[Contribution from the Laboratory of Physical Chemistry of the University of Upsala]

THE ULTRA-CENTRIFUGE, A NEW INSTRUMENT FOR THE DETERMINATION OF SIZE AND DISTRIBUTION OF SIZE OF PARTICLE IN AMICROSCOPIC COLLOIDS

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Introduction

In a previous contribution the present authors pointed out the possibility of studying the distribution of size of particle in colloid solutions by means of determining the variation of concentration in the sol as a function of the distance from the axis of rotation during centrifuging.[1] The determination of the concentration was to be made by measuring the light absorption. The theory of the method was also roughly sketched. Preliminary experiments along these lines were then carried out by Svedberg and Nichols in the Laboratory of Physical Chemistry of the University of Wisconsin. A special centrifuge was built which permitted observations of the sol during centrifuging. Svedberg and Nichols described this centrifuge and a series of determinations of the average size of particle in some sols as calculated from the rate of movement of the boundary of the particles during centrifuging.[2] In cases where the size could be determined also by means of the ultra-microscope such determinations were carried out and the values obtained by this method agreed very well with the values arrived at by the centrifugal method. The smallest particles studied were those of gold, of radius $21\mu\mu$. In the same paper a more detailed explanation of the theory of this method was given.

Experiments with the same centrifuge have been continued by Nichols who will report his results later on. In the opinion of the present writers the problem in question is of such importance that every possible measure should be taken in order to develop this procedure to the point of greatest reliability for the determination of size and distribution of size of particle in very fine-grained sols. Practically nothing at all is known about the distribution of size of particle in even moderately fine-grained sols, and our knowledge of the average size of particle in sols which cannot be resolved by the ultramicroscope, that is, amicroscopic colloids, is very uncertain. On the other hand it is the fine-grained or amicroscopic sols which play the important part in colloid chemistry.

The Apparatus

The new centrifuge constructed by us allows the determination of particles that cannot be made visible in the ultra-microscope. In analogy with

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[1] Svedberg and Rinde, This Journal, **45**, 943 (1923).

[2] Svedberg and Nichols, *ibid.*, **45**, 1922 (1923).

the naming of the ultra-microscope and ultra-filtration apparatus we propose the name *ultra-centrifuge* for this apparatus.

The centrifuge was designed upon the self-balancing principle already used in cream separators. The vertical shaft 15, Fig. 1, rests upon a pivot bearing and is held in position by the bearing 6, which is isolated from the casing of the centrifuge by means of a system of special springs. On top of the shaft 15 rests the rotor 5. It fits so loosely that it can pick the right position as the centrifuge is speeding up. The shaft and the rotor together form a "spinning top." The friction in the springs surrounding the bearing 6 prevents a precessional motion. The energy of rotation is transferred to the shaft 15 by means of an endless screw device. The casing 23, of the centrifuge is fixed to the cast iron stand B, Fig. 2. Rubber plates and rubber tubings are inserted between adjacent metallic parts to absorb vibrations and isolate the centrifuge from the surroundings. The stand B is isolated in the same way from the heavy concrete base on which it rests. These damping and isolating devices diminish the vibrations in the centrifuge essentially. The horizontal shaft around which the toothed wheel 16, Fig. 1, rotates is connected

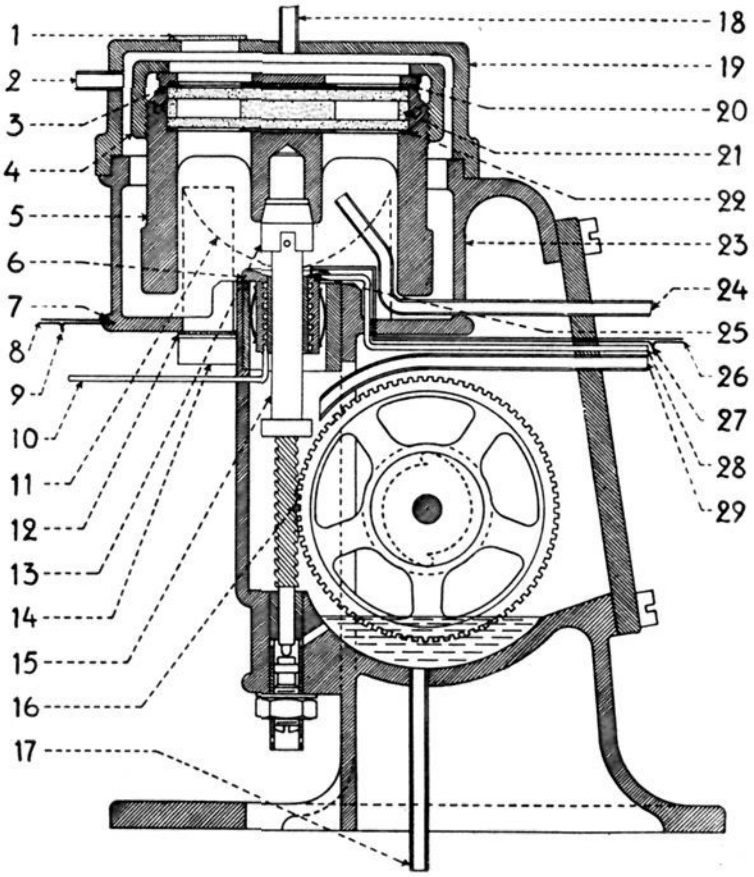

Fig. 1.

1, Upper window; 2, Hydrogen outlet; 3, Ebonite plate; 4, Lid of rotor; 5, Rotor; 6, Water-cooled spring bearing; 7–9, Thermocouple; 10, Water outlet; 11, Copper screen; 12, Lower window; 13, Carrying cone; 14, Reflecting prism; 15, Shaft of rotor; 16, Toothed wheel; 17, Oil outlet; 18, Hydrogen inlet; 19, Lid; 20, Rubber plate; 21, Cell; 22, Rubber plate; 23, Casing of centrifuge; 24, Hydrogen inlet; 25–27, Thermocouple; 28, Water inlet; 29, Oil inlet.

to the shaft of the pulley C, Fig. 2, with a special flexible joint of spiral springs which transfers the rotation from the pulley C. This is a very essential feature of the construction. Without this very loose coupling between pulley and centrifuge the latter cannot be satisfactorily isolated with regard to vibrations. The pulley is driven by a belt from a 1.5 h. p. shunt motor fed by a storage battery of 220 volts. The pulley is connected to its own shaft by a frictional coupling in order to allow the rotor of the centrifuge to get its speed gradually at the start. A special clutch is also inserted between the toothed wheel 16 and its shaft to enable the wheel and therefore also the shaft 15 to run freely when the motor is switched off. This very flexible system of transport of the rotational energy from the motor to the rotor of the centrifuge together with the fact that the latter is given a rather considerable mass, namely, 8660 g., ensures a high degree of constancy in the speed of the rotor. Any fluctuations in the speed of the electric motor will cause only a very slow and small fluctuation in the speed of the rotor. This is essential for the success of the measurements.

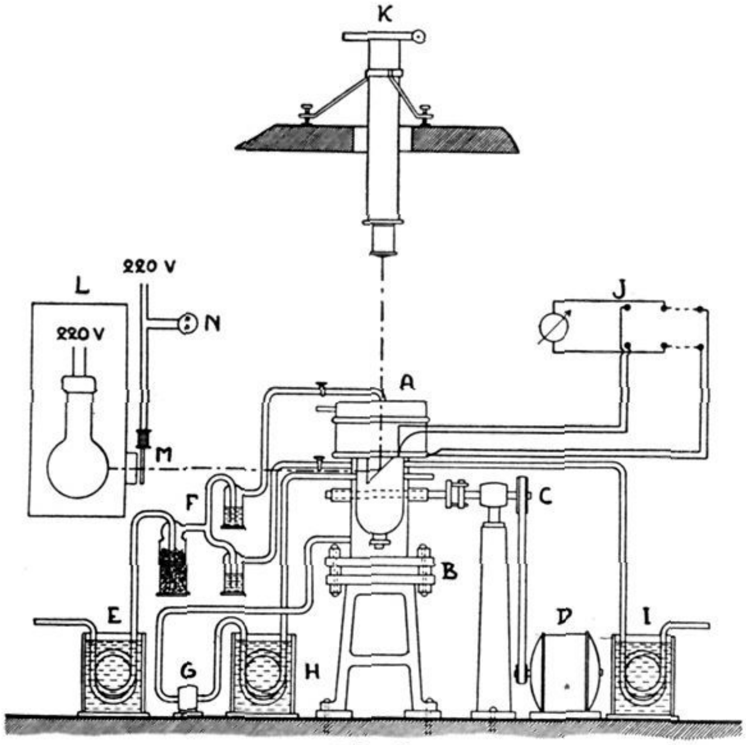

Fig. 2.

A, Centrifuge; B, Stand; C, Pulley; D, Motor; E, Cooling spiral for hydrogen current; F, Valves; G, Oil circulation pump; H, Cooling spiral for oil current; I, Cooling spiral for water current; J, Galvanometer and key; K, Camera; L, Lamp; M, Shutter; N, Switch for shutter.

Preliminary tests showed that besides the elimination as far as possible of vibrations and fluctuations in the speed there is another factor of equal importance to be considered, namely, the constancy of the temperature in the sol during centrifuging. Convection currents in the sol due to temperature differences are magnified enormously by the centrifugal force. Even if the temperature in the sol be uniform at the start of an experiment the heat generated by the friction of the rotor against the surrounding gas and by the friction in the bearings will tend to disturb the constancy of the temperature of the sol. Special precautions have therefore to be taken in order to cut down these disturbances as much as possible. A study of the consumption of electric energy in the motor when the rotor of the centrifuge was running in air and in hydrogen at a speed of 5600 r.p.m. showed that the friction in air generated 5.7 calories per second while the friction in hydrogen only gave 1.4 calories per second. Moreover, the heat conductivity of hydrogen is about six times the heat conductivity of air. A constant flow of hydrogen through the casing surrounding the rotor was therefore maintained. The heat generated in the bearings of the centrifuge was found to be 4.8 calories per second. The distribution of this heat among the different bearings was approximately determined by inserting a thermocouple in little holes bored in the bearings. It was found that most of the heat was produced in the bearing 6. The temperature of this bearing was raised about 10° when the centrifuge had been running for about 15 minutes and then gradually became constant. The bearing 6 was therefore redesigned and provided with a spiral slot through which cold water could be circulated (10, 28, Fig. 1). One thermocouple (25, Fig. 1) in the bearing and one in the casing 7, Fig. 1, permitted the experimenter to control the temperature difference between casing and bearing during centrifuging. The rotor was protected from direct radiation from the bearing by means of suitable copper screens 11, Fig. 1. It was found, however, that in spite of this precaution the temperature of the casing increased slowly during centrifuging. In order to avoid this an oil circulation pump G, Fig. 2, was installed and a jet of oil from a copper tubing 29, Fig. 1, directed against the screw and toothed wheel. The circulating oil was passed through a copper spiral immersed in water H, Fig. 2.

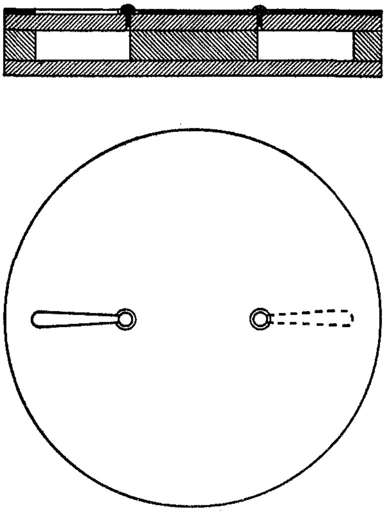

Fig. 3.

The rotor 5, Fig. 1 was made of red brass. Six sectors connected the central part with the outer cylindrical part. The cell 21, Fig. 1, holding the sol to be studied had the form of a low cylinder and was held in position by a brass ring and the lid 4, Fig. 1. Sheets of rubber were inserted between the brass surfaces and the glass cell. The rotor was suspended a little above its center of gravity and rested loosely upon the top of the shaft.

The cell (Fig. 3) was made up of three circular glass plates 12.4 cm. in diameter cemented together. The middle plate was 1.0 cm. thick and the outer ones 0.5 cm. In the middle plate two sectorial apertures had been cut out with a diamond saw and in the upper one two holes had been bored above the inner ends of the sectorial apertures in the middle plate to allow liquid to be poured into the little sectorial cells formed between the glass plates. The glass was of a good resistant type and the cement used was such that sensitive sols were not coagulated by it. A circular disk of ebonite 3, Fig. 1, with an aperture coinciding with one of the sectorial cells was placed on top of the glass plates and cut off all light except that from the sector in question. The other sector served only as counterweight.

In order to permit observations of the sol during centrifuging the casing was provided with two windows 12 and 1, Fig. 1, one in the bottom and one in the lid. Below the window in the bottom a reflecting prism 14, Fig. 1, was fixed so as to direct a horizontal beam of light vertically through the centrifuge. At some distance from the prism a 500-watt Philips Argenta lamp fed by storage cells was mounted providing an intense and even source of white light L, Fig. 2. A cell 5 cm. deep containing water was inserted between lamp and prism to cut out the infra-red. Observations were made from a room above the one where the centrifuge was mounted, through an aperture in the ceiling. Preliminary measurements of the average size of particle were made by observing the rate of movement of the boundary between the sol and the supernatant colorless liquid, formed during centrifuging, by means of a telescope provided with a scale in the ocular. For more accurate measurements of the average size and for measurements of the distribution of size of particles photographs of the sol were taken. The camera K, Fig. 2, used for this purpose has a Voigtländer Euryscope lens of 54.5 cm. focal length. It was usually stopped down to F:22.5. The shutter M, Fig. 2, was controlled by means of an electromagnet and could be operated from the room where the camera was mounted. The galvanometer for the thermocouples and the device for the control of the water current for the bearing 6 were also placed in the upper room.

A determination was carried out in the following way. By means of a capillary pipet the sol to be studied was introduced into the uncovered sector cell and the cell was closed by a stopper made of fiber. It is essential to have the cell closed. When the hole is left open evaporation of the sol takes place during centrifuging and the cooling effect of this evaporation is enough to create convection currents in the cell. The covered sector could in most cases without appreciable unbalance be allowed to remain filled with water. The rotor was put on the shaft, the lid 19, Fig. 1 was placed in position and the hydrogen current started. After about ten minutes the motor was started, the galvanometer observed and the cooling water for the bearing 6 regulated until constancy was attained with a temperature difference less than 0.3° between bearing and casing. The oil circulation pump was started at the same time. The sol was then either observed by means of the telescope or was photographed. It was found difficult to avoid completely a slight vibration or rocking of the centrifuge as a whole when the motor was running, caused by dissymetry in the coupling between motor and centrifuge. To get perfect definition in the pictures the current to the motor was therefore switched off during an exposure. Owing to the great mass of the rotor and the slight friction in the centrifuge the speed of the rotor did not decrease measurably during such a period which never exceeded 20 seconds.[3]

The Theory of the Procedure

In many sols, such as gold sols, the particles are rather uniform in size, so that measurements of the rate of movement of the boundary between particles and colorless liquid can be used for an approximate determination of the average size. Stokes' formula as modified for the influence of variation of acceleration with distance from the axis of rotation is used for the calculation of the radius of the particle.[4]

$$r = \sqrt{\frac{9\,\eta\,ln\,(x_2/x_1)}{2\,(\rho_p - \rho_d)\,(t_2 - t_1)\,\omega^2}}$$

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[3] The main parts of the centrifuge were made for us by "Upsala Separator-Fabrik." We wish to express our indebtedness to Mr. A. G. Bergström of this Company for his kind interest and helpful suggestions.

[4] Svedberg and Nichols, THIS JOURNAL, **45,** 2910 (1923).

where r is the radius of particle, η the viscosity of the dispersion medium, x_2 and x_1 the distance between the axis of rotation and the position of the boundary at the time t_2 and t_1, respectively, $\rho_p - \rho_d$ the difference in density between particle and dispersion medium and ω the angular velocity.

In the case of prolonged centrifuging of very fine-grained sols the influence of diffusion must be taken into account. The effect is a more or less pronounced blurring of the boundary. If the centrifuging is fast enough to permit a zone of clear liquid to be formed close to the meniscus of the sol, that is, if the reflection of the particles against the meniscus can be neglected and if the boundary is far enough from the bottom of the cell so that reflection of particles from the bottom can also be neglected, the following simplified solution of the diffusion equation can be used to express the diffusion of the particles.[5]

$$c_z = c_0/2.\left(1 - \frac{2}{\sqrt{\pi}}\int_0^y e^{-y^2}\,\mathrm{d}y\right) \qquad y = z\sqrt{\frac{3\,\pi\,N\,\eta\,r}{2\,R\,T\,t}}$$

where c_z is the concentration at the distance z from the sharp boundary which would have been formed if there had been no diffusion (z being positive in the direction toward the axis of rotation), c_0 is the concentration of the sol at the time $t = 0$, N the Avogadro constant, R the gas constant and T the absolute temperature. The function $\frac{2}{\sqrt{\pi}}\int_0^y e^{-y^2}\mathrm{d}y$ is the well-known probability integral and can be computed from tables.[6] In Fig. 4 a family of diffusion curves for different sizes of particle at 16° and t = 2 hours calculated from the above formula are given. The origin of each curve has been located at a distance from the meniscus of the sol corresponding to sedimentation during two hours at a speed of 5700 r.p.m. and with 3.00cm. distance between meniscus and axis of rotation. From this

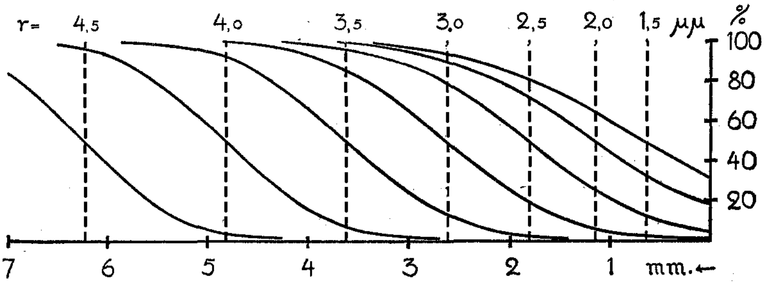

Fig. 4.

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[5] Compare Stefan, *Sitzungsber. Wiener Akad. Wiss. Math.-Nat. Classe,* **79,** II, 176 (1879). Baur, *Biochem. Z.,* **100,** 52 (1919). Einstein, *Ann. Physik,* [4] **17,** 549 (1905); **19,** 289 (1906).

[6] Czuber, "Wahrscheinlichkeitsrechnung," B. G. Teubner, Leipzig, **1908.**

diagram the degree of blurring of the boundary can be estimated. The exact position of the boundary which would have been formed if no diffusion had taken place can be determined by means of photographs of the rate of change of concentration with distance. In case of $z = 0$ we have $c_z = 0.5.c_0$ and the position of the boundary is therefore the point where the concentration of the sol has fallen to half its value.

It was pointed out that the measurements have to be made before any notable reflection of particles at the bottom of the cell reaches the region where the measurements of concentration are made, that is, before sedimentation equilibrium has begun to be manifest. In order to facilitate the estimation of this point we have calculated sedimentation-equilibrium curves for different sizes of particle in the case of gold hydrosols. In the case of sedimentation equilibrium on the centrifuge where the acceleration varies with the distance x from the axis of rotation, a modified formula has to be used. In the well-known differential equation for sedimentation equilibrium[7] the acceleration has to be placed equal to $\omega^2 x$. Thus $\frac{RT}{N} \cdot dc = -4/3\pi r^3(\rho_p - \rho_d)\omega^2 c.x dx$, which gives us $c_x = c_b.e^{-N/RT\, 4/3.r^3(\rho_p-\rho_d)\,\omega^2.\left(\frac{b^2 - z^2}{2}\right)}$, where b is the distance between the bottom of the cell and the axis of rotation and c_x and c_b the concentration at the points x and b. In Fig. 5 the sedimentation equilibrium curves calculated by means of this formula are reproduced for $b = 5.2$ cm., $\omega = 190\pi$, which corresponds to the conditions in some of our experiments.

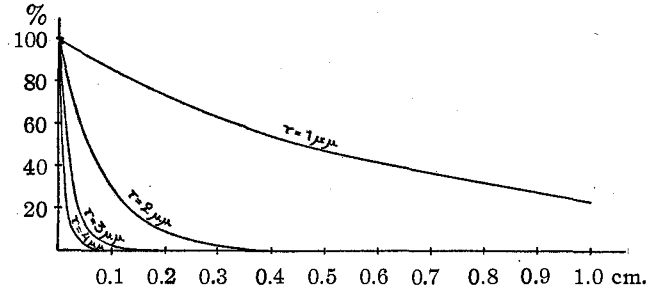

Fig. 5.

The theory for the method of the determination of distribution of size of particle was outlined by us in a previous communication[1] and then given in a more accurate form by Svedberg and Nichols.[2] Their formula, however, gives us only the distribution of size of particle in the sol after it has been centrifuged for the time t, and this distribution does not coincide with the distribution in the original sol. If a sol with equal-sized particles is

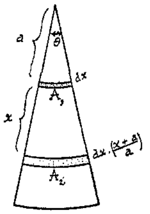

Fig. 6

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[7] Perrin, *Compt. rend.*, **147**, 530 (1908).

centrifuged and we take into account an annulus of a sector of angle Θ and the thickness k we find that the particles contained in the small annulus A_1 (Fig. 6) at the time zero will after the lapse of the time t be spread out within the annulus A_2. Two particles situated at the distance dx at the time zero will be situated at the distance dx. $\left(\frac{x+a}{a}\right)$ at the time t. Let n be the number of particles per cc. and dc and dc_t the concentration within the annulus A_1 and A_2, respectively. Then

$$dc = \frac{n}{\pi a \frac{\Theta}{180} k\, dx}, \quad dc_t = \frac{n}{\pi (a+x) \frac{\Theta}{180} k\, (a+x)\, dx}$$

thus,

$$dc = dc_t.\left(\frac{x+a}{a}\right)^2.$$

The concentration of each size class in the distribution curve has therefore to be multiplied by the factor $\left(\frac{x+a}{a}\right)^2$ where a is the distance between meniscus of sol and axis of rotation and x the distance between meniscus and the point where the boundary of the size class in question has become stationed. Our distribution formula therefore assumes the form, $dc/dr = [(dc_t/dx)/(dr/dx)].[(x+a)/a]^2$.

But

$$r = \sqrt{\frac{9\,\eta\, ln\left(\frac{x+a}{a}\right)}{2\,(\rho_p - \rho_d)\,\omega^2 t}}$$

thus

$$dc/dr = dc_t/dx.\left\{\frac{2\,(x+a)^3\sqrt{ln\left(\frac{x+a}{a}\right)}}{a^2\sqrt{\frac{9\,\eta}{2\,(\rho_p-\rho_d)\,\omega^2 t}}}\right\}$$

It is of interest to note that the equation $dc = dc_t.\left(\frac{x+a}{a}\right)^2$ also can be given the form,

$$r = \sqrt{\frac{9\,\eta\, ln\sqrt{c/c_t}}{2\,(\rho_p-\rho_d)\,\omega^2 t}}$$

which provides us with a new method of determining the size of particle in uniform sols from determinations of the decrease in concentration with time of centrifuging. Such determinations have actually been carried out by us and have given results which are in accordance with those arrived at by determining the rate of movement of the boundary.

In the case of very small particles the influence of diffusion upon the variation of concentration with distance from the axis of rotation has to be taken into account. The exact mathematical analysis of this phenomenon has not been worked out so far but an approximate solution of the problem can be arrived at in the following way. If the sol to be studied is comparatively uniform—this is the case with the fine-grained gold sols—

it is sufficient to determine the percentage mass of a few size-classes, say in the case of a sol of average radius of particle 3.5 $\mu\mu$ the mass of the classes of radius 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0 $\mu\mu$. The diffusion curves for these particles are calculated by means of the equations

$$c_z = c_0/2. \left(1 - \frac{2}{\pi}\int_0^y e^{-y^2}\,\mathrm{d}y\right); \quad y = z\sqrt{\frac{3\,\pi\,N\,\eta\,r}{2\,R\,T\,t}}$$

For a certain time of centrifuging, say two hours, the positions of the boundary lines which these particles would have given are calculated from the modified Stokes formula. The positions of these boundaries constitute the zero points for the different diffusion curves (compare Fig. 4). These theoretical data enable us to calculate for different distances x from the meniscus of the centrifuged sol the contribution $c_{I,x}$ which each size-class gives to the total concentration c_x. These contribution terms have to be multiplied by the factor $[a/(x + a)]^2$ and by the fraction f_I which expresses the relation between the mass of each size-class and the total mass of the disperse phase. Thus we have

$$c_x = \sum_{I}^{k} f_I \,.\, c_{I,x} . \left(\frac{a}{x+a}\right)^2$$

When k size-classes are chosen, k observations are necessary to determine the unknown quantities f_I, f_{II}, ... f_k. The system of equations obtained can be solved conveniently by means of determinants if the number of unknowns, that is, the number of size-classes chosen is low. If the number of size-classes is high the method of successive approximation has to be used. In the first equation (near the meniscus) the smallest particles are predominant and therefore the factors representing the other particles are omitted in the first approximation. The second equation is allowed to contain only two terms, etc. In this way a first set of f-values is obtained. In the second approximation the first equation is given two terms, the second three terms, etc.

Measurements and Results

As an example of the use of the ultra-centrifuge a series of measurements on fine-grained gold sols is given below.

A. Determinations by Means of Photographic Records.—A number of exposures of the sol in question were made during centrifuging at successive intervals of time. Ilford Special Rapid Panchromatic Plates were used. On the same plate was printed a neutral tint wedge, the same time of exposure being used as in the case of the sol. On another plate a series of exposures of the same sol in different degrees of dilution and of the same duration as in the first series was made shortly after starting the centrifuge. The same wedge was printed in the same way on this second plate. Fig. 7 gives an example of such a photographic record of the centrifuging of a gold sol. The average radius was 11.6 $\mu\mu$ (Table VII), the time between successive exposures 5 minutes and the speed 5700 r. p. m. The photographs of the sol at various intervals of time and at various concentrations at the time zero as well as the prints of the wedge on the plates were then recorded by means of a Siegbahn self-registering microphotometer.[8] In Fig. 8 examples of such microphotometric records are given. The curve A represents the second and the curve B the fifth exposure in Fig. 7. By means of these microphotometric records the curves giving the relation between concentration of the sol which is being centrifuged and the distance from the meniscus (and from the axis of rotation) can be constructed. The details of this rather simple procedure are, we think, not of sufficient interest to be given here. Perhaps it ought to be mentioned that in cases

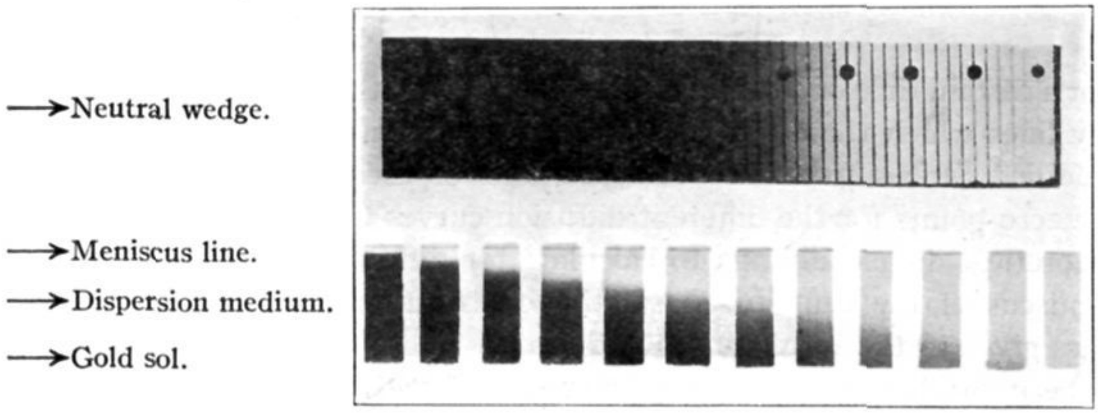

Fig. 7.

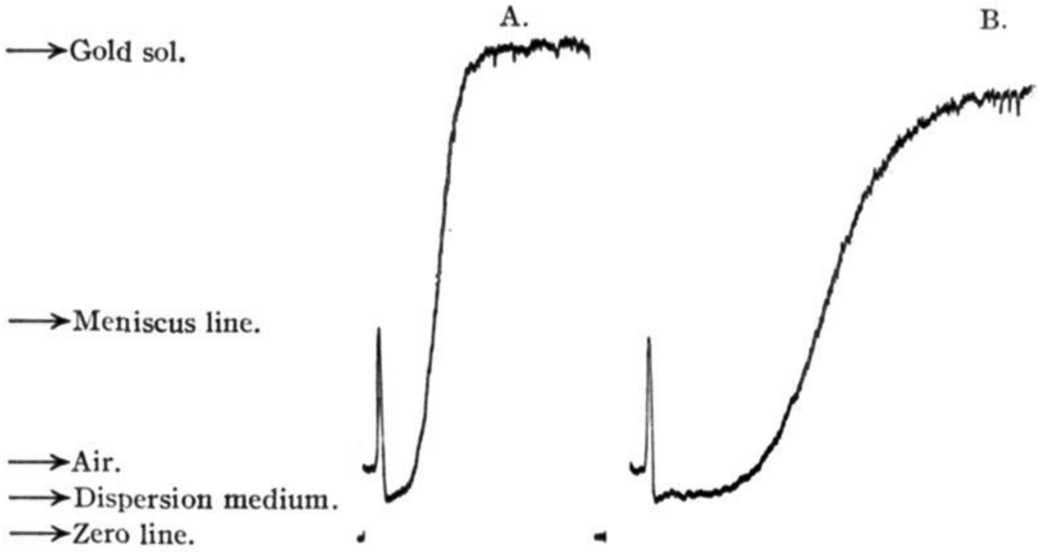

Fig. 8.

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[8] The instrument used by us was built in the workshop of the Department of Physics by Professor Siegbahn's mechanicians and under his supervision. The authors wish to express their indebtedness to Professor Siegbahn for the service thus rendered.

where the distribution of size of particle is measured only over a small range the light absorption of the sol can be regarded as practically independent of the size, while in cases where the distribution is measured over a wide range of size of particle a correction for the variation of light absorption with size has to be introduced. This correction can be taken from Rinde's measurements of light absorption in gold sols (not yet published). In Fig. 9 an example of a series of 12 concentration curves is given, representing the 12 exposures reproduced in Fig. 7.

Gold Sol No. 1: 100 cc. of 0.001 N $HAuCl_4$; 5 cc. of 0.1 N K_2CO_3; 95 cc. of H_2O; 1 cc. of alcoholic solution of phosphorus; reduction completed and alcohol removed by boiling the mixture.

The distribution curve was not calculated but the radius of particle corresponding to the maximum of the distribution curve was determined from the position of the inflection point of the concentration curves. The average size of particle was also calculated from the decrease in concentration in the sol during centrifuging. For the sake of comparison we also determined the average size by means of Zsigmondy's nuclear method.

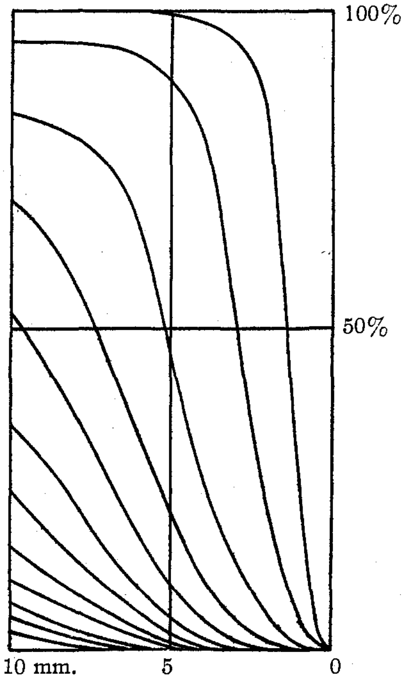

Fig. 9.

TABLE I

GOLD SOL NO. 1

Speed, 8700 r. p. m. ($\omega = 290\pi$); T, 290°; time of exposure, 5 secs.

Time of centrifuging Seconds	Distance between axis of rotation and inflection point of concentration curve Cm.	Radius of particle in $\mu\mu$ calculated from the formula $r = \sqrt{\dfrac{9\,\eta\,ln\,(x_2/x_1)}{2(\rho_p - \rho_d)\,\omega^2\,(t_2 - t_1)}}$
3600	3.70	...
5400	3.78	2.0
7200	3.87	2.1
9000	3.96	2.1
9900	4.00	1.9
		Av. 2.0

Determinations by means of the nuclear method gave the value r = 2.5 $\mu\mu$. The centrifugal determinations have probably given too low values of r because of the reflection of the particles at the meniscus. The theory of the necessary correction has not been worked out yet.

TABLE II

GOLD SOL NO. 1

Speed, 8700 r.p.m. ($\omega = 290\pi$); T, 290°; time of exposure, 5 sec.

Time of centrifuging Seconds	Concentration in percentage of original sol	Radius of particle in $\mu\mu$ calculated from the formula $r = \sqrt{\frac{9\,\eta\, ln \sqrt{c/c_t}}{2\,(\rho_p - \rho_d)\,\omega^2 t}}$
0	100	...
4500	76	3.2
8100	75	2.4
9000	68	2.6
9900	59	2.9
		Av. 2.8

Gold Sol No. 2: 5 cc. of 0.01 N $HAuCl_4$; 100 cc. of gold sol No. 1; a few drops of hydrogen peroxide. The distribution curve was calculated from one of the exposures by means of the formula

$$c_x = \sum_{I}^{k} f_I \cdot c_{I,x} \cdot \left(\frac{a}{x+a}\right)^2$$

and the method of successive approximation. From the other exposures the radius of particle corresponding to the maximum of the distribution curve was calculated as for Sol No. 1; further determinations were made as for Sol No. 1.

TABLE III

GOLD SOL NO. 2

Speed, 5700 r.p.m. ($\omega = 190\pi$); T, 289°; time of exposure, 15 seconds

Time of centrifuging Seconds	Distance between axis of rotation and inflection point of concentration curve Cm.	Concentration in percentage of original sol	Radius of particle calculated from $r = \sqrt{\frac{9\,\eta\, ln\,(x_2/x_1)}{2\,(\rho_p - \rho_d)\,\omega^2\,(t_2 - t_1)}}$	$r = \sqrt{\frac{9\,\eta\, ln \sqrt{c/c_t}}{2\,(\rho_p - \rho_d)\,\omega^2 t}}$
0	..	100	..	..
1800	3.43	..	..	..
2700	3.49	90	3.83	3.06
3600	3.55	86	3.84	3.17
4500	3.60	83	3.43	3.15
5400	3.66	79	3.73	3.23
6300	3.71	75	3.38	3.31
7200	3.78	74	3.97	3.98
8100	3.83	73	3.33	3.05
9000	3.91	70	4.18	3.88
9900	3.97	..	3.58	..
			Av. 3.70	3.35

Determinations by means of the nuclear method gave the value r = 3.2 $\mu\mu$.

TABLE IV

GOLD SOL NO. 2

Distribution of size of particles calculated from the exposure at 7200 seconds after starting the centrifuge

Radius of particle, $\mu\mu$	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
Mass of particle in % of mass of orig. sol	0.7	0.3	4.5	20.7	35.2	34.4	0.0	0.0

Gold Sol No. 3: 95 cc. of 0.001 N $HAuCl_4$; 40 cc. of gold sol No. 2; a few drops of hydrogen peroxide. The distribution curve was calculated from one of the exposures by means of the formula

$$dc/dr = \frac{dc_t/dx}{dr/dx} \cdot \left(\frac{x+a}{a}\right)^2$$

Other determinations were made as for Sols Nos. 1 and 2. In Table V the mean values of r obtained by the different methods are given.

TABLE V

GOLD SOL NO. 3

Radius of particle in $\mu\mu$	Method of determination
6.9	Centrifuging: inflection point of concn. curve
7.3	Centrifuging: decrease in concentration
4.8	Zsigmondy's nuclear method.

Here the nuclear method gives a markedly lower value than the methods of determination based upon centrifuging. This has always been found to be the case with sols containing particles possessing a radius of 7 to 15 $\mu\mu$.

TABLE VI

GOLD SOL NO. 3

Distribution of size of particle calculated from the exposure at 1500 seconds after starting the centrifuge.

Interval of radius of particle $\mu\mu$	dc/dr in percentage of mass of original sol per 1$\mu\mu$ radius interval	Interval of radius of particle $\mu\mu$	dc/dr in percentage of mass of original sol per 1$\mu\mu$ radius interval
3.90–4.76	1.9	7.64–8.08	26.5
4.76–5.48	7.0	8.08–8.49	19.5
5.48–6.11	19.3	8.49–8.87	12.5
6.11–6.67	33.0	8.87–9.23	9.7
6.67–7.17	31.9	9.23–9.58	6.2
7.17–7.64	34.9	9.58–9.91	1.8

In Fig. 10 the distribution is represented graphically.

Gold Sol No. 4: 95 cc. of 0.001 N $HAuCl_4$; 40 cc. of gold sol No. 3; a few drops of hydrogen peroxide. The determinations were the same as for Sol No. 3.

TABLE VII

GOLD SOL NO. 4

Speed, 5700 r.p.m. ($\omega = 190\pi$); T, 289°; time of exposure, 15 seconds

Time of centrifuging Seconds	Distance between axis of rotation and inflection point of concentration curve Cm.	Radius of particle in $\mu\mu$ calculated from the formula $r = \sqrt{\dfrac{9\,\eta\, ln\,(x_2/x_1)}{2\,(\rho_p - \rho_d)\,\omega^2\,(t_2 - t_1)}}$
0	3.200	..
300	3.345	10.6
600	3.490	10.7
900	3.725	12.7
1200	3.935	11.8
1500	4.170	12.1
		Av. 11.6

Determinations by means of the nuclear method gave the value $r = 7.2\ \mu\mu$.

TABLE VIII

GOLD SOL NO. 4

Distribution of size of particle calculated from the exposure at 900 seconds after starting

Interval of radius of particle $\mu\mu$	dc/dr in percentage of mass of original sol per 1$\mu\mu$ radius interval	Interval of radius of particle $\mu\mu$	dc/dr in percentage of mass of original sol per 1$\mu\mu$ radius interval
3.87– 5.09	0.7	11.57–12.04	28.5
5.09– 6.22	1.7	12.04–12.49	19.3
6.22– 7.15	3.1	12.49–12.92	13.8
7.15– 7.97	7.1	12.92–13.33	7.4
7.97– 8.69	8.3	13.33–13.72	8.0
8.69– 9.36	9.2	13.72–14.10	6.3
9.36– 9.97	12.4	14.10–14.46	4.6
9.97–10.53	16.3	14.46–14.81	4.8
10.53–11.07	28.5	14.81–15.15	2.5
11.07–11.57	33.0		

In Fig. 11 the distribution is represented graphically.

B. Determinations by Means of Telescope and Scale.—The rate of movement of the boundary between pure dispersion medium and sol was observed directly by means of a telescope provided with a scale in the ocular. This method of observation gives tolerably accurate results in the case of sols of rather large particles of comparatively equal sizes, that is, in cases where the boundary remains comparatively sharp during the time of centrifuging. The method is of course less laborious than the more accurate procedure of measuring the variation of concentration with distance from the axis of rotation.

The action of a protective colloid, such as gelatin, upon the rate of sedimentation of a gold sol was studied with the object of obtaining some information about the mechanism of the protective action. If the gelatin is really adsorbed upon the gold particles this ought to give rise to an increased friction between particle and dispersion medium and therefore to an apparent decrease in the radius of the particle if simply calculated from the modified Stokes' formula. In Table IX such a series of determinations is given.

Table IX

Gold Sol No. 5

0.0001 *N* $HAuCl_4$ was reduced with alcoholic solution of phosphorus; 100 cc. of this sol + 10 cc. of 0.01 *N* $HAuCl_4$ was reduced with a few drops of hydrogen peroxide. Various amounts of gelatin were then added

Gel. concn., %	0.0	0.00001	0.0001	0.001	0.004	0.01
App. radius of part. μμ	10.3	9.5	7.9	coagulated	5.8	5.6

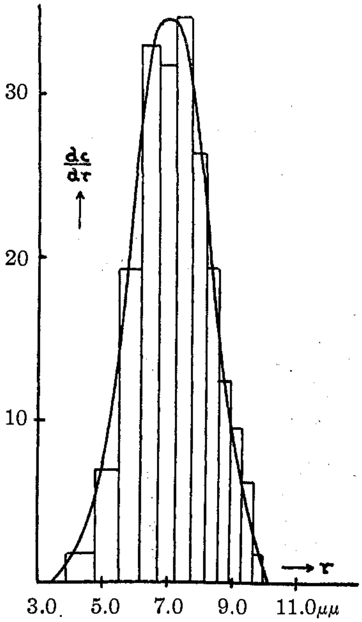

Fig. 10.

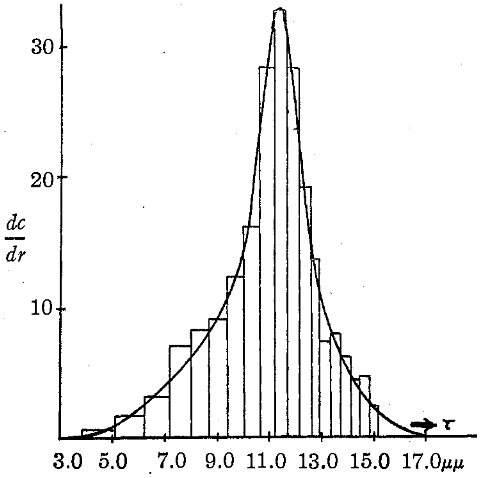

Fig. 11.

The nuclear method gave the value $r = 8.4\mu\mu$. An analogous series of determinations (Table X) was made with the same gold sol to which ammonium hydroxide had been added so as to give a concentration of 0.005 *N*. The Sörensen (*P*H) values were also measured.

Table X

Gold Sol No. 5

Ammonium hydroxide added to the concentration 0.005 *N*

Gelatin concentration %	Apparent radius of particle μμ	*P*H
0.0	11.0	4.6
.00001	8.9	5.6
.0001	9.5	5.8
.001	partly coagulated	6.2
.01	4.4	5.9
.1	2.9	5.3

It is of interest to note that the sol is unstable at the point where the P_{H} has a maximum, that is, where the hydrogen-ion concentration is lowest.

From these determinations it is obvious that the gelatin, or part of it, is adsorbed upon the gold particles. By the following reasoning we can even obtain some idea of the thickness of this adsorbed layer.

A minimum value of the layer of gelatin around the particles is obtained as follows. The gold particle is supposed to be surrounded by a shell of gelatin sol or gelatin gel the density of which does not differ very much from the density of the dispersion medium. In this case we have according to Stokes' law $4/3.\pi r^3(\rho_{\mathrm{Au}}-\rho_d)\omega^2 x = 6\pi\eta R_1.\mathrm{d}x/\mathrm{d}t$, where r is the radius, ρ_{Au} the density of the gold particle and R_1 the radius of the whole system.

Now the apparent radius r_a calculated from the centrifuging experiments and given in the above tables is defined by the equation $4/3.\pi r_a^3(\rho_{\mathrm{Au}}-\rho_d)\omega^2 x = 6\pi\eta r_a.\mathrm{d}x/\mathrm{d}t$; hence, by elimination $R_1 = r^3/r_a^2$.

(R_1-r) gives the minimum value of the gelatin-water layer. A maximum value can be arrived at in the following way. Suppose that all the gelatin in the sol is adsorbed around the gold particles and also a sufficient quantity of water is present to give the rate of sedimentation found in the centrifuging experiments. For the sake of simplicity we assume that the gelatin forms an inner sphere of radius R' around the gold and then the water an outer sphere of radius R_2. This gives $n.4/3.\pi r^3\rho_{\mathrm{Au}} = c_{\mathrm{Au}}$, and $n.4/3.\pi(R'^3 - r^3)\rho_{\mathrm{g}} = c_{\mathrm{g}}$, where n is the number of gold particles per cc. of sol, c_{Au} is the grams of gold per cc. of sol, ρ_{g} is the density of gelatin taken as 1.4, c_{g} the grams of gelatin per cc. of sol. Hence

$$R' = r\sqrt[3]{1+\frac{c_{\mathrm{g}}\cdot\rho_{\mathrm{Au}}}{c_{\mathrm{Au}}\cdot\rho_{\mathrm{g}}}}$$

We further have

$$[4/3.\pi r^3(\rho_{\mathrm{Au}}-\rho_d) + 4/3\pi(R'^3-r^3)(\rho_{\mathrm{g}}-\rho_d)]\omega^2 x = 6\pi\eta R_2.\mathrm{d}x/\mathrm{d}t$$

hence $$R_2 = r^3/r_a\left[\frac{\rho_{\mathrm{Au}}-\rho_{\mathrm{g}}}{\rho_{\mathrm{Au}}-\rho_d} + (R'/r)^3.\frac{\rho_{\mathrm{g}}-\rho_d}{\rho_{\mathrm{Au}}-\rho_d}\right]$$

or $$R_2 = R_1\ [0.978 + (R'/r)^3.0.022]$$

The maximum value of the gelatin-water layer is (R_2-r). From the determinations in Tables IX and X we find the values tabulated in Table XI.

Table XI

Minimum and Maximum Values of Thickness of Gelatin Layer on Gold Particles

Gelatin concn.	Alone		In the presence of ammonia	
%	R_1-r μμ	R_2-r μμ	R_1-r μμ	R_2-r μμ
0.00001	1.80	1.84	6.0	6.2
0.0001	7.2	8.9	3.8	5.2
0.001	coagulation	..	coagulation	..
0.004	22.1	148.0	...	..
0.01	24.5	362.6	57.8	726
0.1	...	..	147	..

At low gelatin concentrations the values of (R_1-r) and (R_2-r) are rather close together, thus giving us a good idea of the thickness of the gelatin layer on the gold particles. This comparatively close agreement between the (R_1-r) and the (R_2-r) values also shows that in dilute sols practically all of the gelatin is adsorbed upon the gold particles. At higher concentrations the minimum and maximum values of the thickness of the layer differ widely showing that in this case only part of the gelatin is adsorbed.

Summary

1. A centrifugal apparatus for the study of the changes taking place in fine-grained sols during centrifuging has been described. The name "ultra-centrifuge" has been proposed for this instrument.
2. The theory of the methods for determining size and distribution of size of particle from observations—direct or photographic—of the sol during centrifuging has been further developed.
3. Results of measurements of size and distribution of size of particle for gold sols of average radius 2.3, 3.6, 7.1, 11.6$\mu\mu$ have been given. The determinations made by means of the ultra-centrifuge give radius values which are from 11 to 38% higher than those arrived at by means of Zsigmondy's nuclear method.
4. The nature of the protective action of gelatin upon fine-grained gold sols has been studied by means of the ultra-centrifuge. Minimum and maximum values for the thickness of the gelatin layer adsorbed around the gold particles have been calculated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF MCGILL UNIVERSITY]

THE PROPERTIES OF PURE HYDROGEN PEROXIDE. V. VAPOR PRESSURE

BY O. MAASS AND P. G. HIEBERT

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The determination of the vapor-pressure curve of pure hydrogen peroxide is important because the data makes possible the calculation of the latent heat of evaporation, Trouton's constant, etc., physical constants which are of particular interest when compared with the corresponding ones for water. The experimental difficulties which have to be overcome in the measurement of the vapor pressure of hydrogen peroxide are many. At high temperatures hydrogen peroxide decomposes when in contact with glass. A mercury manometer cannot be used directly because of the immediate decomposition which takes place when peroxide comes in contact with the mercury surface, the latter being attacked and covered with a scum which makes accurate pressure readings impossible.