

RICHARD A. ZSIGMONDY

## Properties of colloids

*Nobel Lecture, December 11, 1926*

Even in prehistoric times the peoples must have become familiar with the properties of colloidal solutions and with their changes. The curdling of milk and the clotting of blood were certainly known to our oldest ancestors.

Colloids have appeared, though sometimes only temporarily, also in chemical operations as carried out by the alchemists, the iatro-chemists and the classical chemists.

Even in the Middle Ages the properties of "aurum potable" were observed, and of works of the older chemists of the classical period mention may be made of only one investigation by the Swedish scientist Carl Wilhelm Scheele who was at the time the greatest of them all and who described in his work *Om Brunsten eller magnesia nigra* not only the discovery of three elements and their compounds, but also a colloidal solution of manganese dioxide in hydrochloric acid with the following words:

"När Salt-syran stått öfver Brunsten uti kölden, bekom hon en dunkel röd-brun färg (par. 6, a). Emedan Brunstenen, utan at förbinda sig med phlogiston, icke gifver någon färg-lös solution, så följer, att Salt-syran kan lösa honom utan detta principium: Men en sådan solution har antingen en blå eller röd färg (par. 14, No.4). Färgen är här mera brun än röd; orsaken är, at i denna röda solution de aldra finaste delar af Brunsten simma, hvilka icke så lätt sjunka; ty utom dessa fina partiklar, är denna solution röd, och rödt blandadt med svart, gör brunt. Brunsten har här fäst sig så löst vid Acidum salis, at vatten kan praecipitera honom, och detta praecipitat förhåller sig som ordinar Brunsten. Då nu blandningen af Brunsten och Spiritus salis sattes i digestion, upkom fräsning ock lukt af Aqua regis (par. 6, b)."

For the benefit of the reader who might not understand the Swedish text I give here the translated extract from the German translation of the Proceedings of the Royal Swedish Academy of Sciences from *Neueste Entdeckungen in der Chemie* (Latest discoveries in chemistry), by D.L. Crell, Vol. 1, page 127, Weygandsche Buchhandl., Leipzig, 1781:

"The hydrochloric acid receives from the manganese dioxide in the cold a dark red-brown colour ( par. 6, a). It consequently dissolves it without addition of phlogiston (par. 14, No. 4). The brownness is derived from the very fine particles of manganese dioxide which float about and without which the solution appears red. The manganese dioxide adheres so loosely to the acid that it can be precipitated by water, and this precipitate behaves like ordinary manganese dioxide. When the mixture of manganese dioxide and hydrochloric acid is digested, there appears an effervescence and a smell of aqua regia (par. 6, b)."

Scheele, therefore, has described here an unstable colloidal solution of manganese dioxide in hydrochloric acid which, when diluted with water, allows the manganese dioxide to be precipitated.

This reported case of the occurrence of a colloid does not stand alone. Even in the year 1665 gold purple had been described by Andreas Cassius and his son. This purple proved to be a tested dye for glass melts, naturally without its colloidal nature being recognized.

It is known that the great Swedish scientist Berzelius, the most eminent chemist at the time, made a detailed study of the purple of Cassius. He had, however, paid attention also to other colloids; for instance, he observed the occurrence of the hydrosols of certain sulphides, e.g. arsenic sulphide. He first described the straw-yellow liquid which is obtained by passing hydrogen sulphide into arsenious acid, as a solution of arsenic sulphide owing to its homogeneous appearance; later, however, he added the remark that this liquid should probably be regarded as a suspension of arsenic sulphide because it settled out. Here already the difficulty of classifying such preparations appears. It does not, therefore, seem to be particularly remarkable that a detailed concern with such little defined systems appeared to be unrewarding and was neglected at the time, in view of the wealth of knowledge in the organic field.

Biological and technical problems, however, led again and again back to the question as to the nature of colloids.

For instance, Nägeli carried out more than 50 years ago a masterly investigation into the nature of starch. Also the zoologist Bütschli and the physicist Quincke as well as the chemist Selmi were concerned in detail with phenomena which we know today to be partly characteristic of colloids. The first fundamental explanation we owe to the observations of Graham who gave a masterly interpretation of them and who created a division of solutions into crystalloids and colloids on a broad experimental basis.

He was also responsible for the expressions hydrosol (an aqueous colloidal solution) and hydrogel (the jelly derived from it).

As regards myself, dealing with several technical problems provided the incentive to concern myself with colloids.

I was dealing with gold orpiment glass and with certain ceramic dyes which were based in principle on extremely fine gold divisions. It seemed to me particularly remarkable that the effect of very closely allied chemical compounds could be fundamentally different in regard to the preparation and appearance of these dyes. This observation seemed to me all the stranger as compounds with completely opposite properties frequently produce similar effects on the dyes of extremely finely divided (i.e. colloidal) gold.

These results could not be brought into harmony with the previous experience of chemistry. Consequently, I sought to discover the reason for these phenomena in a way other than the purely chemical one. The first special object of such investigations was the *purple of Cassius*. It is known that Berzelius had regarded it as a chemical compound. The reasons which he gave for this were extremely convincing so that I at first believed that I should not ignore them. On the other hand, however, I also knew that earlier and later workers on the purple of Cassius had regarded it also for weighty reasons as a mixture of finely divided gold and stannic acid. My object now was to decide with full certainty which of these two views was correct. For this purpose an attempt to synthesize the purple of Cassius from very finely divided metallic gold and colloidal stannic acid was to be made. Success or failure of this experiment had to provide the decision in view of the chemical inertness of gold, provided it was possible to prepare it in a sufficiently fine division free from gold compounds and colloidal impurities. Only when I had succeeded in reaching this aim, did I hear of the investigations of Faraday who had prepared extremely fine divisions of gold by the reduction of gold salts. If I had known of Faraday's results, it would have saved me much unnecessary work.

I had taken another path which led me eventually to the preparation of practically equal-sized red gold hydrosols (colloidal gold solutions) by the reduction of gold chloride with formaldehyde in a weakly alkaline solution.

After Faraday's publication was available to me, I followed him and used phosphorus as the reducing agent.

However, as I was able to use the experience which I had gained with the formaldehyde gold, I arrived, when using phosphorus, at extremely fine gold

divisions of almost molecular size, such as were used later by The Svedberg in his diffusion experiments.

But the safest method, at the time, of preparing pure highly red gold hydrosols remained first of all the formaldehyde method. This gave me adequate amounts of sufficiently pure highly red colloidal gold. It was used for trying to synthesize the purple of Cassius, and when this attempt succeeded, it provided proof for the view which regards purple of Cassius as a mixture of finely divided gold with colloidal stannic acid. As on the other hand, the purple behaved exactly like a chemical compound as Berzelius had already pointed out, I arrived at an experience which is important for evaluating colloidal precipitates and which has to be applied right down to the present day for evaluating colloidal systems unless one wants to be a victim of errors, and which can be expressed briefly as follows:

*A colloidal mixture may sometimes behave like a chemical compound and has frequently simulated one.*

Several of the red gold divisions prepared with formaldehyde as well as those reduced with phosphorus appeared perfectly clear in ordinary daylight (like good red wine). They did not settle out their gold, and I was therefore able to call them rightly *solutions*. In Graham's dialysis, however, they behaved like colloidal solutions. The gold particles did not pass through the parchment membrane. This showed my gold divisions their proper place, namely, that they belonged to the colloidal solutions.

My first publication on gold solutions was followed by quite disagreeable discussions. Other scientists who repeated my experiments without taking the necessary care, obtained strongly turbid and sometimes precipitating liquids, and generalizing their own experiences, called also the gold liquids obtained by me suspensions. This view was supported by the low osmotic energy emission, the absence of a measurable freezing-point reduction, etc. as well as by the fact that even clear gold solutions showed a Faraday-Tyndall light cone and appeared in this sense non-homogeneous.

Had I conceded that my gold solutions were simply to be regarded as suspensions, it would not only have given a completely wrong picture of their character, but if I had classified my gold divisions under such well known systems as suspensions, there would have been no reason for me to concern myself with the following questions which have become extremely important for colloid chemistry:

1. What particle size have colloidal particles? Are they molecules or aggregates of molecules? How many atoms approximately does a single gold particle contain?

2. Why is the emission of osmotic energy so low with gold solutions? Do colloidal solutions perhaps really exert no osmotic pressure, as was frequently believed at the time?

3. Is the Faraday-Tyndall light cone, which by the way is observed in all colloidal solutions, an essential characteristic of them, or is this light cone rather incidental?

Question 1 regarding the particle size was decided in 1902 and later by ultramicroscopy.

The correct answer to Question 2 is given by the masterly work of The Svedberg and Perrin.

Question 3 I hoped to be able to decide already in 1900 by viewing the light cone under the microscope.

Just as liquids of equal gold content can appear differently under ordinary viewing, so the intensity of the Faraday-Tyndall light cone can vary in solutions which appear externally clear when viewed with the naked eye.

In apparently similar solutions of clear appearance the light cone sometimes occurs very intensely, and almost disappears in other cases, e.g. in several gold solutions reduced with phosphorus.

In a preliminary experiment it was found that the light cone could easily prove the presence of one-hundredth part of the substance which Bunsen and Kirchhoff had proved by spectrum analysis.

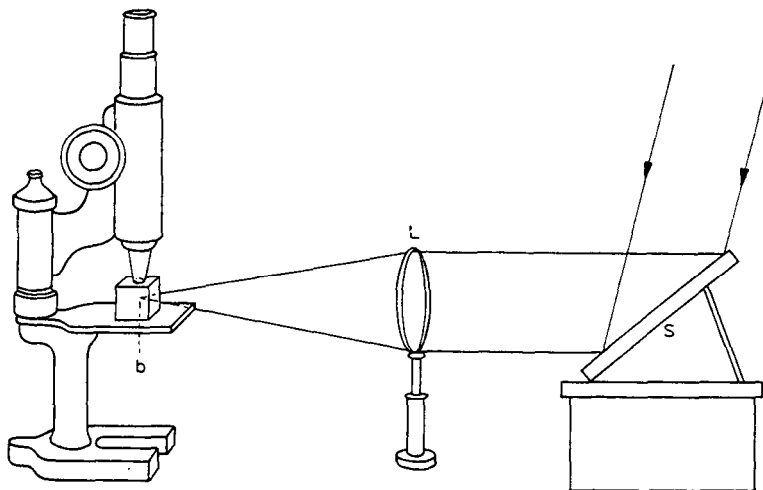


Fig. 1. The first arrangement for making ultramicroscopic particles visible.

Viewing of the light cone under the microscope (Fig.1) gave the following:

- (1) In strongly turbid liquids thousands of individual particles of different colour were recognizable.
- (2) Clear gold solutions with a medium strong Tyndall cone, however, showed under the microscope a light cone which disappeared when the solutions were diluted without being able to make individual particles visible.
- (3) Very fine gold divisions obtained with phosphorus showed several gold-coated dust particles, but the liquid between them appeared optically empty.

The addition of common salt showed, however, that the clear liquid contained elementary gold. The salt coagulated the colloidal gold solution, the gold was precipitated in the form of coarser aggregates, and thousands of yellow-brown gold particles filled the liquid.

Much was explained by this, but for some questions simple viewing of the light cone under the microscope was not sufficient. My endeavour was to develop the microscopic viewing of the light cone to its highest perfection.

Jointly with H. Siedentopf in Jena, therefore, the method was developed further. An instrument of high capacity was made with which gold particles

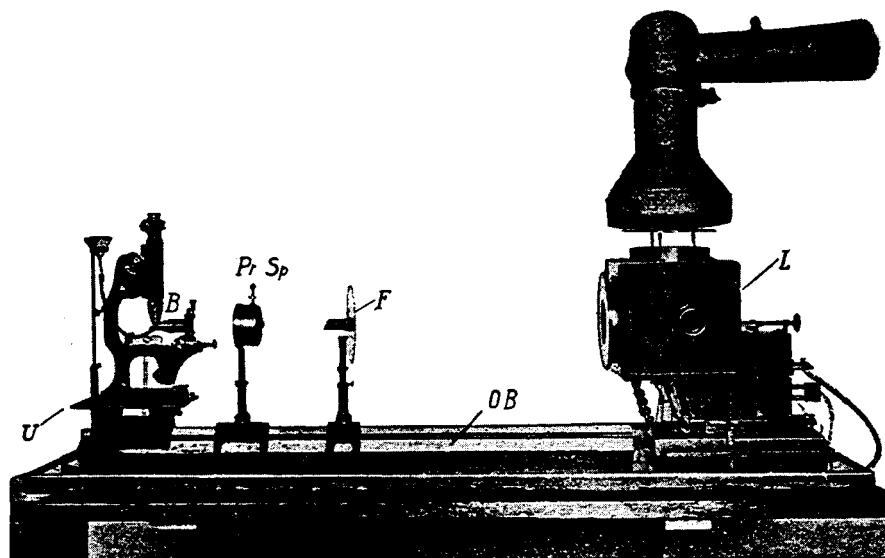


Fig. 2. Immersion ultramicroscope.

$L$  = Light source;  $F$  = Telescope objective which gives a picture of the light source on the precision slit  $PrSp$ . The condenser  $B$  forms an image of the precision slit in the colloidal solution, which is in a small dish.

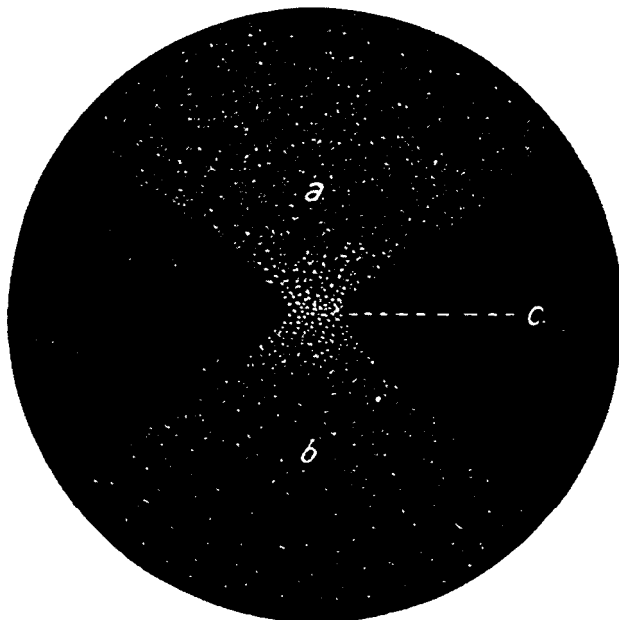


Fig. 3. Ultramicroscopic picture when using the bilateral slit *PrSp*. The picture of the slit is at C, the narrowest constriction.

with a diameter of down to 10m  $\mu$  could still be made visible in sunlight: the slit-ultramicroscope.

With this instrument it was then possible to carry out size determinations of the gold particles by counting the particles in a certain volume of colloidal gold solution the gold content of which was known.

Similarly the number of gold particles in gold orpiment glass was determined.

A preliminary check of the accuracy of the size determination was obtained by comparing the brightness of the ultramicroscopic pictures.

In passing the following may be mentioned: The knowledge that very small particles can be made visible by very bright illumination on a dark background (i.e. in a dark field) led to substantial improvements of the so-called dark-field condensers which in connection with microscopes were later often called ultramicroscopes.

Several inventors were concerned with the improvement of such condensers: Siedentogf built the paraboloid and the cardioid condenser; Reichert the mirror condenser; Ignatowski and Jentzsch other condensers, for instance, the concentric ball condenser. I myself improved the method of intense illu-

mination from one side by designing the immersion ultramicroscope which is manufactured by the optical workshops of the firm of R. Winkel in Göttingen (cf. Figs. 2 and 3).

Observations by H. Ambronn on dichroism, and work carried out by me in Jena jointly with H. Ambronn, and also the behaviour of orpiment glass made it appear probable even in 1904 that the small submicroscopic gold particles were crystalline.

The application of Tammann's theory of crystallization to the formation of the gold hydrosols appeared, therefore, promising. It led not only to an explanation of hitherto unexplained phenomena in the preparation of orpiment glass, but also to the discovery of the nucleus method. This gives gold solutions of definite particle size.

Later much use was made of the nucleus method, both in the preparation of gold solutions for physical investigations and for determining the pore size of fine filters.

I mention in particular the well-known investigations of The Svedberg and Arne Westgren.

*Electrical Charge and Coagulation* - The gold particles of colloidal solutions have a negative electrical charge, just as those of many other irreversible colloids. The electrical charge is very important with these colloids as it is the main cause of their stability. If this charge is taken away from the particles, say by adding salts, particle aggregation immediately occurs and the system coagulates. Externally this is noticeable with colloidal gold by the change in colour from red to blue. In the ultramicroscope not only a colour change

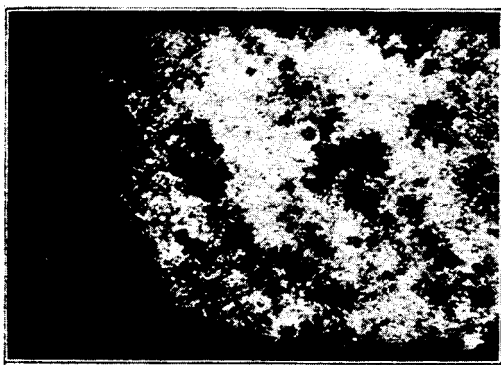


Fig. 4. Gelatine gel photographed by Bachmann. The black areas are optically empty liquid in which single submicrons are moving. The bright areas are jelly flakelets which diffract light.



of the individual particles is noticed, but also an important change in the number of the particles.

The coagulation can be interrupted at any moment by the addition of protective colloids. It is, therefore, possible to determine the number of ultramicros present after each definite period of time after adding the coagulating agent, and consequently the speed of the coagulation. With ordinary gold hydrosols the particle aggregation occurs extremely rapidly. Dilution with water, however, retards the aggregation of the particles owing to the increase in the mean distance between the particles. In spite of the dilution coagulation generally takes place very rapidly, provided that a sufficient amount of precipitating salts is added, so that it originally appeared as if the submicroscopic particles attracted one another over rather large distances.

This induced me to ask the theoretical physicist M. von Smoluchowski to derive an experimentally verifiable formula by which the presence of spheres of attraction could be deduced from the speed of coagulation; von Smoluchowski willingly agreed to my suggestion and gave, in addition, a complete theory of coagulation on a mathematical basis.

My own experiments as well as those of Westgren and Reitstötter led to the surprising result that the spheres of attraction of the gold particles slightly exceed twice the particle radius, in other words, that these particles must almost be touching one another before they unite irreversibly.

Further investigations in this field have been made with other systems, among others by Richard Lorenz, by Kruyt (Utrecht) and G. Wiegner (Zurich) with their pupils.

With these expositions we approach an interesting field which is called changes of state of colloidal solutions. The majority of these changes is due to unification or separation of the particles. The former of these processes can proceed in different ways; only two of them may be emphasized here - the unification of particles by aggregation and by crystallization.

*Gel Structures* - The changes of state are particularly striking in the formation of a jelly. They are accessible to direct observation in the ultramicroscope, and W. Bachmann has made in the Institute placed under my direction a detailed examination of various jellies both during and after their formation. He worked with various dark-field condensers, for instance with Siedentopf's cardioid condenser (Figs. 4, 5 and 6).

The most important result of these investigations can be summarized in that in general jelly structures can be of very different nature. They appear



Fig. 5. Picture of 20% sodium oleate jelly; solidified slowly (at approx.  $10^{\circ}$ ). Apochromat 3, ocular 1, magnification 140. Cardioid condenser (Siedentopf).



Fig. 6. Picture of 5% sodium palmitate jelly. Concentric condenser (Jentzsch).



Fig. 7. Filament structure in the vitreous body of the eye from a drawing by Dr. Heesch. (From *Kolloidchem. Beih. Ambrohn-Festschr.*, 1926).

sometimes as predominantly grainy structures (as in the case of gelatine) or also as networks of very fine filaments or long-drawn crystals as, for example, in gels of soaps.

Of particular interest in this connection is the ultramicroscopic structure in the vitreous body of the eye which was discovered by Thiessen and Baurmann with the aid of the immersion ultramicroscope. It consists of a maze of fine filaments of proteins, filaments which are submicroscopic in two dimensions but microscopic in one. This maze of filaments imparts to the vitreous body its elasticity, and the change of the filaments which occurs with time and is visible in the ultramicroscope produces a melting away of the jelly. More recent investigations of the vitreous body have been made by C. Heesch, Göttingen. (Fig. 7).

The gel structures are frequently so fine that their observation is no longer accessible to ultramicroscopy. Such systems occur, e.g. in the dry gel of silicic acid.

This appears to be homogeneously transparent, but is permeated with an immense number of amicroscopic voids which may be filled with all kinds of liquids.

Van Bemmelen was the first to determine in careful investigations the reduction in vapour pressure which the water in such systems undergoes.

Further investigations in my Institute (in particular an excellent work by J. S. Anderson) led to the valuable result that the vapour-pressure reduction in the gel of silicic acid is essentially due to the development of concave menisci in the ultramicroscopic pores of the gel when the liquid dries out.

By using a formula from capillarity theory it now became possible to determine the diameter of the voids in a given gel from several series of experiments independently of one another with good agreement. This diameter is variable, very small and can be measured in millionths of a millimetre.

Since then the gel of silicic acid is also used technically for the condensation of liquid vapours, similarly to absorption charcoal.

*Transport of Electricity by Colloidal Particles* - More than twenty years ago the statement was sometimes made that the conductivity of colloidal solutions was due only to impurities from crystalloid-dissolved electrolytes. This seemed to me *a priori* improbable because electrically charged colloidal particles which move in an electric current, would have to participate in the transport of electricity in the same way as ordinary ions; there only remained the question what share the colloidal particles have in the transport of electricity. It

was, therefore, first of all necessary to separate the colloidal solutions from the admixed electrolytes. This was done by ultrafiltration, a method which had already been used by Duclaux. The further pursuit of this object by my pupil G. Varga (he examined colloidal stannic acid) then led not only to an answer to this question, but also to a preliminary evaluation of the composition of the particles in the hydrosol of stannic acid.

Other investigations by R. Wintgen and his pupils then confirmed Varga's findings and gave, in addition, information on the electrical equivalent and the composition of the particles in the colloidal solutions of iron oxide and chromium oxide so that we are now completely informed about the actual character of certain colloidal particles. Over and above this, the method used in these investigations promises, when applied to other colloids, to give further information on the composition and nature and magnitude of the charge of micelles. This expression which was first clearly defined by J. Duclaux denotes the colloidal particle with the charging ions adhering to its surface and the ions dissociated from it which compensate the charge of the particle externally. The concept "micelle" has proved to be extremely fruitful in evaluating the composition and the electrical behaviour of colloidal particles.

*Structure of the Particles* - An important question concerns the form and shape of colloidal particles and the nature of their space filling. The ultramicrons are in many cases not iso-dimensional, i.e. not spheres, cubes, or octahedrons, as is usually assumed as a first approximation for the purposes of mathematical treatment. Frequently they are extended in length (filaments, lamellae or platelets), analogous to the description in the discussion of gel structures.

Sometimes it is possible to observe rodlets directly in the ultramicroscope. In hydrosols of vanadium pentoxide and benzopurpurin such formations have frequently been observed.

Experiments on the peptization of stannic acid and purple of Cassius had early shown that the peptization, i.e. the transition from hydrogel to hydrosol under the influence of electrolytes, is always connected with an electrical charging of the particles to which the mentioned change of state is due.

The electrically charged particles are distributed evenly in the surrounding liquid, thus forming a hydrosol. Depending on the amount of peptizing electrolyte finer or coarser divisions are obtained, as can be proved by ultra-microscopy and ultrafiltration (Dissertation by Heinz).

The study of these systems has led to the result that the particles of such hydrosols or colloidal solutions obtained by peptization are as a rule not to

be regarded as being solidly filled. In other words: these solutions contain secondary particles which can be imagined as being composed of many smaller, solidly filled primary particles. The words primary and secondary particles were first used by Werner Mecklenburg.

The picture which we obtain when we consider also the colloidal solutions in addition to the gases and the crystalloidal solutions, is roughly as follows:

In the gaseous state and in crystalloidal solution the substances are always subdivided down to their molecules, they move freely and independently of one another, and they obey the gas laws.

The fact that the molecular weight of chemical compounds could be calculated from the vapour pressure and osmotic measurements, is due to the fact that the molecules of a given chemical compound are all equal to one another.

The peculiarities of electrolyte solutions found their explanation in the dissociation theory of Svante Arrhenius.

The particles of colloidal solutions are larger than the molecules, and must frequently be regarded as aggregates of molecules; they may be of different size even when we are dealing with solutions of the same substance. However, the same laws apply to them which the molecular theory set up for molecules. Owing to the difference in their mass, however, it is not possible to determine exactly the molecular weight of the dissolved substance from osmotic measurements, but on the other hand, the particles often have the advantage of being directly visible. In this way we gain an insight into their absolute size in another way.

The foregoing remarks were able to deal, if they were to fit the occasion, only very briefly with the state of the knowledge of colloids which has been reached in connection with my own investigations. We possess today extensive knowledge of the size and structure of colloidal particles and proved methods for their investigation. I was able to express myself here all the more briefly as I have given a detailed description with literature references in my *Lehrbuch der Kolloidchemie* (5th ed., Leipzig, 1925 and 1927).

Although we should not be satisfied with what has been achieved, the hope does not seem to us too bold that we shall be able to build safely on the basis that has been won the further knowledge of colloids as a continuation of the proved molecular theory and its impressive extension through the ionic theory of Svante Arrhenius.