SOME RECENT ADVANCES IN THE FIELD OF COLLOIDS[1]

THE SVEDBERG

The chief problem of the physics and chemistry of colloids is the study of the structure of the colloid systems. The astonishingly rapid growth of this science may be attributed to the fact that both chemistry and physics have for a long time been developed without regarding the influence of microscopic and ultramicroscopic structure on a great many phenomena. The central point in colloids is the particle—like the molecule in chemistry and the cell in biology. The colloid particle is indeed a sort of intermediate between those two; in certain respects it possesses the properties of the molecule, e.g., as molecular-kinetic unit, in certain other respects it has the complicated properties of the cell. The latter properties are to a great extent due to the surface field around the particle. The material reported on in the following has been arranged from this point of view.

FORMATION OF THE PARTICLE

Dispersion processes

Some interesting experiments on preparing fine grained fogs by using a centrifugal force have been carried out by Regener (1) (1922). The liquid to be dispersed is broken up by means of a kind of atomizer and the gas loaded with droplets of various size is pressed through a glass spiral. It is easy to get a force about 1000 times that of gravity acting on the particles. Thus the coarse particles are pressed against the wall of the spiral and the gas leaving the spiral will contain only droplets of sizes below a certain limit.

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[1] An essay prepared in connection with the dedication of the Sterling Chemistry Laboratory.

Nordlund (2), working in the laboratory of the writer (1918) studied the formation of mercury emulsions in water under various conditions. He found that the emulsification can take place in two different ways, either by crushing of mercury drops or by bursting of mercury lamellae. If we force water (containing potassium citrate to the concentration $2.5.10^{-3}$N in order to prevent coagulation) through a layer of mercury, very thin mercury films are produced when the water bubbles rise through the mercury. On bursting those mercury lamellae give rise to extremely fine drops of mercury. As a matter of fact, the degree of dispersity of such a mercury sol is—after removing the coarser particles—higher than in any other mercury sol known. If, on the other hand, we eject mercury through a fine glass tube against a glass wall under the same weak citrate solution, we get only a coarse emulsion.

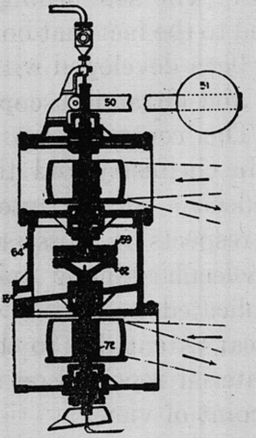

FIG. 1. PLAUSON COLLOID MILL

The Russian chemist, Plauson, has constructed the so-called colloid mill (3) (1920). The principle of this machine is the following. The substance to be dispersed is suspended in the dispersion medium in the form of coarse particles, and those particles are crushed or torn to pieces by giving part of the suspension a very high velocity and allowing it to strike another part of the suspension having no velocity, or a velocity of opposite direction. This can be arranged in different ways, e.g., by passing the liquid through a channel in the shaft that holds a metallic disc rotating with high speed close to another similar disc rotating in the opposite direction (fig. 1). The suspension has to pass between the two rotating discs and accordingly there will be a very high shearing force in the middle layer of the suspension tearing the suspended particles to pieces.

High speed is essential. A peripheral speed of less than 10 m. per second gives only coarse particles. Above 30 m. per second the size is brought down to colloidal dimensions. The colloid mill is one of the most important and promising new procedures for preparing colloid solutions by dispersion, and machines of that type have already been tried with success in some of the plants interested in production of colloids. Addition of protective substances—electrolytes or colloids—are often necessary to prevent coagulation of the fine particles.

Condensation processes

Some experiments by Hamburger (4) (1918), dealing with condensation of metal gas on a glass wall in a perfect vacuum, are of considerable interest for our understanding of the formation of colloids by condensation processes. Filaments of various metals were heated by an electric current and the condensate collected on a glass plate and examined in the ultramicroscope. He also measured the electric conductivity of those metal films. The metals of low boiling point give films built up of comparatively coarse particles, while the metals of high boiling point, such as iron, nickel, molybdenum, tungsten, give condensates of a very high degree of dispersion, some of them e.g., the tungsten films, unresolvable in the ultramicroscope. On the whole, the degree of dispersion of the films seems to rise with the temperature difference between the metal gas and the wall on which it is condensed, viz., with the degree of supersaturation. The films are not stable; the break-up in time forming a deposit of ultramicroscopic particles. Heating accelerates this crystallization or coagulation process. The metals of very low vapour pressure, such as tungsten, give the most stable films, while silver with its comparatively high vapour pressure gives rather unstable films.

These experiments emphasize the importance of high supersaturation and low vapour pressure, or low solubility, when a disperse system of high degree of dispersity is wanted.

Since Bredig's discovery of the pulverizing action of the submerged d. c. arc in 1898 (5) and the writer's studies of the high frequency a. c. arc in 1907 (6), the importance of the arc as a means of producing colloids has been more and more recognized. Recently (1919–1922) the writer and his co-workers have studied the action of various kinds of arcs with the object of elucidating the mechanism of the process that gives rise to the metal colloids and of finding out the best conditions for the preparation of metal sols by means of the arc (7). A closer study of the d. c. arc showed that the production of metal gas can be considerably increased by protecting the electrodes from the cooling effect of the surrounding liquid. If a d. c. arc was struck between silver or gold wires within a silica tube immersed in ethyl alcohol, and the arc was blown out into the alcohol through a fine hole in the silica tube in front of the arc by means of a stream of nitrogen or a magnetic field, or both (figs. 2 and 3) the writer arrived at a colloid production many times higher than with the unprotected arc. Those sols are built up of extremely fine particles about 5 $\mu\mu$ in diameter, while the sols produced by the unprotected arc have particles of say 25$\mu\mu$. Spectrograms were taken of the protected and the free arc and they show (fig. 4) that while in the case of the free arc, the band spectrum of carbon is very strong the protected arc gives only the silver spectrum and a

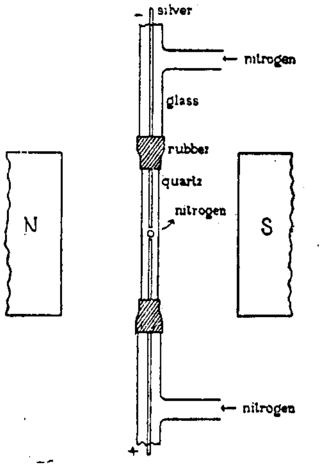

Fig. 2. Production of Silver Vapor by Means of Enclosed Arc

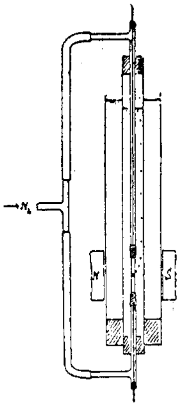

Fig. 3. Formation of Colloids by Means of Enclosed Arc

trace of a continuous spectrum in the red and the yellow, originating from glowing particles of silver and silica. This indicates that the decomposition of the dispersion medium is very low in the case of the protected arc.

The arc enclosed in the silica tube also produces some silica vapour which is condensed to silica particles, and taken up by the alcohol. We hope to be able to avoid this contamination by using some less volatile material e.g., alumina for the tube enclosing the arc.

An almost undamped form of high frequency arc, observed by the writer (1914) was studied by Börjeson and the writer (1919). Figure 5 gives the wiring diagram. *L* is a leyden jar, *H* a hot-wire ammeter, *P* the pulverization apparatus, *R* an adjustable resistance and *A* an ammeter. This arc produces more metal colloid per unit virtual current and less decomposition products of the dispersion medium per unit metal colloid than does the damped oscillatory current arc, previously studied by the writer. The order of the metals with regard to the amount pulverized by the arc is not quite the same as in the case of the damped oscillatory arc. This order seems to be easily influenced by slight variations in the electrical conditions of the arc. Thus Bodforss and Frölich (8) (1922) found that upon exchanging the induction coil in the writer's original experimental arrangement for a transformer fed with low frequency a. c., the pulverization of the electrodes was considerably altered.

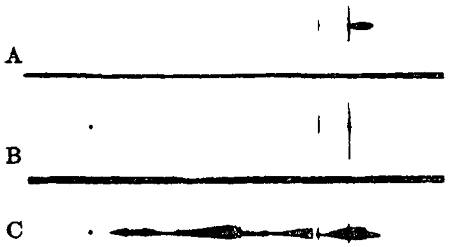

FIG. 4. SILVER ARC SPECTRA

A, enclosed arc in alcohol; *B*, free arc in nitrogen; *C*, free arc in alcohol.

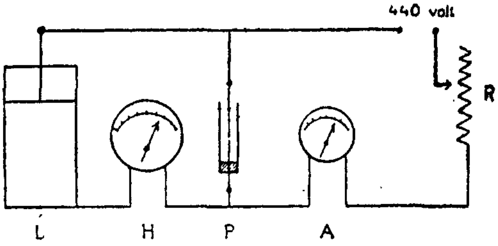

FIG. 5. UNDAMPED OSCILLATORY ARRANGEMENT FOR PRODUCTION OF COLLOID SOLUTIONS

In table 1, the loss in weight of electrodes in mgm. per 1.5 amp. for those three different forms of high frequency arc are tabulated.

The mechanism of the formation of sols by means of the arc was studied by Börjeson (1921). On measuring the distribution of the size of particles in the dispersed systems produced, he found that the dispersed phase consists of two distinctly different parts, one very coarse-grained and one very fine-grained. The coarse particles are melted globules formed out of the molten parts of the electrodes by a dispersion process, while the small particles are formed by condensation of metal gas. In the case of cadmium pulverized in ethyl alcohol, the radius of the melted globules lies between 500 and 25,000$\mu\mu$, while the particles formed by condensation have an average radius of about 5$\mu\mu$. The percentage amount of dispersion product varies with the electrical conditions of the circuit and with the melting point of the metal. For cadmium in ethyl alcohol, this percentage increases from 20 at a capacity of 0.0004 M.F. to 55 at a capacity of 0.09 M.F. The following Table 2 gives the amount of dispersion product for some metals together with their boiling points.

TABLE 1

METAL	PULVERIZATION		
	Damped oscillatory arc		Undamped oscillatory arc
	Induction coil	Low frequency a. c. transformer	
Pb	45	28	64
Bi	33	21	75
Sb	25	18	130
Cd	21	13	48
Zn	8	4.8	25
Al	2	1	1.1
Ag	1.3	1.4	2
Cu	1	0.8	2

Arc experiments with electrodes of binary alloys gave the result that the metal with the lowest boiling point is concentrated in the condensation product. The dispersion product was found to be richer in the metal with high boiling point and it was distributed among the particles of various size in such a way that the smaller particles contained more of it than did the coarser ones (table 3).

This shows that the melted globules must have been suspended in the hot arc gases for some time after their formation allowing them to evaporate some of the metal with the lower boiling point. For equal times, this evaporation must be relatively more intense from the particles with small radius, because their relative surface is greater.

TABLE 2

Dispersion medium ethyl alcohol. Capacity 0.003 M.F. Current int. 1.5 amp.

METAL	PERCENTAGE DISPERSION PRODUCT	MELTING POINT OF ELECTRODES °C.
Pt	20.2	1700
Au	25.8	1064
Zn	41.0	419
Cd	41.6	320
Sn	56.8	232
Bi	59.3	268

TABLE 3

ALLOY AND BOILING POINT OF COMPONENTS	RATIO OF COMPONENTS			
	In electrodes	In dispersion product		In condensation product
		Coarse fraction	Fine-grained fraction	
Au(2500°) — Cd(780°)	0.84	1.7	3.0	0.52
Au(2500°) — Sn(2270°)	0.74	0.75	0.81	0.71
Bi(1420°) — Cd(780°)	1.0	1.4	2.0	0.77

The problem of the relation between experimental conditions and degree of dispersion of the arc sols is a difficult one. Börjeson found that the initial size of the particles formed—the primary degree of dispersion—does not vary much, but that the secondary degree of dispersion—that is, the degree of aggregation of those primary particles—varies very much with the experimental conditions. Low velocity of production of the colloid and low temperature seem to favour a high secondary degree of dispersion.

The primary degree of dispersion of some arc sols as determined by Börjeson are given in table 4.

The efficiency of the high frequency arc seems to be connected with the very high momentary values of the current intensity and the very short duration of that high intensity. Thus, a stream of highly supersaturated metal gas is suddenly blown out into the dispersion medium and allowed to condense before the next explosion follows. The arrangements that have given colloids of highest purity produce an electric current out of phase with the voltage so that when the current reaches its very high intensity, the potential difference between the electrodes is very low. This low voltage at the time of the most abundant vaporization of the electrodes probably protects the dispersion medium from being decomposed.

TABLE 4

Oscillatory arc. Ethyl alcohol. Temperature = − 75°.

METAL	RADIUS OF PARTICLES IN $\mu\mu$
Au	2.8
Zn	2.9
Pt	3.8
Cd	5.0

The mechanism of the gold reduction process—formation of gold sols by reducing a solution of $HAuCl_4$—studied by Nordenson (10) in 1914 has been investigated again by the writer (1921). Nordenson's and his results may be summed up as follows. If the reaction

$$2HAuCl_4 + 3H_2O_2 = 2Au + 8HCl + 3O_2$$

is followed by means of conductivity measurements, we find, of course, that the conductivity increases from the value for the $HAuCl_4$ solution to the value for the 4HCl solution—no other electrolytes being involved in the reaction. Now, the course of the time-conductivity curve is of great interest for our understanding of the mechanism of the colloid formation process. If no gold particles (or other nuclei) are present in the reduction mixture, there is a sudden rise in conductivity of about 30 per cent of the total rise corresponding to the formation of 4 HCl per Au. This rise is accompanied by a drop in colour intensity; the absorption in blue and violet goes down. After the sudden rise in conductivity (fig. 6, *AB*) follows a period of very slow rise *BC* and then another period of sudden rise up to the final value. The red colour characteristic of the gold sol appears at *C* and deepens along the line *CD*. If we examine the sol formation in the ultramicroscope, we find that only a negligible number of gold particles are visible during the period *BC*. At *C* masses of particles suddenly appear and increase in number along *CD*.

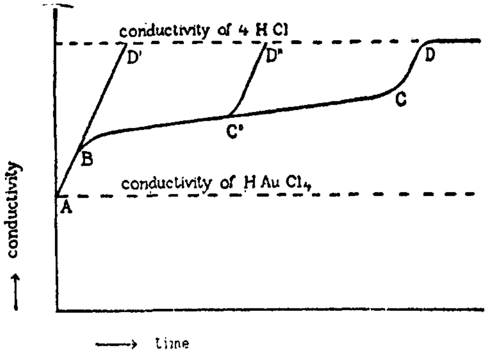

FIG. 6. FORMATION OF GOLD SOL BY REDUCTION OF CHLORAURIC ACID WITH HYDROGEN PEROXIDE

If condensation nuclei, e.g., gold particles, are added to the gold chloride before the reducing agent is added, the reduction proceeds along an almost straight line *BD'* and if such are added during the period *BC* the reaction instantly changes in velocity and is completed along the line *C''D''*.

The explanation may be the following. Upon adding the hydrogen peroxide about 30 per cent of the gold is reduced to gold molecules, forming an enormously supersaturated solution of gold in water. This balances up the reaction according to the law of mass action. The gold molecules slowly condense to colloid gold particles along the line *BC* and at the point *C* the size of a great number of particles has reached the minimum size of nuclear action (according to Zsigmondy's measurements about $2\mu\mu$). The reduction follows slowly along the line BC. After the nuclear limit is reached at C the reduction proceeds rapidly, depositing the rest of the gold on the gold nuclei formed during the period BC. In those cases where nuclei are added, the reduction is accelerated along BD'' or $C''D''$ in the same way as along CD.

The riddle of the mysterious influence of small—almost undetectable—traces of various substances on the velocity of formation of gold nuclei and on the growth of gold particles is still unsolved.

The light action in photography, giving rise to the so-called latent image, is probably a dissociation process and the result a highly disperse and exceedingly dilute disperse silver system, within the halide grains of the photographic film. Experiments carried out during the last four years (1920–1923) in Sweden (the writer (11) and Andersson (12)), England (Slade and Higson (13), Toy (14)) and America (Sheppard, Trivelli, Mees and Silberstein (15)) on the basis of colloid chemical conceptions, have considerably deepened our knowledge of the mechanism of the photographic process.

If a photographic plate coated so thinly that all the halide grains are practically in a single layer (a "single-layer plate") is exposed to α-rays each grain struck by one or more than one α-particle is made completely developable (Svedberg and Andersson, 1921). The percentage number P, of developable grains of a certain size is therefore given by the simple law.

$$P = 100(1 - e^{-\nu t})$$

where ν is the average number of α-particles striking the grain per second and t the time of exposure. Thus, for α-rays the relation between exposure and percentage number of developable grains is an exponential curve (without inflexion point).

Similar experiments with β-rays (Svedberg and Andersson) gave the result that more than one β-particle striking the halide grain is necessary to make it developable. The curve giving the relation between exposure and number of developable grains is probably exponential.

Regarding X-rays of short wave length, a few preliminary tests seem to indicate that those rays, too, give an exponential curve.

On the other hand, ordinary light gives exposure-percentage curves showing a very pronounced inflexion point (Svedberg and Andersson, Toy). Experiments are now in preparation to study the curves from slowly moving electrons and long waved X-rays.

If we expose a single-layer plate to α-rays, and develop it with a suitable developer, e.g., oxalate developer, for a short time, say 15 seconds and take a photomicrograph in red light, the halide grains are apparently unchanged. Now dissolve away the halide with an ordinary fixing bath and take a picture of the same spot of the specimen. It shows small black points and if we print a faint image of the halide grains over the picture of those points, we find that they are situated on the grains (Svedberg). These points or centers represent the starting point for the reduction of the grains. They of course increase in size during development, but only slightly in number. Various grains contain various numbers of centers and for a certain sized class of grains, the centers are distributed according to the laws of chance, as shown by table 5 (Svedberg).[2]

TABLE 5

There were 765 grains studied and divided into two classes, the first containing the grains with a diameter less than 1.18 μ and the second those with a diameter more than 1.18 μ.

NUMBER OF CENTERS PER GRAIN	SIZE CLASS 1. NUMBER OF GRAINS 263. AVERAGE RADIUS OF GRAIN 0.479μ. AVERAGE NUMBER OF CENTERS PER GRAIN 0.461			SIZE CLASS 2. NUMBER OF GRAINS 502. AVERAGE RADIUS OF GRAIN 0.727μ. AVERAGE NUMBER OF CENTERS PER GRAIN 1.136		
	Number of grains	Frequency in per cent		Number of grains	Frequency in per cent	
		Observed	Calculated		Observed	Calculated
0	168	64.0	63.1	165	32.9	32.2
1	73	27.8	29.0	178	35.5	36.6
2	18	6.8	6.7	103	20.7	20.8
3	4	1.5	1.0	41	8.0	7.9
4				12	2.4	2.2
5				3	0.6	0.5

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[2] A report of these measurements was given before the Chemical Society of Upsala, December 2, 1921, but have not yet been published.

Analogous experiments with grains exposed to the action of X-rays or ordinary light gave the result that also in those cases the development only sets in at few points of the halide grain and that those points are distributed according to the laws of chance (Svedberg). If we assume that at least one developable center is required to make a grain fully developable, we can calculate the percentage number of developable grains for various exposures and compare those figures with those directly found. The two curves are affine, the values calculated from the number of developable centers being slightly lower according to the impossibility of making all the centers visible without growing them together to an inextricable network of silver.[3]

By a statistical study of the distribution of the centers within the central and the outer part of the grains, as shown in the photomicrographs, the writer was able to prove that the developable centers, or at least the centers that are responsible for the developability of a halide grain, are located in the surface layer of the halide grains.

The number of developable centers per unit area of the halide grain should, according to the above experiments, determine the sensitivity of the silver halide material of the grains. Experiments by the writer and Andersson show that this number is indeed fairly constant for grains of different size within the same (unmixed) emulsion, but varies enormously from one emulsion to another.

To explain the nature of the developable centers, three different hypotheses have been put forward. (*a*) The centers are a chance product of development. The reduction must start somewhere and it starts at those points. Against this assumption could be said that if they are a chance product of development it is rather surprising that they increase but slightly with time of development and that their absolute number is so small. (*b*) The centers are present in the grains as especially light sensitive points already before exposure. (*c*) The number and distribu-

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[3] Svedberg, *Phot. J.*, April, 1922, p. 3, the experimental values not published; also Toy, *Phil. Mag.*, 1922.

tion of the centers are entirely due to the action of the radiation striking the halide grains.

I think we may discard the first hypothesis as rather unlikely to account for the phenomena observed. How about the two others? Toy is of the opinion that the centers are present in the grains before exposure and constitute the only light sensitive parts of the grain. They should be very few in number of different sensitivity, and have their sensitivity given by a distribution or frequency curve. Now, this extreme form of hypothesis (*b*) seems to me rather improbable. How to account for the fact that the percentage number of developable grains in the case of exposure to α-rays can be calculated upon the assumption that each α-particle striking a grain makes it developable—that is, that every grain struck by one or more than one α-particle is made developable? If the sensitive spots were so few as Toy assumes them to be, only very few α-particles would have a chance to hit a sensitive spot of the grain. Silberstein favours the view that a single light quantum is sufficient to form a developable center, but as recent experiments in the Kodak laboratory seem to indicate that several hundred absorbed quanta are required to make a grain developable, he modifies his hypothesis a little, assuming a limited number of sensitive spots in the grain. Now, as already pointed out by the writer and Mr. Andersson, the fact that the curves giving the relation between exposure and percentage developable grains for light have a very pronounced inflexion point, shows that it is impossible to account for the formation of the developable centers assuming that a single light quantum is able to produce a developable center.

In seems to me that all the facts so far known may be explained on the basis of the following hypothesis. The surface of the halide grain is capable of supplying the material for the formation of a developable center in all its points but the sensitivity—defined as the least amount of energy required to make a certain spot reducible by a developer of a certain reduction potential—varies from point to point considerably. The variation in sensitivity is probably due to the action of the gelatin and other substances added to the emulsion, and to the way of making the emulsion.

The energy of the α-particles is high enough to produce a developable center—probably an ultramicroscopic silver particle big enough to act as a condensation center—wherever it strikes the grain. We accordingly get the exponential curve and the number ν in the formula

$$P = 100(1 - e^{-\nu t})$$

is equal to the number of α-particles striking the grain. The energy of a β-particle or of a high frequency quantum (short waved X-rays) is still high enough to produce a developable center but every β-particle and every X-ray quantum striking the halide grain does not give off energy enough in the surface layer of the grain. We therefore get an exponential curve obeying the above equation, but ν is less than the number of β-particles or of quanta striking the grain, or even absorbed in the grain. It is also possible that not all the spots of the halide grain surface are sensitive enough to β-particles or X-ray quanta. The energy of a quantum of ordinary light is too small to give a developable center. It is necessary that a certain minimum number of light quanta are absorbed within a certain maximum area of the grain surface to produce a developable center. Hence we get a curve with an inflexion point, and a big number of quanta must be absorbed per grain to make a developable center.

The mechanism of the formation of disperse systems by double decomposition has been studied very carefully by Odén in the case of formation of $BaSO_4$ from solutions of $Ba(SCN)_2$ and $(NH_4)_2SO_4$. He measured the distribution of size of particles by means of the self-recording sedimentation balance constructed by him some years ago (1916) and tried to find out the influence of the various experimental conditions upon the degree of dispersion of the system formed, viz., on the form of those distribution curves. Odén found that the formation of aggregates is one of the principal causes of error in such investigations. To prevent the formation of aggregates or to peptize the aggregates already formed, he added potassium citrate to the sols. As shown by the diagrams, figures 7 and 8, where the area between ordinates drawn from two points on the abscissae axis denotes the mass of disperse phase in the radius interval in question, the degree of dispersity rises with concentration, e.g., with the degree of supersaturation. It also increases with decreasing temperature, probably due to the decrease in solubility (figs. 7 and 8).

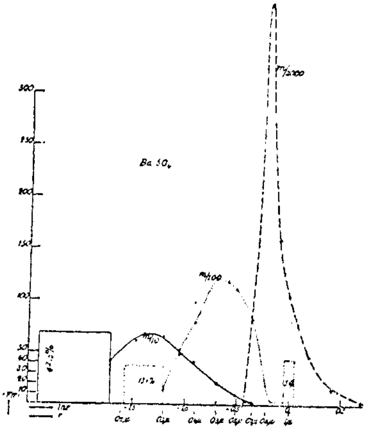

FIG. 7. VARIATION IN DISTRIBUTION OF SIZE OF PARTICLES WITH CONCENTRATION OF REACTING IONS

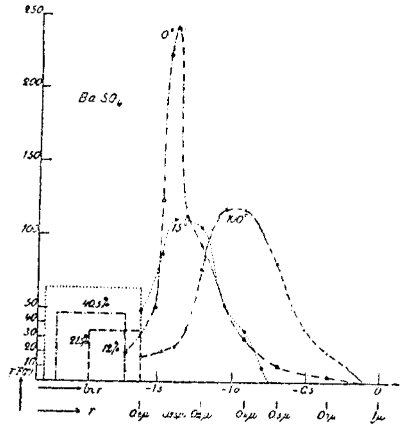

FIG. 8. VARIATION IN DISTRIBUTION OF SIZE OF PARTICLES WITH TEMPERATURE

Purification of sols

The method of purifying sols by means of electrolysis—so-called electrodialysis—has been improved and found very useful especially in the case of organic colloids, e.g., gelatin. One of the best materials for the diaphragm seems to be the electrofiltros made by the General Filtration Company, Rochester, New York. Porous clay, alumina, parchment paper and collodion diaphragms have also been used with success. Kröger electrolyzed with the Hildebrand cell.[4]

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[4] *Kolloid-Z.*, **30**, 16, 1922.

THE COLLOID PARTICLE AS A MOLECULAR KINETIC UNIT

The Brownian movements

The validity of the law of sedimentation equilibrium deduced by Einstein (16) in 1906 and by Perrin (17) in 1908, and experimentally tested and verified by Perrin for coarse particles of gamboge and mastic, and by Westgren (18) for ultramicroscopic particles of gold and selenium, has been doubted by Burton (19) (1922) and by Porter (20) (1922).

The Einstein formula is

$$n_2 = n_1 \cdot e^{-\frac{N}{RT}(x_2 - x_1)\, mg}$$

where n_1 is the number of particles at the height x_1
n_2 the number of particles at the height x_2
m the apparent mass of the particle
g the gravity constant
N the Avogadro constant
R the gas constant
T the absolute temperature

This formula applied to ordinary colloid solutions requires that after sedimentation equilibrium is reached, the concentration would decrease very rapidly with height, falling to $\frac{1}{10}$ a few millimeters from the bottom of the vessel holding the sol. Now, as a rule, we do not find that the particles of our sols go down to the bottom like this. This fact was pointed out by the writer in an article in Stähler's Handbuch, (1916) together with the suggestion that the discrepancy was probably due to the mixing effect of convection currents. For small particles, the velocity of fall is extremely small, and even slight temperature differences within the sol would probably disturb the equilibrium considerably.

Burton studied a copper sol in water (the particles probably consisting partly of oxide) contained in a glass tube 94 cm. high and left for fifty days "in a room in which the temperature varied but little." The content of the tube was then drawn off in six portions and analyzed. No perceptible change in concentration with height was found.

Porter used a gamboge sol with comparatively coarse particles and a cell only 5 mm. high and measured the concentration at different heights by means of counting the particles in a microscope. He found a decrease in concentration downwards in the top layer of the cell, but constant concentration already 2 mm. down in the sol.

The question whether Einstein's law for the sedimentation equilibrium holds over a wide range of height or not is, of course, of considerable importance, and it is to be hoped that further experiments will soon allow us to settle the question. In the opinion of the writer, Burton's and Porter's experiments do not give conclusive evidence. Burton's copper sol probably was built up of oxide particles of a loose spongy structure, settling very slowly, and he did not keep the temperature constant enough. Porter does not state how much time he gave the particles to reach the equilibrium. To judge from Westgren's experiments in the writer's laboratory, it takes a considerable time to reach equilibrium.

Size and structure of particles

Börjeson (21) (1920), working in the laboratory of the writer, has adopted Zsigmondy's method of determining the size of particles not visible in the ultramicroscope by depositing gold on them until they are large enough to be seen. Under proper conditions, he was able to determine the size of particles of all kinds of metal sols, even alcosols, in this way. Table 6 shows how well the values of determinations with different quantity of nuclei check.

The same method can be used for the study of sols of arsenious and antimony sulfide sols. Börjeson thus succeeded in determining the size of particles of arsenious sulphide sols prepared by Linder and Picton's classical method, and found that the size of the particles actually decreases with decreasing concentration of the As_2O_3 solution used for the preparation, as shown by table 7.

Lindeman and the writer (22) showed (1921) that the same method can be used for determining the size of platinum particles of ethyl ether sols by mixing a portion of the original sol with alcohol and then using this sol as nuclear liquid. Probably the procedure can be applied to other metal organosols.

New methods for measuring the distribution of size of particles in disperse systems have recently been worked out by the writer and Rinde (23) in the Upsala laboratory, and are now the object of further development in the laboratory of the University of Wisconsin under the supervision of the writer. The first distribution curves were determined by Svedberg and Estrup (24) in 1910, by a statistical study of the velocity of fall of the particles, and a very ingenious method of recording the distribution of sizes by means of allowing the particles in a sedimenting sol to accumulate on the plate of a balance and measuring the rate of accumulation, was given by Odén in 1916. Rinde and the writer have recently (1923) built a new apparatus for determining the distribution curves, using Odén's accumulation principle, but introducing a more satisfactory way of recording the rate of accumulation. They were able to record the distribution curve using such small quantities as 0.02 gram

TABLE 6

VOLUME NUCLEAR LIQUID—Cd SOL—PER 50 CC. OF REDUCTION MIXTURE	RADIUS OF Cd PARTICLES AS DETERMINED BY MEASUREMENT OF DEGREE OF DISPERSION OF GOLD SOL FORMED
cc.	$\mu\mu$
0.2	11.4
0.1	10.7
0.05	11.0
0.025	10.9

TABLE 7

CONCENTRATION OF As_2O_3	RADIUS OF PARTICLES OF As_2S_3
normality	$\mu\mu$
1.10^{-2}	39
5.10^{-4}	16
1.10^{-4}	11

of disperse phase in the sol, while with Odén's original apparatus, it is necessary to use say about 1 gram to get satisfactory results. Rinde and the writer also worked out an entirely new method based on the determination of the variation of concentration with height in a sedimenting system. The introduction of this principle is of importance because it enables us to make use of centrifugal force, instead of gravity. Experiments in this direction are now in progress in the Wisconsin laboratory. The variation of concentration with height can be determined by means of measuring the light absorption. Rinde and the writer passed a narrow beam of light through the cell containing the sedimenting sol (at different heights) and measured the light absorption by means of a spectrophotometer. The relation between light absorption and height can also be found by taking a photograph of the system, using a suitable source of colored light, and this is actually the procedure to be used when examining the sol exposed to the action of a strong centrifugal force. The calculations are very simple. The distribution function $\frac{dc}{dr}$ gives the variation of mass of disperse phase per unit volume of sol with radius and is found in the following way. The difference in concentration of successive heights gives us our values of dc, because this difference is actually due to the particles having radii between r and r+dr. The r values corresponding to the different heights are calculated from Stokes' law of fall and the differences for successive heights are our dr values. Figure 9 gives the distribution curve for a coarse-grained gold sol recorded by means of this method. In the case of a centrifugal force acting upon the particles, the variation of the force with the distance from the axis of rotation has to be taken into account.

The Debye-Hull method of X-ray analysis has been adapted to the study of colloids by Scherrer (26) (1918). He found that Au, Ag and SiO_2 sols are built up of particles having the same crystal lattice as macroscopic crystals of the same material. Even gold particles of linear dimensions down to $1.9\mu\mu$ give the same kind of X-ray diagram as a gold wire. When we get down to particles of such smallness, there is however a certain difference—the lines in the X-ray diagram are broader in the case of the fine-grained colloid than in the case of a gold wire. Scherrer has shown that it is possible to calculate the size of the particles from the width of the lines taken as the distance between the points on each side of the maximum of blackening where the intensity of the radiation is reduced to half its value. When worked out properly, this method of determining the size of very small particles in colloids will probably prove a very useful one. One of the experimental difficulties is that the colloid to be studied by this method must contain the disperse phase in a rather high concentration, and that sols coagulate very rapidly under the influence of the intense X-ray illumination. Björnståhl, working in the writer's laboratory and in the laboratory of the University of Stockholm, has used an X-ray camera with the sol streaming in a fine cylindrical jet through the center of the camera.

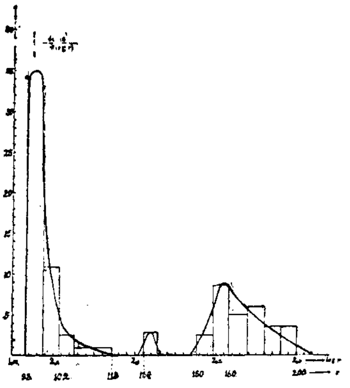

FIG. 9. DISTRIBUTION OF SIZE OF PARTICLES IN GOLD HYDROSOL PREPARED BY "GILDING" METHOD

The relation between coefficient of light absorption and size of particles has been studied by Pihlblad (28) in the writer's laboratory (1918). He investigated sols of gold, silver, sulphur, and some organic dyestuffs, in the visible and the ultraviolet. With decreasing size of particles, the light absorption curve approached more and more the curve for the molecular solution of the substance in question, as already pointed out by the writer in the case of selenium sols. Pihlblad found Beer's law to hold good and he found that the absorption constants calculated from Mie's theory of light absorption checked fairly well with the values determined experimentally.

New careful determinations of the light absorption in the visible and the ultraviolet in gold sols of different degrees of dispersion combined with determinations of the intensity of scattered light—the Tyndall light—as a function of wave length—are now being made by Rinde in the writer's laboratory in order to find out if a reliable method of determining the size of particles from measurements of the light absorption or the intensity of the Tyndall light can be worked out.

The investigation of Björnståhl and Bergholm (28) (1920) on the double refraction of colloids in an electric field, and Björnståhl (29) (1921) on the double refraction in a magnetic field are of considerable interest for the study of the structure of the particles. Ordinary gold and silver sols show a very marked double refraction, in the case of gold down to sizes of about $10\mu\mu$. The effect is probably due to orientation of the particles in the field and indicates that they are dissymmetrical in shape. Björnståhl found that in the case of the magnetic double refraction, the phase difference Δ was proportional to the square of the field intensity H^2. The quantity $\frac{\Delta}{H^2}$ is therefore independent of the field. It increases rapidly with increased size and for gold sols, it seems to reach a maximum value at a radius of particles of about $60\mu\mu$. It then goes down to a minimum and increases again with increasing size. The process of formation and of coagulation of sols can be studied by means of measuring the double refraction in a magnetic field.

THE COLLOID PARTICLE AS MICELL

The surface of the particle with its adsorbed ions or molecules and the field of force in and around this surface layer is almost entirely responsible for the following important colloid phenomena: electroendosmosis, cataphoresis, changes of degree of dispersity (coagulation), gel formation.

Langmuir's theory of adsorption (30) (1918) is at present one of the leading ideas in this branch of colloid chemistry. He assumes that at the surface of a crystal—and almost all particles in colloids are small crystals—there is a certain number of elementary spaces where the forces derived from unsaturated chemical affinities are especially strong. Each elementary space usually can hold only one atom or molecule adsorbed. The result is that in almost all cases the adsorption layer should be only one molecule thick. At first sight, this seems rather improbable, but when we examine the cases where the maximum amount of adsorbed substance per unit surface is determined, we find that there is actually no case known where the adsorbed layer is more than one molecule deep. Langmuir himself proved this for the adsorption of gases on plane surfaces of mica, glass and platinum (1918). Paneth (31) confirmed it in the case of dyes adsorbed on lead sulphate crystals (1922) and Gustaver (32) (1922) calculated from Odén's data that the amount of NaCl adsorbed on the particles in sulphur hydrosols after coagulation is not more than about one molecule deep.

The structure of the electrical double layer causing the endosmotic flow, the endosmotic potential difference and the cataphoresis, is still very incompletely known. Experiments by Freundlich (33) and his co-workers (1920) show that the potential difference active in the double layer—the electrokinetic potential—is not the same as the total potential between particle and liquid—the Nernst or thermodynamic potential—but much smaller. The thermodynamic potential is not influenced by the addition of salts forming ions of high valency or by certain dye stuffs which have a very strong influence upon the electrokinetic potential difference as measured by the endosmotic potential. Freundlich assumes that the electrokinetic drop in potential takes place in the liquid at a certain distance from the surface of the particle.

Mathews and Strickler (34) (1922), studying the electroendosmosis in organic solvents, showed that the valency rules which are found to hold in aqueous solutions did not hold with non-aqueous solutions. To account for the effect of the various solvents, the authors suggest that the molecules of the solvent upon adsorption are oriented upon the membrane surface producing an electric charge by their polarity.

A new procedure of measuring the cataphoresis of proteins has been worked out by the writer and Jette (35). The writer had found (1923) that the proteins, when illuminated with intense ultraviolet light, fluoresce strongly enough to be photographed. We made use of this property to determine the velocity of migration of the boundary surface between protein solution and a buffer solution in a U-tube provided with reversible electrodes. This investigation is now being continued in the Wisconsin laboratory.

The ultramicroscopic methods of measuring the cataphoresis have been improved by the writer and Andersson (36) (1919) and recently by Kruyt and van Arkel (37) (1923). In both of those new procedures, special cells were constructed to be used in combination with the Zeiss paraboloid condenser. The writer and Andersson compared two different ways of measuring the migration of gold particles in water. The particles were either photographed for a short time with direct current and the tracks of the particles measured on the photographs, or exposed to a special kind of alternating current produced by means of a commutator and the amplitude of the vibrations measured by means of a scale in the ocular. Platinum electrodes were used. Kruyt and van Arkel studied selenium sols containing rather high concentrations of electrolytes and used reversible electrodes—copper oxide on copper and silver chloride on silver—to avoid the disturbance caused by the formation of gas at the electrodes. Kruyt and van Arkel, as well as the writer and Andersson, calculated the velocity of migration by means of the formulae given by Smoluchowski.

A phenomenon closely related to the electroendosmosis is the so-called anomalous osmosis studied by Loeb (38) (1919–1921). Already Graham noticed that under certain conditions, the osmotic flow goes the wrong way—that is, from the concentrated into the dilute solution. Loeb has succeeded in showing that this is due to a potential difference built up in the membrane. Another and still more important kind of anomalous osmosis studied by Loeb manifests itself in a positive osmose many times higher than the regular one due to the osmotic pressure of the solute. The height of the anomalous osmotic pressure depends on the nature and valency of the ions present and the nature of the membrane. It shows a maximum at a concentration of about $\frac{1}{512}$ normal then falls off into a minimum and rises again as normal osmosis. Determinations of the endosmotic flow with the same membrane and the same solutions gave a maximum of endosmotic flow, corresponding to the maximum of anomalous osmosis.

Smoluchowski's splendid theoretical work on the velocity of coagulation (39) (1917) founded on the theory of the Brownian movements has been subjected to some new experimental tests. Westgren and Reitstötter, working in Zsigmondy's laboratory (1918), found that the total number of particles in a gold sol that undergoes fast coagulation decreases according to Smoluchowski's formula

$$\Sigma\nu = \nu_1 + \nu_2 + \quad = \frac{\nu_0}{1 + \beta t}$$

where ν_o is the number of single particles, ν_2 the number of double particles, etc., at the time t after addition of the coagulating agent, ν_o the original number of particles present in the sol. $\beta = 4DR\nu_o$. D is the diffusion constant of the particles and R the radius of action. R was found to be about double the radius of the gold particles, i.e., the particles must come into direct contact before the attractive forces begin to act. Later investigations by Westgren (41) in the writer's laboratory have given values for R still more close to the double radius of the particle (1918). The so-called slow coagulation, the case where, according to Smoluchowski's view, not all collisions cause instantaneous combination, has been studied by Westgren (41). The results were corroborative for the theory. Some recent investigations by Kruyt and van Arkel (42) (1920) on the coagulation of selenium hydrosols have given results not quite in conformity with the theory. As pointed out by Westgren and Reitstötter (43) (1922) in a recent paper, the sols used by Kruyt and van Arkel were probably not free from microscopic particles and from electrolytes and this may account for the deviations.

Among the many publications on coagulation values, there is one by Freundlich and Scholz (44) (1922) worthy of especial attention. They found that in the case of hydrophile sulphur sols, there is a very striking antagonism between certain coagulating electrolytes. Thus, the threshold value for magnesium chloride is many times higher when lithium chloride is present than when it is not. Odén had observed and studied such antagonistic actions in the case of the chlorides of the different alkali metals and hydrochloric acid, but explained the result as an antagonistic action between the cations and the anions. Freundlich believes that such an action exists, but claims that his measurements show that the antagonism between the cations plays a prominent part. Hydrophobe sols, such as gold hydrosol, do not show this phenomenon, but a slightly hydrophile sol such as As_2S_3 shows it to a certain extent.

The heat of coagulation of ferric oxide sols of various degrees of purity has been very carefully measured by Mathews and Browne (45) (1921). As the purity increased, the heat effect decreased and became almost negligible at the highest degrees of purity corresponding to about 40 equivalents ferric oxide per equivalent chlorine. The authors attribute the heat effects observed at low degrees of purity to the interaction between coagulant and electrolytes of sol. Now the coagulation—at least in the first period—consists only in an aggregation of the particles and not in a real change of degree of dispersity, the particles conserving their individual size in the coagulum for some time. It is quite reasonable that such an aggregation should involve only a very slight heat effect.

The colloid chemistry of proteins has been studied ardently during the last few years, and a very large number of papers on that subject have been published. Sörensen, Michaëlis, Pauli, Loeb, J. A. Wilson and their co-workers are the chief contributors. The importance of the hydrogen ion concentration is still one of the leading principles in the study of both protein sols and gels. On the other hand, the conviction that the hydrogen ion concentration is not the only factor of importance for the state of a protein seems to gain ground. To explain the minima and maxima in swelling, osmotic pressure, and viscosity, Pauli (46) (1920) assumes that the hydration of the protein particles varies, while Loeb (47) (1922) has put forward the hypothesis that practically all the properties of proteins can be explained by assuming a Donnan membrane equilibrium to exist between particles and liquid. Proctor and Wilson had successfully introduced this principle in the theory of swelling of a protein gel, and it is not improbable that it may play a part in certain kinds of coarse grained protein sols, the particles of which resemble gel clumps in their structure.

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