Tyndallmeter readings, owing to the greater reflecting surface of the particles.

3. It was found that the rate of disappearance of a finely divided smoke of a given concentration was greater than for a coarser smoke owing to the increased opportunity for coalescence.

4. By setting up smokes with the same size of particles but with different concentrations it was found that the rate of disappearance increases with concentration owing to the increased chance for coagulation and removal by the walls.

5. Since increased concentration and increased subdivision both lead to a higher rate of disappearance, it is impossible to raise the optical density of a smoke beyond a certain point by the introduction of further smoke material.

AN OSCILLATION METHOD FOR MEASURING THE SIZE OF ULTRAMICROSCOPIC PARTICLES.[1]

By P. V. Wells and R. H. Gerke.

Received January 17, 1919.

Introduction.—It is one of the familiar properties of ultramicroscopic particles that some portion of any given type are electrically charged. Moreover, it is now accepted that the charges carried by any such particles are always multiples of the elementary unit, the electron. When the particles are not ionized by some powerful agent, the charged particles form but a fraction of the whole number and most of the charged particles possess but a single electron. Compared with the number carrying one electron, in statistical work the number doubly charged is negligible. The observed motion of the particles in a given electrostatic field is thus a measure of their size.

The usual method of observing the motion of the charged particles is much improved in precision by reversing the direction of the field by means of a rotating commutator. In this way the particle is made to perform repeated oscillations, the amplitude of which may be measured with considerable precision, making possible for the first time the precise measurement of the size of a single ultramicroscopic particle.

The following paper presents some of the results obtained by this method with ultramicroscopic particles suspended in air.

Properties of Gaseous Disperoids.—The most important characteristic of suspensions of small particles in air is that they are not in equilibrium. The particles are continually diffusing to the surrounding walls, and collid-

[1] This paper describes part of a joint investigation by the Bureau of Standards and the Dispersoid Section, Research Division, Chemical Warfare Service, and has been approved for publication by Major-General William L. Sibert, Director of Chemical Warfare Service, U. S. A. and by S. W. Stratton, Director of the Bureau of Standards.

ing with each other and coalescing, which results in larger particles that settle to the bottom of the chamber, so that the dispersed phase is gradually disappearing from the system. The transient character of the phenomena forbid the application of the thermodynamic laws of equilibrium to such systems.

The motion of the particles is resisted by the viscosity of the air. For spheres of diameter d, moved with uniform slow velocity v, the force of viscous resistance is in accordance with Stokes' law,

$$F = 3\pi\eta dv \qquad (1)$$

where η is the viscosity of the medium.

In settling, this force is equal to the weight of the particle, so that

$$F = \pi/6\ \rho g d^3 \qquad (2)$$

where ρ is the density of the particle (neglecting the density of the air) and g is the acceleration of gravity. Hence, taking as approximate values $g = 980$, and for the viscosity of air $\eta = 1.81 \times 10^{-4}$ c. g. s., the velocity of steady fall under gravity of spheres of unit density is approximately

$$v = 3 \times 10^5 d^2. \qquad (3)$$

The rate of settling for particles of different sizes is as follows:

Diameter of particle d. (Cm.)	Rate of settling v. (Cm. per sec.)	
10^{-2}	30	= 1100 meters per hour
10^{-3}	0.3	= 11 meters per hour
10^{-4}	3×10^{-3}	= 11 cm. per hour
10^{-5}	3×10^{-5}	= 1.1 mm. per hour

Owing to deviations from Stokes' law, Equation 3 does not hold accurately for particles smaller than 10^{-4} cm. in air, the steady velocity of fall being greater than indicated by the equation, but it is evident that such particles would practically never settle in the ordinary atmosphere subjected to convection currents. Hence particles must grow by coalescing to the order of 10^{-3} cm. before appreciable settling can occur, except in very quiet air. In an inclosed chamber after some time particles of order 10^{-4} cm. may settle out in appreciable quantities, but particles of order 10^{-5} cm. are probably collected on microscope slides only as the result of diffusion and convection.

While larger particles settle faster, they diffuse more slowly. As a result of the unequal bombardment by the molecules of the surrounding air, the dispersoid particles are in incessant Brownian motion. While this seems to be aimless, there is in the long run a resultant velocity in any given direction which corresponds to diffusion. The formula for the diffusion of such small particles, assuming Stokes' law, was first given by Sutherland,[1] in the form

$$D = RT/N\ 1/3\pi\eta d \qquad (4)$$

[1] *Phil. Mag.*, **9**, 781 (1905).

where R is the gas constant, T the absolute temperature, N Avogadro's number, and D the diffusion coefficient. Einstein also deduced the formula for the mean displacement x in a given direction in time t as

$$x = \sqrt{2Dt} \tag{5}$$

which, combined with (4), eliminating D, gives for the diameter of the particle,

$$d = RT/N\ 2/3\pi\eta\ t/x^2. \tag{6}$$

Putting the gas constant $R = 8.316 \times 10^7$, Avogadro's number $N = 6.06 \times 10^{23}$, and the absolute temperature $T = 293$, approximately we have

$$d = 4.7 \times 10^{-11}\ t/x^2. \tag{7}$$

From this equation it is evident that the time required for a given particle to travel a given distance increases as the square of the distance so that the removal of particles by diffusion is a slow process, unless they are very small. The chief effect of the motion of the particles seems to be to provide collisions between neighboring particles.

Whenever two particles collide there is the possibility of their sticking together, or coalescing. The result of this is growth of the particles, and a reduction in their number. The chance, or expectation that two particles will coalesce depends upon the magnitude of the surface forces. The rate of growth is the combined result of these forces and of the motion, number, and superficial area of the particles. It is obvious that with attractive surface forces all these tendencies oppose the permanence of highly dispersed substances. Gaseous dispersoids thus tend to grow in size of particle, or to become coarser, especially at high concentrations.

It is difficult to appreciate the enormous numbers of such small particles which must exist to contribute any appreciable amount to the concentration. For the same concentration this number increases inversely as the cube of the diameter of the particle. Moreover, in such a finely divided state an enormous surface is presented. For a given concentration the surface increases inversely as the diameter of the particles. These relations are illustrated in the following table for a concentration of water particles of 10^{-4} grams per cc.:

Diameter of particle d. (Cm.)	Number of particles (per cc.).	Total surface of particles. (Cm^2, per cc.)	Average distance between particles. (Cm.)
10^{-2}	2	0.0006	0.8
10^{-3}	2,000	0.006	0.08
10^{-4}	2,000,000	0.06	0.008
10^{-5}	2×10^9	0.6	0.0008
10^{-6}	2×10^{12}	6	0.00008

Probably the most striking property of a smoke, or any other dispersoid, is its effect upon a beam of light. When the particles forming the dis-

persed phase are of the order of magnitude of a wave length of light, or larger, the incident beam is reflected from the surface of the particles When, however, the particles are small compared with the wave length, the laws of reflection and refraction are no longer followed, a small fraction of the incident light being scattered in all directions. These particles are quite invisible in the ordinary sense, even with the microscope, because they are below the limit of resolution. Their shape can therefore never be seen. They are rendered visible by dark ground illumination, since any object, no matter how small, which emits enough light to affect the retina is visible, provided the background is sufficiently dark. Thus stars are visible at night and dust particles are easily seen in a sunbeam in a darkened room.

The particles appear brightest when looking almost directly at the source of light but with the direct light shielded from view. This is commonly rather inconvenient so that the particles are usually viewed normally to the incident beam. The larger particles do not appear larger but brighter. The apparent size of the particles is determined by the diffraction pattern and is thus dependent only on the optical system used to view them. The more intense the incident light the brighter the particles appear. Hence the most intense light sources must be used, the electric arc, or sunlight, in order to make the smallest particles visible.

Description of the Ultramicroscope.—The ultramicroscope is a low power microscope using intense dark ground illumination for viewing particles which are too small to be seen by transmitted light. For illuminating the particles in our work the method of Tyndall as used by Seidentopf and Zsigmondy is adopted. The image of an intense source, such as a concentrated filament lamp, or an arc, is focused upon the particles in the microscope field, but the axis of the illuminating beam instead of coinciding with the axis of the microscope, as ordinarily used, is perpendicular to it. The beam itself therefore never enters the microscope at all, but passes under the objective into a blackened chamber where it is absorbed. The field of the microscope is made dark by placing underneath the objective another "black hole" or blackened chamber with an opening just a little larger than the field.

After a trial apparatus, a cell was constructed using two microscope cover glasses each 15 mm. square. These were placed 1 mm. apart to damp out the convection currents. It was designed also so that it could be immersed in a liquid thermostat to bring the sample to temperature equilibrium. Even with this cell, however, it was found impossible to eliminate convection currents. The intense light from the source heated one side of the particle, setting it in slow motion away from the source. Moreover the cell was so small that a considerable amount of stray light entered the microscope, diminishing the sensitiveness.

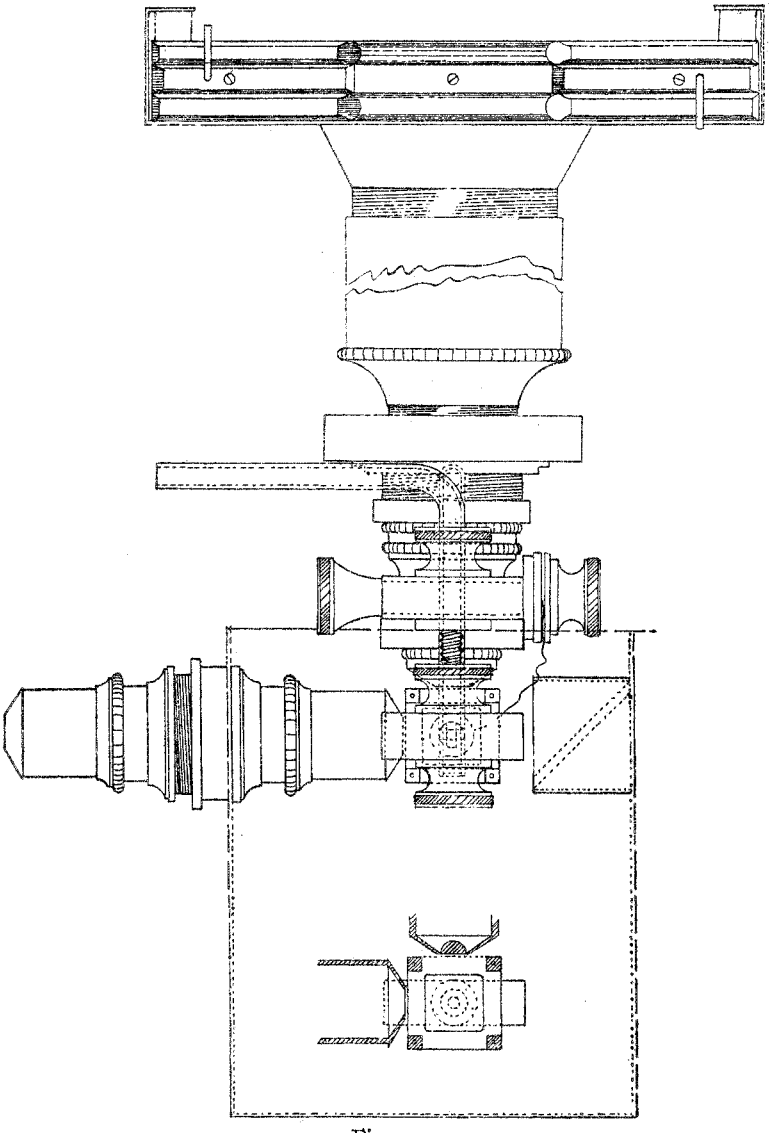

Fig. 1.

A third cell was therefore constructed large enough to eliminate stray light completely, no attempt being made to eliminate convection currents, since a method was actually used in which convection currents were not disadvantageous. This cell is shown in Figs. 1 and 2. Four cover glasses, each 15 mm. square, form four of the sides of the cell, which is cubical in shape. The frame is composed of four small, square, brass rods, which serve as supports, against which the edges of the cover glass

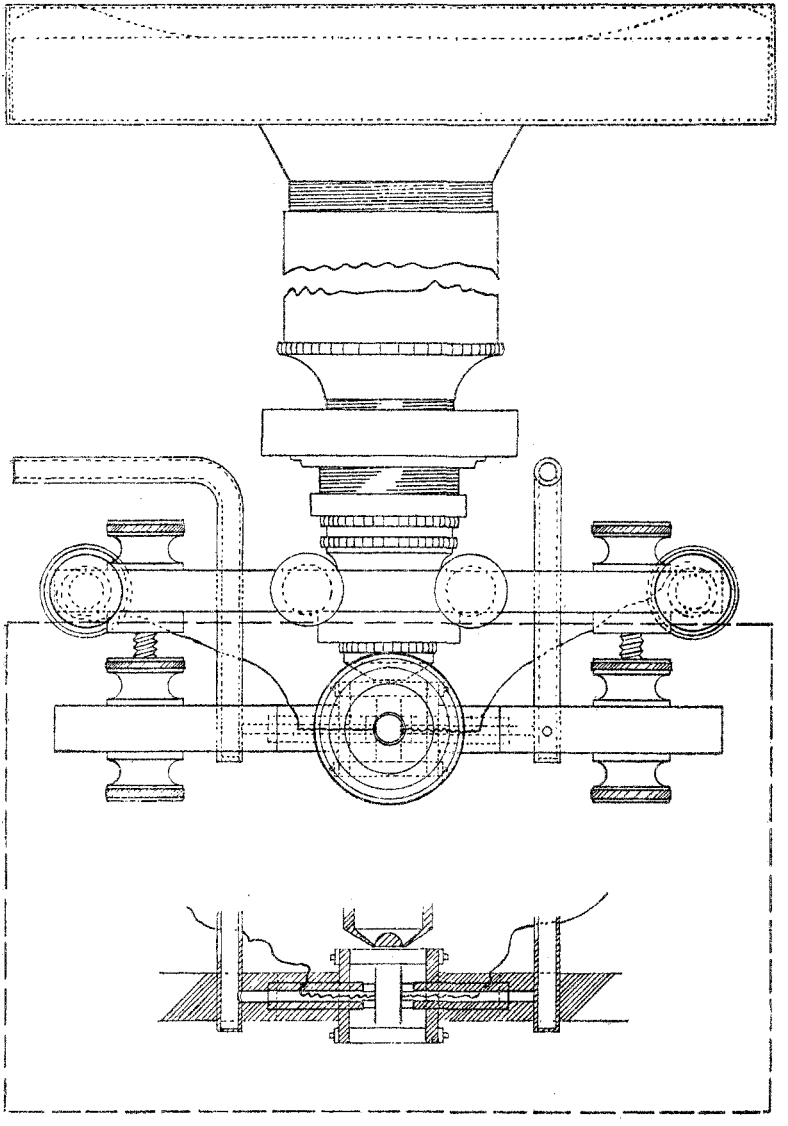

Fig. 2.

windows are glued. The remaining two faces of the cube are square blocks of copper, into which the frame rods are fastened, and projecting sufficiently to provide material for the supporting clamps and entrance tubes for the sample. A very simple and convenient stopcock is made by rotating the entrance tube in a tapered bearing, a small hole communicating with the tube leading through the center of the copper block into the cell. In one position the tubes connect, while by rotating through

a right angle they are disconnected. In this way a closed chamber is formed which may be entirely immersed in a thermostat. Adjustable supports connect the cell with the microscope objective. Plate electrodes 4 mm. apart and 10 mm square are placed parallel to the copper faces of the cell.

A 16 mm. objective on the microscope is required for this cell, and two 16 mm. objectives are used to condense the illuminating beam from an arc after passing through a water cell to remove the heat rays. The beam passes between the electrodes and does not strike them at all. The field is thus quite dark. Convection is no more marked in this cell than in the capillary form. The thermostat produces little effect upon convection, and was not used.

For photography the light must be of the utmost intensity, as the incessant Brownian movement prevents any cumulative effect in exposure. No eyepiece is used, the microscope objective itself acting as the photographic lens. The arc current used is 40 amperes. The shutter is placed between the objective and the body tube, into the upper end of which is screwed the plate-holder attachment. A magnification of eleven is produced. Seed's Graflex plates are satisfactory.

Methods of Measuring the Size of Particle.—There are three methods of measuring the size of ultramicroscopic particles, which we have tried. The first measures the velocity of fall due to the force of gravity. This method is insufficient for particles smaller than 10^{-4} cm. as the convection currents are then faster than the rate of fall; moreover, the method is complicated by ignorance as to the actual density of the particles involved.

The second method involves the use of Einstein's[1] equation for the displacement of a particle due to Brownian motion. Here also the effect of convection must be eliminated, which for small particles is generally larger than the Brownian displacement itself. The mean displacement is recorded by means of a camera lucida, the times with a stop watch. The mean of a large number of displacements is necessary to secure a reliable result, a laborious and time-consuming process. Moreover the sample soon diffuses out of the field and a new sample must be taken, and the sample may change during the measurements. The displacement may be recorded photographically as was tried by de Broglie,[2] but there is an uncertainty as to the time since the particle may come into focus or go out of focus during the exposure.

The third method measures the velocity of the particles in an electric field. This method can be applied only to charged particles, but this is no limitation as at least a fraction of the particles are charged in all the

[1] A. Einstein, *Ann. Physik*, **17**, 549–560 (1905); **19**, 289–306 (1906).

[2] M. de Broglie, *Le Radium*, **6**, 203–209 (1909).

smokes observed. The charge carried by the particle may be assumed to be one electron as the number carrying two charges is negligibly small.

All of the above methods involve Stokes' Law, which gives the viscous resistance of the air to the steady motion of a sphere. This law has received a large amount of study and is known not to hold exactly for particles in air of sizes less than 10^{-4} cm. Such particles experience less resistance than is indicated by Stokes' Law due to the discrete structure of the medium. Cunningham[1] has derived a correction factor from kinetic theory of the form

$$v = v_s(1 + k\, l/d) \qquad (8)$$

where v is the corrected velocity, v_s the velocity given by the law of Stokes, d the diameter of the particle, l the molecular mean free path of the gas, and k is a constant. The mean free path is inversely proportional to the pressure. The following table gives the diameters of particles computed from an observed velocity, in the first column by Stokes' Law, in the second column by Cunningham's corrected formula using Millikan's[2] data for oil drops.

DIAMETER OF PARTICLE (IN CM.).

Assuming Stokes' law.	Assuming Cunningham's formula.
1×10^{-4}	1.14×10^{-4}
1×10^{-5}	2.57×10^{-5}
1×10^{-6}	4.5×10^{-6}
1×10^{-7}	17.0×10^{-7}

Oscillation Method of Measuring the Size of Particle.—The technique finally adopted for measuring the size of particles is a modification of the third method. A simple device was used which made possible the precise determination of the velocity of a charged particle in an electric field. By reversing the direction of the field with a rotating commutator the particle was made to describe a definite stroke many times in succession. The convection due to the source of light is perpendicular to this motion so that a zigzag line is obtained. The amplitude of this oscillation is an accurate measure of the distance traversed by the particle under the electric force for a definite small interval of time. The time interval and the electric field are varied to give the best results. The speed of the rotating commutator and the electric field are both susceptible of precise measurement, so that the size of a single particle is precisely determined.

Photographic records of these oscillations (see for example Figs. 3 and 4) have been obtained, giving simultaneously the sizes of a large number of particles, and thus making possible for the first time a study of the size distribution of the particles.

[1] E. Cunningham, *Proc. Roy. Soc.*, 83A, 357–365 (1910).

[2] R. A. Millikan, *Phys. Rev.*, 1, 218–221 (1913); 2, 109–143 (1913).

The method is not open to objection due to the particle passing out of the focus during the exposure. All that is needed is a number of consecutive complete oscillations. When incomplete they are immediately evident. In fact, the time during which the particles remain in focus

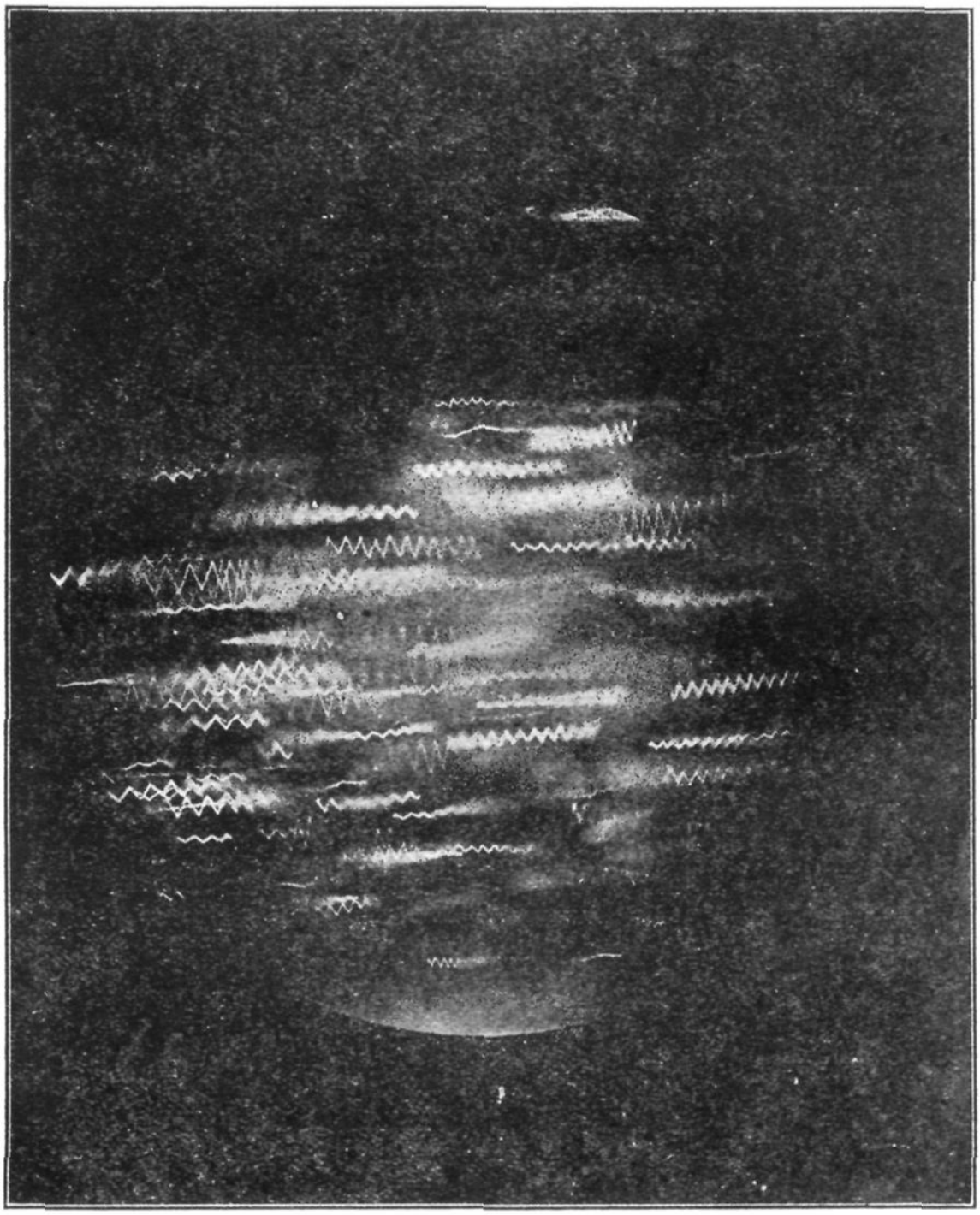

Fig. 3.

may be accurately measured from the photograph, and the actual existence of such a passing out of focus proved, thus demonstrating the incorrectness of de Broglie's photographic method of determining the Einstein displacement. The convenience and precision of the method are far

superior to those of most measurements in this difficult field of research.

Assuming Stokes' Law, the motion of the particle due to the electric field may be written:

$$Xe = 3\pi\eta dv. \tag{9}$$

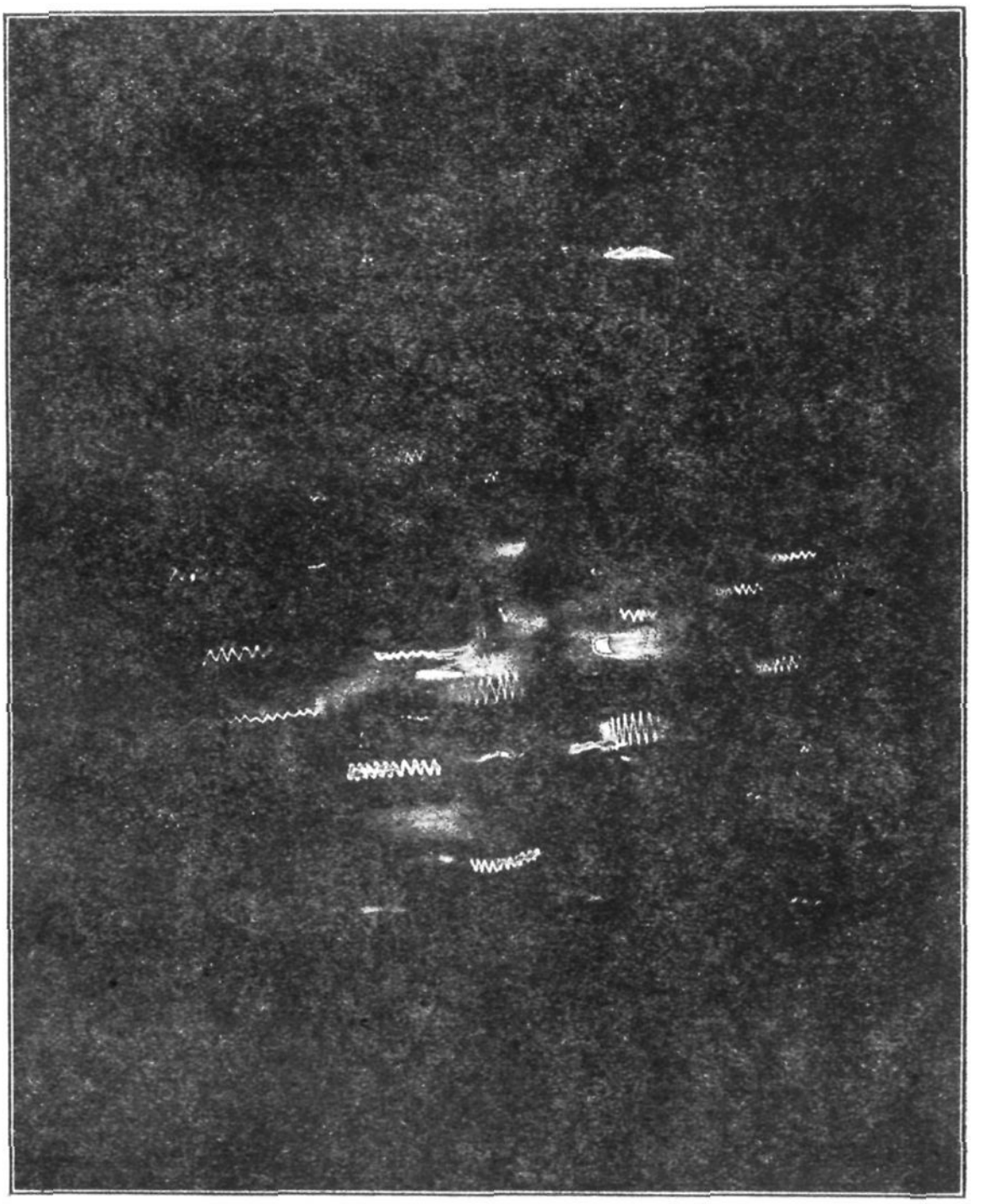

Fig. 4.

Expressing the field X in volts per centimeter, and taking for the electronic charge $e = 1.59 \times 10^{-20}$ e. m. f., the diameter d in centimeters is measured approximately by

$$d = 9.3 \times 10^{-10}\, X/v. \tag{10}$$

The field is measured with a voltmeter, and the velocity is given by the product of the oscillation amplitude and the frequency of field reversal. The amplitude of the oscillation is measured directly from the photographs, using a low power microscope with 40 mm. objective and an ocular filar micrometer. The magnification of the photographs is determined by photographing a stage micrometer with the ultramicroscope, and thus calibrating the ocular micrometer. The frequency of field reversal is obtained by measuring the speed of rotation of the commutator with a revolution counter. The larger particles require higher fields and slower commutation than the smaller particles.

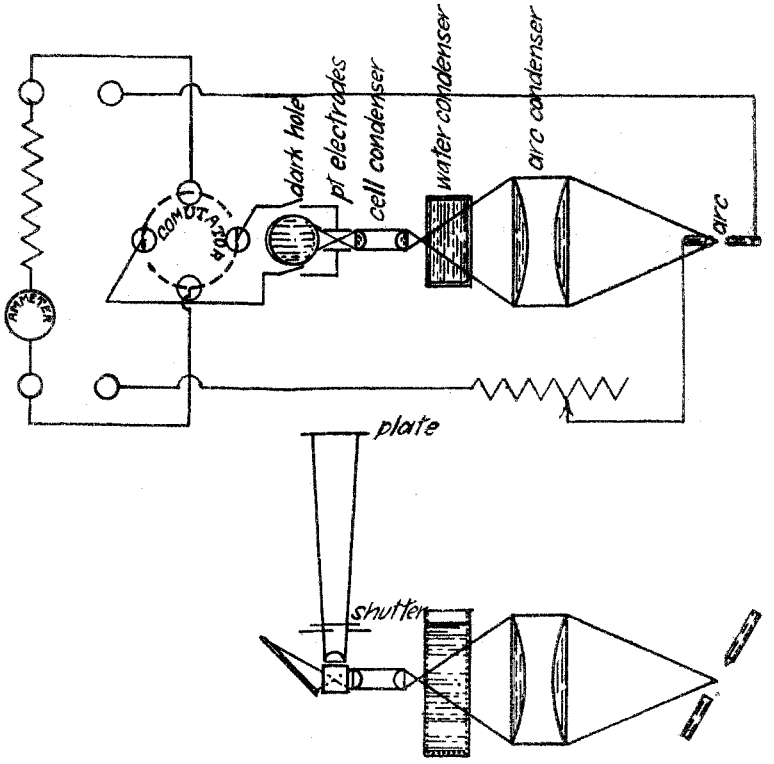

Fig. 5.

A diagram of the set-up is given in Fig. 5. The commutator produces four reversals of the direction of the electric field per revolution. It is rotated at uniform speed by a D. C. shunt motor with reducing pulleys to give speeds of 30 and 60 r. p. m., corresponding to time intervals of one-half and one-quarter seconds.

Procedure and Precision.—The sample of the dispersoid is withdrawn into a glass cylinder about 6 cm. in diameter and 30 cm. in length, by means of a piston. From this it is forced into the ultramicroscope cell as needed.

The whole system is inspected for adjustment, the particles being focused on the ground glass for each exposure, and an exposure of five seconds made. An increase in the length of the exposure produces no increase in contrast in the plate because the particles are in incessant Brownian motion. The exposure merely regulates the length of the path photographed. While the photographic method is more convincing, in actual practice it is just as precise, and more convenient, to measure the oscillation amplitude visually with the ocular micrometer directly on the ultramicroscope.

In discussing the value of the method three points must be considered: (1) the precision with which the variables in Equation 10 can be determined, (2) the significance of the sample which is measured, and (3) the validity of Stokes' Law. No attempt has been made to exhaust the possibilities of precision in measuring the field and the oscillation amplitude, because of the limitations imposed by points (2) and (3). It is obvious, however, that both variables are susceptible of precise measurement. This is shown by measurements made visually with the same sample of tobacco smoke, but with different fields with the following results:

Time of one-half oscillation.	Field strength, (volts/cm.).	Av. diameter of particles (10^{-5} cm.).
0.23	275	1.0
0.25	550	0.8

The fields in this case were not measured but the line voltages were assumed to be 110 and 220 volts. A test was also made on another sample of tobacco smoke, varying the oscillation time, taking ultramicrographs, and measuring the voltage with a voltmeter. The results are as follows:

Time of one-half oscillation (sec.).	Field strength, (volts/cm.).	Velocity, (10^{-2} cm./sec.).	Av. diameter of particles d (10^{-5} cm.).
0.25	587	1.97	2.76
0.25	590	2.07	2.65
0.545	587	2.03	2.70
0.545	585	1.87	2.80

The mean of these four determinations of d is 2.73×10^{-5} cm. with an average deviation from the mean of 1.8% and a maximum difference between two determinations of 5.4%. The method thus possesses a high degree of precision. It might be suspected that an error would arise because of the time required for the particle to accelerate to its final, steady velocity. A simple analysis shows, however, that the time required to reach a velocity within 1% of the terminal velocity is roughly

$$\delta t = 1/4\ \rho/\eta\ d^2, \qquad (11)$$

where ρ is the density of the particle, d its diameter, and η the viscosity of the medium. Since for air $\eta = 1.81 \times 10^{-4}$, we have for particles of unit density and diameter less than 10^{-4} cm., δt less than 10^{-5} seconds,

which is negligible compared with one-half oscillation, usually a quarter second in duration.

While the measurement of the Stokes' Law size is sufficiently precise, the significance of the sample varies enormously with the character of the dispersoid. Gaseous dispersoids are not in equilibrium, so that a given sample remains constant scarcely long enough to make a single determination. The particles measured in one exposure soon pass out of the field usually never to return, and in a few minutes the whole character of the sample has changed. Moreover, it is often impossible to reproduce the unknown conditions under which the sample was formed so that the interpretation of the results is uncertain. Such conditions are familar to the biologist, whose experimental material is in continuous change and beyond his complete control. The underlying laws of such phenomena can be obtained only by comprehensive statistical studies. But this is characteristic of all molecular phenomena. It is only when nature has provided a statistical result herself that the problem is simplified. Such is more often the case with liquid dispersoids which are frequently in thermodynamic equilibrium, and then the variables controlling the state of the system may be under control. In this case the sample is reproducible and the statistical study is much simplified.

The failure of Stokes' Law for small particles due to the phenomenon called "slip," indicates that the apparent diameter of the particle thus measured is smaller than the true diameter, but it does not impair the usefulness of the method for classifying and quantitatively studying dispersoid phenomena. In those cases where the same sample can be measured at different pressures, the correction factor indicated in Equation 8 may also be determined.

Discussion of Results.—When a sample of smoke is viewed in the ultramicroscope it appears like the starry heavens, except that the stars are dancing about violently, but aimlessly, due to the Brownian motion. At first little distinction is made between the particles, as there seems to be no order in their motion, but soon it becomes evident that the brighter particles are more sluggish than the dim ones. This is due to the greater mass of the brighter particles, for they are larger. The particles are all moving slowly away from the source of light, and eventually diffuse to the walls of the cell.

When the electric field is turned on, about one-third of the particles immediately migrate, about equally in each direction, toward the two electrodes. If the field is reversed the direction of migration is reversed, and if the commutator is used the particles oscillate regularly. Sometimes the particles may be seen to combine and become neutral. In this case the oscillation ceases, the particle continuing its irregular Brownian motion as if no field existed.

A curious phenomenon was noticed in the capillary cells first used. Here the electrodes consisted of small wires placed so close together that both could be seen in the microscope. When a particle diffused to the neighborhood of the wire it rushed up and stuck to the wire. This occurred when no potential gradient was impressed across the wires. It is

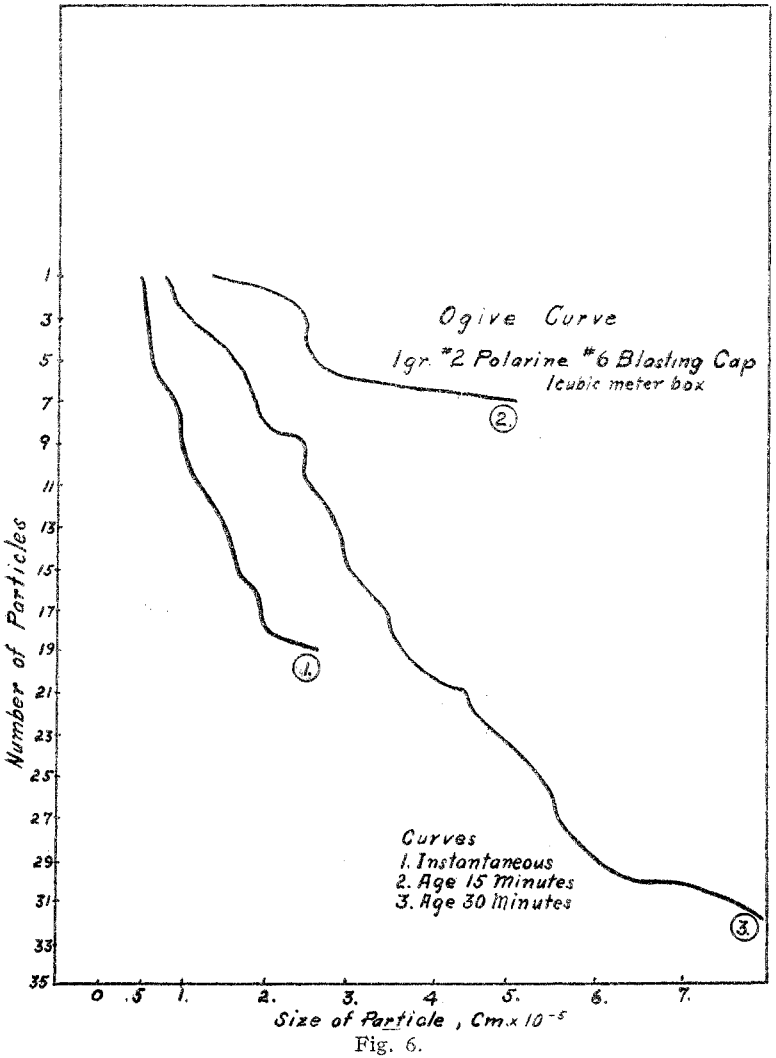

Fig. 6.

probably due to an attraction between the charge on the particle and an induced charge on the wire.

The ultramicrographs show all the phenomena above described. They also show conclusively that the convection is due to heat from the light source. When the distance from peak to peak of the oscillation, or what

might be called the "wave length" is measured, it is found to be independent of the size of particles, which latter is given by the amplitude of the oscillation. This can be explained by the fact that although the resistance of the medium to convection is proportional to the surface of the particle, the radiant heat absorbed by the particle, and therefore the

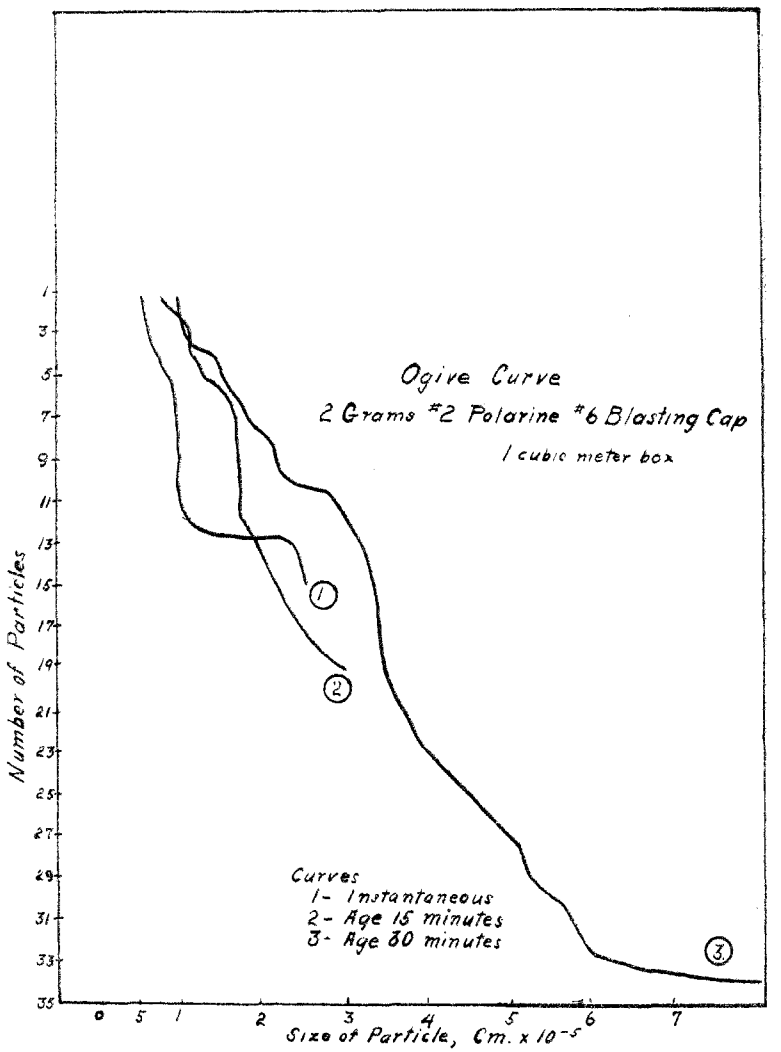

Fig. 7.

driving force, is also proportional to the surface so that the resulting motion is independent of the size of the particle. It may also be that particles of all sizes are carried along with the same velocity by the motion of the gas as a whole.

In order to illustrate the kind of results which may be obtained by this method some results are given of measurements upon two samples of oil smoke (made with commercial Polarine Oil No. 2) of different concentrations. Figs. 6 and 7 are Galton's Ogive curves, made by

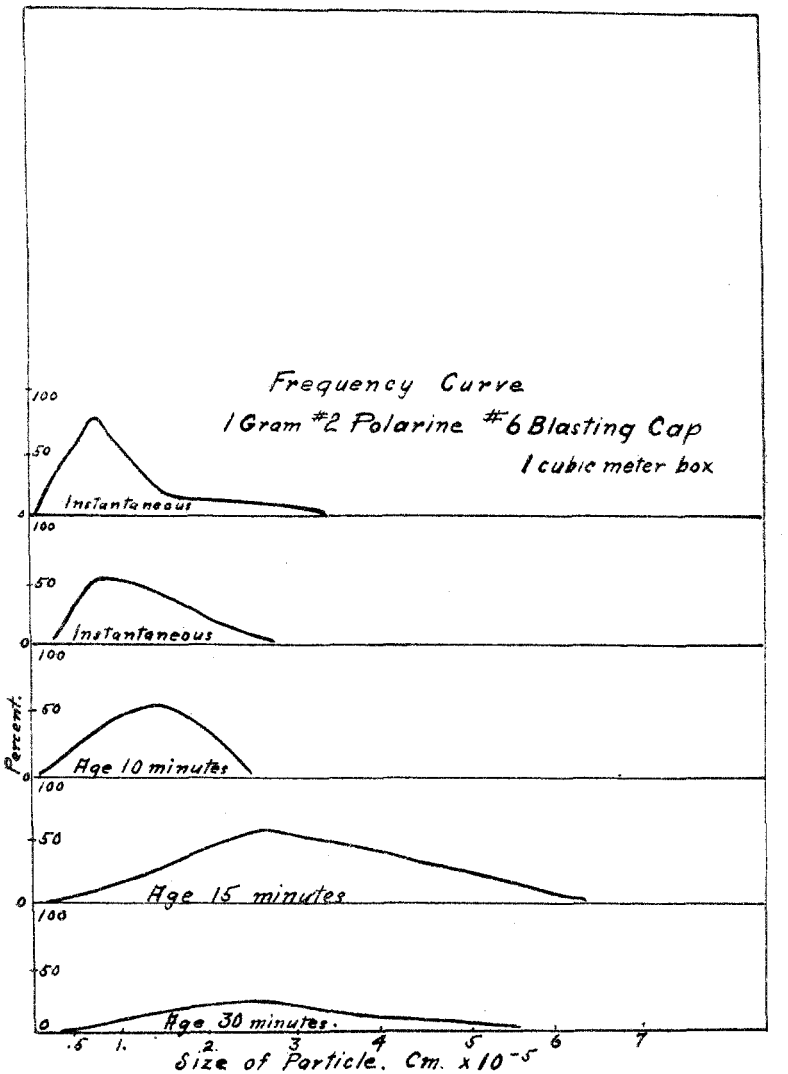

Fig. 8.

plotting the size of each particle, arranged in order of size, allotting to each particle an equal ordinate spacing. These curves therefore present the data directly in graphic form, in fact the curves are sometimes called "direct plots." Figs. 8 and 9 present these data as frequency dis-

tributions of the size of particle. There is an unmistakable growth in the size of particle due to coalescing. The particles vary from 5×10^{-6} to 10^{-4} cm. in diameter and average about 10^{-5} cm.

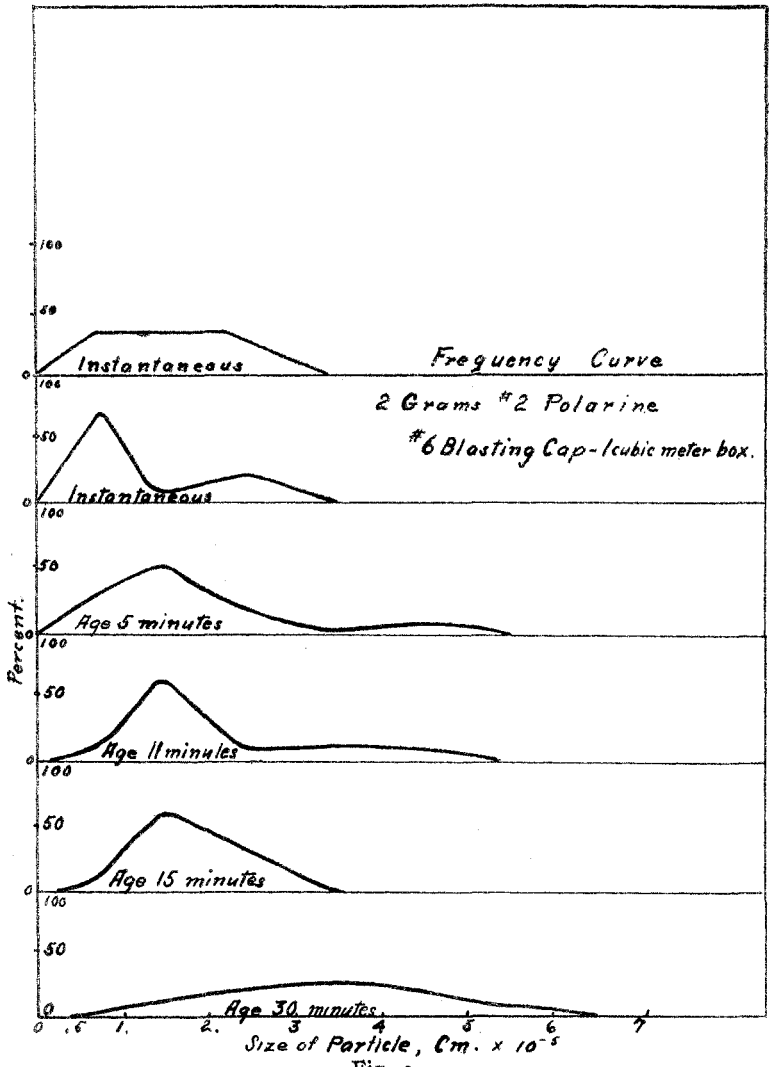

Fig. 9.

Conclusion.—A method is presented for measuring the size of ultramicroscopic particles by their oscillation amplitudes in an electric field which is reversed by a rotating commutator. This eliminates the uncertainties in previous methods due to the effects of Brownian motion and to passing out of focus. Moreover, it renders possible the precise determination of the Stokes' law size of a single particle.

The general properties of gaseous dispersoids and the application of this method to their statistical study are briefly discussed.

We wish to acknowledge the assistance in a portion of the work of Cpl. P. J. Olin, the friendly coöperation of the whole Dispersoid Section in which laboratory the work was done, but especially the constant inspiration and suggestion of its Chief, Major R. C. Tolman.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF WISCONSIN.]

A CONTRIBUTION TO THE CHEMISTRY OF TELLURIUM SULFIDE.[1]

BY AARON M. HAGEMAN.

Received December 2, 1918.

A careful study of any compounds which tellurium is able to form with sulfur is of special interest to the inorganic chemist from a twofold viewpoint. First, it may serve more definitely to establish the true chemical character of tellurium, and second, it may furnish positive information regarding the possible complexity of that element whose atomic weight has already been more exhaustively studied than any other element known to chemists.

Although Berzelius,[2] in 1826, reported that two sulfides of tellurium could be prepared by passing hydrogen sulfide gas into acidified aqueous solutions of tetravalent and hexavalent tellurium, respectively, Becker[3] showed that the resulting precipitates were not true chemical compounds since a large part of the sulfur could be extracted with carbon disulfide. The existence of true sulfides of tellurium was therefore questioned.

However, Becker was unable to remove completely all the sulfur from these precipitates by carbon disulfide. He states that a minimum of 3.69% of sulfur is always retained by the tellurium. This phenomenon has attracted the attention of chemists who have seen a clue to the suspected complexity of tellurium, since the unidentified hypothetical impurity in tellurium must have a higher atomic weight than tellurium, and consequently ought to form a more stable sulfide.

Such has been the assumption of Brauner,[4] of Gutbier and Flury,[5] and of others.

However, none of these workers has been able to obtain positive evidence of the existence of any compound between these two elements, while

[1] Abstract of a part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] *Pogg. Ann.*, **8**, 411 (1826).

[3] *Ann.*, **180**, 257 (1876).

[4] *Monats.*, **1889**, p. 456.

[5] *Z. anorg. Chem.*, **32**, 272 (1902).