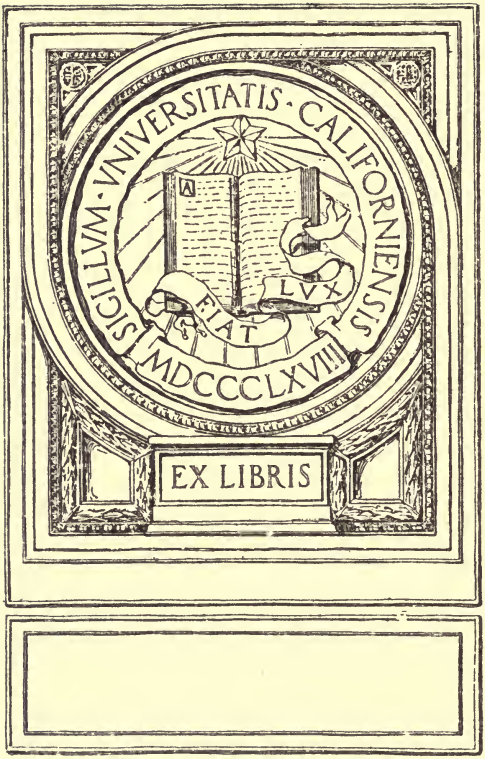
A POPULAR TREATISE

ON

THE COLLOIDS IN THE INDUSTRIAL ARTS

ARNDT—KATZ



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A Popular Treatise on

The Colloids in the Industrial Arts

BY

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TRANSLATOR'S PREFACE.

The warm reception and great approval with which the little volume of Prof. Dr. Kurt Arndt's "Die Bedeutung der Kolloide für die Technik" met in Germany make it very desirable that it becomes accessible also to the English-speaking chemists. It will be especially welcomed by those busy works-chemists who do not have the time to make a special study of the chemistry of the colloids, but who desire to keep abreast with the development of their science and the application of its various theories in the different industries.

This translation has been made from the second German edition which has been revised and considerably enlarged by the author. It was thought advisable to add an Index, which is missing in the German edition.

I feel it a pleasant duty to express here my thanks to the publisher of this translation, Prof. Dr. Edward Hart, proprietor of the Chemical Publishing Company, for his revision of my manuscript and for the great care in the preparation of the book for publication.

NAHUM E. KATZ.

MERIDAN, MISS., January, 1913.

PREFACE.

The present treatise originated from a lecture, which I delivered before the "Verein zur Befoerderung des Gewerbefleisses," in Berlin. Since this short lecture was favored with a very detailed abstract in the "Chemiker-Zeitung," and, since it found otherwise more attention than expected, I willingly complied with the request of the energetic publisher of the "Kolloid-Zeitschrift" to make my lecture accessible to larger circles, and to present a *popular* treatment of the subject of the intimate relation between colloidal chemistry and the Arts and Manufactures, in a separately issued volume. The chemist, who makes a special study of colloidal chemistry, will naturally find in the present unassuming treatise little which is new to him.

Since the purely scientific problems of colloidal chemistry were treated in the *"Introduction To Colloidal Chemistry"* by Pöschl,[1] I was in the position to limit myself to short introductory remarks in explanation of the most important ideas and terms, after which I entered into a more thorough discussion of technical matters. I have brought together a large quantity of material, which I have taken from technical magazines (preferably, from the "Zeitschrift für Chemie und Industrie der Kolloide"), partly from the book by A. Müller, "Allgemeine Chemie der Kolloide," (Leipzig, 1907), partly from my own book, "Technische Anwendungen der physikalischen

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[1] This book has been translated into English.

Chemie," (Berlin, 1907), but I have not striven after completeness, but endeavored, to give the reader a *Vivid Picture of the Great Significance,* which the colloids have in numerous important processes. K. ARNDT.

Charlottenburg, New-Year, 1909.

PREFACE TO THE SECOND GERMAN EDITION.

In the two years, since the first edition of this treatise appeared, colloidal chemistry has rapidly developed. Numerous treatises, preferably, in the "Zeitschrift für die Chemie und Industrie der Kolloide" and their "Chemische Beihefte," have brought forth much which is of interest, and some which is of value to the industries. I have endeavored to do justice to all these developments within the scope of my treatise, by changes and considerable additions. The chapters on Dispersed Systems, Suspension- and Emulsion-colloids, in which I duly considered the new classification of colloidal chemistry and its terms, and, the chapter on the Colloids in the Mineral-kingdom, and in the Brewing-Industry are new.

To those who desire further information about scientific colloidal chemistry, the "Grundriss der Kolloidchemie" by W. Ostwald, (Dresden, 1911), the second edition of which has just appeared, may be recommended.[1]

K. ARNDT.

Charlottenburg, Easter, 1911.

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[1] A third edition of this book has already appeared.

1. Definition of the Term "Colloid."—The name *"Colloid"* is connected with the Greek word κολλα = glue, and means "glue-like"; it was first used by Th. Graham half a century ago. This English chemist termed as *Colloids* various substances, which, indeed, chemically, have nothing to do with glue, but which resemble in appearance the soaked-up cabinet-maker's glue, as, for instance, the gelatinous precipitate which is obtained when muriatic acid is added to a concentrated solution of waterglass. From sodium silicate, hydrochloric acid separates a voluminous jelly, which, by washing, we can free almost completely from the salt. By heating, we gradually expel the large quantity of water which is absorbed by the jelly, and at last obtain a pulverulent mass which gives off the last traces of its water only when it is strongly ignited. Heated over an oxyhydrogen flame the silicic acid melts and on cooling congeals to a transparent glass, quartz glass. But if we let the mass cool extremely slowly, then the quartz-glass transforms into small crystals. So we have for one and same substance, silicic acid, three different states: the *colloidal,* the *glassy* and the *crystalline* state. In a strict sense, silicic acid has several crystalline states, since it is found in several crystalline forms, of which rock-crystal presents an especially beautiful example. One of these states, the hexagonal crystalline form of rock-crystal, is, at the ordinary temperature, the state of rest of silicic acid into which the other forms tend to change.

The *glassy* state forms a continuation of the *liquid* state; the glasses are considered as liquids which have a very great internal friction. The *colloidal* state, on the contrary, may be defined as the *solid non-crystalline state;* we really cannot call it amorphous, formless, because, as was shown by C. Bütschli, *colloidal silicic acid* presents a very fine *cell-structure*. It has a honey-comb (wabige) structure, and therefore, like a sponge, it is able to absorb liquids. Such a cell-structure of great surface development is shown by numerous inorganic and organic jellies, particularly the cells of vegetable and animal bodies, and of substances which are obtained from them: wool, and other textile fibers, leather, glue, caoutchouc, cellulose and celluloid, proteins; all come under the term *colloid*. How infinite the field.[1] The reader will anticipate that the industrial arts as well, have much to do with "Colloids," although up to the present time they have generally not made use of this name.

2. Colloidal Solutions.—If we add muriatic acid to a *dilute* solution of waterglass, no jelly separates, but after

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[1] It is accepted at present that all substances are able, under appropriate conditions, to assume the colloidal state.

evaporating the solution, it congeals suddenly with separation of silicic acid. In spite of the fact that from the dilute solution no silicic acid visibly separates, the sodium silicate and the hydrochloric acid have nevertheless entered into a chemical inter-action; this can be proven by physical measurements. For instance, by measuring the electrical conductivity of the solution. We have in this case a *colloidal solution.* We can remove the salt from this solution by transferring the latter into a vessel, the bottom of which is formed of a parchment membrane, and placing it in pure water. The salt diffuses through the membrane, while the colloidal silicic acid does not. In this way, by *Dialysis,* we are able, if we renew the water from time to time, to obtain a colloidal solution of silicic acid which contains only traces of salt. By evaporation we can concentrate it to a certain degree. But the more concentrated the solution becomes the easier it congeals. We can coagulate it, for instance, immediately, by adding to it a minute quantity of soda, or by passing into it only a few bubbles of carbonic acid gas. This *colloidal solution* of silicic acid manifests besides its remarkable instability, still other very important differences from a *true* solution, for instance, that of common salt. While a solution of salt boils only above 100° C. and freezes below 0° C., the boiling and freezing points, the vapor tension and electrical conductivity of the colloidal solution are not much different from those of pure water.

For colloidal solutions Graham introduced the name *Sol;*[1] when water is the solvent, the name became *Hydrosol.* Correspondingly there are *Alcosols,* etc. The precipitated colloid on the contrary was a *Gel.*[2]

Like the hydrosols of silicic acid, the hydrosols of iron hydroxide, aluminium hydroxide, stannic acid, tungstic acid, arsenious sulphide, Berlin blue, etc., can be obtained by chemical transformation in dilute solutions and purified by dialysis.

3. Colloidal Solutions of Metals.—Metals may also be obtained in the condition of colloidal solutions, when their salts in *very dilute solution* are reduced to metals. In this way, the great physicist M. Faraday, as early as 1857, obtained a *colloidal solution of gold* when he treated a very dilute solution of gold-chloride with yellow phosphorus. A very good method for the preparation of colloidal solutions of gold is given by R. Zsigmondy, who studied these solutions very thoroughly, and even devoted to them a special book.[3] He employs formaldehyde as the reducing agent and by a small addition of potash increases the stability of the colloidal solution.

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[1] From "Solution."

[2] From "Gelatine."

[3] R. Zsigmondy, Zur Erkenntins der Kolloide (Jena 1905).

If the water employed in this process is sufficiently free from impurities, a colloidal solution of gold is obtained which has a magnificent deep-red color and which will keep for years. In reflected light, on the contrary, this solution has a dirty brown color. This turbidity is an indication that in this case we do not have a true solution, but that in the water solid particles which reflect the light are suspended. If the colloidal solution is illuminated by a very bright light, then the separate gold-particles can even be seen under a microscope.

H. Siedentopf, of Jena, constructed for this purpose the following appliance: strong arc-light, or still better, sun-light is condensed by lenses to a light-cone with a perpendicular axis, the point of which falls into the solution to be tested. The microscope is focused on the point of the light-cone, the place where the greatest brightness prevails. In pure, dust-free water the vision field remains dark; in the colloidal solution of gold, on the contrary, numerous brilliantly variegated red, yellow, and green discs are seen, which restlessly fly to and fro in a constant zig-zag movement.[1]

If the visible gold-particles in a limited space are counted and the quantity of gold in this space is deter-

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[1] The brightness of the ultra-microscopic vision was considerably enhanced by the introduction of the Paraboloid- and Kardioid-Condensers. Now even very small quantities of solution are sufficient.

mined by analysis, then the average size of these particles can be calculated. If it be assumed that these particles are spherical, it is found that their diameters in different solutions of gold range from about 10 to 40 $\mu\mu$.[1] This size is far under the limit of visibility under an ordinary microscope. For this reason H. Siedentopf named his appliance *Ultra-microscope* and termed the particles which are made visible by it, ultra- or submicroscopic From the fact that the gold-particles appear as small discs nothing can be concluded as to their real form; this is due only to the imperfections of our vision.[2]

In light red solutions of gold, R. Zsigmondy was able to point out still smaller particles, down to 6 $\mu\mu$. In others he found also larger particles, up to 200 $\mu\mu$; these solutions already began to disintegrate, the gold particles clumped together to larger complexes and were gradually sinking to the bottom.

In two interesting graphical descriptions, in his abovementioned book, R. Zsigmondy compared the magnitude of these ultra-microscopical gold particles, on the one hand, with microscopically small objects, such as blood corpuscles, starch particles, suspensions of porcelain clay, bacteria, on the other hand, with the still smaller (calculated) dimensions of *the molecules* of chloroform,

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$\mu\mu$?

[1] μ is the sign for one millionth part of one millimeter (micron).

[2] The stars also appear to us, not as points, but as small discs.

alcohol, etc. We learn from this comparison that, in general, *the molecules* are still very much smaller than the ultra-microscopical gold-particles, but that very large molecules, which comprise very many atoms, such as, for example, the molecule of soluble starch (according to C. A. Lobry de Bruyn) are much like them. The ultra-microscope has considerably shifted the limits between visible and invisible. In several pink-colored solutions of gold the existence of mass-particles even still smaller than 6 $\mu\mu$. must be assumed. Indeed, these particles can no more be seen separately by means of the ultra-microscope, but their presence is detected by a feeble glittering of the light; R. Zsigmondy terms these particles *amicroscopic*.[1] If a few drops of the usual colloidal solution of gold are added to such an amicroscopic solution of metallic gold, the flocculation of the latter is considerably accelerated.

Another way of preparing the *hydrosols of metals*, worked out by G. Bredig, is the following: an electric arc or strong sparks are formed under water between two wires of the respective metal; the metal then evaporates and partially remains in the water as a colloidal

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[1] The lower limit of visibility of metallic particles is especially favorably located because these particles reflect the light rays very strongly. The molecule of soluble starch, despite its large size, will be invisible under the ultra-microscope, because it does not shine sufficiently bright.

solution; another part clumps together and sinks to the bottom. The solution of gold, obtained in this way, is usually colored violet blue. Most of the metals have been prepared in this second way in the condition of colloidal solutions in water and in other liquids. So, for instance, Th. Svedberg prepared a blue colloidal solution of metallic sodium in ligroin. But none of these numerous solutions can be compared in beauty of coloration with that of the solution of gold. A colloidal solution of platinum, for example, appears yellowish brown in transmitted light and almost black in reflected light. The hydrosol of silver has a brick-red color. Most of the colloidal solutions of metals are very instable and soon precipitate the metal.

4. Flocculation of Colloidal Solutions.—Since the colloidal solutions do not correspond to any condition of equilibrium and their particles tend to clump together, the colloid flocculates by itself in a longer or shorter period; boiling usually accelerates this decomposition.

A small addition of an alkali to the water considerably increases the keeping qualities of the metallic Sols. The Sol of silicic acid, on the contrary, becomes more stable by the addition of some hydrochloric acid. Some investigators assert that, in general, the presence of certain small quantities of "electrolytes" is needed for the existence of colloidal solutions. At any rate, it is a fact, that most of these solutions are very sensitive towards any change in the quantity of electrolytes, which they contain; for example, the red solution of gold is colored blue by the addition of one drop of hydrochloric acid, and the gold gradually separates.

The quantity of the addition, which causes the change in the coloration, or the beginning of precipitation, varies with the nature of the solution and that of the addition. Quantities of electrolytes, which remain below this limit, the *swelling value* (Schwellenwert), will not cause the flocculation of the hydrosol even in a longer period. The explanation of this phenomena at present preferred, is based on the fact, that colloids, as, in general, all solid particles, move in the field of an electrical current. If we send a current, having a pressure of about 110 Volts, or more, through a colloidal solution, it is observed, that the solution is almost a non conductor, but that the colloidal particles collect at one pole.[1] Colloidal metals

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[1] While the mass particles of the colloid migrate together towards one and the same pole, in solutions of "electrolytes," one part of the molecules migrates toward one, and the other part—towards the other pole; for example, the chlorine of hydrochloric acid migrates towards the positive pole (Anode), and the hydrogen, towards the negative pole (Kathode). In accordance with this, the ionic theory assumes that the hydrochloric acid is split into negatively charged chlorine-ions and positively charged hydrogen-ions. Potassium hydroxide (caustic potash), when dissolved in water, is split into positive potassium-ions and negative hydroxyl-ions.

usually migrate towards the positive pole, the Anode; therefore they are negatively charged; since (as is known from friction electricity) opposite electricities attract each other. Iron hydroxide and aluminium hydroxide, on the contrary, migrate towards the cathode, and are therefore positively charged. More accurate observations revealed the fact, that "migration-sense" (Wanderungssinn) is not so much dependent on the kind of the colloid, but that it is determined mostly by the small quantities of electrolytes, which are found even in very pure solutions. A very small increase of the *hydrogen-ions* in the water electrifies the hydrosol positively so that its particles migrate towards the negative pole; a minute increase of the *hydroxyl-ions* electrifies it, on the contrary, negatively so that its particles migrate towards the positive pole.

An addition of ions, which carry a charge *opposite* to that of the colloidal particles, causes their precipitation;[1] so a *negatively* charged colloid is coagulated by *positively* charged ions. Similarly charged ions cause no precipitation, or have a slight protective action.

Hydrosols which carry opposite charges precipitate each other; so, for example, colloidal solutions of gold

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[1] The precipitating power of the respective ion is the greater the higher its chemical valence; a bivalent ion acts more than one-and-a-half times as strongly as a univalent one. But hydrogen- and hydroxyl-ions possess the greatest precipitating power.

and of stannic acid give a purple precipitate which corresponds to the well known purple of *Cassius.* If a *larger* quantity of the oppositely charged colloid is added to the solution, often no precipitation occurs, on the contrary the solution becomes more stable. Especially organic colloids, such as gelatine and proteins, increase the stability of colloidal metals; therefore these are termed *protective colloids.* The pharmaceutical industry is making use of these colloids in the manufacture of colloidal silver and mercury.[1] We have seen in the example of hydrosol of gold, which becomes more stable by the addition of a little alkali (*i. e.,* hydroxyl-ions) that similarly charged ions also make a colloidal solution more stable, if they are added in a sufficiently small quantity.

The flocculation processes are of paramount importance in physiological chemistry; here belongs, for instance, the mutual precipitation of toxins and antitoxins (Immuno-serum).

Singular is the behavior of solutions of proteins. If the protein solution is purified from salts, as much as

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[1] This protective action is manifested also in very fine mechanical suspensions, as, for example, in a suspension of soot in water. Despite its very fine division, soot can be prevented from precipitating only by a protective colloid (lime), which fact is taken into consideration in the manufacture of water colors. In a similar manner Acheson was able, by treating his graphite with tannic acid and water, to bring it into such a condition that it could be permanently suspended in water and oils, and in this way become useful as a lubricating material.

possible, by long dialysis, it does not coagulate, when heated, but it does so when salts are subsequently added to it. Complete coagulation ensues only when the solution reacts slightly acid. When milk, for example, curdles, proteins which have been chemically changed by ferments are precipitated; the curdling represents an intermediate step; the curdled protein is completely coagulated by the subsequent heating.

When the precipitated colloid changes to the form of a *Gel*, it still does not completely separate from the water, but forms, as I have mentioned before, a peculiar honey-comb-like structure, which contains enclosed water.

5. Reversible and Irreversible States of Aggregation.—When *pure* hydrosols of metals are precipitated, no real Gel-formation results, but a sort of metallic sponge is produced. In the case of precipitated gold a light pressure with the burnisher is sufficient to transform the dried powder into coherent metal. If it should be desired to bring this gold again into the condition of a colloidal solution, this could be accomplished only in a roundabout way, probably by dissolving it in aqua-regia and reducing the solution with formaldehyde. But colloidal silver, which is prepared by the method of C. Lea[1] and

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[1] C. Lea reduces the solution of silver-nitrate with iron sulphate in the presence of sodium citrate.

which contains organic impurities, easily dissolves in water; it can even be precipitated from the colloidal (blood-red) solution by ammonium nitrate, and then again dissolved in water. Such Sols used to be designated as *reversible* (umkehrbar) and the hydrosol of gold was considered as an example of another class, the *irreversible* Sols. This difference in behavior is, however, not so much due to the nature of the respective substance, as to the treatment which is accorded to it. For this reason, in a strict sense, it can be spoken only of reversible and non-reversible states of aggregation of the colloids.

Colloidal silicic acid, which in the process of evaporation has lost but little water, can be liquefied by an addition of water; even in a somewhat later stage of the process of evaporation the silicic acid can be brought into solution by treating it with a solution of caustic soda; according to Th. Graham one part of sodium hydroxide in 1,000 parts of water is sufficient to convert into hydrosol 200 parts of silicic acid when the whole is cooked for one hour. This liquefaction process used to be termed peptisation; by this term it was compared with the process of transformation of protein into pepton which goes on in the intestines when food is digested.

Reversible states of aggregation are caused by change of temperature in lime, agar-agar, and fish-glue, which, when they have a certain composition, congeal in the cold to a semi-solid Gel that liquefies again on being warmed.

6. General Remarks on Dispersed Systems.—The term *dispersed systems,* has recently been introduced to designate compositions in which one substance is very finely divided within another one. The finely divided substance is termed the *dispersed phase,* while the other, which is mostly in very large excess, is not termed the "solvent," but, in a more general way, the *dispersing medium.* From these dispersed systems, which come under the term colloidal solutions, are distinguished, on the one hand, suspensions, or *aggregated dispersed systems* (grob disperse,) and, on the other hand, true solutions, or *molecular dispersed systems.* A sharp dividing line cannot be drawn between either of these systems; in reality, all such dispersed phases, the particles of which measure between one ten thousandth to one five hundred thousandth of a millimeter, have to be considered as colloidal solutions.

The *suspensions* differ in their behavior from the colloidal solutions in that they can be separated from the solvent by sedimentation, or more rapidly, by centrifugalizing; by stirring up the separated slime the suspension is mostly restored. When filtered, the slime is retained by the filter paper, while colloids usually pass smoothly through the paper.

From the molecular dispersed systems, the *true solutions,* colloidal solutions are distinguished in that in reflected light they appear turbid, and that they exhibit the so-called *Tyndal-Effect.* If a bundle of bright light-rays, condensed by lenses to a cone, is thrown (as in an ultra-microscope) into a colloidal solution, the light-cone shines with a more or less bright light, depending on the size and the reflective-power of the colloidal particles, while a true solution, on the contrary, remains dark. In that special case, when the true solution contains a fluorescent substance, (for example, a water extract of chestnut-bark) it will, indeed, also emit light, but this peculiar bluish or greenish light is not *polarized* like that of the Tyndall-effect, *i. e.,* when observed through a Nicol-prism, it does not change its brightness on turning the prism. A second very characteristic property of colloidal solutions is their *very small diffusion power.* Colloids cannot permeate membranes which let true solutions pass through; this difference was made use of to purify the colloidal solution of silicic acid from salt by dialysis by means of a parchment skin. On account of this great difference in the diffusion, it is possible to conveniently examine the nature of, for example, solutions of dyes, by pouring same on gelatine:

if the dye penetrates the gelatine, there is a true solution; but if the separating surface remains, then we have a colloidal solution.

7. Suspension and Emulsion-Colloids.—Lately the colloids have been very properly divided into two classes. The distinction is between those colloidal solutions in which the finely divided substance is liquid, here the dispersed phase consists of ultra-microscopical fluid particles, the *emulsion-colloids,* and those in which the small particles are solid, which are termed *suspension-colloids.* In the colloidal solution of gold we have an excellent example of the suspension-colloids, or shorter the *suspensions.* To the *emulsion-colloids* belong, in the first place, gelatine, and protein-solutions. Suspension-colloids are flocculated even by a small addition of an electrolyte; emulsion-colloids are much more stable. Suspension-colloids scarcely influence the mobility of the solvent, but emulsion-colloids make the solvent more viscous, and, in general, the viscosity (the internal friction) of emulsions increases very much upon cooling. These differences disappear inasmuch as they depend on the solvent, and very diluted emulsoids may behave like suspensoids, while the latter, on the contrary, at higher concentrations, resemble the first. The upper concentration limit of the suspensoids is mostly small; R. Zsigmondy was able to prepare colloidal solutions of gold with the highest content of only 0.1 per cent. of gold, and G. Bredig was able to obtain, by electrical spraying, not more than 0.014 per cent. Indeed, W. R. Whitney and J. C. Blake prepared, in roundabout ways, more concentrated gold-sols, but there is no assurance that we do not have to do in this case with a suspension. Emulsoids have no upper limit of concentration.

To the emulsions belong also the *foams*. That, for example, of the white of an egg, which is beaten to a foam, is a mixture of two liquids, and does not probably consist of skins filled with liquid. This becomes evident when the foam settles in the cold: it melts then to a clear solution, which can easily be freed from the impurities of the white of an egg (threads, coagulums).

Common to all colloids is the very fine division and, therefore, the, in comparison with the mass, enormous surface-development.[1] The more the surface is developed, the more come into the foreground the actions of the surface energy, which endeavor to reduce the surface, and for that purpose strive to clump the small particles together to a larger structure. On the other hand, all

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[1] The total surface increases in the same proportion as the diameter of the separate particles decreases. For example, a clay ball of one centimeter in diameter has a surface of 3 square centimeters (in round figures); if this mass is divided into 100,000 little balls, the total surface is then equal to more than 30 square meters.

bodies endeavor to draw from their surroundings and to accumulate on their surface gases, liquids, and solid particles. In the colloids, with their very much developed surface, this endeavor, likewise, comes to the foreground. In the following chapters we shall see of what value these general properties of the colloids are to the technics, and which special part certain colloids play in technical processes.

8. Ruby Glass.—The magnificent color of the colloidal solution of gold we find reproduced in the *gold ruby glass.* Genuine ruby glass is obtained when gold-chloride is added to the glass-mass. If the mixture is cooled off quickly, a colorless glass is obtained, which, when subsequently heated to the softening-point, suddenly becomes tarnished by a splendid ruby-red. The quantity of gold which is contained in ruby glass is minute, only 0.05 to 0.06 per cent. In the red glass H. Siedentopf and R. Zsigmondy were able to distinctly discern the ultra-microscopical particles of gold. Their following experiment is very instructive: They heated to the melting-point one end of a strip of *colorless,* very slowly cooled ruby-glass, while the other end remained cold. The hot end of the glass became shining red, the red coloration weakening towards the cold end, while the latter unheated part of the glass remained entirely colorless. The ultra-microscope showed in the shining red part of the glass brilliant-green particles in very short distances from one another; in the weakly red one there was but a symmetrical green light-cone, which was weakening towards the colorless end.

When a strip of poor ruby-glass was heated in a similar manner unilaterally, its hot end was colored blue, the coloration becoming weaker towards the cold end, being, first violet, and then light pink, while the cold end again remained colorless. In this case the ultra-microscope showed brighter single particles, which were separated from one another by much longer distances, and which shone copper red in the blue part of the glass, yellow further on, and green in that part of the glass which appeared pink in the transparency. The average distance from one particle to another was, however, as in the good ruby-glass, about the same in the entire strip The brightness of the particles diminished from the blue toward the colorless end; in this case feebly lighted particles could be discerned also in the cold part of the strip.

These entangled phenomena can be interpreted in the following manner: On cooling, gold particles separate, which, however, are too small to give the glass any coloration. These gold germs (Goldkeime), when heated again, grow and produce the beautiful ruby-red; they grow the quicker the hotter the glass, therefore, the time of heating being equal, the largest particles of gold are to be found in those places which were exposed to the greatest heat. This separating of the gold can last only until the supersaturation-point of the respective kind of glass and temperature is reached.

Under the ordinary conditions of work only a part of the total gold separates in the ruby-glass as the coloring matter in the form of ultra-microscopic particles.[1] If the red ruby-glass is remelted at a white heat, the gold goes again into solution and the fusion remains colorless when cooled, but by reheating it may again be colored red.

Some kinds of ruby-glass are tarnished red already upon cooling; in these glasses the conditions for the formation and growth of crystallization center-points upon cooling are more favorable.

The reason why the edges of a pressed ruby-glass remained colorless on heating are also of interest: the edges cooled in the press more rapidly and on reheating warmed up more rapidly and hotter than the center. In the ultra-microscope the edges showed much less but considerably larger green particles of 110 to 145 $\mu\mu$ than the rest of the glass-mass. The edges had to pass through the temperature of the germ-formation too rapidly, so that only few germs could develop which on

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[1] This has been proven by colorimetrical experiments. See: R. Zsigmondy, Zur Erkenntniss der Kolloide (Jena 1905), pp. 128-135.

reheating rapidly grew to a considerable magnitude. But the center of the glass upon cooling had enough time to develop a large number of germs which on heating were less strongly warmed and therefore did not grow as rapidly.

In *spoiled ruby-glass* the germ formation and growth are disturbed; there are less germs developed and these grow slower than in good ruby-glass. R. Zsigmondy assumes that instead of simple crystals, crystalline germs were formed.

The coloration process in *copper ruby-glass* may be similar to that in gold ruby-glass. Copper ruby-glass upon cooling is colored greenish, and only on being gently heated it becomes red.[1]

9. Milky-White Opaque Glass. Troostite. Phosphorus.— *Milky-white opaque glass,* which has been prepared by the addition of fluor-spar, contains, according to A. Lottermoser,[2] calcium fluoride in the condition of a colloidal solution. The fact that such glass appears turbid in re-

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[1] H. Siedentopf explained in a similar manner the blue coloration, which at times appears in rock salt. In this case the ultra-microscopical crystals of metallic sodium are the coloring matter. H. Siedentopf was able to prepare artificially such colored sodium-chloride crystals, by treating them in vacuum with vapors of sodium or potassium. When reheated the color changes, because the ultra-microscopical particles undergo a similar change as those of ruby-glass.

[2] A. Lottermoser, Zeitschr. f. angew. Chemie, 1906, 19: 369-377.

flected light and allows transmitted light to pass through clearly with a yellowish color, speaks in favor of the acceptance of this theory. The *glaze-colorations,* which are formed by metals, may also be considered as colloidal solutions.[1]

Colloidal solutions occasionally appear also in *metal-alloys.* So, C. Benedicks[2] considers the structural-element (Gefügebestandtheil) of slowly cooled steel, the *Troostite* (an intermediate stage between Martensite and Pearlite), discovered by F. Osmond, as a colloidal solution of cementite (iron-carbide). If this Troostite is heated to 150 degrees for a sufficiently long period, the ultra-microscopical germs grow and needles of cementite become visible.[3]

Colloidal intermediate forms do not seem to be rare in other transformations. H. Siedentopf found that when white phosphorus changes into the red form, a colloid is obtained at first.

He observed that when a piece of white phosphorus was placed under the Kardioid-Ultra-microscope at a magnification of 1,500 times, he noticed in the phos-

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[1] Just as the colorations of the borax- and sodium-phosphate glasses so useful to the analyst.

[2] C. Benedicks, Zeitschr. f. physikal. Chem., 1905, **52** : 733.

[3] Sufficient information as to the value of Martensite, etc., can be found in my book, "Technische Anwendungen der physikalischen Chemie" (Berlin 1907), p. 235.

phorus, right after the illumination, small white points, which rapidly grew to radiant brightness, and then turned red. In a solution of phosphorus in carbon bisulphide the process is the same.

10. Colloids in the Mineral Kingdom.—The costliest members of the mineral kingdom, the *precious stones,* owe their magnificent color, often, to minute quantities of a colloidally dissolved coloring substance. C. Doelter includes in this class, among others, the smoky (yellow) topaz and most of the sapphires, the beautiful blue color of which is due to colloidal cobalt oxide; in ruby, however, he assumes the coloring substance to be a true solution of chromium oxide in alumina. A very beautiful artificial ruby, which belongs to me, appears indeed in reflected light turbid and dark, just like a colloidal solution of gold on heating, it turns green; upon cooling it is again colored red.

Of the semi-precious stones, the *opal* is to be considered as a colloid, and in fact as a *Gel.* According to F. Cornu,[1] the Gels are in general far more numerously represented in minerals than was hitherto supposed; they are the typical products of all normal disintegration processes. So, for example, bauxite (aluminium-hydroxide) and the already mentioned opal (hydrated silica) are such colloidal products of the disintegration of

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[1] F. Cornu, Koll-Zeitschr., 1909, 4 : 15, and in other places.

rocks. Numerous Gels appear also in the oxidation zone of the ore-beds, for example, *Psilomelane* in the manganese ores. The Gels of the mineral kingdom are distributed, according to F. Cornu, in the groups of the hydroxides, the sulphates, the hydrated phosphates, the arsenates, the antimonates (Bleiniere), the silicates, and the salts, which contain organic acids (*Dopplerite* of the moss-worts); they are entirely absent in the other groups, for example, in the sulphides, the carbonates, and the anhydrous silicates, etc.; that, indeed, is to be expected, if the mode of their formation as disintegration products is taken into consideration.

The external characteristic of the mineral Gels is the conchoidal fracture, presupposing that they have not lost any water; they often stick to the tongue.

Many mineral colloids have their crystalline antitypes. So, for example, opal has an antitype in *Calcedony*, which appears as a crystalline transformation product of the colloidal form.

As especially important colloids of the mineral kingdom, I will also mention kaolin, anthracite and bog-iron-ore.

In the *soil* there are present in the form of colloids iron oxide, silicic acid, amorphous silicates, and the humus substances; as non-colloidal ingredients there are quartz, fragments of crystalline silicates, and the simple salts, such as calcium carbonate, phosphates, chlorides, and sulphates. The humus substances form an amorphous complex of decomposition products of the sugars and proteins; they are agglomerated with the colloidal silicates and adhere also to the crystalline particles.[1]

11. Silver and Gold Mirrors.—The flocculation of hydrosols of metals is made use of in the preparation of silver and gold mirrors on glass. Under certain conditions, the silver separates from the colloidal solution on the glass plate as a brilliant mirror. The whole process lasts few or several minutes, according to which formula is employed in the preparation of the *silver-mirror* (all are based on the reduction of a silver salt in a dilute solution by formaldehyde, sugar, or Seignette-salt, etc.); as an intermediate stage there appears a brick-red colloidal solution of silver. If the process is conducted incorrectly, instead of a coherent brilliant metallic layer, a grayish-yellow skin and a slimy or granulated powder separate. The fact, that the slightest deviation from the formula is so fatal, is not surprising if the sensitiveness of colloidal solutions is taken into consideration. As it is well known, the preparation of the glass, which is to be silvered, is also important; the sep-

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[1] Gedenkboek, J. M. van Bemmeln (Halder), 1910, p. 62.

aration is facilitated if the surface is already overlayed by a silver coating, even if this is an invisible one. In the analogous process of gilding the preliminary production of an invisible gold layer is even necessary. The ultra-microscopical particles rapidly attach themselves to the already separated metallic particles. The metallic mirror can be reinforced as desired by the addition of a fresh quantity of the colloidal solution.

Since the silver-mirror, in spite of its exceedingly small thickness, is a good conductor of the electrical current, it is possible to electro-deposit on it a thick layer of copper and then on the latter a thin layer of palladium. S. Cowper-Coles manufactures hollow metallic mirrors on a large scale by producing them on curved glass-molds in the way described, and then separating the metallic layer by heating.

12. Manufacture of Tungsten Lamps.—While in the preparation of metallic mirrors the separation of the colloid in the form of a coherent metallic layer is desired, and that part which is flocculated as an invisible powder, is considered as an inconvenient waste; in the manufacture of *tungsten lamps,* on the contrary, we desire to obtain the metal in the form of a *Gel,* because this Gel is sufficiently plastic to be pressed into thin filaments. One would wonder why the compact tungsten metal is not rolled out and squirted into filaments directly, as it is done with the tantalum metal for tantalum-lamps. Unfortunately, metallic tungsten is much too brittle to be drawn into wire, not to mention filaments of less than 0.05 millimeter in diameter, as those that are used as metallic filaments in incandescent lamps.[1] On the other hand, tungsten, which melts only at about 2,900° (1,000° higher than platinum and 500° higher than tantalum), by the reason of its cheapness, is especially fitted for the preparation of filaments for lamps on account of its exceedingly high melting-point. The aspiration of the lighting industry is concentrated in an endeavor to heat the illuminative body to the highest temperature possible, because the light-radiation increases extraordinarily rapidly with the increase of temperature. The higher the temperature of the illuminative body, the larger the part of energy, with which it is supplied, is transformed into light. Carbon, indeed, does not melt, but the carbon filament, in general, cannot be heated over 1,800 degrees without deteriorating. The metallic filament lamps are able to glow so much brighter, since such lamps consume for each normal candle-power only about one volt, *i. e.,*

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[1] The metals are better conductors than carbon; for that reason the lamps, which are intended for the use with the current of the usual pressure of 110 volts require long metallic filaments, in order to furnish the necessary electrical resistance.

only about one-third of the electrical energy, which is consumed by the old carbon filament lamps.

The filaments for *osmium lamps,* made from metallic osmium, which cannot be drawn into threads, can be prepared in a chemical way, by igniting carbon threads in an atmosphere of the vapors of osmic acid, a very volatile oxygen compound of osmium. At this high heat, the osmic acid is decomposed into osmium and oxygen, the osmium is deposited on the thread, while the carbon and oxygen burn off, so that a thread of metallic osmium results at last.

The common method, however, was to pulverize the metal, as finely as possible, mix it with a binding material, such as dextrin, gum-solution, sugar-syrup, to a thick mush and squirt this under high pressure through fine holes to form filaments of the desired thickness and form. These filaments were heated strongly, whereby the organic binding material was carbonized; in this way fused filaments were obtained, which conducted well and which contained the carbon in the form of carbide or as a solid solution.

The same methods can also be applied to tungsten, when either the volatile tungsten-oxy-chloride is employed, or the pulverized tungsten is worked to a dough with some binding material. But the second method, which hitherto was employed by preference, has its defects. The squirting requires very high pressure and, further, the carbon in the finished filament is often unequally distributed and forms knots; the cross-section of the filament is in other ways also not uniform throughout the whole length. The thin section offers to the current more resistance, is heated stronger, and, in consequence soon burns through.[1] Binding materials were tried which volatilize at moderate temperatures, for example, paraffin and camphor mixed with alcohol. Finally H. Kuzel has given up the use of any artificial binding materials and made the tungsten extraordinarily plastic in the way indicated above, by converting it into the form of a Gel. The above mentioned binding materials are, indeed, themselves colloids. If the tungsten metal is pulverized very finely in a ball-mill and is pulverized further again and again for weeks and months, a powder is obtained, which, being mixed with water, gives a ductile mass. But, when this mass is pressed to thin filaments in a stamping press, it is noticed that the ductility of the mass is not yet sufficient, that the filaments break; they are too brittle for further treatment. It is

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[1] More information can be found in the valuable article of A. Lottermoser: Einige Bemerkungen ueber die Herstellung von Metallfaeden fuer elektrische Gluehlampen, besonders aus kolloiden Metallen, Chem. Ztg., 1908 : 311-313. See also Koll.-Zeitshr., 1908 : 2, 347.

possible, however, to bring the mechanically extraordinarily pulverized tungsten into the colloidal condition, in fact, into a comparatively concentrated solution, by treating it alternately with alkalies and acids, and giving it, intermediately, plentiful washing. If the tungsten is precipitated from this solution, a viscous mass of an exceedingly fine division is obtained, which has all the desirable properties, and which can be drawn out to filaments of 0.03 millimeters in cross-section, through very fine holes bored in rubies, without the use of great power.

At first, these filaments conduct the current badly, but the small current, which passes through them, is sufficient to heat the filament. In the heat the small particles combine to larger ones; the filament allows a stronger current to pass through and at last at a white heat the tungsten fuses to a solid, good conducting metallic filament, which meets all the requirements in mechanical and electrical respects.

Instead of gradually heating the unfinished filament by the electrical current in the lamp, the filaments, as they come from the press, and after they are dried, are, preferably, ignited in an atmosphere of nitrogen, or in vacuo (because the ignited tungsten is oxidized by the oxygen of the air). The desired metallic filaments are at last obtained at a white heat. They are then cut into the proper length, and are cemented to the current-leading-in-wires in the lamp socket by means of tungsten Gel; by heating also this cement is transformed into a coherent metal. After that the glass globe is placed over the filaments and fastened to the socket, finally the lamp is evacuated, or filled with nitrogen gas, and sealed. The *siriuscolloid lamps,* which are manufactured in Germany by J. Pintsch, are claimed to withstand a current of considerable overpressure, without being deteriorated.

The *Auer-Gesellschaft* manufactures its *osra-lamps* by a different process, the details of which have not been made public.

With reference to the theoretical explanation of the Kuzel process, A. Lottermoser assumes that the grains of the already exceedingly fine ground tungsten powder are etched by the alternating treatment with alkalies and acids, and in this way they are finally reduced to the diameter of ultra-microscopical particles. Further, the chemicals applied in this process introduce into the solution certain ions which make the metal-hydrosol stable when they are present in a definite small concentration (for this reason the plentiful washings between the separate etchings are employed); these ions are, probably, the hydrogen-ions of the acids, on the one hand, and the hydroxyl-ions of the alkalies, on the other hand.[1]

It has been found lately that *perfectly pure* tungsten is ductile and can be drawn out to threads of $^1/_{50}$ millimeter thickness, such as are used in metal-filament lamps. This discovery will, probably, overturn the whole industry, and will do away with colloidal tungsten.

13. Colloids in the Ceramic Industry.—As in the younger tungsten-lamp industry, so, from ancient times, in the ceramic industry the Gel formation is utilized in order to make the pliant ceramic mass more plastic. The noblest material of the ceramic industry, porcelain clay, which consists of almost pure aluminium silicate, is first freed from the heavier and coarser particles by very careful washing, and is then mixed with "diluting-materials" (Magerungsmitteln), Feldspar and quartz, which are also very finely ground and washed. In spite of the painful mechanical preparation, this mass, after being freed from the superfluous water in a filter-press and wedged in a wedging machine, is, (like the powdered tungsten), not yet sufficiently plastic to be subjected to further treatment at once; it must be previously stored for a long period. During the storing in a damp cellar the porcelain mass becomes black and evolves gases, carbonic acid, ammonia, hydrogen-sulphide, which originate

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[1] A. Lottermoser, loc. cit.

in the decomposed organic ingredients that were introduced into it partly by the raw materials, partly by the water.[1] This process is termed "mellowing," or "curing" (Faulen, Mauken). The longer the mass is mellowing the more pliant it becomes; usually the mass is stored at least for three months. According to P. Rohland the success of the mellowing consists in the formation of a colloid which is peptised under the influence of the alkali present in the mass. The acid fermentation of the organic substances causes the binding of the alkali and therewith the coagulation of the colloidal solution.

Kaolin also, which is by itself more plastic than the porcelain mass, must be mellowed previous to being subjected to further treatment.

A very interesting application of the peptisation of the colloids is the process, discovered by E. Weber for *the manufacture of glass melting-pots by casting.* By the addition, according to the nature of the fire-resistant clay, of a small, accurately measured, quantity of soda and a little water, under constant vigorous stirring, he transforms the finely ground slip into a thin mush, which is then run out from the mixing vessel into the pot molds placed below. If the slip were mixed with water only, it would soon settle to the bottom of the mold, while in the Weber's process the whole mush gradually hard-

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[1] R. Dietz, Das Porcellan (Halle), 1907 : 41.

ens to a solid mass, which is uniform in structure and thick in the fracture, for which reason the pots do not suffer any longitudinal cracks, even at more considerable fluctuations of temperature in the glass furnace.

Besides the greater durability in comparison with the pots which were formed by hands, the casting process means also a considerable saving in time and labor. The production of one pot, which holds 220 to 225 kilograms of glass, requires from the time when the mixture is measured up to the time when the filled mold is carried away not more than one hour. After 24 hours of standing still the pot has hardened so much that the core of the mold can be taken out; after a further 24 hours the mantel is taken off and at the same time the upper edge of the casting is cut off. Further treatment is not required. This process has been employed since 1905 in the glass works of Aug. Leonhardi in Schwepnitz (Saxony).

Clays, which cannot be liquefied by soda only, as J. Keppeler[1] found, can be brought into that condition by the addition of humic acid.

In drying in the kiln the colloidal ingredients distinguish themselves in that they, in correspondence with their large surface development, tend in a large measure

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[1] See the lecture by J. Keppeler, Zeitschr. f. angew. Chemie, 1909, 22 : 526.

to diminish their surface by *shrinking*. Crystalline substances do not manifest such *fire-shrinking* properties at all. Due to the fine division of their mass, the colloids are usually at the head also in respect to the rapidity with which they change into other states of aggregation. While, for example, quartz crystals, even at a white heat change but very slowly into the crystalline form, tridymit, which is stable at temperatures above 1,000 degrees, and also quartz-glass transforms only slowly, the colloidal silicic acid forms tridymit rapidly even at 1,000 degrees.

14. Colloids in the Hydraulic-Cement Industry.—Just as, according to the theory of P. Rohland, in kaolin and porcelain, so also in cement does the colloidal condition play an important part.

According to W. Michaelis[1] in the first stage of the hardening process of *portland cement,* in that stage, which is called setting (Abbinden), there are formed, with absorption of water, colloidal calcium hydro-silicate and -aluminate, and colloidal calcium hydroxide. The crystals of calcium hydroxide and calcium aluminate, which are formed gradually, find in the yielding, jelly-like colloid-mixture room for their development; in separating out these crystals petrify more and more the

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[1] W. Michaelis, Jahresbericht der chemischen Technology, 1906 : 109, ff.

first perfectly elastic colloid, which, moreover, on drying becomes by itself hard as a stone, thus cementing by itself the sand-grains or the crystals, which are embedded in it. The colloidal cement, this "mineral Gel," as W. Michaelis calls it, protects the iron in the iron-ore-cement from rusting, by surrounding it in the form of a thick protecting layer. The hardening of the hydraulic cement is based on the gradual setting free of the swelling water, the continued hardening of the colloids, the binding of water as water of crystallization, and the continued formation of crystals of calcium hydroxide. The larger cement grains are protected from the absorption of water by the jelly-like calcium-hydro-silicate and calcium-hydro-aluminate, which are not permeable to water, so that when a pure cement, which has hardened under water years ago, is pulverized, it hardens anew and, indeed, the more, the coarser the original powder was. Thus, in the hardening of the cement, we have to do with the combined action of colloidal and crystalline substances; the water, which is contained in the colloid, compels us to make additions of "diluting-materials" (Magerungs-mitteln) in order, that the cement on hardening, may not shrink too much.

E. Stern,[1] indeed, does not accept this theory wholly, but also thinks that the formation of jelly-like substances

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[1] Chem. Ztg., 1908 : 85.

in the period of the setting of the cement is very probable. To prove the presence of colloids, he carried out the following experiment: when hydraulic cement (or a pure aluminate) is mixed up with water, the lime and alumina go into solution. If a finely pulverized aluminate is dialysed, in the dialysate can be found only lime, alumina is not found at all, or is present in traces only.

E. Stern studied the setting and hardening processes more closely under the microscope, retarding these processes by the addition of gelatin. He spread coarse-grained cement on the object-plate and covered it with a few cubic centimeters of a two per cent. solution of gelatine. After drying, the gelatine preparation was immersed in water (100 cc.). At the end of 24 hours the cement grains were superfically attacked by the water, but no crystals were to be seen there; the larger part of the lime had diffused out, while aluminium hydroxide and calcium carbonate were formed, which surrounded the cement grains. When the access of air was perfectly excluded, instead of carbonate, crystals of calcium hydroxide were formed.

According to Stern, the cement grains, in setting, are surrounded by a colloidal layer; in hardening, crystals (sodium carbonate and hydroxide, aluminate and silicate) separate out and, indeed, in the interior of the cement block chiefly calcium hydroxide, and on the external part—calcium carbonate.

According to P. Rohland, the colloids are of especial importance in the hardening of cement in *sea-water,* because they are impermeable to all salts of magnesium, which would be detrimental to the mortar.

15. Colloids as Adhesives and Glues.—According to the above given explanation, we may consider the colloidal elementary mass of the hydraulic cement as a *binding material.* In a very general way the *colloids,* indeed, are employed for *glueing* and *cementing* purposes. While in soldering the liquid solder forms an alloy with the metallic thread which is to be soldered, in glueing such a mutual dissolving process does not take place, but, so to say, intimate interlacing of two cell-structures is produced. In glueing of wood and other substances of a cellular structure, the glue, owing to its great plasticity, penetrates the pores of the wood and on solidifying unites well glued pieces with such force that they can be separated only with great trouble and damage. Being interposed between flat surfaces such as metallic and glass, the glue fills up the slightest depressions and cracks, even if such are not visible to the naked eye; in this way it forms in a manner, a uniform whole.

If the adhesive power, as it is often assumed, were the result only of the elimination of all the air between the two surfaces, which are glued together, and the air pressure alone were holding these surfaces together, then, first, the adhesive would bind best only as long as it remains moist; adhesives, however, bind well only on drying, and many of these attain their full adhesive power only after a long period. Second, the adhesive power could not be any greater than that which corresponds to the air pressure, *i. e.*, one kilogram to each square centimeter of the surface to be glued; but it is usually several times greater. For instance, the adhesive strength of good joiner's glue is 150 kg. to 1 sq. cm.[1] From this example we may see how great a tensile strength may be manifested by this delicate colloidal structure.

16. Usefulness of the Colloids in the Absorption of Liquids.—In consequence of their peculiar porosity the colloids are able to absorb large quantities of liquids and, indeed, often, by being swelled at the same time, much more than the original volume of their pores. The *absorption-ability* is made use of, for example in electrotechnics in the preparation of *dry batteries;* besides plaster of Paris, gelatine, agar-agar, blotting-paper, saw-dust, cellulose, cotton and other organic substances are used; of the inorganic colloids, in the case of acidic

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[1] See F. Krueger, Kleben und Klebbstoffe, Verhandlungen des Vereins zur Befoerderung des Geverbefleisses, 1905 : 132.

liquids, the Gel of the silicic acid, and in the case of alkaline liquids, iron-oxy-hydrate are used.

This absorption power of the colloids is also made use of in order to remove disagreeable liquids; *Peat-molds* (Torf-mull), for example, are readily employed for the absorption of liquid fecal matters.

This water absorption plays an important part also in nature. The richer a soil is in colloidal ingredients, the more water it is able to retain. Cultivated peat soil, for example, which is superficially dried and is still somewhat moist to the touch, contains, according to the determinations of P. Ehrenberg and H. Pick,[1] 110 per cent. of the weight of the dry substances in water; in humic garden soil (fresh and moist) it is 38 per cent.; in air dried, ground Dollart-clammy-soil it is 11 per cent.; in air dried loess it is 3 per cent.; and in fine sand (containing 0.3 per cent. of organic substances) it is, according to my own determinations, but 0.2 per cent.

17. Dehydration of Peat by Electro-Osmosis.—The large quantity of liquid which is absorbed by peat is a great obstruction to its employment as a fuel. Simple *pressing* removes the water from the peat just as ineffectively as it does from, for example, the Gel of silicic acid. If it is not desired to leave to the air and sun the

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[1] Gedenkboek, J. M. van Bemmeln (Helder 1910), pp. 201-204.

tedious job of drying the peat, and it is attempted to evaporate the water ballast rapidly by heating, one experiences difficulties due to the comparatively high cost of this process. Several years ago a process for the dehydration of peat, which was invented by Prince Botho Schwerin drew considerable attention; it is based on the following: an electrical current of several hundred Volts pressure is conducted through a thick mush of ground peat and water; the peat is then forced towards the positive pole and the water towards the negative one; in this interesting way he succeeded in removing from the peat-slime a good portion of its water.

18. Colloids as Diaphragms and Filters.—The application of the Gels as porous "diaphragms" and as filters is based on the cell structure of the Gels. Water, and substances which are really dissolved in water, pass through the pores without great difficulty, but colloids diffuse only very slowly, or not at all.[1] In nature, such colloidal diaphragms are the cell-walls of plants. Their impermeability toward colloids is made use of in the *beet-sugar manufacture,* in the process of leaching the beet slices, the sugar passes out while the colloidal ingredients of the cell-juice remain. Of the artificial dia-

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[1] The diffusion appears to go on mainly through the liquid, which is present between the cell-walls, while the walls themselves do not allow any passage.

phragms we have mentioned parchment paper, which is employed in the dialysis of the Sols of silicic acid. On the other hand, how great the permeability is in the case of electrolytes, is illustrated, for example, by the following: In storage batteries diaphragms are sometimes used made from sulphite-cellulose pasteboard. In order to make them more durable, these diaphragms are soaked in rosin. In a short time, after they are immersed in the storage battery, these diaphragms, in spite of the fact, that they have been soaked with the non-conducting rosin, absorb so much of the sulphuric acid, that they conduct the current very well.

When the particles of the colloidal solution are very small, they also will go through very fine filters. Usual filter paper still retains particles measuring about 5 μ; hardened filters permit the passage of particles measuring up to 2 μ, and Pukal-filter-candles, indeed, only up to 0.3 μ. If the pores of a filter paper are made smaller by the addition of jellies of different concentrations, according to the process of H. Bechhold, a mixture of different colloids may be subjected to *fractional filtration,* and for example, colloidal silver (Lysargin) may be separated from Hæmoglobin (the coloring ingredient of blood).

19. Adsorption.—It is incorrect to consider the process of filtration only as a kind of percolation; here comes to the foreground another property of the colloids, based on their cell structure, namely, the *adsorption-power,* which is based on their enormous surface development. By the name *adsorption* is designated the remarkable phenomenon that gases, liquids, and finely divided substances adhere, often with great force, to the surface of many materials. Each window pane, for example, is covered with a not insignificant layer of water and gases, from which it can be completely freed only by heating for several hours in an evacuated room. The adsorption power increases with the surface and depends, not only on the nature of the adsorbing, but also on the nature of the adsorbed substance. *Colloids are preferably adsorbed again by colloids.* So, for example, the ultramicroscopical particles of gold, despite their small size, are retained, in filtering, by the filter and clog up the pores.

How peculiarly adsorption acts can be seen, for example, in the fact that R. Zsigmondy was able to prevent adsorption on the filter by adding white of an egg, or another protective colloid, to the hydrosol of gold; gold particles measuring 30 $\mu\mu$ smoothly passed through Maassen-filter-candles and Pukal-filters. In this case probably, also chemical combinations assert themselves. The usual proteins, in general, appear to be quite indifferent to the material of the filter, while ferments and toxins enter into combination with it.

20. Varnish-Making.—Varnish-making is largely based on the adsorption properties of the colloids. Just as freshly precipitated aluminium-hydroxide takes up the gold from a colloidal solution of gold and produces a beautiful red varnish, so the Gel of aluminium-hydroxide causes other coloring matters to adhere to it. The well-known receipt for the making of a varnish consists in the following: A solution of coloring matter is mixed with a solution of alum and the aluminium-hydroxide, which takes up the coloring matter, is precipitated by soda. This process, formerly used to be explained as the producing of a chemical combination, while, according to the modern views, there is, in the first place, a case of adsorption.

21. Dyeing.—Adsorption plays a great part also in the *dyeing* of textile-fibers. Many dye solutions, when investigated by L. Michaelis under the microscope, proved to be colloids, as, for example, carmine, naphthol-yellow, induline, violet-black, aniline blue, congo-blue, bavarian-blue in a water solution, scarlet dissolved in alcohol, etc.

Fluorescin, eosin, toluidine blue, nile-blue, methylene blue, and other fluorescent substances do not show any ultra-microscopical particles, but do show a *light-cone.*

The suspensions of chrom-yellow and of ultramarin contain comparatively very coarse particles. In the deep blue "solution" of ultramarin, which appears clear to the eye, which can be filtered through paper, and which, often, does not settle for months, small points can be seen even under an ordinary microscope with a magnification of 1,200.

L. Michaelis makes the following interesting conclusions from his ultra-microscopical studies: those coloring matters, which form colloidal solutions in water, can be employed as elementary coloring matters, and as such, which possess a diffusive power.

Numerous coloring matters cannot readily be fastened on the textile-fiber, the material to be colored must previously be subjected to the process of mordanting. For this purpose it is mostly impregnated with colloidal aluminium hydroxide, which effects a wash-proof union between the coloring matter and the fiber.

Dyeing was considered from the point of view of colloidal chemistry first of all by Otto N. Witt, who two decades ago pointed out the colloidal character of the textile-fibers.[1] Later the theory of dyeing was developed by P. S. Zacharias and by W. Biltz.

The solid fibers behave like the Gels; they have a cell-

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[1] See, for instance, the treatise by O. N. Witt, "Zur Theory des Faerbeprocesses;" Faerber-Zeitung, 1890-91, No. 1.

structure and are swelled on "steaming." By the alkali and acid "fulling," as well as by the previous preparation, the fibers are brought, according to Ed. Justin Miller, into a jelly-like condition, and by the mechanical action of the fulling they are cemented and felted together. According to P. S. Zacharias, each direct dyeing takes place in two steps: first, absorption, in which the coloring matter penetrates the swelled up fiber, second, fixation, in which the penetrated coloring matter is made insoluble by chemical reaction or by coagulation.

The fiber as W. Biltz states, takes up comparatively more substantive coloring matter from a dilute solution, than from a concentrated one. He showed further that in the case of dyes, which are of the type of benzopurpurin, the textile-fiber may be substituted by an inorganic colloid, as aluminium hydroxide, without causing a quantitative change in the adsorption.

The laws of adsorption have been especially investigated by the thorough researches of H. Freundlich.[1] He discovered that the ratio between the adsorbed quantity and the concentration of the solution is expressed by an exponential equation; the constants of this equation are different in different cases.

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[1] A grouping of these investigations is made by H. Freundlich in his book, "Kapilarchemie" (Leipzig 1909).

22. Tanning.[1]—The animal hide represents a mixture of protein-like substances, which are in the form of a Gel. The vegetable tannins, which are used in the industry, are also in the condition of colloidal solutions; consequently, tanning represents a reaction, which takes place between colloids. The precipitation processes, which are caused in colloidal solutions by electrolytes, assert themselves even in the process of the extraction of tannin from the tannin raw materials by water; distilled water extracts considerably more tannin than raw water; the losses are the heavier, the more impurities contained in the water, which is used in the process. The hide, which, by soaking and treatment with lime, was de-haired and freed from flesh, and which, by treatment with acid, was de-limed, absorbs from the tanning materials, preferably, colloids.[2] These colloidal tanning materials (tannin, etc.,) are absorbed more or less rapidly, according to their nature, being taken up, preferably, by the upper parts of the hide, or penetrating also to its interior. Since from leather which was tanned by vegetable tannins, more tannin can be washed out immediately upon

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[1] A fuller treatment of the subject is given by E. Stiasny in Koll.-Zeitsch., 1908, 2 : 257-263.

[2] An important part is played thereby by the "swelling up" of the fiber. As J. v. Schroeder found in his research work, "Zur Kenntniss der Gerbprocesse" (Dresden, 1909), hide-powder, in order to be able to take up tannins, must first, be soaked in water.

the finishing of the tanning process, than after the leather has been stored, it is to be assumed, that, in time, the adsorbed tannin changes from the reversible-, into the irreversible- Gel-form, a process, which is catalytically accelerated by the fibers of the hide. But the tannin, which is taken up by the hide, is surely changed also chemically; oxydation, anhydration, and polymerisation are presumed to be these chemical transformations. Since, further, diffusion and capillarity are determining factors of the penetration of the hide by the tannins, the process of tanning appears to be a very complicated one, the theory of which is still obscure.

In *mineral-tanning* chromium salts (chrom-tanning) and alum are used. The real tanning material is the colloidally dissolved basic salt. Since the alum splits up less basic salts, than the chromium sulphate, the aluminium salts penetrate the hide more rapidly, indeed, but their tanning action is weaker. While chrom-tanned leather resists the action even of hot water, a larger portion of the aluminium hydroxide can again be washed out from alum-tanned leather; the longer the leather is stored, the more of the aluminium hydroxide becomes insoluble.

The fact, that the iron salts, which are closely related to those of chromium and aluminium, are not well fit for tanning purposes (the leather is made brittle), E. Stiasny traces back to the iron hydroxide, which does not diffuse sufficiently and is too easily precipitated. By the addition of blood (as a protective colloid) the iron tanning can be improved.

In fat-tanning the colloidal fat (Tran, etc.,) is adsorbed by the fiber and then transformed into insoluble oxydation products by the oxygen of the air. Also in this case we find the general principle of the tanning: the colloidally dissolved tanning material is first adsorbed, then it is changed into an insoluble form, so that the tanning cannot retrocede.

The essence of any tanning process consists, according to the conception of P. S. Zacharias,[1] in the following: the hide is transformed into leather by the coagulation of the swelled up hide fiber, and by the nullifying of its ability to take up water through an appropriate deposition of the tannins.

The processes which take place in pickling have lately been studied more closely by Henry R. Procter.[2] In pickling, the hide is treated with a very diluted solution of sulphuric acid, whereby the fibers of the binding tissues swell up strongly; they are then immersed in a

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[1] Lecture at the Fifth International Congress of Applied Chemistry, Berlin, 1903.

[2] Kolloidchemische Beihefte, 1911, **2** : 243-284.

concentrated solution of salt which causes contraction, the fiber is strongly dehydrated and becomes leather-like. The saturated solution of salt is not able to dehydrate a hide, which has not been subjected to a preliminary treatment with acid.

Gelatine, which, owing to its formless structure, offers simpler conditions for investigation than the hide substance, and, which in other respects behaves similar to the hide substance, according to the observations made by H. R. Procter, is able to take up, in strongly diluted solutions of muriatic acid, more than fifty times its weight of water, while in pure water it takes up only seven or eight times its weight of water. Very dilute acids exert only a slight swelling action. Neutral salts (*i. e.,* salts, which have neither an acid, nor an alkaline reaction), when in a neutral solution, increase the swelling, but, when in presence of a trace of muriatic acid, they effect, on the contrary, a considerable contraction. H. R. Procter assumes, that gelatine, which acts as a weak base, forms with the acid a salt-like compound.

23. Soap-Manufacture.—Soap represents by its spongy consistency the typical structure of a Gel. The large quantities of water, which are contained in soap, in storage, are gradually given off. But, if, on the contrary, dried soap is placed into water, it swells up and dissolves to a jelly. This liquefaction process takes place more rapidly when, according to F. Goldschmidt, some alkali is added to the water; this is the reason why the soap-maker remelts his scrap not with water, but with weak lye.

The *salting out* (graining) of the soap, *i. e.*, the separation of the soap from the aqueous solution, by the addition of a mixture of common salt, soda, and caustic soda, has hitherto been considered as an "ion-reaction"; now this process is considered as the flocculation of a colloid. That concentrated soap solutions are of a colloidal nature, is proven by the fact, that they boil at 100°, just as pure water, while the boiling-point of a true solution is higher than that of the solvent. The electrical conductivity of a strong soap solution is also very small at room temperature, while otherwise the alkali salts are very good conductors. But, in order to avoid misunderstandings, I wish to emphasize, that soap solutions are by no means always colloidal, and that there are various differences.

Owing to its great porosity, the soap-Gel is able to absorb much water without appearing moist, which property is made use of by manufacturers. For adulterating purposes, various *cheap fillers,* such as common salt, potash, and sodium-silicate may be added. The soft soaps, which, as is known, are not solid, but have a jelly-like consistency, are "filled" with *potato-flour,* which is, indeed, in its turn perfectly well gelatinized by the action of alkalies. The potato-flour is mixed with potash and a solution of soap, the mixture is added to the soft soap, and the whole is crutched till it is uniform, when, finally, a solution of caustic potash is added. A product is then obtained, which, despite its high water content, has, owing to the flour-gelatine, the firmness of a good article.

24. Brewing-Industry.—The observation, made by H. Bechhold, that colloidal solutions are clarified by filters, the pores of which have been reduced by jellies, has been made use of by F. Emslander to explain certain processes in the brewing-technic. From the wort (malt extract), to which hops have been added, and which was boiled with the hops for several hours, a sediment separates upon cooling, the so-called *malt-residuum* (Kuehlgelaeger), which settles to the bottom of the cooling vessel and consists mostly of coagulated albumen. The malt-residuum can be easily separated from the wort by filtering through coarse linen cloth. On the other hand, the so-called keg-residuum (Fassgelaeger) which separates in mellowing of the beer in keg storage, is not easily separated by filtration, because its solid particles are very small, and contain very many bubbles of carbonic acid, which clog the pores of the filter. But if the beer be passed through a filter, which already contains the malt-residuum, a perfectly clear filtrate may be obtained, and time is also saved.

Soluble proteins may act in the beer as *protective colloids,* and prevent the flocculation of the yeast; in such case the beer remains turbid.

The remarkable influence of *water* on the quality and kind of the beer can be explained, in some respects, by colloidal chemistry. Water which contains much iron acts harmfully because the flocculated iron hydroxide carries away with it taste- and extractive—matters; the beer is not *matured* (Vollmundig). Water, which contains *lime,* has, on the contrary, a favorable influence, because it improves considerably the yield from the malt, and helps the maturing.

25. Lubricating Greases.—If lime soap (15-23 per cent.) be dissolved in heavy mineral oils, to which is added a little water (1-4 per cent.), a lubricating grease is obtained, which has a salve-like consistency, and is used especially for lubricating inaccessible bearings. Without water, the solution of lime soap in mineral oil is liquid; under the ultramicroscope it appears turbid. A solution of lime soap in pure benzene also shows a bluish light-cone. The black, non-transparent mineral oils also appear under the ultra-microscope as colloidal solutions.

Reddish-yellow lubricating oils give an amicroscopic bluish light-cone, likewise white paraffin oil. Crystallized paraffin, which is dissolved in benzene in smaller quantities, does not show a distinct light-cone, but, after a considerable quantity of paraffin is dissolved, a light-cone appears consisting of beautifully flashing sub-microscopical particles.

The solution of asphalt in benzene appears dark under the ultra-microscope; but, if plenty of alcohol is added to it, sub-microns appear, which are, evidently, precipitated asphalt. To the naked eye this solution appears clear.

Resin also, when in an alcoholic solution, exhibits submicroscopical particles.

If the water-free solution of lime soap in mineral oil be intimately mixed with only three-fourths of one per cent. of water, it becomes salve-like in consistency; its viscosity often increases with time. From the view-point of colloidal chemistry, this transformation can be explained as a process of coagulation.

In concluding these observations D. Holde suggests that the ultra-microscope be employed in the examination of mineral oils, paraffin, ceresin, rosins, etc.

Under the ultra-microscope, Russian, almost paraffin-free, petroleum oil, for example, can immediately be distinguished from the American.

26. Sewage Purification.—The sewage of cities contains a large quantity of organic substances, and, indeed, the larger part of these in the condition of colloidal solutions. The sewage can be purified from these harmful, putrescible substances, by the addition of suitable chemicals (*chemical purification*). Since the putrescible sewage substances migrate in the electric current towards the positive pole, and are negatively charged towards water, positively charged colloids are adapted for their precipitation, as, for example, the hydrosol of iron hydroxide. The iron hydroxide, which is obtained by the decomposition of iron chloride, in flocculation, carries down with it the major part of the putrescible substances. *Drinking water* also may be purified in the same manner, by the addition of measured quantities of iron chloride and sodium carbonate. L. Schweikert recommends, instead of these additions, a colloidal solution of iron hydroxide, which he prepares from freshly precipitated iron hydroxide, by washing with water until it goes into solution. With one litre of this solution (which costs about 3 Pfennige—less than 1 cent) Schweikert was able to purify 1 cm. of water, taken from the river Elbe.

Colloidal aluminium hydroxide is also adapted for use as a clarifying agent, for example, of waste waters from starch manufacturing plants.[1]

When these clarifying agents are applied, it must be taken into consideration that they, indeed, carry down the organic putrescible substances, but they do not destroy them. If these organic substances are carried away by running water soon, this clarification is sufficient, but, if the precipitate remains in the same place, putrefaction sets in. In order to avoid this, in such cases, a purification agent is to be employed, which oxidizes and decomposes, as, for example, ozone.

In the *chamber process* of sewage purification, the gradual flocculation of the organic substances is made more rapid by the putrefaction, which sets in. The walls of the chamber are covered with sediments consisting of rolled together colloids; the gases, which are evolved during the process of putrefaction, stir up the sludge, and, from time to time, bring it to the top, or hold it suspended in the liquid. These sludge particles adsorb on their surfaces further quantities of colloids; as soon as the gas escapes, the sludge sinks again to the bottom. By frequently repeating this movement, the sewage becomes continually clearer.

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[1] According to P. Rohland, also the highly plastic kaolins of Striegan, in Schlesien-Germany, thanks to their richness in colloids, can be used for clarification of waste waters. Koll.-Zeitschr., 1908, **2** : 177-179.

After this clarification, the sewage is conducted through tubes or through sprinkling filters; these are filled with materials having a large surface, which adsorb the colloidal, refuse substances, as well as a part of the ammonia and the salts.

If the purification mass is coarse, and the air has free access to the tubes, the jelly-like sediment gradually becomes granular and may easily be rinsed out.

When *filters* are employed for the purpose of purifying water, their action is based primarily on the adsorption-power of the filtering-medium, be it sand, carbon, wood-wool, or the like; by depositing themselves on the filtering medium, the colloids enlarge still more the effective surface, and therewith improve the adsorption. As is known, filters mostly do not work well at the beginning, they must, first, be worked up.

Along with these colloidal reactions, the transformations brought about by bacteria, especially in the *Biological* process of purification of sewage are, however, the most essential feature.

27. Colloids in Agriculture.—The inventive man unconsciously derives benefit from the colloids, which are present in the fertile soil, as well as those in the numerous trades. That very process of reducing and etching, which H. Kuzel employed in order to obtain tungsten in a colloidal condition, is practiced by nature on a large scale. The influence of the disintegration process, which results in the formation of colloids, has been mentioned on page 23. In addition to that, there are other powerful forces. The rivers, the Elbe, for example, in flowing, carry with them rocks and soil; on the way to the sea, the soil becomes ever more finely divided, partly mechanically, partly by putrefaction processes (in the same manner as in the process of mellowing of kaolin), and at last the viscous silt is deposited in the sea between the alluvial land and the shore; this deposit is, owing, probably, to its extraordinary fine division, an exceptionally fertile soil, so that the cost of building dams is covered by the sale of this land with profit. A hectar (about 2½ acres) of this land costs at present about 3,000 Marks (about $710).

Even usual soil manifests a large binding capacity for the nourishable materials, which are contained in irrigating waters, and, in general, in the manures. According to J. M. van Bemmeln[1], the ability of soils to take up salts of the alkalies and alkaline-earths from their solutions is based on their content of basic, soluble in hydrochloric acid, silicates, which contain lime, magnesia, potash and soda, and which are able to exchange these bases with the salts contained in the water. It is seen, that also in this case, as in many others, which were con-

[1] J. M. van Bemmeln, Die Absorption (Dresden 1910).

sidered before, the chemical transformations enhance the adsorption action.

The *silt of the Nile* also contains a considerable quantity of hydrated silicates, suitable for the colloid formation, which take up from the Nile-water every year, during the innundations, potash, nitrogen, and phosphoric acid and transfer these stored up nourishing materials to the plants after the waters recede. In this manner E. Pohl explains the astonishing, inexhaustible fertility of the Nile-land.

The great water absorption ability of soils rich in colloids, which prevents a too rapid drying out of the soil during dry periods, and which in this way is useful to the plant-growth, was already mentioned on page 40.

It would be easy to find in literature as well as in practice other cases, in which the colloids play an important part.[1] However, I believe that the birds-eye-

[1] For example, in the *photographic technics* we find the remarkable fact that the bromo-silver gelatine plates, at first, are not fit for use; they must be previously stored. In storing, the plates, which are transparent at the beginning, become very turbid; the ultra-microscopical bromo-silver particles clump together into somewhat larger particles, which are now especially light-sensitive. In general, the colloidal forms of the silver halogens, their adsorption further the tanning and adsorption of the gelatine play a weighty part in the photography. I only wish, in a few words, to call attention to the work of Luppo-Cramer, "Kolloidchemie und Photography (Dresden 1908).

view of the colloids, which I have here presented, is in a quantitative way satisfactory, in a qualitative way there is as yet much to be desired. In most of the cases we know very little of the real essentials of the phenomena. But we may cherish the conviction, that colloidal chemistry, which is yet more than one hundred years behind the chemistry of crystalline substances, in the future may be able to give the desired enlightment. Each step forward in this dark field is, directly or indirectly, of importance and value also to the arts and manufactures.

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