of aluminium sulphate added to the colloidal solution was 10 drops $\frac{N}{1000}$ per 40 ccs. of colloid. If the tetravalent metals are some 30 times as powerful as the trivalent (as the theory of Whetham demands), it is quite probable that Linder and Picton missed the isoelectric point altogether by adding much too large a quantity of the zirconium and platinum ions at first.

A more complete series of similar experiments were carried out on the copper colloidal solutions. They deal with: first, the effect of solutions of two salts having the same acid radical and, respectively, a monovalent and a trivalent metal, viz. potassium sulphate and aluminium sulphate; and secondly, the effect of solutions of salts having the same metal ion and, respectively, monovalent, divalent, and trivalent, acid radicals, viz. potassium chloride, potassium sulphate, potassium phosphate, and potassium ferricyanide. The results of these experiments fit in remarkably with the theory first suggested by the work of Picton and Linder, and Hardy, and supported by the conclusions drawn from analogous experiments on silver and gold solutions.

The solutions of copper were easily prepared according to Bredig's method by sparking with copper wires under the surface of conductivity water, the specific conductivity of which was usually about 2×10^{-6}. Using a current of from 5 to 6 amperes from a voltage of 110, about 250 ccs. could be produced in a short time. The resulting solution was a very clear yellowish brown liquid in which the particles remained suspended apparently unchanged for months. Several samples were made, the average copper content being 50 mgs. per 100 ccs. Usually about 250 ccs. of the solution sufficed to carry out one series of experiments, and as each series was completed a fresh stock of solution was made from the same pieces of copper. In every case the velocity of the particles in the pure solution was found; the results of these observations are collected in Table XI.

TABLE XI.

Pure Copper Colloidal Solutions.

No.	Date of preparation.	Date of measurement of vel.	Specific Conductivity at 18°C.	Velocity at 18°C.
1	June 19 '07	June 20, '07	7.7×10^{-6}	$+23.4 \times 10^{-5}$
2	" 20, '07	" 26, '07	6.5×10^{-6}	$+25.4 \times 10^{-5}$
3	" 5, '08	" 5, '08	8.2×10^{-6}	$+24.9 \times 10^{-5}$
4	" 16, '08	" 17, '08	5.8×10^{-6}	$+25.4 \times 10^{-5}$
5	" 23, '08	" 24, '08	4.3×10^{-6}	$+30.4 \times 10^{-5}$
6	" 27, '08	" 29, '08	3.1×10^{-6}	$+33.0 \times 10^{-5}$

With solutions nos. 5 and 6 it will be noticed that the velocities are rather larger than for the others, but it will also be seen that the specific conductivities of these solutions are also much lower than the others; that is to say, these latter two solutions were freer from electrolytes than the others.

With each of the salts named the procedure was the same as with the solutions of silver and gold. Solutions of the salts of determined normality were prepared with the conductivity water and the amount of such solution added to a given quantity of colloidal solution was measured by counting drops as they came from a fine burette. The tap of the burette was turned so that the liquid dropped at a convenient rate, the number of drops given by 2 ccs. of the liquid counted, a required number of drops allowed to fall into the chosen amount of colloidal solution, and finally the number of drops in 2 ccs. again counted with the tap still turned as at the beginning; the two calibrations always agreed, the burettes giving from 24 to 30 drops per cc. The burettes were always washed with distilled water, and just before being used for any solution were rinsed with the latter several times. One was thus enabled to introduce into a given amount of colloidal solution a very exact, small quantity of a given electrolytic solution.

A typical series of experiments on the effect of each of the electrolytes was as follows: The velocity of the particles in the pure copper solution was first taken; gradually increasing quantities of the chosen electrolytic solution were then added to fresh samples of the stock copper solution and the corresponding velocity measured each time. The measurement of one velocity was usually completed within one hour of the addition of the electrolyte. All of the salts used were Kahlbaum's purest and were not specially retested.

a. *Potassium Chloride*—In Table XII, the velocities corresponding to the various amounts of this salt are given. Column 1 gives the number of grams of Cl (as KCl) per 50 ccs. of colloidal solution, a $\frac{N}{100}$ ($\frac{1}{100}$ grm. mol.) solution of KCl being added drop by drop. Column 2 gives the specific conductivity of the mixture in each case. In the next column the velocities of the particles (in cms. per sec. per volt per cm.) are written, the positive sign indicating that the motion of the colloidal particle was toward the cathode. In each table are included particulars as to the coagulation caused in each case.

TABLE XII.

KCl added to Copper Colloidal Solution.

No.	Grams of Cl per 50 ccs. Cu. Sol.	Specific Conductivity at 18°C.	Velocity at 18°C.	Coagulation.
1	0	8.2×10^{-6}	$+24.9 \times 10^{-5}$	No sign.
2	3.0×10^{-5}	$11\ 7 \times 10^{-6}$	$+25.7 \times 10^{-5}$	"
3	6.8×10^{-5}	15.3×10^{-6}	$+26.2 \times 10^{-5}$	"
4	13.1×10^{-5}	22.0×10^{-6}	$+22.8 \times 10^{-5}$	"
5	27.3×10^{-5}	34.2×10^{-6}	$+18.7 \times 10^{-5}$	"

Anticipating the results which follow, we shall find that with colloidal solutions, the particles of which are positively charged, the negatively charged ions are the ones to which the coagulative action is due; consequently, the amounts of electrolyte are given always in terms of the weight of the acid radical.

It will be noticed from the Table that at first the addition of KCl produced a slight increase in the velocity, but, as larger amounts were added, the velocity reached a maximum and then slowly decreased. It is important to observe that in the above samples there was no sign of coagulation even at the expiration of several weeks. Two of the solutions did coagulate at the end of six weeks, but this interval is so long that such a result may have been due to some ulterior cause.

b. *Potassium Sulphate*—Similar results for this salt, a $\frac{N}{200}$ (gram-molecular) solution of which was used, are given in Table XIII.

TABLE XIII.

K_2SO_4 added to Copper Colloidal Solution.

No.	Grams of SO_4 per 50 ccs. Cu. Sol.	Specific Conductivity at 18°C.	Velocity at 18°C.	Coagulation.
1	0	5.8×10^{-6}	$+25.4 \times 10^{-5}$	No sign.
2	3.6×10^{-5}	9.3×10^{-6}	$+25.3 \times 10^{-5}$	"
3	8.9×10^{-5}	12.4×10^{-6}	$+24.0 \times 10^{-5}$	"
4	17.8×10^{-5}	18.7×10^{-6}	$+21.8 \times 10^{-5}$	In 2 weeks.
5	44.5×10^{-5}	38.5×10^{-6}	$+14.4 \times 10^{-5}$	In 2 hours.
6	71.2×10^{-5}	58.3×10^{-6}	0	In 1 hour.

When more KCl and K_2SO_4 than the greatest amounts shewn in the above Tables was added to 50 ccs. of the colloidal solution the conductivity became so large that the current through the liquid spoiled the velocity readings.

c. *Aluminium Sulphate*—In similar experiments on colloidal gold and silver solutions from 18×10^{-5} to 25×10^{-5} grams of $Al_2(SO_4)_3$ per 100 ccs. of colloidal solution was sufficient to reduce the velocity of the gold and silver particles to zero. The very strong action of this salt was attributed to the trivalent aluminium ion. According to the theory then suggested this salt should not have nearly so strong an action on the copper colloidal solution on account of the fact that the copper particle bears a positive charge and therefore the active ion in the aluminium solution will be the SO_4. The results given in Table XIV confirm this view entirely.

TABLE XIV.

$Al_2(SO_4)_3$ added to Copper Colloidal Solution.

No.	Grams of SO_4 per 50 ccs. Cu. Sol.	Specific Conductivity at 18°C.	Velocity at 18°C.	Coagulation.
1	0	7.7×10^{-6}	$+23.4 \times 10^{-5}$	(*)
2	6.7×10^{-5}	12.9×10^{-6}	$+21.5 \times 10^{-5}$	No sign.
3	13.4×10^{-5}	14.9×10^{-6}	$+19.2 \times 10^{-5}$	(*)
4	26.0×10^{-5}	20.2×10^{-6}	$+18.5 \times 10^{-5}$	(*)

* The solutions were not kept for coagulation observations.

It will be seen from the Table, that, although about 62×10^{-5} grams of aluminium sulphate were added to 100 ccs. of copper colloidal solution, there is very slight diminution of the velocity, while in none of the samples was there any immediate sign of coagulation: a result in marked contrast with those obtained when the same electrolyte was added to gold and silver colloidal solutions.

d. *Potassium Phosphate*—This salt was chosen as one representative of those possessing a trivalent acid radical. That its action on the copper is very keen is shewn by the numbers in Table XV.

TABLE XV.

K_3PO_4 added to Copper Colloidal Solution.

No.	Grams of PO_4 per 50 ccs. Cu. Sol.	Specific Conductivity at 18°C.	Velocity at 18°C.	Coagulation.
1	0	6.5×10^{-6}	$+25.4 \times 10^{-5}$	No immed. sign.
2	1.7×10^{-5}	7.8×10^{-6}	$+21.5 \times 10^{-5}$	" "
3	3.4×10^{-5}	8.3×10^{-6}	$+16.8 \times 10^{-5}$	" "
4	6.8×10^{-5}	9.9×10^{-6}	$+3.4 \times 10^{-5}$	3 to 4 hours.
5	10.2×10^{-5}	11.7×10^{-6}	-4.8×10^{-5}	In two hours.
6	15.6×10^{-5}	15.7×10^{-6}	-7.9×10^{-5}	In a few hours.

e. *Potassium Ferricyanide*—The results (Table XVI) for this electrolyte which also has a trivalent acid radical are in complete accord with those given by the phosphate.

TABLE XVI.

$K_6(FeCy_6)_2$ added to Copper Colloidal Solution.

No.	Grams of $FeCy_6$ per 50 ccs. Cu. Sol.	Specific Conductivity at 18°C	Velocity at 18°C.	Coagulation.
1	0	4.3×10^{-6}	$+30.4 \times 10^{-5}$	....
2	7.5×10^{-5}	7.6×10^{-6}	$+14.0 \times 10^{-5}$	No immed. sign.
3	15.0×10^{-5}	9.3×10^{-6}	$+3.8 \times 10^{-5}$	In one hour.
4	22.5×10^{-5}	13.0×10^{-6}	$+1.0 \times 10^{-5}$	" "
5	30.0×10^{-5}	18.8×10^{-6}	-1.5×10^{-5}	" "
6	45.0×10^{-5}	28.6×10^{-6}	-9.1×10^{-5}	" "

We see that very small quantities of either potassium phosphate or potassium ferricyanide are sufficient to reduce the velocity of the copper particles to zero and even to reverse the direction of their motion in an electric field.

In order the better to illustrate the relation between the number of molecules of the various electrolytes added per cc. of the copper colloidal solution and the resulting velocity of the copper particles in a given field, all of the results recorded in Tables XII to XVI inclusive, are brought together in slightly different form in Table XVII and illustrated in the curves in Figure 10. In Column I are given the numbers from which the solutions may be identified in the above tables. Column II gives the normality, in respect of the electrolyte, of the mixture of the colloid and the electrolyte; i.e. the number of gram-molecules of the salt per cc. of the mixture. According to the accepted dissociation theory we may look upon the salts in these extremely dilute solutions as being completely ionized, and so the normality as defined above will be directly proportional to the number of ionized molecules of the particular salt per cc. However, if we are to compare the efficiency of various ions in discharging the colloidal particles we must deduce numbers directly proportional to the number of such ions per cubic centimetre. For example, taking the above definition of normality, we may look upon a 3×10^{-6} normal solution of potassium phosphate as containing the same number of molecules as the number of molecules of $K_6(FeCy_6)_2$ in a 3×10^{-6} normal solution of potassium ferricyanide. But the latter solution will contain twice the number of $FeCy_6$ ions that the former contains of PO_4 ions. Consequently in Column III are written the numbers directly proportional to the number of acid radical ions present per cubic centimetre; of course, those numbers opposite the aluminium sulphate and the potassium ferricyanide are the only ones which will differ in the two columns. In the last column are copied the various velocities in cms. per sec. per volt per cm.

TABLE XVII.

Relation between the number of negative ions added per cc. to the copper colloidal solutions and the resulting velocities of the particles.

Solution.	Normality: gram-mols. per cc.	Numbers proportional to the number of ions per cc.: Grm.-ions per cc.	Velocity at 18°C.
KCl: 1	0	0	$+24.9 \times 10^{-5}$
2	17.0×10^{-6}	17.0×10^{-6}	$+25.7 \times 10^{-5}$
3	38.0×10^{-6}	$38\ 0 \times 10^{-6}$	$+26.2 \times 10^{-5}$
4	74.0×10^{-6}	74.0×10^{-6}	$+22.8 \times 10^{-5}$
5	154.0×10^{-6}	154.0×10^{-6}	$+18.7 \times 10^{-5}$
K_2SO_4: 1	0	0	$+25.4 \times 10^{-5}$
2	7.7×10^{-6}	7.7×10^{-6}	$+25.3 \times 10^{-5}$
3	19.2×10^{-6}	19.2×10^{-6}	$+24.0 \times 10^{-5}$
4	38.4×10^{-6}	38.4×10^{-6}	$+21.8 \times 10^{-5}$
5	96.0×10^{-6}	$96\ 0 \times 10^{-6}$	$+14.4 \times 10^{-5}$
6	153.0×10^{-6}	153.0×10^{-6}	0.0×10^{-5}
$Al_2(SO_4)_3$: 1	0	0	$+23.4 \times 10^{-5}$
2	4.6×10^{-6}	13.8×10^{-6}	$+21.5 \times 10^{-5}$
3	9.2×10^{-6}	27.6×10^{-6}	$+19\ 2 \times 10^{-5}$
4	18.3×10^{-6}	$54\ 9 \times 10^{-6}$	$+18.5 \times 10^{-5}$
K_3PO_4: 1	0	0	$+25.4 \times 10^{-5}$
2	3.6×10^{-6}	3.6×10^{-6}	$+21.5 \times 10^{-5}$
3	7.2×10^{-6}	7.2×10^{-6}	$+16.8 \times 10^{-5}$
4	14.4×10^{-6}	14.4×10^{-6}	$+3.4 \times 10^{-5}$
5	21.6×10^{-6}	21.6×10^{-6}	-4.8×10^{-5}
6	32.8×10^{-6}	32.8×10^{-6}	-7.9×10^{-5}
$K_6(FeCy_6)_2$: 1	0	0	$+30.4 \times 10^{-5}$
2	3.55×10^{-6}	7.1×20^{-6}	$+14.0 \times 10^{-5}$
3	7.15×10^{-6}	$14\ 3 \times 10^{-6}$	$+3.8 \times 10^{-5}$
4	10.7×10^{-6}	$21\ 4 \times 10^{-6}$	$+1.0 \times 10^{-5}$
5	14.3×10^{-6}	28.6×10^{-6}	-1.5×10^{-5}
6	21.4×10^{-6}	42.8×10^{-6}	-9.1×10^{-5}

The curves in Figure 10 are drawn with the velocities as abscissae and the numbers proportional to the number of ions per cc. as ordinates. The very marked overlapping of the curves for potassium phosphate and potassium ferricyanide at once suggests the fact that the two ions PO_4 and $FeCy_6$ have the same power of reducing the velocity of the copper particle, and, therefore, of producing the coagulation of the copper.

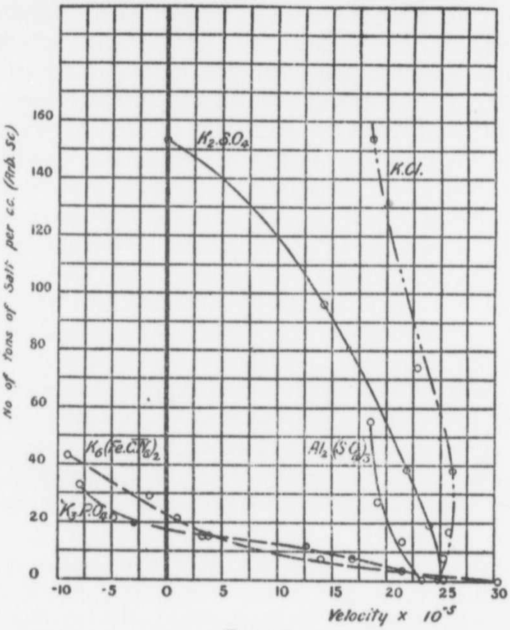

FIG. 10.

The evidences of coagulation given in the last columns of Tables XV and XVI support the latter statement, as does the work of many other writers. Although the experiments on aluminium sulphate were not carried out as far as those on potassium sulphate, nevertheless the corresponding curves shew a remarkable coincidence in the region common to the two.

These latter two curves have an additional importance in that they shew that the action of the SO_4 ion is practically independent of the metal ion. Since aluminium is trivalent and potassium monovalent, if the metal ions exerted any marked influence on the copper particle, we should expect these two curves to be very far apart.

Again, comparing the five curves, one has the very strongest evidence of the great differences in the powers of monovalent, divalent, and trivalent acid ions to reduce the velocity of the positively charged copper, and, consequently, to produce coagulation. Examination of the curves will shew that the velocity results indicate that the ratios of the powers of various acid ions to reduce the velocity of the copper particles are not very far removed from the observed ratios of the powers of the same ions to produce coagulation. These latter ratios for univalent, divalent and trivalent ions as found by Picton and Linder were 1 : 35 : 1023; the analogous ratios suggested in accordance with Whetham's theory of coagulation were 1 : 32 : 1024.

Some time since Duclaux[40] published the results of his work on colloids synthetically prepared by a double decomposition, as, for example, the colloidal solution of copper ferrocyanide resulting from the action of cupric chloride ($CuCl_2$) on potassium ferrocyanide. In this case he finds that the colloidal particle retains varying quantities of the potassium, to which he gives the credit for the existence of the colloidal particle. This portion of the colloidal unit he calls the "partie active" and draws the conclusion that the coagulation of the colloid is brought about by the substitution of the "partie active" by some other ions. In the course of his argument he expresses "most formal doubts as to the exactitude of Hardy's law according to which the coagulative power of an ion is the greater the higher its valency." The law of Hardy referred to above is based on the experimental work of Picton and Linder and others, as well as that of Hardy himself, and is uniquely supported by the theoretical contribution of Whetham. The conclusions arrived at by Duclaux seem so diametrically opposed to all this work as to suggest the possibility that Duclaux was dealing with colloidal solutions quite different in their constitution from those upon which the above law was based. This conclusion is supported by the criticism of Duclaux's work by Lottermoser, in which he constantly refers to a class of colloids which can be changed by the addition of certain electrolytes from hydrosols to hydrogels and vice versa; whereas in no case have the metallic colloids of gold, silver, etc., at present under discussion shown that they are thus reversible.

Exception must, however, be taken to the remark of Duclaux when he says that " it is by no means evident that the immobility of a micelle in an electric field implies that the micelle does not carry a charge." Historically, the only reason we have for attributing the possession of a charge to the colloidal particle is the fact that it does move in an electric field, and, if dependence is not to be placed on this assumption, there is no ground for speaking of the particles as being charged at all. If we mean anything by the statement that a colloidal particle is positively or negatively charged, it is surely a just conclusion to say that, if the particle does not move in an electric field, it has lost its charge.

IX. BROWNIAN MOVEMENT

In 1827 the botanist Brown[45] first called attention to the fact that generally fine particles in suspension in liquids are in constant motion, suggestive of the motion of gas molecules according to the kinetic theory. The unique properties of this Brownian movement have been carefully summed up by Smoluchowski[14] in his application of the kinetic theory to the explanation of the motion.

" The general occurrence of the Brownian movement in suspensions is a most striking phenomenon. Observations have been made by Brown, Wiener,[60] Cantoni[61] and Gouy[62, 63] on the suspensions in liquids of an extraordinarily large number of quite different substances, and in every case the Brownian movement was observed if the pulverization of the suspended substances was fine enough. The same phenomenon is exhibited by suspended drops of liquids in other liquids and also by suspended gas bubbles. Gouy says: ' The most important point is the general occurrence of the phenomenon; thousands of particles have been examined, and in no single case has any one seen a particle in suspension which does not shew the customary motion.'

"The velocity of the motion is the greater, the less the diameter, S, of the particle. For S = 0.004 mms. the motion is scarcely perceptible, while at the lower limit of microscopic visibility the movement is extraordinarily lively. From results given by Wiener and Exner, we have the following series for S and the corresponding v, the velocity of motion:

$$S = 13 \times 10^{-5},\ 9 \times 10^{-5},\ 4 \times 10^{-5} \text{ cms.}$$

$$v = 27 \times 10^{-5},\ 33 \times 10^{-5},\ 38 \times 10^{-5} \text{ cms. per sec.}$$

"Regarding the influence of the material of the particle on the velocity, we have differences of opinion expressed. Gouy and Jevons maintain that particles of a determined size give practically no differences in their velocities, whether the particles are solid, liquid, or gas; while Cantoni holds that the chemical constitution of the particles influences the velocity (e.g., silver moves more quickly than iron, and platinum faster than lead, etc.) It may be that the different materials cannot be pulverized equally well; in any case the influence of the material of the particle seems to be of little importance.

"Undoubtedly the motion depends very intimately on the kind of liquid medium; the motion is the fastest in water and liquids of greater fluidity, less in the more viscous liquids and hardly noticeable in the case of the viscous liquids such as oils, glycerine, sulphuric acid, etc. The motion becomes quite visible, however, in glycerine that is heated to 50°C., its viscosity being very much reduced at that temperature (Exner). Cantoni affirms that alcohol, benzine, and ether are slightly less active than water.

"Closely allied to the general existence of this motion is its unchangeableness. Nearly all observers agree as to this characteristic. So long as the particles float in the liquid, this Brownian movement persists without change. It ceases only when the particle sinks to the bottom or becomes fastened to the wall of the vessel. On account of the action of gravity, one can observe the motion longer in the case of comparatively large particles of very nearly the same density as water itself (e.g., mastic, gamboge, etc.), than in the case of the heavier particles, which soon sink to the bottom of the containing vessel. The motion is interrupted by the addition of salt solutions, which, as is well known, produce coagulation.

" Cantoni observed a preparation between the two microscopic glasses imbedded in paraffin, and was unable to notice any change in the Brownian movement during a whole year.

" It is quite characteristic of this motion that it is independent of external conditions. One may cover the sample with ground glass so as to prevent evaporation, or place it in a bath of uniform temperature, or let it stand in a place completely free from vibration, or leave it for weeks at a time in a darkened room, or heat the solution for hours, or cut out the heat rays from the incident light, or change the colour of the incident light, or reduce the intensity of the incident light in the ratio of 1000: 1—all this without influencing this motion.

" When very intense illumination is continued for some time, it increases the temperature and reduces the viscosity of the liquid; as a consequence the motion is quickened, especially in the case of the viscous liquids, the fluidity of which increases very rapidly with the temperature. In the case of water, Exner has observed an increase in the velocity of the Brownian motion from 32×10^{-5} cms. per sec. at 20°C. to 51×10^{-5} cms. per sec. at 71°C.

" As is apparent from the foregoing, all explanations of the Brownian movement which rely on the assumption of the application of external energy, must be discarded. In this category must be placed the theory that we have to do with convection currents which are set up by the unequal heating of the liquid, or that the motion is due, as in the case of the radiometer, to the intensity of the incident lights. . . . A calculation will show that in order to produce the effects by convection currents we should have to produce a temperature gradient in the liquid of 100,000° per cm."

Smoluchowski[14] proceeds to dismiss also the explanations which rest on the assumption of sources of energy internal to the liquid. The hypotheses which have been suggested are:

(1) Mutual repulsions between the particles whether of

electrical or other origin. (Meade Bache, Jevons, and Rachlmann).

(2) Surface tension phenomena. The view expressed by Maltezos is that the fundamental cause of the motion is the destruction of surface tension equilibrium on account of slight impurities. Mensbrugghe recalls in this connection the action of small particles of camphor on water.

The view that the motion is due to surface tension phenomena is hardly tenable, since, as Smoluchowski points out, the intentional addition of some impurities is without effect, many completely insoluble substances such as diamond, graphite, etc., shew the motion, and most of all, this motion does not shew the alteration with time which one would expect were the phenomena due to an attempt to reach an equilibrium state. Smoluchowski also discards the first explanation because electric actions might produce a certain grouping of the particles, but not a continuous motion; besides, the existence of these forces would be another problem to resolve.

He then treats of the kinetic theory. Before discussing these views we shall refer to some important cinematographical evidence of the Brownian movement, due to Victor Henri,[65] and other measurements by Perrin.

By an application of the principle of the cinematograph to the microscope, Henri has been able to obtain photographic evidence by which to make a quantitative study of the Brownian movement. The emulsion studied was that of the milk of caoutchouc diluted in about 500 times its volume of distilled water. This emulsion contains spherical microscopic particles of uniform size, about 1 μ diameter (10^{-4} cms.). On account of the density of the particle (.98) they remain suspended for a great length of time. The photographs were taken with a magnification of some 600 diameters; the cinematograph was so arranged as to give twenty exposures per second, each exposure lasting for $\frac{1}{320}$ of a second. Consequently, in the figure (Fig. 11) reproduced from the photograph, we have the projection on a horizontal plane of the trajectories of five particles, with the positions indicated at the end of each $\frac{1}{20}$ of a second. The scale divisions attached give the length $\mu = 10^{-4}$

cms. The mean displacement corresponding to $\frac{1}{20}$ second varied very little from particle to particle. The mean of 16 successive determinations for each of 10 particles gave the following numbers:

$.58, .55, .52, .56, .70, .64, .67, .71, .55, .70, \times 10^{-4}$ cms.

which give a mean velocity of

$$12.4 \times 10^{-4} \text{ cms. per sec.}$$

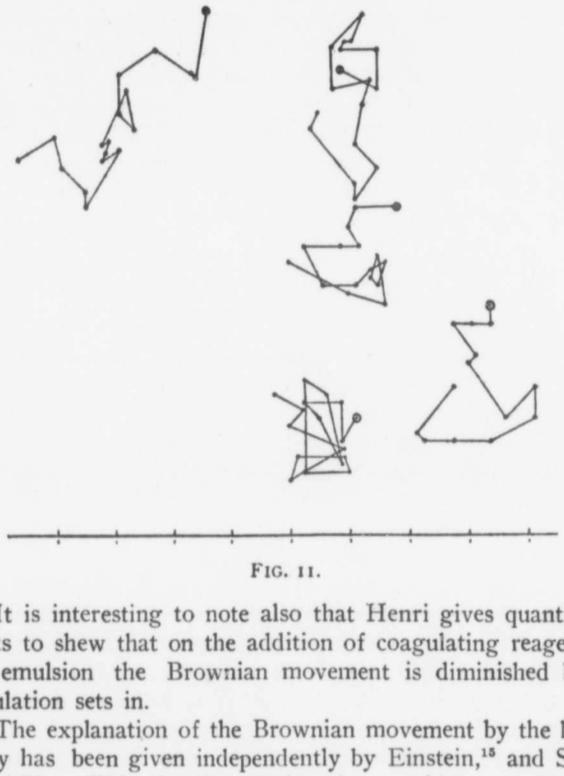

FIG. 11.

It is interesting to note also that Henri gives quantitative results to shew that on the addition of coagulating reagents to this emulsion the Brownian movement is diminished before coagulation sets in.

The explanation of the Brownian movement by the kinetic theory has been given independently by Einstein,[15] and Smoluchowski[14]. This is the explanation which seems apparent as one views the particles under the microscope. As Smoluchowski says: "Wenn man die Brownsche Bewegung unter dem Microscop beobachtet, erhalt man unmittelbar den Eindruck, dass so die Bewegungen der Flüssigkeits-moleküle aussehen müssen. Es ist das keine fortschreitende, sondern ein Zittern oder ein Wimmeln; die Teilchen beschreiben unregelmässige Zickzackbewegungen, als ob sie infolge der zufälligen Zusammenstösse mit den Flüssigkeits-molekülen angetrieben würden, und trotz ihrer fieberhaften Bewegung rücken sie nur langsam von der Stelle."

The idea which the authors mentioned above have worked out is that the Brownian movement of the particles represents the resultant of the shocks given the particles by the molecules of the liquid and is consequently the resultant of the thermal agitation of the fluid. They have developed the following formula, giving the relation between the distance $\varDelta$ cms. traversed by a particle in time *t* secs. and the radius *r* of the particle (supposed spherical):

$$\varDelta=\sqrt{\frac{t}{r}}\cdot\sqrt{\frac{RT}{N}\cdot\frac{1}{3\pi K}}$$

where R = gas constant, 8.31×10^7,

T = absolute temperature,

N = number of molecules in one gram molecule $= 7 \times 10^{23}$, and

K = coefficient of viscosity of liquid medium.

At 17°C., K for water $= 1.35 \times 10^{-2}$,
so that we have

$$\varDelta = 5.4 \times 10^{-7}\sqrt{\frac{t}{r}} \text{ at } 17^\circ\text{C}$$

$\varDelta$ for $\frac{1}{20}$ sec. for particle for which $r = .5 \times 10^{-4}$ cms. is equal to $.17 \times 10^{-4}$ cms. Victor Henri's experimental value for this number is $.62 \times 10^{-4}$ cms., from which we gather that the particles move much faster than the kinetic theory alone would indicate.

When we compare the mass, the mean free path, and the mean velocity of the particle in the colloidal solution with those of the molecules of liquids and gases, one can hardly demand that the kinetic theory shall give an entire explanation of the

Brownian movement, although one cannot but be surprised at the closeness of the observed and calculated results.

For a particle of radius 10 $\mu\mu = 10^{-6}$ cms., we get for the value of Δ for 1 sec.,

$$\Delta = 5.4 \times 10^{-7} \sqrt{\frac{1}{10^{-6}}} = 5.4 \times 10^{-4}$$

which is about the order of the path observed; so that there is little doubt that the bombardment of the molecules of the liquid accounts in some measure at least for the motion observed.

In connection with this formula, Smoluchowski points out that:

(1) The motion is independent of the mass of the particle. It is a remarkable coincidence that particles of such a variety of constitution have motions of about the same order.

(2) The velocity varies as the inverse square of the radius.

(3) The velocity increases with the temperature. Exner found that the relation of the velocity at 71°C. to that at 20°C. for a particular kind of particle was 1.6, while the above equation gives 1.7.

(4) The velocity will be small for the more viscous liquids.

One of the most remarkable contributions to the kinetic theory of the Brownian movement, as well as to the kinetic theory in general, is afforded by the observations of Perrin.[17] From an ordinary solution of gamboge ("gomme gutte," a gum resin) the larger microscopic particles were removed by centrifuging, leaving a solution containing only ultramicroscopic particles, which, on account of their uniform appearance, Perrin takes to be spheres of uniform size. He viewed a layer of this solution 0.12 mms. in thickness by means of the ultramicroscope so arranged that it could be focussed on layers of the liquid at different heights. The numbers of particles visible in the microscope at different depths were counted, and, as a mean of thousands of observations, he obtained the numbers given in the following series. If the number of particles visible at depth h be 100 then at depths

$$h \qquad h+25\mu \qquad h+50\mu \qquad h+75\mu \qquad h+100\mu$$

he found

100 116 146 170 200

Now the numbers

100 119 142 169 201

are in geometrical progression. Therefore, as the depth increases in A.P. the number of particles increases in G.P. This distribution of the particles is the same as that for a gas in equilibrium under the force of gravity, according to the kinetic theory. However, the reduction of the concentration to one-half of its value, which is produced in the atmosphere at a height of 6 kilometres, is given here at a height of $\frac{1}{10}$ mm. This exponential law of distribution Perrin explains as follows:

If $\rho =$ density of particles,
$m =$ mass of particle,
$n =$ number per cc.,

they will exert by their bombardment on every wall that stops them without stopping the water molecules an osmotic pressure proportional to n, say Kn. The ndh particles in a horizontal layer of depth dh and of unit cross-section are kept in suspension by the buoyancy of the water and the difference between the osmotic pressure from above and from below. That is,

$$ndh \, . \, mg = Kdn + \frac{m}{\rho} \, . \, ndh$$

$$\frac{dn}{n} = \frac{1}{K} \, . \, gdh \left(1 - \frac{1}{\rho}\right) m.$$

Integrating between the heights o and h

$$log \frac{n_0}{n} = \frac{1}{K} \, mgh \left(1 - \frac{1}{\rho}\right)$$

From this equation, by finding m as shewn previously, K can be calculated from the observation given:

$$K = 42.5 \times 10^{-15}$$

Thus the osmotic pressure of n granules in unit volume is

$$n . 42.5 \times 10^{-15}$$

The pressure (p) exerted by a gas having n molecules per cc. is given by

$$p = n \cdot \frac{RT}{N}$$

which gives $n \cdot 34.3 \times 10^{-15}$, affording a wonderful coincidence between the values of the pressures in the two cases. Thus the granules play the rôle of visible molecules of a perfect gas, with a molecular weight equal to 3.3×10^{9}. (The radius of the granules observed by Perrin was 1.2×10^{-5} cms.)

These results give excellent confirmatory evidence of the truth of the kinetic explanation of the Brownian movement. The great obstacle to the acceptance of this theory lies in its inability to afford any adequate explanation of the power of electrolytes to produce coagulation of the particles—a phenomenon which is quite easily explained if the source of the Brownian movement and consequently of the stability of the colloid lies in the charges borne by the particles. In fact, Victor Henri has given direct evidence that on the addition of electrolytes the Brownian movement decreased in amount before coagulation sets in.

It seems impossible to conceive of these myriads of charged particles existing in solution without these charges having a very intimate connection with the resultant motion of the particles. One has but to view these particles with the ultramicroscope to be struck with the mutual action of these particles. As has been already noted by various writers (*vide* Henri[64] and Zsigmondy), when two particles approach one another there is an abrupt alteration in their velocities; for example, one may often notice two or three approach one another, and begin revolving about a common centre, and so on. Further work in this phenomenon is being prosecuted by Perrin[65].

X. MOLECULAR WEIGHTS OF COLLOIDS

Two general methods have been used to find the molecular weights of colloids in solution, viz. the determination of the depression of the freezing point and the finding of the diffusion coefficient.

As is well known, if Δ = the experimentally determined depression of the freezing point which 100 grm. of the solvent suffers through the addition of p grams of the substance, K = molecular depression of the solvent, and M = molecular weight of substance to be determined,

$$\frac{\Delta}{K} = \frac{p}{M}$$

$$\therefore M = \frac{p\,K}{\Delta}$$

These determinations give the following results for the substances indicated:

Malto-dextrine	965
Gum	1800
Glycogen	1625
Ferric Hydrate	6000
Tungstic Acid	1750
Egg Albumen	14,000
Starch	25,000
Albumose	2400
Tannin	2643—3700

The diffusion method rests on a determination of the rate at which the colloid diffuses into pure water. If we have a solution in a parallel-sided trough of one sq. cm. cross-section and the solution at one plane perpendicular to the column of liquid is $(n + \frac{1}{2})$ normal and that at a second plane, 1 cm. from the former and parallel to it, is $(n - \frac{1}{2})$ normal, then the difference in osmotic pressure at the two planes is equal to the osmotic pressure of a normal solution,

$$= R\ T \text{ per sq. cm. at } 0^\circ\text{C.}$$

This pressure tends to drive the dissolved molecules in the direction of the lower concentration, and acts on all dissolved molecules between the two planes perpendicular to the liquid, i.e. on $\frac{n}{1000}$ grm.-molecules. If the force necessary to drive a grm.-molecule of the dissolved substance with a velocity of 1 cm. per sec. is P kilograms—this force is known as the coefficient of friction of the substance—the velocity v is given by

$$v = \frac{R\,T\ .\ 1000}{1000\,P\ .\ n} \text{ cms. per sec.}$$

The quantity of dissolved substance passing the plane of lower concentration in 1 sec. is found from the number of molecules lying between that plane and a parallel plane v cms. distant.

The number of milligram molecules in the volume (v ccs.) is $v \times n = N$.

$$N = \frac{R\,.\,T}{P}$$

N is called the diffusion coefficient.

The friction coefficients of substances of non-conducting solutions are found from the diffusion coefficient. According to a calculation made by Euler the friction of a gram-molecule is approximately proportional to the square root of the molecular weight of the dissolved substance. If we apply this method to calculate the molecular weight of the four colloids examined by Graham, we have:

Gum Arabic	= 1750
Tannic Acid	= 2730
Egg Albumen	= 7420
Caramel	= 13,200

These determinations shew that there is a continuous gradation in the size of the dissolved particles from that of the ordinary crystalloidal molecule to that of particles visible in the microscope.

XI. GENERAL CONCLUSIONS.

Theoretically, colloidal solutions give a most substantial confirmation of the molecular theory of matter. We may trace particles of various sizes, from those of coarse suspensions to those of large molecular weights, and finally to those small molecules of true crystalloidal solutions. Not only have we good evidence, optically, of this gradation in the size of the particles in various solutions, but other phenomena shown by small particles, e.g. Brownian movement, filtration, etc., show a corresponding gradation in their action.

As regards the theory of the constitution of colloidal solutions we have the most satisfactory explanation in the case of the reversible colloids. Chiefly on account of the work of Hardy, these solutions are now looked upon as consisting of two phases. For example, in the case of the hydrosol of gelatine, we have a solution of gelatine in water, and a solution of water in gelatine, in the same sample. Any cause which alters the equilibrium state of these two phases will bring about a change in the sol. This view is important in the explanation of anomalies exhibited by these solutions in their relation to semipermeable membranes. The particles visible in the ultramicroscope in these solutions represent the water-in-solid phase. In general these particles are the smallest of those visible in any colloidal solution, while the particles of many of such solutions are invisible even in the ultramicroscope. This explanation has also been extended to apply to irreversible colloids, the particles of which are larger and appear to be merely very fine pieces of solid.

Many theories of the structure of irreversible colloids and the action of electrolytes in coagulating them have been formed, but as yet no completely satisfactory general explanation has been suggested. Besides the partial chemical action which may take place, there is the phenomenon of absorption exhibited by these particles, in a manner somewhat analogous to the absorption of gases and dye-stuffs by carbon, and the occlusion of hydrogen by platinum and many other metals. Their work on the Kerr phenomenon and the magneto-optical phenomena given by ferric hydroxide colloidal solution, has led Cotton and Mouton to the conclusion that we have in this case particles which are anisotropic[13, 66, 67].

The deportment of the Schutzkolloid is another indication of the complexity of these solutions. In addition to the remarkable action of reversible colloids in the rôle of protecting irreversible colloids from coagulation by electrolytes, Bechhold has shown that they have an analogous action in relation to filtration.

A circumstance which has often been advanced as an obstacle in the way of accepting any given theory is the difficulty of explaining why many irreversible colloids coagulate when frozen and then thawed. If the particles are held in solution by the mutual action on one another, due to charges of electricity or otherwise, then, as a frozen mass thaws, the particles in the very thin layer of solution on the outside at any instant, as the ice surface melts and the water runs away, are carried down by the stream and do not remain in suspension on account of the cessation, for the time being, of the action of their neighbouring particles. That is, by the process of thawing the particles are taken from solution one by one, as it were, and the suspended mass coagulates.

All of these questions, together with others of the greatest practical importance, await future developments in this study. In colloidal solutions we have an unlimited scope for the many workers now engaged in the problems presented by them. The solving of these problems will undoubtedly add greatly to our knowledge of the structure and action of matter in its various states.