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THE ISOLATION OF AN ION, A PRECISION MEASUREMENT OF ITS CHARGE, AND THE CORRECTION OF STOKES'S LAW.[1]

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§ 1. Introduction.

In a preceding paper[2] a method of measuring the elementary electrical charge was presented which differed essentially from methods which had been used by earlier observers only in that all of the measurements from which the charge was deduced were made upon one individual charged carrier. This modification eliminated the chief sources of uncertainty which inhered in preceding determinations by similar methods such as those made by Sir Joseph Thomson,[3] H. A. Wilson,[4] Ehrenhaft[5] and Broglie,[6] all of whom had deduced the elementary charge from the average behavior in electrical and gravitational fields of swarms of charged particles.

The method used in the former work consisted essentially in catching ions by C. T. R. Wilson's method on droplets of water or alcohol, in then isolating by a suitable arrangement a single one of these droplets, and measuring its speed first in a vertical electrical

[1] A preliminary account of this work was read on April 23 before the American Physical Society and was published in Science, Vol. 32, p. 436, September, 1910.

[2] Millikan, Phys. Rev., December, 1909, and Phil. Mag., 19, p. 209.

[3] Thomson, Phil. Mag., 46, p. 528, 1898; 48, p. 547, 1899; 5, p. 346, 1903.

[4] H. A. Wilson, Phil. Mag., 5, p. 429, 1903.

[5] Ehrenhaft, Phys. Zeit., Mai, 1909.

[6] Broglie, Le Radium, Juillet, 1909.

and gravitational field combined, then in a gravitational field alone.[1]

The sources of error or uncertainty which still inhered in the method arose from: (1) the lack of complete stagnancy in the air through which the drop moved; (2) the lack of perfect uniformity in the electrical field used; (3) the gradual evaporation of the drops, rendering it impossible to hold a given drop under observation for more than a minute, or to time the drop as it fell under gravity alone through a period of more than five or six seconds; (4) the assumption of the exact validity of Stokes's law for the drops used. The present modification of the method is not only entirely free from all of these limitations, but it constitutes an entirely new way of studying ionization and one which seems to be capable of yielding important results in a considerable number of directions.

With its aid it has already been found possible:

1. To catch upon a minute droplet of oil and to hold under observation for an indefinite length of time one single atmospheric ion or any desired number of such ions between 1 and 150.

2. To present direct and tangible demonstration, through the study of the behavior in electrical and gravitational fields of this oil drop, carrying its captured ions, of the correctness of the view advanced many years ago and supported by evidence from many sources that all electrical charges, however produced, are exact multiples of one definite, elementary, electrical charge, or in other words, that an electrical charge instead of being spread uniformly over the charged surface has a definite granular structure, consisting, in fact, of an exact number of specks, or atoms of electricity, all precisely alike, peppered over the surface of the charged body.

3. To make an exact determination of the value of the elementary electrical charge which is free from all questionable theoretical assumptions and is limited in accuracy only by that attainable in the measurement of the coefficient of viscosity of air.

4. To observe directly the order of magnitude of the kinetic energy of agitation of a molecule, and thus to bring forward new

[1] In work reported since this paper was first presented, Ehrenhaft (Phys. Zeit., July, 1910) has adopted this vertical field arrangement so that he also now finds it possible to make all his measurements upon individual charged particles.

direct and most convincing evidence of the correctness of the kinetic theory of matter.

5. To demonstrate that the great majority, if not all, of the ions of ionized air, of both positive and negative sign, carry the elementary electrical charge.

6. To show that Stokes's law for the motion of a small sphere through a resisting medium, breaks down as the diameter of the sphere becomes comparable with the mean free path of the molecules of the medium, and to determine the exact way in which it breaks down.

§ 2. The Method.

The only essential modification in the method consists in replacing the droplet of water or alcohol by one of oil, mercury or some other non-volatile substance and in introducing it into the observing space in a new way.

Fig. 1 shows the apparatus used in the following experiments. By means of a commercial "atomizer"[1] A a cloud of fine droplets of oil is blown with the aid of dust-free air into the dust-free chamber C. One or more of the droplets of this cloud is allowed to fall through a pin-hole p into the space between the plates M, N of a horizontal air condenser and the pin-hole is then closed by means of an electromagnetically operated cover not shown in the diagram. If the pin-hole is left open air currents are likely to pass through it and produce irregularities. The plates M, N are heavy, circular, ribbed brass castings 22 cm. in diameter having surfaces which are ground so nearly to true planes that the error is nowhere more than .02 mm. These planes are held exactly 16 mm. apart by means of three small ebonite posts a held firmly in place by ebonite screws. A strip of thin sheet ebonite C passes entirely around the plates, thus forming a completely enclosed air space. Three glass windows, 1.5 cm. square, are placed in this ebonite strip at the

[1] The atomizer method of producing very minute but accurately spherical drops for the purpose of studying their behavior in fluid media, was first conceived and successfully carried out in January, 1908, at the Ryerson Laboratory, by Mr. J. Y. Lee, while he was engaged in a quantitative investigation of Brownian movements. His spheres were blown from Wood's metal, wax and other like substances which solidify at ordinary temperatures. Since then the method has been almost continuously in use here, upon this and a number of other problems, and elsewhere upon similar problems

angular positions 0°, 165° and 180°. A narrow parallel beam of light from an arc lamp enters the condenser through the first window and emerges through the last. The other window serves for observing, with the aid of a short focus telescope placed about 2 feet distant, the illuminated oil droplet as it floats in the air between the plates. The appearance of this drop is that of a brilliant star on a black background. It falls, of course, under the

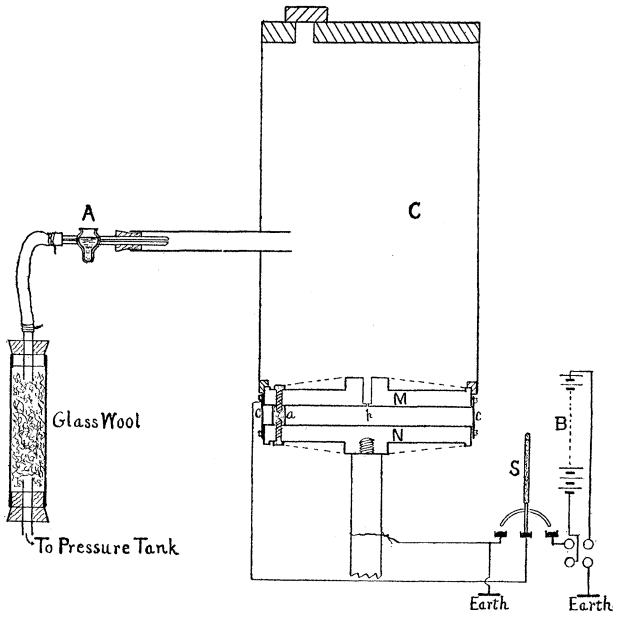

Fig. 1.

action of gravity, toward the lower plate; but before it reaches it, an electrical field of strength between 3,000 volts and 8,000 volts per centimeter is created between the plates by means of the battery *B*, and, if the droplet had received a frictional charge of the proper sign and strength as it was blown out through the atomizer, it is pulled up by this field against gravity, toward the upper plate. Before it strikes it the plates are short-circuited by means of the switch *S* and the time required by the drop to fall under gravity the distance corresponding to the space between the cross hairs of the observing telescope is accurately determined. Then the rate

at which the droplet moves up under the influence of the field is measured by timing it through the same distance when the field is on. This operation is repeated and the speeds checked an indefinite number of times, or until the droplet catches an ion from among those which exist normally in air, or which have been produced in the space between the plates by any of the usual ionizing agents like radium or X-rays. The fact that an ion has been caught, and the exact instant at which the event happened is signalled to the observer by the change in the speed of the droplet under the influence of the field. From the sign and magnitude of this change in speed, taken in connection with the constant speed under gravity, the sign and the exact value of the charge carried by the captured ion are determined. The error in a single observation need not exceed one third of one per cent. It is from the values of the speeds observed that all of the conclusions above mentioned are directly and simply deduced.

The experiment is particularly striking when, as often happens, the droplet carries but one elementary charge and then by the capture of an ion of opposite sign is completely neutralized so that its speed is altogether unaffected by the field. In this case the computed charge is itself the charge on the captured ion.

The measurement of the distance between the cross hairs, correct to about .01 mm., is made by means of a standard scale placed vertically at exactly the same distance from the telescope as the pin-hole p.

§ 3. The Deduction of the Relative Values of the Charges Carried by a Given Droplet.

The relations between the apparent mass[1] m of a drop, the charge e_n, which it carries, its speed, v_1 under gravity, and its speed v_2 under the influence of an electrical field of strength $\mathcal{F}$, are given by the simple equation

$$\frac{v_1}{v_2} = \frac{mg}{\mathcal{F}e_n - mg} \quad \text{or} \quad e_n = \frac{mg}{\mathcal{F}}\left(\frac{v_1 + v_2}{v_1}\right). \tag{1}$$

[1] The term "apparent mass" is used to denote the difference between the actual mass and the buoyancy of the air.

This equation involves no assumption whatever save that the speed of the drop is proportional to the force acting upon it, an assumption which is fully and accurately tested experimentally in the following work. Furthermore, equation (1) is sufficient not only for the correct determination of the relative values of all of the charges which a given drop may have through the capture of a larger or smaller number of ions, but it is also sufficient for the establishment of all of the assertions made above, except 3, 4 and 6. However, for the sake of obtaining a provisional estimate of the value of m in equation (1), and therefore of making at once a provisional determination of the absolute values of the charges carried by the drop, Stokes's law will for the present be assumed to be correct, but it is to be distinctly borne in mind that the conclusions just now under consideration are not at all dependent upon the validity of this assumption.

This law in its simplest form states that if μ is the coefficient of viscosity of a medium, x the force acting upon a spherical drop of radius a in that medium, and v the velocity with which the drop moves under the influence of the force, then

$$x = 6\pi\mu a v. \tag{2}$$

The substitution in this equation of the resulting gravitational force acting on a spherical drop of density σ in a medium of density ρ gives the usual expression for the rate of fall, according to Stokes, of a drop under gravity, viz.,

$$v_1 = \frac{2}{9}\frac{g a^2}{\mu}(\sigma - \rho). \tag{3}$$

The elimination of m from (1) by means of (3), and the further relation $m = \frac{4}{3}\pi a^3(\sigma - \rho)$ gives the charge e_n in the form

$$e_n = \tfrac{4}{3}\pi \left(\frac{9\mu}{2}\right)^{\frac{3}{2}} \left(\frac{1}{g(\sigma-\rho)}\right)^{\frac{1}{2}} \frac{(v_1 + v_2)v_1^{\frac{1}{2}}}{\mathcal{F}}. \tag{4}$$

It is from this equation that the values of e_n in tables I.–XII. are obtained.

§ 4. Preliminary Observations upon the Catching of Ions by Oil-Drops.

Table I. presents the record of the observations taken upon a drop which was watched through a period of four and one half hours as it was alternately moved up and down between the cross-hairs of the observing telescope under the influence of the field F and gravity G. How completely the errors arising from evaporation, convection currents or any sort of disturbances in the air are eliminated is shown by the constancy during all this time in the value of the velocity under gravity. This constancy was not attained without a considerable amount of experimenting which will be described in section 11. It is sufficient here to state that the heating effects of the illuminating arc were eliminated, first by filtering the light through about two feet of water, and second, by shutting off the light from the arc altogether except at occasional instants, when the shutter was opened to see that the star was in place, or to make an observation of the instant of its transit across a cross-hair. Further evidence of the complete stagnancy of the air is furnished by the fact that for an hour or more at a time the drop would not drift more than two or three millimeters to one side or the other of the point at which it entered the field.

The observations in Table I. are far less accurate than many of those which follow, the timing being done in this case with a stop-watch, while many of the later timings were taken with a chronograph. Nevertheless this series is presented because of the unusual length of time over which the drop was observed, and because of the rather unusual variety of phenomena which it presents.

The column headed G shows the successive times in seconds taken by the droplet to fall, under gravity, the distance between the cross-hairs. It will be seen that, in the course of the four and one half hours, the value of this time increases very slightly, thereby showing that the drop is very slowly evaporating. Furthermore, there are rather marked fluctuations recorded in the first ten observations which are probably due to the fact that, in this part of the observation, the shutter was open so much as to produce very slight convection currents.

The column headed F is the time of ascent of the drop between

TABLE I.

Negative Drop.

Distance between cross-hairs = 1.010 *cm.*
Distance between plates = 1.600 *cm.*
Temperature = 24.6° *C.*
Density of oil at 25° *C.* = .8960.
Viscosity of air at 25.2° *C.* = .0001836.

	G sec.	F sec.	n	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
	22.8	29.0	7	34.47	4.923
	22.0	21.8	8	39.45	4.931
	22.3	17.2			
$G =$ 22.28	22.4	—			
$V =$ 7950	22.0	17.3	9	44.42	4.936
	22.0	17.3			
	22.0	14.2	10	49.41	4.941
	22.7	21.5	8	39.45	
	22.9	11.0	12	59.12	4.927
	22.4	17.4	9	44.42	
	22.8	14.3	10	49.41	
$V =$ 7920	22.8	12.2			
$G =$ 22.80	22.8	12.3	11	53.92	4.902
	23.0	—			
	22.8	14.2			
$F =$ 14.17	—	—	10	49.41	4.941
	22.8	14.0			
	22.8	17.0			
$F =$ 17.13	—	17.2	9	44.42	4.936
	22.9	17.2			
	22.8	10.9			
$F =$ 10.73	22.8	10.9	12	59.12	4.927
	22.8	10.6			
	22.8	12.2	11	53.92	4.902
$V =$ 7900	22.8	8.7	14	68.65	4.904
$G =$ 22.82	22.7	6.8	17	83.22	4.894
$F =$ 6.7	22.9	6.6			
	22.8	7.2			
	—	7.2			
	—	7.3			
$F =$ 7.25	—	7.2	16	78.34	4.897
	23.0	7.4			
	—	7.3			
	—	7.2			
	22.8	8.6			
$F =$ 8.65	23.1	8.7	14	68.65	4.904
	23.2	9.8	13	63.68	4.900
	—	9.8			
	23.5	10.7			
$F =$ 10.63	23.4	10.6	12	59.12	4.927

TABLE I.—*Continued.*

	G sec.	*F* sec.	*n*	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
	23.2	9.6			
	23.0	9.6			
	23.0	9.6			
	23.2	9.5			
$V=7820$	23.0	9.6	13	63.68	4.900
$G=$ 23.14	—	9.4			
$F=$ 9.57	22.9	9.6			
	—	9.6			
	22.9	9.6			
	—	10.6	12	59.12	4.927
	—	8.7	14	68.65	4.904
$F=$ 8.65	23.4	8.6			
	23.0	12.3			
	23.3	12.2	11	53.92	4.902
$F=$ 12.25	—	12.1			
	23.2	12.4			
	Change forced with radium.				
	23.4	72.4			
	22.9	72.4			
$F=$ 72.10	23.2	72.2	5	24.60	4.920
	23.5	71.8			
	23.0	71.7			
	23.0	39.2	6		
$V=7800$	23.2	39.2			
$G=$ 23.22	—	27.4	7	34.47	
	—	20.7	8	39.38	4.922
	—	26.9	7	34.47	4.923
	—	27.2			
	23.3	39.5			
	23.3	39.2	6	29.62	4.937
$F=$ 39.20	23.4	39.0			
	23.3	39.1			
	23.2	71.8	5	24.60	4.920
	23.4	382.5	4		
	23.2	374.0			
	23.4	71.0	5	24.60	4.920
	23.8	70.6			
$V=7760$	23.4	38.5	6		
$G=$ 23.43	23.1	39.2			
	23.5	70.3			
	23.4	70.5			
	23.6	71.2	5	24.60	4.920
	23.4	71.4			
	23.6	71.0			
	23.4	71.4			

TABLE I.—*Continued.*

	G sec.	F sec.	n	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
	23.5	380.6			
	23.4	384.6			
	23.2	380.0			
$F=$ 379.6	23.4	375.4	4	19.66	4.915
	23.6	380.4			
	23.3	374.0			
	23.4	383.6			
	—	39.2			
$F=$ 39.18	23.5	39.2			
$V=7730$	23.5	39.0	6	29.62	4.937
$G=$ 23.46	23.4	39.6			
	—	70.8			
$F=$ 70.65	—	70.4	5	24.60	4.920
	—	70.6			
	23.6	378.0	4	19.66	
	Saw it, here, at end of 305. sec., pick up two negatives.				
	23.6	39.4	6	29.62	4.937
	23.6	70.8	5	24.60	4.920
				Mean of all e_1s = 4.917	

Differences.

24.60 − 19.66 = 4.94
29.62 − 24.60 = 5.02
34.47 − 29.62 = 4.85
39.38 − 34.47 = 4.91
Mean dif. = 4.93

the cross-hairs under the action of the field. The column headed e_n is the value of the charge carried by the drop as computed from (4). The column headed n gives the number by which the values of the preceding column must be divided to obtain the numbers in the last column. The numbers in the e_n column are in general averages of all the observations of the table which are designated by the same numeral in the n column. If a given observation is not included in the average in the e_n column, a blank appears opposite that observation in the last two columns. On account of the slow change in the value of G, the observations are arranged in groups and the average value of G for each group is placed opposite that group in the first column. The reading of the voltmeter, taken at the mean time corresponding to each group, is labelled V

and placed just below or just above the mean G corresponding to that group. The volts were in this case read with a ten thousand volt Braun electrometer which had been previously calibrated, but which may in these readings be in error by as much as one per cent., though the error in the relative values of the volts will be exceedingly slight. The PD was applied by means of a storage battery. It will be seen from the readings that the potential fell somewhat during the time of observation, the rate of fall being more rapid at first than it was later on.

§ 5. Multiple Relations shown by the Charges on a Given Drop.

Since the original drop in this case was negative, it is evident that a sudden increase in the speed due to the field, that is, a decrease in the time given in column F, means that the drop has caught a negative ion from the air, while a decrease in the speed means that it has caught a positive ion.

If attention be directed, first, to the latter part of the table, where the observations are most accurate, it will be seen that, beginning with the group for which $G = 23.43$, the time of the drop in the field changed suddenly from 71 sec. to 380 sec., then back to 71, then down to 39, then up again to 71, and then up again to 380. These numbers show conclusively that the positive ion caught in the first change, *i. e.*, from 71 to 380, carried exactly the same charge as the negative ion caught in the change from 380 to 71. Or again, that the negative ion caught in the change from 71 to 39, had exactly the same charge as the positive ion caught in the change from 39 to 71.

Furthermore, the exact value of the charge caught in each of the above cases is obtained in terms of mg from the difference in the values of e_n, given by equation (1), and if it be assumed that the value of m is approximately known through Stokes's law, then the approximately correct value of the charge on the captured ion is given by the difference between the values of e_n obtained through equation (4). The mean value of this difference obtained from all the changes in the latter half of Table I. (see Differences), is 4.93×10^{-10}.

Now it will be seen from the first observation given in the table that the charge which was originally upon this drop and which was obtained, not from the ions in the air, but from the frictional process involved in blowing the spray, was 34.47×10^{-10}. This number comes within one seventh of one per cent. of being exactly seven times the charge on the positive, or on the negative, ion caught in the observations under consideration. In the interval between December, 1909, and May, 1910, Mr. Harvey Fletcher and myself took observations in this way upon hundreds of drops which had initial charges varying between the limits 1 and 150, and which were upon as diverse substances as oil, mercury and glycerine and found in every case the original charge on the drop an exact multiple of the smallest charge which we found that the drop caught from the air. The total number of changes which we have observed would be between one and two thousand, and *in not one single instance has there been any change which did not represent the advent upon the drop of one definite invariable quantity of electricity, or a very small multiple of that quantity.* These observations are the justification for assertions 1 and 2 of the introduction.

For the sake of exhibiting in another way the multiple relationship shown by the charges on a given drop the data of Table I. have been rearranged in the form shown in Table II.

TABLE II.

n	$4.917 \times n$	Observed Charge.	n	$4.917 \times n$	Observed Charge.
1	4.917	——	10	49.17	49.41
2	9.834	——	11	54.09	53.92
3	14.75	——	12	59.00	59.12
4	19.66	19.66	13	63.92	63.68
5	24.59	24.60	14	68.84	68.65
6	29.50	29.62	15	73.75	——
7	34.42	34.47	16	78.67	78.34
8	39.34	39.38	17	83.59	83.22
9	44.25	44.42	18	88.51	——

No more exact or more consistent multiple relationship is found in the data which the chemists have amassed on combining powers, and upon which the atomic theory of matter rests, than is found in tables I. to XIII.

§ 6. Direct Observation of the Energy of Agitation of a Molecule.

Before discussing assertion 4 it is desirable to direct attention to three additional conclusions which can be drawn from Table I.:

1. Since the time of the drop in the field varied in these observations from 380 sec. to 6.7 sec., it will be seen that the resultant moving force acting upon the drop was varied in the ratio 1 to 55, without bringing to light the slightest indication of a dependence of e_1 upon the velocity. Independently of theory, therefore, we can assert that the velocity of this drop was strictly proportional to the moving force. The certainty with which this conclusion can be drawn may be seen from a consideration of the following numerical data. Although we had upon our drop all possible multiples of the unit 4.917×10^{-10} between 4 and 17, save only 15, there is not a single value of e_1 given in the table which differs by as much as .5 per cent. from the final mean e_1. It is true that the observational error in a few of the smaller times is as much as 1 or 2 per cent., but the observational error in the last half of the table should nowhere exceed .5 per cent. In no case is there here found a divergence from the final value of e_1 of more than .4 per cent.

2. Since the charge on the drop was multiplied more than four times without changing at all the value of G, or the apparent value of e_1, the observations prove conclusively that in the case of drops like this, the drag which the air exerts upon the drop is independent of whether the drop is charged or uncharged. In other words, the apparent viscosity of the air is not affected by the charge in the case of drops of the sort used in these experiments.

3. It will be seen from the table that in general a drop catches an ion only when the field is off. Were this not the case there would be many erratic readings in the column under F, while in all the four and one half hours during which these experiments lasted, there is but one such, and the significance of this one will presently be discussed. A moment's consideration will show why this is. When the field is on, the ions are driven with enormous speed to the plates as soon as they are formed, their velocities in the fields here used being not less than 10,000 cm. per sec. Hence an ion cannot be caught when the field is on unless the molecule which is

broken up into ions happens to be on the line of force running from the plates through the drop. With minute drops and relatively small ionization this condition is very unlikely to occur. When the field is off however, the ions are retained in the space between the plates, and sooner or later, one or more of them, by virtue of its energy of agitation, makes impact upon the drop and sticks to it.

These considerations lead up to assertion 4 in the introduction. It will be seen from the readings in the first half of the table that even when the drop had a negative charge of from 12 to 17 units it was not only able to catch more negative ions, but it apparently had an even larger tendency to catch the negatives than the positives. Whence then does a negative ion obtain an amount of energy which enables it to push itself up against the existing electrostatic repulsion and to attach itself to a drop already strongly negatively charged? It cannot obtain it from the field, since the phenomenon occurs when the field is not on. It cannot obtain it from any explosive process which frees the ion from the molecule at the instant of ionization, since again in this case, too, ions would be caught as well, or nearly as well, when the field is on as when it is off. *Here then is an absolutely direct proof that the ion must be endowed with a kinetic energy of agitation, which is sufficient to push it up to the surface of the drop against the electrostatic repulsion of the charge on the drop.*

This energy may easily be computed as follows: As will appear later the radius of the drop was in this case .000197 cm. Furthermore, the value of the elementary electrical charge obtained as a mean of all of our observations, is 4.891×10^{-10}. Hence the energy required to drive an ion carrying a unit charge up to the surface of a charged sphere of radius r, carrying 16 elementary charges, is

$$\frac{16e^2}{r} = \frac{16 \times (4.891 \times 10^{-10})^2}{.000197} = 1.95 \times 10^{-14} \text{ ergs.}$$

Now the kinetic energy of agitation of a molecule as deduced from the value of e herewith obtained, and the kinetic theory equation, $p = \frac{1}{3}nmu^2$, is 5.75×10^{-14} ergs. According to the Maxwell-Boltzmann Law, which certainly holds in gases, this should also be the kinetic energy of agitation of an ion. It will be seen

that the value of this energy is approximately three times that required to push a single ion up to the surface of the drop in question. If, then, it were possible to load up a drop with negative electricity until the potential energy of its charge were about three times as great as that computed above for this drop, then the phenomenon here observed, of the catching of new negative ions by such a negatively charged drop, should not take place, save in the exceptional case in which an ion might acquire an energy of agitation considerably larger than the mean value. Now, as a matter of fact, it was regularly observed that the heavily charged drops had a very much smaller tendency to pick up new negative ions than the more lightly charged drops, and, in one instance, *we watched for four hours another negatively charged drop of radius .000658 cm., which carried charges varying from 126 to 150 elementary units, and which therefore had a potential energy of charge (computed as above on the assumption of uniform distribution) varying from* 4.6×10^{-14} *to* 5.47×10^{-14}, *and in all that time this drop picked up but one single negative ion, and that despite the fact that the ionization was several times more intense than in the case of the drop of Table I.* This is direct proof independent of all theory that the order of magnitude of the kinetic energy of agitation of a molecule is 5×10^{-14}, as the kinetic theory demands.

§ 7. The Question of Valency in Gaseous Ionization.

The correctness of assertion 5 in the case of the ionization existing in the observing chamber at the time at which the data in Table I. were taken is directly proved by the readings shown in that table, since the great majority of the changes recorded in column 4 correspond to the addition or subtraction of one single elementary charge. There are, however, some changes which correspond to the addition or subtraction of two or three times this amount and which therefore seem at first sight to indicate the existence of multiply charged ions. The conclusion, however, that valency is exhibited in gaseous ionization is not to be so easily drawn. During the observations recorded in the first half of the table, a closed tube of radium, containing 500 mg. of radium bromide of activity 3,000, stood about five feet away from the testing chamber, so that its

γ rays and a portion also of its β rays could enter this chamber. At the end of the observations in the group in which $G = 23.14$, this radium was brought up to within a few inches of the testing chamber, and six elementary charges were forced upon the drop in a manner which will be explained in section 8. The radium was then taken entirely out of the room, so that the changes recorded in the last half of the table are entirely due to such ionization as exists in air under normal atmospheric conditions.

Now, so long as changes take place only when the field is off there is no way of telling whether an observed change of two units is due to the addition to the drop of a double ion or to the successive additions of two single ions. It might be possible to account, therefore, for all the multiple changes which occurred when the field was off on the theory of successive single changes. There is, however, one single change recorded in the last part of Table I. which is not to be so easily accounted for upon this hypothesis. It will be seen that the drop made one particular trip up in 378 sec., then one down (recorded in the same horizontal line) in 23.6 sec. Immediately thereafter it was being pulled back again under the influence of the field at the 380 sec. rate—a rate so slow that it could scarcely be seen to be moving at all if observed for a short time. After the lapse of 305 seconds, during which time the shutter had been opened every 30 seconds or so to see that the star was still in view it changed instantly *while I was looking at it, the field being on*, from the 380 sec. to the 39 sec. speed skipping entirely the 71 sec. speed.

This sort of a multiple change, when the field was on, has been observed a dozen or more times when the ionization was so weak that it seemed very improbable that two or three different molecules could have been simultaneously ionized in the minute tube of force having for its diameter the diameter of the drop. In fact at the time at which the preliminary report upon this work was made it was thought that these changes constituted pretty good evidence that the ionization produced by radium does not always consist in the detachment of one single elementary charge from a neutral molecule but consists in occasional instances, in the separation of two or three such charges from a single molecule. The method

of studying ionization herewith presented is capable of furnishing a definite answer to the question here raised in the case of any particular ionizing agent. Recent work which will be reported in detail in another paper has shown that if either radium radiations or X rays of the intensities thus far used ever produce multiply-valent ions in air, the number of such ions formed cannot exceed one or two per cent. of the number of univalent ions formed. At the present time therefore it seems probable that, despite the contrary evidence presented by Townsend[1] and Franck and Westphal,[2] *the process of gaseous ionization by both radium and X rays always consists in the detachment from a neutral molecule of one single elementary electrical charge.*

§ 8. Mechanism of the Change of Charge of a Drop.

It has been tacitly assumed thus far that the only way in which a drop can change its charge is by the capture of ions of one sign or the other from the air. When a negative charge increases there seems to be no other conceivable way by which the change can be produced. But when it decreases there is no *a priori* reason for thinking that the change may not be due as well to the direct loss of a portion of the charge as to the neutralization of this same amount by the capture of a charge of opposite sign. Table I. shows conclusively, however, that if direct losses occur at all they take place with exceeding infrequency as compared with the frequency with which ions are captured from the air even when there is no external source of ionization whatever. For if there were two comparable processes tending to diminish the charge (viz., direct loss and capture of opposite ions) and only one tending to increase it (viz., capture of ions of the same sign) and that one of approximately the same efficiency as one of the first two, the drop, instead of maintaining as it did in these experiments for three and one half hours after the radium was removed from the room, essentially the same mean charge despite its repeated changes, would have quickly lost its charge and gone to the lower plate. The fact that it did not do this furnishes perhaps the most convincing evidence

[1] J. Townsend, Proc. Roy. Soc., 80, p. 207, 1908.

[2] J. Frank u. Westphal, Verh. d. D. Phys. Ges., 11, pp. 146 and 276, 1909.

which has yet been brought forward that the process of evaporation, which must have been going on continuously at the surface of the drop (see § 13) does not have the power of removing at all an electrical charge which resides upon an evaporating surface.[1]

There is but one more comment to be made upon Table I. At a point indicated in the table by the remark "change forced with radium," it will be noticed that the charge was suddenly changed from eleven negative units to five negative units; *i. e.*, that six positive units were forced upon the drop. This sort of a change was one which, after the phenomenon had once been got under control, we could make at will in either direction; *i. e.*, we could force charges of either sign or in any desired number, within limits, upon a given drop. We did this as follows: when it was desired to load the drop up negatively, for example, we held it with the aid of the field fairly close to the positive plate, and placed the radium so that it would produce uniform ionization throughout the chamber. Under these conditions if the positive and negative ions were alike in both number and mobility the chance that the drop would catch a negative ion would be as many times its chance of catching a positive ion as the distance from the drop to the negative plate was times the distance from the drop to the positive plate. Similarly, if we wished to load the drop positively it was held by the field close to the negative plate. On account of the slightly greater mobility of the negative ion, and also on account of the somewhat greater numbers in which they occur, we found, in general, a greater tendency of the drops to take up negative than positive charges. In view, therefore, of the greater ease with which negative drops could be held for long intervals without being lost to the plates most of the drops studied have been of negative sign.

§ 9. THE FAILURE OF STOKES'S LAW.

When the values of e_1 were computed as above for different drops, although each individual drop showed the same sort of consistency which was exhibited by the drop of Table I., the

[1] This question has been considerably discussed in the past and the experiments of Henderson (Phil. Mag., 50, p. 489, 1900) and at Schwalbe (Ann. de Phys., 1, p. 295, 1900) strongly support the conclusions here reached, despite the opposite evidence brought forward by Pellat (Jour. de. Physique, 8, p. 225, 1899).

values of e_1 at first came out differently, even for drops showing the same value of the velocity under gravity. This last irregularity was practically eliminated by blowing the drops into air which was strictly dust free, but even then drops of different sizes, as determined by v_1, always gave consistently different values of e_1. This is illustrated by the observations shown in tables III., IV., V., VI., VII. and VIII.

TABLE III.

Negative Drop No. 5.

Distance between cross hairs = 1.303 *cm.*
Temperature = 24.6° *C.*
Density of oil at 25.0° *C.* = .9041

	G sec.	*F* sec.	*n*	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
	120.8	26.2	2	10.98	5.490
F = 11.9	121.0	11.9	4	21.98	5.495
	121.2	16.5			
	120.1	16.3	3	16.41	5.470
F = 26.40	120.2	26.4	2		
	119.8	67.4	1	5.495	5.495
G = *120.07*	120.1	26.6	2	10.98	
V = 91.50	——	16.6			
F = 16.50	120.2	16.6	3	16.41	
	——	16.5			
F = 67.73	120.2	68.0	1	5.495	
	119.9	67.8			
		26.4		10.98	

v_1 = .01085 Mean e_1 (weighted) = *5.490*

TABLE IV.

Negative Drop No. 8.

Distance between cross hairs = 1.033 *cm.*
Temperature = 20° *C.*

	G sec.	*F* sec.	*n*	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
	88.0	——			
V = 3512	88.8	95.3	2	10.98	5.490
G = *87.85*	87.8	31.0	4	21.93	5.482
F = 30.9	87.4	30.8			
	87.8	47.0	3	16.41	5.470
	87.3	——			

v_1 = *.01176* Mean e_1 (weighted) = *5.482*

TABLE V.

Negative Drop No. 2.

Distance between cross hairs = 1.005 *cm.*

Temperature = 24.3° *C.*

	G sec.	*F* sec.	*n*	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
F = 49.15	53.8	49.2	4	21.46	5.365
	53.7	49.1			
G = 53.80	54.0	95.2			
V = 3990	—	95.5	3	16.00	5.333
	53.7	96.6			
F = 95.78	53.7	95.8			
$v_1 = .01868$				Mean $e_1 = 5.349$	

TABLE VI.

Positive Drop No. 15.

Distance between cross hairs = 1.033 *cm.*

Temperature = 20° *C.*

	G sec.	*F* sec.	*n*	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
	30.4	12.8	10	52.06	5.206
	30.5	17.9	8	41.61	5.200
	30.6	43.8	5	26.08	5.216
	30.2	85.9			
G = 30.48	30.5	85.9			
V = 9010	30.7	86.4			
	30.5	85.6	4	20.84	5.210
	30.7	86.2			
F = 86.09	30.5	86.2			
	—	86.4			
	30.2	2520.0	3	15.55	5.183
$v_1 = .04265$				Mean e_1 (weighted) = 5.208	

The drops shown in tables III. and IV. were of almost the same size, as is seen from the closeness of the values of the two velocities under gravity, and although the field strength was in one case double that in the other the values of e_1 obtained are almost identical. Similarly Tables VII. and VIII. are inserted to show the consistency which could be attained in determining the values of e_1 so long as the drops used were of the same size. On the other hand, the series of tables III., V., VI. and VII., or IV., V., VI. and VIII. show conclusively that the value of e_1 obtained in this way

TABLE VII.

Positive Drop No. 16.
Distance between cross hairs =1.317 *cm.*
Temperature =27.6° *C.*

	G sec.	*F* sec.	*n*	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
	24.61 [1]	151.9			
	24.4	152.9			
$F=$ 152.9	24.63	152.4	5	25.75	5.150
	24.6	153.5			
	24.4	153.9			
$V=9075$	24.7	39.4	7	36.03	5.147
$G=$ 24.57	24.8	29.2			
	24.6	28.6			
$F=$ 28.92	24.50	28.9	8	41.07	5.134
	24.59	29.0			
	24.54	16.0			
	24.53	16.0	11	56.25	5.114
$F=$ 15.93	——	15.8			
$v_1=.05360$			Mean e_1 (weighted) $=5.143$		

TABLE VIII.

Negative Drop No. 17.
Distance between cross hairs =1.305 *cm.*
Temperature =26.8° *C.*

	G sec.	*F* sec.	*n*	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
	23.8	31.5			
$F=$ 31.33	23.6	31.3	8	41.10	5.139
	23.4	31.2			
	23.7	43.8			
$G=$ 23.58	23.7	43.6			
$V=8975$	23.8	43.7	7	36.09	5.156
$F=$ 43.72	23.5	43.4			
	23.2	43.4			
$F=$ 24.2	23.5	24.2	9	46.29	5.144
$v_1=.05534$			Mean e_1 (weighted) $=5.145$		

diminishes as the velocity of the drop increases. This means of course that Stokes's law does not hold for these drops.

In order to find in just what way this law breaks down we made an extended series of observations upon the drops the velocities

[1] The reading carried to hundredths of a second were taken with a chronograph, the others with a stop watch: The mean *G* from the chronograph readings is 24.567, that of the stop watch readings 24.583.

of which varied in the extreme cases 360 fold. These velocities lay between the limits .0013 cm. per sec. and .47 cm. per sec. Complete records of a few of these observations are given in tables IX., X., XI. and XII.

On account of the obvious importance of obtaining accurate readings on the larger drops, for which Stokes's law should most nearly hold, the times of fall of such drops under gravity were taken with a chronograph with as great care as possible. Also, wherever it was possible the same drop was timed by both Mr. Fletcher and myself in order to eliminate the personal equation. The degree of precision which we attained can be judged from the readings recorded in the columns headed G in the tables IX., X., XI. and XII. The letter F before a reading means that it was taken by Fletcher, the letter M that it was taken by Millikan. It will be seen that we very seldom made a reading of the time interval involved in the passage of our star between the cross hairs which differed from the mean time interval by more than one twenty-fifth of a second. Furthermore, F.'s and M.'s mean times on a given drop in no case differ by as much as one fiftieth of a second.

All of the times recorded under F in these tables were taken with a stop watch for the reason that in view of the way in which v_1 and v_2 enter into formula 4, and also in view of the fact that F was in all these observations very much larger than G, no increase

TABLE IX.

Negative Drop No. 20.
Distance between cross hairs = 1.314 *cm.*
Temperature = 23.4° *C.*

	G Sec.	F Sec.	n	$e_n \times 10^{10}$	$e_1 \times 10^{11}$
$V = 8431$	M 14.87	114.7			
$F = 114.9$	" 14.88	114.8	11	56.14	5.104
	" 14.87	115.3			
$G = 14.857$	" 14.90	64.2			
	" 14.85	64.8	12	61.20	5.100
$V = 8428$	" 14.82	64.2			
$F = 64.35$	" 14.84	64.2			
$V = 8423$	" 14.84	117.0	11	56.12	5.102
$F = 117.0$	" 14.84	117.0			
$v_1 = .08843$				Mean $e_1 = 5.102$	

TABLE X.

Negative Drop No. 27.
Distance between cross hairs = 1.317 *cm.*
Temperature = 25.2° *C.*

	G sec.	*F* sec.	*n*	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
$V = 8793$	F 8.03	48.6	28	114.78	5.063
$F = 99.35$	" 8.03	98.9	26	131.58	5.061
$V = 8792$	" 8.08	99.8			
$F = 67.05$	" 8.06	67.2	27	136.34	5.050
$V = 8790$	" 7.96	66.9			
	" 7.98	32.7	30	151.69	
	M 7.96	32.6			
	" 8.04	27.6	31		
$F = 32.66$	—	32.6	30	151.69	5.056
$V = 8788$	" 7.92	32.7			
$G = 8.013$	—	32.7			
	" 8.02	32.7			
$F = 24.67$	—	24.7	32	161.41	5.044
$V = 8786$	—	24.6			
	" 8.06	24.7			
	Forced change with radium.				
$V = 8785$	" 8.03	50.5	28	141.20	5.043
$F = 68.3$	—	68.2	27	136.17	5.043
$V = 8784$	" 8.01	68.4			
$F = 107.15$	—	107.2	26	131.05	5.040
$V = 8782$	" 8.01	107.4			

$v_1 = .16436$ Mean $e_1 = 5.050$

F's mean $G = 8.023$. M's mean $G = 8.007$

Differences.

	e_n	n	e_1	Prob. Error. Per Cent.
141.78 − 131.58 =	10.20	÷ 2	= 5.10	1
136.34 − 131.58 =	4.76	÷ 1	= 4.76	2
151.69 − 136.34 =	15.35	÷ 3	= 5.12	2
161.41 − 141.20 =	20.20	÷ 4	= 5.05	1
141.20 − 136.17 =	5.03	÷ 1	= 5.03	2

Weighted mean difference = 5.03

in the accuracy of e_1 could be obtained by the use of a chronograph in the observations on v_2.

The volts were read just before and just after the observations on a given drop by dividing the bank of storage cells into 11 parts and reading the *PD* of each part by means of a 900 volt Kelvin and White electrostatic voltmeter which we calibrated with an

TABLE XI.

Negative Drop No. 29.
Distance between cross hairs = 1.007 *cm.*
Temperature = 21.8° *C.*

	G sec.	*F* sec.	*n*	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
$V = 8845$	—	16.8	46	232.07	
$F = 15.07$	—	15.0			
$V = 8845$	—	14.8	47	238.43	
	—	15.4			
$F = 18.60$	—	18.5			
$V = 8844$	—	18.7	45	227.21	
	—	18.6			
	—	20.6	44	222.67	
	F 4.66	27.5			
	" 4.69	27.5			
	" 4.57	27.8			
	" 4.61	27.9			
	—	27.9			
	" 4.66	27.7			
$F = 27.73$	" 4.58	27.6	42	212.70	5.064
$V = 8843$	" 4.60	27.7			
	" 4.65	27.6			
	—	27.7			
	M 4.60				
	" 4.62	28.0			
	" 4.61	27.9			
	" 4.60	33.6			
	" 4.68	33.8			
$F = 33.75$	" 4.61	33.8	41	207.33	5.057
$V = 8841$	—	33.7			
	" 4.64	33.7			
	" 4.62	33.9			
$F = 42.55$	" 4.61	42.5	40	202.28	5.057
$V = 8840$	" 4.61	42.6			
	" 4.64	33.8			
$F = 34.05$	—	34.2	41	207.30	5.055
$V = 8839$		34.2			
	" 4.66	34.0			
	" 4.67	34.8			
	—	34.4	41		
$G = 4.630$	" 4.68	34.8			
	" 4.61	28.8	42		
$F = 34.67$	" 4.66	34.5			
$V = 8837$	—	34.8	41	206.86	5.045
	" 4.62	34.7			
		Forced change with radium.			
$F = 59.50$	F 4.58	59.4	39	196.75	5.045
$V = 8836$	" 4.63	59.6			

TABLE XI.—*Continued.*

	G sec.	F sec.	n	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
	" 4.64	60.0			
$F=$ 44.1	—	44.1			
$V=8835$	" 4.64	44.0	40	201.69	5.041
	" 4.63	44.2			
		Forced change with radium.			
$F=$ 219.3	F 4.66	216.7	37	186.39	5.038
$V=8834$	—	222.0			
		Forced change with radium.			
	" 4.64	35.0			
$F=$ 35.2	" 4.60	35.2	41	206.59	5.039
$V=8833$	" 4.65	35.4			
	" 4.65	35.2			
	" 4.67	44.8			
$F=$ 45.66	—	45.2			
$V=8831$	" 4.60	45.4	40	201.30	5.033
	—	45.4			
	—	45.5			
	—	35.6	41		
		Forced change with radium.			
	—	19.1			
	—	19.6			
	—	19.2			
	—	19.6			
	—	19.5			
$F=$ 19.42	—	19.4			
$V=8829$	—	19.3	45	226.21	
	—	19.2			
	—	19.7			
	—	19.6			
	—	19.3			
	—	19.2			
	—	19.7			
	—	19.5			
		Forced change with radium.			
	—	64.0			
$F=$ 63.45	—	63.4	39	196.12	
$V=8827$	—	63.0			
	—	63.4			
$F=$ 100.2	—	100.0	38	191.11	
$V=8826$	—	100.3			
$v_1=.2175$				Mean $e_1=5.046$	

F's mean $G=4.629$. M's mean $G=4.632$.

Differences.

	e_n	n	e_1	Prob. Error. Per Cent.
196.12 − 191.11 =	5.01	÷ 1 =	5.01	1
226.21 − 196.12 =	30.09	÷ 6 =	5.08	1
226.21 − 201.30 =	24.11	÷ 5 =	4.98	2
206.59 − 186.39 =	20.20	÷ 4 =	5.04	1
201.69 − 186.39 =	15.30	÷ 3 =	5.10	1

Mean difference (weighted) = 5.035

TABLE XII.

Negative Drop No. 32.
Distance between cross hairs = 1.003 *cm.*
Temperature = 23.2° *C.*

	G sec.	F sec.	n	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
	—	8.7			
F = 8.5	—	8.3	123	622.40	
V = 8577	—	8.5			
	Changed without radium.				
	M 2.44	28.4			
	—	28.7			
	—	28.7			
F = 28.70	" 2.46	28.4			
V = 8573	" 2.54	29.0	104	524.25	5.040
	" 2.46	29.0			
	" 2.45	28.8			
	" 2.43	28.6			
	Change forced with radium.				
G = 2.462	" 2.44	15.7			
F = 15.72	" 2.48	15.7			
V = 8568	—	15.7	111	558.78	5.034
	—	15.7			
	—	15.8			
	Change forced with radium.				
F = 59.1	—	59.1			
V = 8565	" 2.50	59.1	100	503.42	5.034
F = 60.0		59.8			
V = 8563	F = 2.45	60.2	100	503.23	5.032
	Change forced with radium.				
F = 81.5	—	81.0			
V = 8561	—	82.1	99	498.12	5.031
	Change forced with radium.				
	" 2.44	19.9			
F = 20.0	" 2.50	20.1	108	543.41	5.032
V = 8555	" 2.42	20.0			
v = .4074			Mean e_1 (weighted) =		5.033

F's mean G = 2.452. M's mean G = 2.467.

Differences.

	e_n	n	e_1	Prob. Error. Per Cent.
543.41 − 498.12 =	45.29 ÷	9 =	5.032	.5
503.23 − 498.12 =	5.11 ÷	1 =	5.11	3.0
558.78 − 503.42 =	55.36 ÷	11 =	5.033	.5
558.78 − 524.25 =	34.53 ÷	7 =	4.94	3.0
Mean difference (weighted) =			5.031	

accuracy of .1 per cent. by comparing it with a Weston voltmeter which had been standardized at the Bureau of Standards. Furthermore, care was taken to use the cells under such conditions as would render the diminution in potential small and as uniform as possible.

It will be seen from the tables that even in the case of the largest drops used, which were charged with as many as 130 elementary units, the values of n are in every case unmistakably determined by the differences summarized at the bottoms of the tables. In fact, in general, even with the largest drops the relative value[1] of e_1 can be determined with an accuracy of .5 per cent. from the differences alone. The accuracy is, of course, increased by dividing the values of e_n by n as soon as n has been found with certainty from the differences.

The readings shown in these tables are merely samples of the sort of observations which we took on between 100 and 200 drops between December, 1909, and May, 1910. The sort of consistency which we attained after we had learned how to control the evaporation of the drops and after we had eliminated dust from the air may be seen from Table XIII. which contains the final results of our observations upon all of the drops except three which were studied throughout a period of 47 consecutive days. The three drops which have been excluded all yielded values of e_1 from two to four per cent. too low to fall upon a smooth e_1v_1 curve like that shown in Fig. 2 which is the graph of the results contained in Table XIII. It is probable that these three drops corresponded not to single drops but to two drops stuck together. Since we have never in all our study observed a drop which gave a value of e_1 appreciably above the curve of Fig. 2, the hypothesis of binary

[1] Since the same value of G is used in computing all of the e_ns the relative values of e_n are practically independent of the error in G.

drops to account for an occasional low value of e_1 is at least natural. Before we eliminated dust we found many drops showing these low values of e_1, but after we had eliminated it we found not more than one drop in ten which was irregular. The drop shown in Table I. is perhaps the best illustration of the case under consideration which we have observed. It yields a value of e_1 which is four per cent. too low to fall on the curve of Fig. 2. This is as large a departure from this curve as we have thus far obtained.

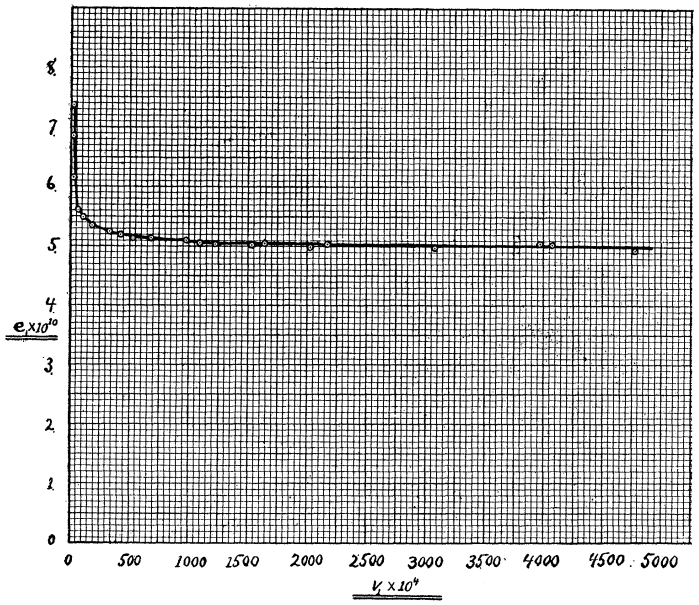

Fig. 2.

§ 10. THE CORRECTION OF STOKES'S LAW.

The simple form of Stokes's law which has been used in obtaining the values of e_1 involves the assumption that there is no slip at the bounding surface between the medium and the drop, or that the coefficient of external friction between oil and air is infinite. From the standpoint of the kinetic theory this surface slip, though in general very small, is, strictly speaking, never zero, and to take it into account a term must be introduced into the equation of motion which is proportional to the ratio between the mean free path of the

TABLE XIII.

No.	Velocity cm./sec.	Radius cm.	$e\times10^{10}$	Per Cent. Prob. Error.
1	.001315	.0000313	7.384	6.
2	.001673	358	6.864	4.
3	.001927	386	6.142	2.5
4	.006813	755	5.605	1.5
5	.01085	967	5.490	.5
6	.01107	979	5.496	.7
7	.01164	.0001004	5.483	.4
8	.01176	1006	5.482	.4
9	.01193	1016	5.458	.8
10	.01339	1084	5.448	.5
11	.01415	1109	5.448	.4
12	.01868	1281	5.349	.5
13	.02613	1521	5.293	.5
14	.03337	1730	5.257	.5
15	.04265	1954	5.208	.5
16	.05360	2205	5.148	.4
17	.05534	2234	5.145	.5
18	.06800	2481	5.143	.7
19	.07270	2562	5.139	.5
20	.08843	2815	5.102	.3
21	.09822	2985	5.107	.4
22	.1102	3166	5.065	.4
23	.1219	3344	5.042	.5
24	.1224	3329	5.096	.5
25	.1267	3393	5.061	.5
26	.15145	3712	5.027	.5
27	.1644	3876	5.050	.3
28	.2027	4297	4.989	.7
29	.2175	4447	5.046	.4
30	.3089	5315	4.980	1.
31	.3969	6047	5.060	1.
32	.4074	6104	5.033	1.
33	.4735	6581	4.911	1.5

gas molecule and the radius of the drop.[1] Since it is conceivable however that there is some other cause for slip than that assigned by the kinetic theory, it will be well to make this discussion as independent as possible of all theoretical considerations.

From whatever point of view, then, the phenomenon of external

[1] See O. E. Meyer, Kinetische Theorie der Gase, p. 211, for the correction of Poiseuille's law for slip, and Cunningham, Proc. Roy. Soc., 83, p. 357, 1910, for the corresponding correction of Stokes's law.

slip be regarded it is clear that the very existence of any surface effect of this sort between the medium and the drop must tend to produce an actual velocity higher than that computed from the simple form of Stokes's law, *i. e.*, it must tend to produce departures from Stokes's law of the kind actually shown in the experiments herewith recorded. Furthermore, it will be evident from the analysis underlying Stokes's law (see § 11) that any surface effect whatever between oil and air which might modify the velocity given by Stokes's law must be more and more effective in so modifying it the more the radius of the drop is diminished, and that when the radius is taken sufficiently large the term which represents this surface effect must become negligible. We could then write a corrected form of Stokes's law which would take into account any kind of surface phenomenon which might alter the speed, in the general form

$$X = 6\pi\mu a v \left\{ 1 + f\left(\frac{l}{a}\right)\right\}^{-1} \tag{5}$$

in which l is a constant of the medium and a the radius of the drop. If we were in complete ignorance of the form of the function f we could express it in terms of the undetermined constants, A B, C, etc., thus

$$f\left(\frac{l}{a}\right) = 1 + A\frac{l}{a} + B\frac{l^2}{a^2} + C\frac{l^3}{a^3}\text{etc.} \tag{6}$$

and so long as the departures from the simple form of Stokes's law were small we could neglect the second order terms in l/a and have therefore

$$X = 6\pi\mu a v \left\{ 1 + A\frac{l}{a}\right\}^{-1} \tag{7}$$

or

$$v_1 = \frac{2}{9}\frac{g a^2(\sigma - \rho)}{\mu}\left\{ 1 + A\frac{l}{a}\right\}. \tag{8}$$

Using this form of equation to combine with (1) and denoting now by e the absolute value of the elementary charge and by e_1 as heretofore the value of the charge obtained from the use of (4) there results at once

$$e\left(1 + A\frac{l}{a}\right)^{\frac{3}{2}} = e_1 \quad \text{or} \quad e^{\frac{2}{3}}\left(1 + A\frac{l}{a}\right) = e_1^{\frac{2}{3}}. \tag{9}$$

If Al were known a could be determined directly from (8) and then e could be determined from (9). In fact Al is not known but the departures from Stokes's law shown in the experimental curve of Fig. 1 are not large except for the very small values of e_1. Leaving these for the present out of consideration, and remembering that a appears in the second power in (3), it will be evident that we can obtain very nearly correct values of a from the assumption of (3). We can then find the approximate value of Al by plotting

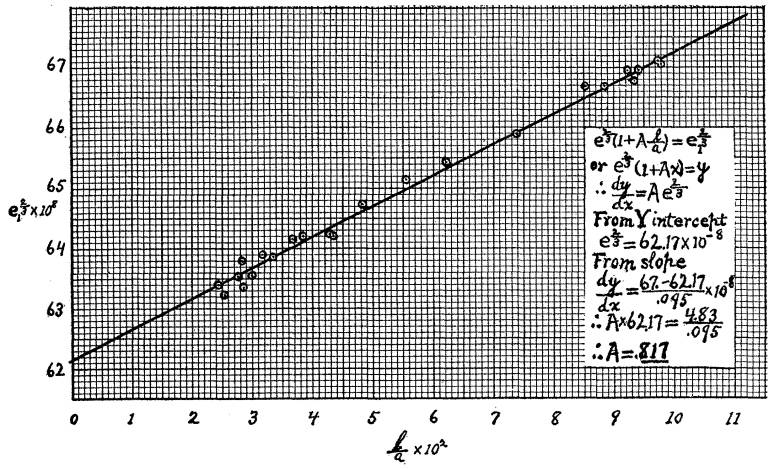

Fig. 3.

the observed values of $e_1^{\frac{2}{3}}$ as ordinates and the observed values of $1/a$ as abscissæ, and obtaining the slope of the resulting straight line (see Fig. 3), providing a linear relation is found between these quantities. If no such linear relation is found then an equation of the form (7) is not sufficient for the representation of the phenomena. As a matter of fact, a very satisfactory linear relationship was found between $e_1^{\frac{2}{3}}$ and $1/a$ as is shown by Fig. 3. In this way we at first determined the approximately correct value of Al and then went back and recomputed a from the corrected formula (8) which is a simple quadratic containing no unknown except a. We then corrected the value of Al by plotting a new curve between $e^{\frac{2}{3}}$ and the corrected values of $1/a$. *When this was done it was found that the constant Al so determined agreed closely with the*

value of Al given by the analysis of Cunningham based upon kinetic theory considerations, provided the value of f in his formula[1] *was made equal to zero.* Thus, if the constant of the medium l was taken as the mean free path of the molecules of air, then the value which we found it necessary to assign to A was .817 (see Fig. 3). Furthermore, A could easily be determined from our curve with an accuracy of two or three per cent. as will be seen from the figure.

The value of A which results from placing $f = 0$ in Cunningham's equation is .815. The agreement however is not as close as at first appears. The empirical equation (7) was set up without any reference to Cunningham's theoretical work, which in fact appeared while we were in the process of finding empirically the correction to Stokes's law, and the values of l used in obtaining the values of l/a plotted in Fig. 3 and tabulated in Table XIV. were computed from the Boltzmann formula $\mu = .3502\rho\bar{c}l$,[2] in which $\bar{c}$ is the average molecular velocity. In order to obtain from Cunningham's theoretical work the value $A = .815$ it is necessary not only to put $f = 0$ but to compute l from the formula $\mu = \frac{1}{3}\rho ul$ in which u is not the average molecular velocity but the square root of the mean square velocity. If l is computed, as above, from Boltzmann's formula Cunningham's theory gives when $f = 0$ $A = .788$ instead of $A = .815$, so that the above empirical value of A is actually 3.6 per cent. higher than that given by Cunningham's theory[3] when $f = 0$.

In the above computation, as in all of this, the value of μ at 15° C. is taken as .00017856, and for temperatures within a range of say 12° on either side of 15° C. μ_t is computed from the formula

$$\mu_t = \mu_{15}(1 + .00276)(t - 15).$$

This equation gives precisely the rate of change of μ with temperature, within this region, which is obtained independently by all three of the observers Breiterbach,[4] Schultze[5] and Fisher[6] in their

[1] Cf. p. 361, *l. c.*

[2] Boltzmann, Gastheorie, 1, p. 81.

[3] If l is computed from $\mu = \frac{1}{3}\rho\bar{c}l$ in which $\bar{c}$ is the *average* molecular velocity Cunningham's corrective term, when the substitutions are correctly carried out, is $(1 + 1.5 \cdot l/a)$ instead of $(1 + 1.63 \cdot l/a)$.

[4] P. Breiterbach, Ann. der Phys., 5, p. 168, 1901.

[5] H. Schultze, Ann. der Phys., 5, p. 157, 1901.

[6] W. J. Fischer, PHYS. REV., 28, p. 104, 1909.

exceedingly careful work upon this subject. The reliability of the absolute value of μ_{15} will be discussed in section 12.

It is most interesting that the agreement between Cunningham's rational formula and the above empirical results is as good as it is, but it is to be particularly emphasized that the correctness of the final value of the elementary electrical charge is completely independent of the correctness of any theory whatever as to the cause of the failure of Stokes's law for small drops. *The corrective constant A is a purely empirical one.* It is entirely possible that a series of experiments of this kind upon substances other than oil might lead to other values of A but the value of e should in no way be effected thereby. It is of immense interest to know whether varying the mean free path by varying the pressure and the nature of the gas will affect the value of e_1 in the way in which it ought according to Cunningham's theory and enough data have already been obtained to indicate that that theory holds, approximately at least, for wide ranges of pressure. This work, however, will be reported in a later article.

§ 11. Coefficients of External Friction and of Slip.

The modified form of Stokes's law which takes into account surface slip[1] is

$$X = 6\pi\mu av \left\{ \frac{1 + 2\gamma}{1 + 3\gamma} \right\}$$

or

$$v_1 = \frac{2}{9} \frac{ga^2}{\mu} (\sigma - \rho) \left\{ \frac{1 + 3\gamma}{1 + 2\gamma} \right\} \qquad (10)$$

in which γ is defined by the equation

$$\gamma = \frac{\mu}{\beta a},$$

β being the coefficient of external friction. If the last factor is expanded in powers of γ the resulting series

$$1 + \gamma + 2\gamma^2 + 4\gamma^3 \cdots (-1)^n 2^{n-2} \gamma^{n-1} + \cdots$$

is convergent for $\gamma < 1$. If we neglect powers of γ higher than the

[1] See Basset's Hydrodynamics, Vol. II., p. 271.

first (10) becomes

$$v_1 = \frac{2}{9}\frac{ga^2(\sigma - \rho)}{\mu}\{1 + \gamma\} \qquad (11)$$

which is identical with the empirical equation (8) when

$$\gamma = Al/a.$$

But since

$$\gamma = \frac{\mu}{\beta a}$$

and the coefficient of slip ζ is defined by

$$\zeta = \frac{\mu}{\beta}^1$$

we obtain, by inserting the value of Al given by the above experiments viz., .0000077,

$$\zeta = .0000077 \quad \text{and} \quad \beta = 23.7.$$

This direct determination of these constants for oil and air at atmospheric pressure agrees well with the result ($\zeta = .0000076$) computed from Warburg's[2] observations on the flow of gases at low pressures though glass capillaries.

§ 12. THE ABSOLUTE VALUE OF e.

Taking the value of A as .817 the value of e was determined from (9) and the values of e_1, a, and l obtained as explained above. The next to the last column of Table XIV. gives the results of this computation of e for all of the observations recorded in Table XIII. except the first four and the last four. These are omitted not because their introduction would change the final value of e, which as a matter of fact is not appreciably affected thereby, but solely because of the experimental uncertainties involved in work upon either exceedingly slow or exceedingly fast drops. When the velocities are very small residual convection currents and Brownian movements introduce errors, and when they are very large the time determination becomes unreliable, so that it is scarcely legiti-

[1] Meyer, Kin. The. d. Gases, p. 207.

[2] Warburg, Pogg. Ann., 1876, Vol. 159, p. 399.

mate to include such observations in the final mean. However, for the sake of showing how completely formula (9) fits the ex-

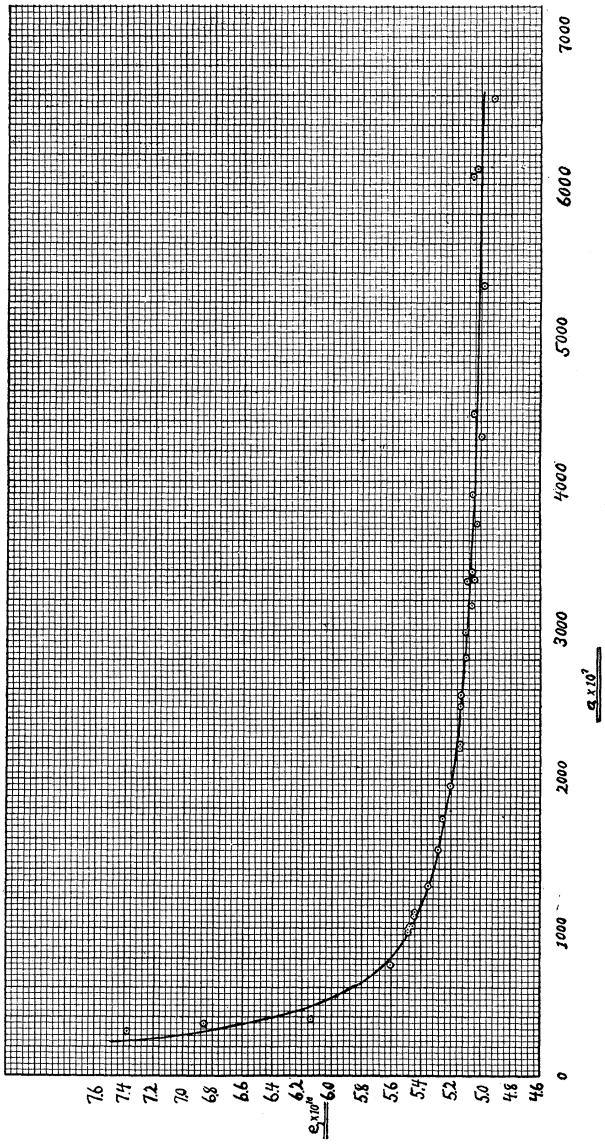

Fig. 4.

perimental results throughout the whole range of the observations of Table XIII., Fig. 4 has been introduced. The smooth

TABLE XIV.

No.	Tem. °C.	Dew Point °C.	$l \times 10^8$ cm.	Velocity cm./sec.	a (=radius) cm.	l/a	$e_1 \times 10^{10}$	Max. Obs'l Error. %	$e \times 10^{10}$	Dif. from Mean. %
1	24.0	5.3	945	.001315	.0000313	.3020	7.384	6.		
2	26.0	10.8	954	.001673	358	.2172	6.864	4.		
3	23.8	9.3	944	.001927	386	.1993	6.142	2.5		
4	19.9	1.8	929	.006813	755	.1230	5.605	1.5		
5	24.6	3.7	948	.01085	967	.0980	5.490	.5	4.892	.20
6	26.4	6.0	955	.01107	979	.0975	5.496	.7	4.889	.26
7	24.0	0.0	945	.01164	.0001004	.0941	5.483	.4	4.903	.03
8	20.0	1.8	929	.01176	1006	.0923	5.482	.4	4.916	.28
9	24.8	0.0	949	.01193	1016	.0934	5.458	.8	4.891	.22
10	26.3	6.0	955	.01339	1084	.0883	5.448	.5	4.908	.10
11	23.6	3.7	943	.01415	1109	.0850	5.448	.4	4.921	.42
12	24.3	11.0	947	.01868	1281	.0739	5.349	.5	4.900	.03
13	24.0	0.0	945	.02613	1521	.0621	5.293	.5	4.910	.17
14	27.0	6.0	959	.03337	1730	.0554	5.257	.5	4.918	.34
15	23.2	−1.2	942	.04265	1954	.0483	5.208	.5	4.913	.21
16	27.6	12.2	959	.05360	2205	.0435	5.143	.4	4.884	.36
17	26.8	6.0	958	.05534	2234	.0429	5.145	.5	4.885	.34
18	25.2	4.0	951	.06800	2481	.0384	5.143	.7	4.912	.21
19	23.8	5.0	944	.07270	2562	.0369	5.139	.5	4.913	.01
20	23.2	13.5	942	.08843	2815	.0325	5.102	.3	4.901	.01
21	24.6	1.7	948	.09822	2985	.0318	5.107	.4	4.915	.27
22	25.0	9.2	950	.1102	3166	.0300	5.065	.4	4.884	.36
23	27.7	15.0	959	.1219	3344	.0287	5.042	.5	4.882	.40
24	22.6	1.6	939	.1224	3329	.0282	5.096	.5	4.923	.44
25	24.0	3.7	944	.1267	3393	.0278	5.061	.5	4.894	.15
26	23.8	5.0	944	.15145	3712	.0254	5.027	.5	4.880	.44
27	25.2	0.3	948	.1644	3876	.0245	5.050	.3	4.903	.03
28	22.3	−0.7	938	.2027	4297	.0218	4.989	.7	4.858	.85
29	21.8	−0.1	936	.2175	4447	.0211	5.046	.4	4.918	.36
30	22.3	4.2	938	.3089	5315	.0177	4.980	1.		
31	24.4	1.0	947	.3969	6047	.0157	5.060	1.		
32	22.8	1.0	940	.4074	6104	.0154	5.033	1.		
33	25.2	2.7	951	.4735	6581	.0144	4.911	1.5		

Mean $e = 4.901$

Six months after the original work on this table was done the laboratory obtained a very reliable Weston laboratory standard voltmeter which made it possible to obtain a more perfect calibration curve of the Kelvin and White electrostatic instrument than had been made at first. With the aid of this new calibration curve every value of e_1 in the above table was recomputed with the result that the final value of e was reduced .06 per cent. Furthermore in the computation of the above table the m of equation (1) was through oversight treated as the real mass instead of as the apparent mass. This necessitates a further reduction of e amounting to .14 per cent. so that the most reliable value obtainable from the work thus far done is

$$e = 4.891 \times 10^{-10}.$$

curve in this figure is computed from (7) under the assumption of $e = 4.891 \times 10^{-10}$ and the experimentally determined values of e_1 are plotted about this curve, every observation contained in Table XIII. being shown in the figure.

The probable error in the final mean value 4.891×10^{-10}, computed by least squares from the numbers in the last column, is four hundredths of one per cent. If there is an error of as much as 3 per cent. in the determination of A the final value of e would be affected thereby by only about .2 per cent. Since, however, the coefficient of viscosity of air is involved in the formula, the accuracy with which e is known is limited by that which has been attained in the measurement of this constant. There is no other factor involved in this work which has not been measured with an accuracy at least as great as .2 per cent.

The value of μ_{15} which has been used in the computation of all of the preceding tables, viz., .00017856, is in my judgment the most probable value which can be obtained from a study of all of the large mass of data which has been accumulated within the past forty years upon this constant. It represents not only the result of what seems to me to be the most reliable single determination of μ which has thus far been made, viz., that of Stokes and Tomlinson[1] who deduced it from the damping of oscillating cylinders and spheres, but it is exactly the mean of the three most recent and very concordant values obtained by the outflow method (Table XV.) and it is furthermore the mean of all of the most reliable determinations which have ever been made. These are summarized in Table XV.

In this summary I have discarded the early work of Maxwell[2] and O. E. Meyer[3] by the damping method, because it is admittedly inaccurate, the work of Puluj[4] by the transpiration method because he used but one capillary tube and obtained a value completely out of line with the results obtained by all others under similar conditions, and two recent results obtained by Zemplén[5] because he himself discards the first while the second has just been definitely

[1] Stokes, Math. and Phys. Papers, Vol. 5, p. 181.
[2] Phil. Trans., 156, p. 240, 1866.
[3] Pogg. Ann., 143, p. 14, 1871.
[4] Wien. Sitz. Ber., 69, p. 287; 70, p. 243, 1874.
[5] Ann. Phys., 19, p. 442, 1906; 29, p. 869, 1909.

TABLE XV.

Date.	Observer.	Method.	Reference.	$\mu_{15} \times 10^7$
1874	Schumann.	Damping method.	Wed. Ann., 23, p. 374, 1884.	1752
1875	Obermeyer.	Transpiration method.	Wiener. Sitz. Ber., 71, p. 281; 73, p. 433.	1748
1885	Schneebeli.[1]	Transpiration method.	Arch. des sc. phys. et nat. Geneve, 14, p. 197.	1780
1886	Tomlinson.	Damping method.	Phil. Trans., 177, p. 767.	1785
1899	Breiterbach.	Transpiration method.	Ann. der. Phys., 5, p. 168.	1807
1901	Schultze.	Transpiration method.	Ann. der. Phys., 5, p. 157.	1811
1906	Tanzler.	Transpiration method.	Verh. d. D. Phys. Ges., 8, p. 222.	1812
1908	Grindly and Gibson.	Flow through long pipe.	Proc. Roy. Soc., 80, p. 114.	1788
1909	Fisher.	Transpiration method.	PHYS. REV., 28, p. 104.	1782
1910	Rankine.	Transpiration method.	Proc. Roy. Soc., ser. A, pp. 516–525.	1788

Mean = 1785

shown by work now in progress in the Ryerson Laboratory to be 6 per cent. in error. O. E. Meyer's[2] early transpiration experiments are also excluded for the reason that, though his mean is in close agreement with the above result the individual observations show great divergence.

Despite the agreement shown in the results obtained by the "outflow"[3] and "damping"[4] methods I am inclined to rate both of them as inferior in reliability and precision to the "constant deflection" method (with concentric cylinders) used by Gurney at the Ryerson laboratory and also by other observers, in determining the coefficient of viscosity of liquids. Mr. Lachlan Gilchrist

[1] Obermeyer and Schneebeli are in perfect agreement when they treat their observations in the same way. One considers the air saturated, the other dry. It is probably in an intermediate condition.

[2] Pogg. Ann., 148, p. 37, and 203, 1873.

[3] The consistently high values found by Briterbach, Schultze and Tanzler may possibly be due to the fact that they all use high values of $(p_1 - p_2)$. Barus' results (Ann. der Phys., 36, p. 358, 1889) seem to indicate an apparent slight increase in μ with increasing $(p_1 - p_2)$.

[4] Schumann's results by the damping method are not at all comparable in accuracy with Tomlinson's.

is now making in this laboratory a very careful determination of μ for air by this method and it is already certain that his result will not differ from Tomlinson's by more than a fraction of a per cent. It seems therefore impossible that the value of μ which has been used in these computations can be in error by more than .5 per cent. and it is probable that its error is even less than this. Tomlinson estimates it at not more than .2 per cent. and the agreement to within less than .1 per cent. which he obtained both in the use of two wholly distinct damping methods and in the use of different suspensions by the same method seems to justify his estimate. It may be confidently expected that within a very few years at most the uncertainty in the absolute value of the coefficient of viscosity of air will be not more than one or two tenths of one per cent.

Tomlinson's work, like the above, was done with ordinary rather than with dry air, his mean humidity being apparently much the same as that shown in column 3, Table XIV. He estimated however that the presence of the aqueous vapor in the air used in his experiment could scarcely affect his results by .1 per cent. Mr. Gilchrist has experimentally demonstrated the correctness of this estimate in the case of the present experiments and has further shown that the drag which the air exerts upon an oiled cylinder is exactly the same as the drag which it exerts upon a brass cylinder, thereby removing all question as to the applicability of the above constant to the conditions of these experiments.

We have devised two modifications of this method of determining e which do not involve the value of μ. It is scarcely likely however that the necessary experimental error in these methods can be reduced below the error in μ. It is probable therefore that any increased accuracy in our knowledge of e is to be looked for in increased accuracy in the determination of μ.

§ 13. Experiments upon Substances other than Oil.

All of the preceding experiments except those recorded in Table I. were made with the use of a specially cleaned gas engine oil of density .9041 at 25° C. Those in Table I. were made with the use of a similar, though more volatile, mineral oil (machine oil) of density .8960. The reason that we worked so continuously upon

a single substance was that it was found that in order to maintain a drop of constant size it was necessary, even with these very non-volatile substances to have the drop in equilibrium with its saturated vapor. This is shown by the following observations. The inner surfaces of the condenser plates had been covered with a very thin coat of machine oil in order that they might catch dust particles. Drops blown from a considerable number of non-volatile substances were introduced between the plates and were found in the main to evaporate too rapidly to make accurate observing possible. This was true even of so non-volatile substances as glycerine and castor oil as the following observations show:

Glycerine,	Den. 1.25	Castor Oil,	Den. .975
G	*F*	*G*	*F*
28.3	11.5	73.8	18.0
32.5	9.8	75.8	12.9
38.7		77.3	18.0
45.6	8.4	78.7	102.2
59.2		79.6	17.8
		84.8	30.2
		87.7	12.7
		90.7	18.1

In order to get rid of this continuous increase in *G*, the drops were next blown from the least volatile liquid at hand, viz., gas engine oil, and the behavior of a given drop showed immediately that it was growing in size instead of evaporating. This can be seen from the following readings:

Gas Engine Oil.	
G	*F*
17.6	6.1
17.4	76.2
17.2	82.0
16.9	87.2
16.8	92.4
17.1	97.8
16.7	104.6
16.4	112.0

This behavior was shown consistently by all the drops experimented upon (six or eight in number) throughout a period of two days. Imagining that the vapor from the more volatile machine oil upon the plates was condensing into the less volatile but similar

oil of the drop I took down the apparatus, cleaned the plates carefully, and oiled them again, this time with the gas engine oil. Every gas engine oil drop tried thereafter showed the sort of constancy which is seen in tables III. to XII. Series of observations similar to that made upon gas engine oil and tabulated in tables XIII. and XIV. will ultimately be made upon other substances. Thus far the aim has been to take enough observations upon other substances to make sure that the results obtained from these substances are substantially in agreement with those obtained from gas engine oil and to concentrate attention upon an accurate series of observations upon one substance. As a matter of fact we have a fairly complete series upon machine oil and a number of observations upon watch oil, castor oil, and glycerine, all of which are in agreement within the limits of observational error, in some cases as much as 2 or 3 per cent., with the observations upon gas engine oil.

The only observations which have been taken upon mercury are tabulated below.

TABLE XVI.

Negative Mercury Drop.

Distance between cross hairs = 1.033 *cm.*
Temperature = 24.4° *C.*
Density of mercury at 25° *C.* = 13.52.
Viscosity of air at 25.2° *C.* = .0001837.

	G sec.	F sec.	n	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
$G =$ 6.747	6.780	68.0			
$V =$ 8383	6.686	63.3	6	32.77	5.448
$F =$ 64.1	6.776	61.0			
$v_1 = .1531$					$e_1 = 5.448$

The drop of Table XVI. yields a value of e within 1 per cent. of the value obtained with the gas engine oil if A is assumed to be .817. This will be readily seen from the consideration that v_1 for an oil drop of the same size as the mercury drop would have been

$$.1531 \times \frac{.9041}{13.52} = .01025.$$

This is very close to the value of the velocity shown by the oil

TABLE XVII.

Positive Mercury Drop.

Distance between cross hairs = .980 *cm.*

Temperature = 21° *C.*

	G sec.	F sec.	n	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
	3.0	4.8			
$F=$ 4.8	3.1	4.8	27	137.1	5.077
	3.0	4.8			
	2.8	4.8			
	2.8	8.0			
$F=$ 7.83	3.0	7.5	23	116.8	5.078
	2.8	8.0			
	3.1	6.7	24	122.2	5.092
	3.1	36.6			
	3.2	36.2			
$G=$ 2.988	3.0	36.4			
$V=9070$	3.0	36.1			
	—	36.2			
$F=$ 36.34	2.8	36.1	18	91.45	5.081
	3.2	36.1			
	2.9	36.6			
	3.0	36.5			
	—	36.6			
$v_1=.3280$				Mean $e_1=5.082$	

drop of Table III., and the values of e_1 obtained from tables III. and XVI. differ by not more than 1 per cent. Since G in Table XVI. is uncertain to 1 per cent., as is shown by the differences between individual readings (which were taken with the chronograph), the uncertainty in e_1 is about 1.5 per cent. (*cf.* equation 4) so that within the limits of observational error this drop is in good agreement with the oil.

The drop of Table XVII., while yielding readings which are most consistent among themselves, gives a value of e about 4.5 per cent. too low. However this drop was timed with a stop watch and G is therefore uncertain by about one tenth second, or 3 per cent., which means that e_1 contains an uncertainty of 4.5 per cent. The experiments upon mercury have not been pushed farther for the reason that its great density makes it unsuitable for precise measurements unless the drops are very small, and then Brownian movements produce enormous irregularities.

The conclusion to be drawn then from all of the work thus far done on substances other than oil is merely that there is nothing in it to cast a doubt upon the correctness of the value of e obtained from the much more extended and much more accurate work upon gas engine oil.

§ 14. Comparisons with Other Determinations.

The value of e herewith obtained is in perfect agreement with the result reached by Regener[1] in his remarkably careful and consistent work on the counting of the number of scintillations produced by the particles emitted by a known amount of polonium and measuring the total charge carried by these same particles. His final value of this charge is 9.58×10^{-10}, and upon the assumption that this is twice the elementary charge—an assumption which seems to be justified by Rutherford's experiments[2]—he finds for e 4.79×10^{-10}, with a probable error of 3 per cent. Since the difference between this value and 4.89×10^{-10} is but 2 per cent. the two results obviously agree within the limits of observational error.

On the other hand, the present value of e is 4 per cent. higher than the simple mean value which I previously obtained in work by a similar method upon drops of water and alcohol[3] and when the correction to Stokes's law is applied the difference becomes as high as 8 per cent. Although the observational error in these earlier experiments was enormously greater than that found in the present work it is not probable that more than 2 per cent. or 3 per cent. of the difference can be accounted for by mere timing errors in the preceding determination. The difference is due I think in the main to the instability of the conditions which prevail in any expansion chamber immediately after a sudden expansion. Since the temperature rises rapidly after such an expansion the convection currents produced by this rise must on the whole have an upward tendency and consequently the apparent rate of fall under gravity is lower than it should be. This always

[1] E. Regener, Sitz. Ber. d. k. Preuss. Acad. d. Wiss., XXXVII., p. 948, 1909.

[2] Rutherford, Phil. Mag., 17, p. 281, 1909.

[3] Millikan, Phil. Mag., 19, p. 209, 1909.

tends to make the value of e come out too small (cf. equation 4). Furthermore the lack of perfect uniformity in the electrical field between plates as small as those which have been used by all experimenters who have worked with the cloud method tends to push down the apparent value of e.

Turning next to Begeman's experiments[1] the observational errors are here still larger, the last criticism applies with equal force, and in addition Cunningham shows that the group velocity of a falling cloud is less than the velocity of an individual drop and finds that because of this fact alone Sir Joseph Thomson's calculation of e is 7 per cent. too low.[2] The same sort of a correction would apply to Begeman's experiment. On the other hand, Begeman's result would be three or four per cent. too high because of the fact that individual drops of the sizes which he uses actually fall faster than they would if Stokes's law held. The net result of the consideration of all of these causes would be to raise Begeman's value so that it would be well within the limits of observational error of the value 4.89×10^{-10}.

The only other investigations which appear to yield results which are in any way adverse to the conclusions herein contained are reported in very recent papers by Ehrenhaft[3] and Przibram[4] both of which have appeared since this work was first presented to the Physical Society on April 23, 1910.

Ehrenhaft, who in his preceding work, which appeared simultaneously with the completion of the work reported in October, 1909,[5] had deduced e from average rates of fall and average velocities in a horizontal electric field, has in this later work used the vertical electric field and therefore now makes all the observations from which e is deduced, as I have done since the spring of 1909, upon a single charged particle. His present observations then differ from these only in these important respects:

1. He observes through an ultra-microscope and therefore deter-

[1] Begeman, PHYS. REV., 31, p. 41, 1910.

[2] *Loc. cit.*, p. 365.

[3] Ehrenhaft, Phys. Zeit., Juli 15, 1910.

[4] Przibram, Wien. Sitz. Ber., CXIX., p. 1, 30 June, 1910.

[5] Millikan, PHYS. REV., 1909.

mines rates of fall and rise through exceedingly minute distances, about .01 cm. in place of the 1.3 cm. which is here employed.[1]

2. He moves a single particle up and back but once, and holds it under observation at most a minute, as I did in the earlier work, instead of from four to five hours as I am now doing.

3. Instead of using oil drops he sucks into the observing chamber the metallic dust arising from the volatilization produced in a metallic arc.

4. He assumes Stokes's law instead of correcting it as is done above.

5. He computes simply the charges upon his dust particles, and in no case the charges upon ions captured from the air, *i. e.*, he makes no study whatever of the phenomena of *change* of charge.

His results are so irregular that he concludes that if there is any elementary charge it is much smaller than the value herein assigned. His irregularities are all easily and simply explained, however, by a consideration of the failure of Stokes's law shown above and the Brownian movements.[2] His particles have diameters which lie between those of our very smallest drops and values only one tenth as large. Now it was found in this work on oil drops that consistency could not be obtained in the readings upon the successive rates of fall under gravity of a given particle when that particle was smaller than the smallest shown in Table XIV., and that for the simple reason that the displacements of such particles due to

[1] The apparatus of Fig. 1 was designed with especial reference to (1) uniformity of field, (2) freedom from convection currents and (3) the largest attainable accuracy in the measurement of rates of fall even with large drops. The distance between the plates was therefore made as large as possible and the magnification used as small as possible (only about 4 diameters). The accuracy and consistency of the results is attributable chiefly to the largeness of the distance of fall and the smallness of the magnification.

[2] Einstein's formula

$$\overline{\Delta X^2} = \frac{RT}{N}\frac{1}{3\pi a\mu}\tau$$

shows that the displacement in time τ is independent of the mass of the particle. Since however the kinetic energy of agitation of all particles is the same the velocity at any instant of a platinum particle is but about one fifth as much as that of an oil or water particle of the same radius. This accounts presumably for the fact that Ehrenhaft did not notice the agitation of the particles when he was using dense substances but did observe it when he was using light substances.

their Brownian movements[1] became comparable with the displacements produced by gravity. Indeed, we have many series of observations upon such particles in which the successive values of G vary because of the Brownian movements from two to four fold. Table XVIII. shows observations upon one such. It will be seen

TABLE XVIII.

Distance between plates = 1.600 *cm.*
Distance between cross hairs = .0148.
Temperature = 23° *C.*
Volts = 326.

G	F	e_1	
10.3	10.6	5.25	
7.7	20.0	4.52	
6.8	13.2	7.50	
5.6	13.4	9.40	
8.3	8.8	7.15	Mean $e_1 = 7.8 \times 10^{-10}$
5.0	11.5	11.3	
7.8	16.5	5.87	
6.8	11.2	8.0	
5.7	7.2	11.6	
4.7	13.0	12.1	
7.3	13.2	6.95	
7.4	15.4	6.50	
8.6	17.0	5.24	
6.5	3.6	14.9	
6.0	2.6	19.8	
8.4	3.0	13.8	
5.6	3.0	18.8	
6.4	3.0	15.1	Mean $e_2 = 15.2 \times 10^{-10}$
6.0	3.6	15.9	
7.2	4.3	12.2	
6.5	3.3	15.8	
7.8	3.0	14.4	
8.2	3.4	12.7	
5.5	2.7	13.9	

$a = .00004$ cm.

that while the drop carried one single elementary charge the value of this charge, if computed from single observations, would have appeared to oscillate between 5.2×10^{-10} and 11.6×10^{-10} and similarly that the value of the double charge would have appeared

[1] A more complete analysis will be given in a separate paper by Mr. Fletcher.

to oscillate between 12.7×10^{-10} and 19.8×10^{-10}. The Brownian movement theory can be made to account quantitatively as well as qualitatively for all of the irregularities of Table XVIII., as well as for those in Ehrenhaft's tables.[1]

The irregularities in Ehrenhaft's results furnish then no evidence whatever against any of the conclusions which have been drawn from the above data.

Przibram's observations, carried on between April and June, 1910, were made under conditions which were practically identical with those which I used in the work published in December, 1909, save that his drops had but one third as large diameters and were formed differently. He obtained more consistent results than did Ehrenhaft, because he used larger particles. However tables V. and VI. of his paper, in which he records the only observations made as much as twice upon the same particle show, as he himself points out, divergencies as high as 40 per cent. between the two successive timings and an average divergence of 12.4 per cent. in the computed values of e. The only way in which data of this sort can be treated, if results of any significance whatever are to be drawn from it, is to take averages of a large number of observations upon the same particle, or since these are not available in this case, averages of as many observations as possible upon different particles. The mean value of e which Przibram obtains by plotting the results of 1,000 observations on "Phosphornebel" of mean radius .000054 cm. is 6.0×10^{-10} which is seen from the curve of Fig. 3 to agree perfectly with the above results.

The only result in any of the Vienna work which is not to be predicted at once from the smallness of the particles used, taken in connection with the laws governing Brownian movements, is the fact that some of Ehrenhaft's irregularities fluctuate about smaller values of e_1 than any shown in the above tables. It is to be observed however that Przibram's observations made upon the same substance "Phosphornebel" fluctuate about the correct value. In view then of (1) the disagreement between Ehrenhaft's and Przibram's results on the same substance, (2) the uncertainty as

[1] A more complete analysis will be given in a separate paper by Mr. Fletcher.

to the density and sphericity of ultramicroscopic particles, and (3) our complete ignorance to date of the law of motion through a resisting medium of such particles especially when charged,[1] it is obvious that there is nothing in either Ehrenhaft's or Przibram's work to raise a suspicion as to the validity of any of the conclusions herein drawn.

There is but one more experiment which needs to be mentioned in this connection, namely, the important work of Zeleny and McKeehan[2] on the direct measurement of the dimensions and rates of fall in air of spheres whose radii lie within the limits .00366 cm. and .00035 cm. This work constitutes direct verification within the rather large limits of experimental error of the constants of Stokes's law, though the individual observations are too scattering to throw any light upon the way in which the rate of fall varies with the radius of the drop—a gap which is filled in by the above observations. For spheres of the average radius which they use the correction term which is here applied to Stokes's law would influence their final mean by only 1 per cent. Since their probable error is very much larger than this there is evidently no discrepancy between their "verification of Stokes's law" and the proof herewith presented of its inadequacy. They originally used a high value of μ, but they now inform me that the value $\mu_{15} = .0001785$ yields better agreement between observed and calculated times of fall than does the value which they first employed.

In conclusion there is presented a summary of the most important of the molecular magnitudes, accurate values of which are made possible by an accurate determination of e. The Faraday constant is taken as $Ne = 9{,}655$ absolute electromagnetic units.

$e = 4.891 \times 10^{-10}$ E.S.U.	the smallest quantity of electricity capable of separate existence.
$N = 5.922 \times 10^{23}$	the number of molecules in one gram molecule of any substance.
$n = 2.644 \times 10^{19}$	the number of molecules in 1 c.c. of any gas at 0° C. and 76 cm.
$\alpha = 2.106 \times 10^{-16}$ ergs.	the constant of molecular energy. Molecular energy $\epsilon = \alpha T$.

[1] When the particles become sufficiently small the apparent viscosity of the medium should be a function of the charge.

[2] PHYS. REV., XXX., p. 525, May, 1910.

$\epsilon_0 = 5.750 \times 10^{-14}$ ergs. the kinetic energy of agitation of a single molecule at 0° C. and 76 cm. $\epsilon_0 = 273\alpha$.

$m = 1.702 \times 10^{-24}$ gms. the weight of the hydrogen atom.

Weights and Diameters of Molecules.

Substance.	Molecular Wt. ($H=1$).	Absolute Wt., Grams.	Diameter,[1] cm.	Absolute Density, g.cm.
Hydrogen	2	3.40×10^{-24}	2.28×10^{-8}	.55
Helium	4	6.81×10^{-24}	2.00×10^{-8}	1.63
Carbon monoxide	27.8	47.4×10^{-24}	2.89×10^{-8}	3.76
Ethylene	27.8	47.4×10^{-24}	3.40×10^{-8}	2.34
Nitrogen	27.8	47.4×10^{-24}	3.06×10^{-8}	3.17
Air	28.9	49.2×10^{-24}	2.99×10^{-8}	3.53
Nitric oxide	29.81	50.8×10^{-24}	2.69×10^{-8}	5.00
Oxygen	31.8	54.2×10^{-24}	2.89×10^{-8}	4.30
Argon	39.6	67.5×10^{-24}	2.78×10^{-8}	6.01
Carbon dioxide	43.7	74.4×10^{-24}	3.11×10^{-8}	4.73
Nitrous oxide	43.7	74.4×10^{-24}	3.48×10^{-8}	3.39
Chlorine	70.4	119.8×10^{-24}	3.01×10^{-8}	3.90
Water vapor	17.9	30.5×10^{-24}	$3(?)\times10^{-8}$	
Ethyl chloride	64.0	108.9×10^{-24}	$4(?)\times10^{-8}$	

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November 28, 1910.

[1] These diameters have been obtained from the above value of n and the viscosity equation

$$\mu = \frac{350\rho\bar{c}}{\sqrt{2}\pi n D^2},$$

Sutherland's correction for cohesional force (Phil. Mag., 17, p. 320, 1909) and Jean's correction for persistence of velocities being added. This procedure is thought to yield more reliable results than applying the above corrections to means of D obtained from viscosity, diffusion, heat conduction, and departures from Boyle's law, since computations based on the last three phenomena involve both theoretical and experimental uncertainties of large magnitude.