SPECIAL ARTICLES

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

§ 1. *Introduction.*—There is presented herewith a new method of studying gaseous ionization, with the aid of which it has 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; in other words, that an electrical charge, instead of being spread uniformly over a 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 this elementary electrical charge, which is free from all questionable theoretical assumptions and is limited in accuracy only by the accuracy which is 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, direct and most convincing evidence of the correctness of the kinetic theory of matter.

5. To demonstrate that the great majority of the ions of the air of both positive and negative sign, carry the elementary electrical charge, and to present convincing evidence that some atmospheric ions carry exact multiples of this charge; in other words, that the phenomena of valency are exhibited to some extent in gaseous ionization.

6. To show that the law of motion of a small sphere through a resisting medium, commonly known as Stokes's law, 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.

The investigation by means of which these results have been obtained differs from most of the equally important ones which are carried on in the physical laboratory, in that the method used is so simple, and the conclusions follow so inevitably from the experimental data that even the man on the streets can scarcely fail to understand the method or to appreciate the results.

§ 2. *The Method.*—The method by which these results have been obtained and by which still further important results bid fair to be obtained grew out of some experiments which were presented in a preceding paper.[2] It is in brief as follows: A cloud of fine droplets of oil, or of mercury, or of some other non-volatile substance is blown by means of an atomizer[3] over a horizontal air condenser and a few of the droplets in this cloud are allowed to fall through a pinhole in the middle of the upper plate of this condenser into the space between the plates. The pinhole is then closed for the sake of shutting out air currents. The condenser used consists in most of the experiments of two heavy, circular, and accurately planed brass plates, 20 cm. in diameter, held exactly 16 mm. apart by means of three small ebonite posts. The plates are

[1] At the request of the editor this abridgment of a paper presented on April 23, 1910, before the American Physical Society is published in SCIENCE.

[2] *Phil. Mag.*, 19, p. 209, 1910.

[3] 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.

enclosed, and the temperature controlled so that the air within the condenser is altogether stagnant. The droplet, once inside the condenser, is illuminated through a small window by a beam from an arc light, so that it appears in the field of view of the observing cathetometer telescope like a bright star on a black background. This star, of course, falls under the 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 thrown on between the plates, and, if the droplet had received a 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 this plate the field is thrown off, the plates short-circuited, 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 are signaled 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. Furthermore, it is from the values of the speeds observed that all of the conclusions above mentioned are directly and simply deduced.

§ 3. *The Deduction of the Relative Values of the Charges Carried by a Given Droplet.*—The relations between the mass 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 F, are given by the simple equation

$$\frac{v_1}{v_2}=\frac{mg}{Fe_n-mg} \quad \text{or} \quad e_n=\frac{mg}{F}(v_1+v_2). \qquad (1)$$

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 after 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, and for the establishment of 4 no other exact relationship is needed. However, for the sake of obtaining a provisional estimate of the value of m in equation (1), and therefore of making 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 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

$$X=6\pi\mu av. \qquad (2)$$

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.,

$$v_1=\frac{2}{9}\frac{ga^2}{\mu}(\sigma-\rho). \qquad (3)$$

The elimination of m from (1) by means of (3), and the further relation

$$m = \tfrac{4}{3}\pi a^3 \alpha$$

gives the charge e_n in the form

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

It is from this equation that the values of e_n in tables I.–XI. 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 error 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 full elsewhere. 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 the case of Table I. 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 the 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 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 equation (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 PD between the plates, taken at the mean time corresponding to each group, is labeled V and placed just below or just above the mean G corresponding to that group. The PD was applied by means of a storage battery.

§ 5. *Discussion of Table I.*—Since the original drop was in this case 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 $G =$

TABLE I

Negative drop

Distance between cross hairs = 1.010 cm.
Distance between plates = 1.600 "
Temperature = 24.6° C.
Density of oil at 25° C. = .8960
Viscosity of air at 25.2° C. = .0001837

	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	—	9	44.42	4.936
$V = 7950$	22.0	17.3			
	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	11	53.92	4.902
$G = 22.80$	22.8	12.3			
	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			
$F = 8.65$	22.8	8.6	14	68.65	4.904
	23.1	8.7			
	23.2	9.8	13	63.68	4.900
	—	9.8			
$F = 10.63$	23.5	10.7	12	59.12	4.927
	23.4	10.6			
	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
$F = 8.65$	—	8.7	14	68.65	4.904
	23.4	8.6			
	23.0	12.3			
$F = 12.25$	23.3	12.2	11	53.92	4.902
	—	12.1			
	23.2	12.4			
	Change forced with radium.				

	G (sec.)	F (sec.)	n	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
	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			
$F = 39.20$	23.4	39.0	6	29.62	4.937
	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			
	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	6	29.62	4.937
$V = 7730$	23.5	39.0			
$G = 23.46$	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	4.915
	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 $e_1 s$ =	**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

23.43, the time of the drop in the field changed suddenly from 71 seconds to 380 seconds, 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 differences 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. Mr. Harvey Fletcher and myself, who have worked together on these experiments since December, 1909, studied in this way between December and May from one to two hundred 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 exact multiple of that quantity.* These observations are the justification for assertions 1 and 2 of the introduction.

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

First, since the time of the drop in the field varied in these observations from 380 seconds to 6.7 seconds, 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.

Second, since the charge on the drop was multiplied more than four times without changing at all the value of G, or the 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.

Third, 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 of the four and one half hours during which these experiments lasted, there is but one such. 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 can not 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 can not obtain it from the field, since the phenomenon occurs when the field is not on. It can not 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 already 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 4.902×10^{-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 sixteen elementary charges, is

$$\frac{16e^2}{r} = \frac{16 \times (4.901 \times 10^{-10})^2}{.000197} = 1.95 \times 10^{-14} \text{ ergs.}$$

Now the kinetic energy of agitation of a molecule as deduced from the value of e herewith obtained, and the kinetic theory equation, $p = \frac{1}{3}mnu^2$, is 5.756×10^{-14} ergs. According to the Maxwell-Boltzmann law, which doubtless 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 Mr. Fletcher and myself watched for four hours a 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} ergs, 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 in 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.

The first portion of assertion 5 is directly proven by the readings contained in the table, since the great majority of the changes recorded in column 4 corresponds to the addition or subtraction of one single elementary charge. The second portion of the assertion seems at first sight to be proven by the remaining changes which correspond to the addition or subtraction of 2 or 3 times this amount. The conclusion, however, that valency is exhibited in gaseous ionization is not to be so easily drawn. The arguments for it which are furnished by our experiments will be presented fully elsewhere. Space here only permits the statement that the only strong argument furnished by table I. is found near the end of the table where, *when the field was on, the drop caught a double negative ion, while I was looking at it.*

Some idea of the intensity of ionization used in these experiments may be gained from the statement that 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 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 presently be explained. 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.

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 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 ions and also on account of the somewhat greater numbers in which they occur, we found, in general, a slightly 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.

§ 5. *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 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 completely 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

TABLE II

Negative drop No. 5

Distance between cross hairs = 1.303 cm.
Temperature = 24.6° C.
Density of oil at 25° 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	3	16.41	5.470
	120.1	16.3			
$F = 26.40$	120.2	26.4	2		
	119.8	67.4	1	5.495	5.495
$G = \mathbf{120.07}$	120.1	26.6	2	10.98	
$V = 9150$	—	16.6			
	120.2	16.6	3	16.41	
$F = 16.50$	—	16.5			
$F = 67.73$	120.2	68.0	1	5.495	
	119.9	67.8			
		26.4		10.98	

$v_1 = \mathbf{.01085}$ Mean e_1 (weighted) $= \mathbf{5.490}$

TABLE III

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
$G = \mathbf{87.85}$	87.8	31.0	4	21.93	5.482
	87.4	30.8			
$F = 30.9$	87.8	47.0	3	16.41	5.470
	87.3	—			
v_1 — **.01176**		Mean e_1 (weighted) = **5.482**			

TABLE IV

Negative drop No. 12

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			
$G = \mathbf{53.80}$	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 (weighted) = **5.349**			

TABLE V

Positive drop No. 15

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

	G (sec.)	F (sec.)	n	$e \times 10^{10}$	$e_1 \times 10^{10}$
	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			
	30.5	85.9			
$G = \mathbf{30.48}$	30.7	86.4			
$V = 9010$	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**			

e_1. This is illustrated by the observations shown in tables II., III., IV., V., VI. and VII. The drops shown in tables II. and III. were of almost exactly 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

TABLE VI

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[4]	151.9			
	24.4	152.9			
$F = 152.9$	24.63	152.4	5	25.75	5.150
	24.6	153.5			
$V = 9075$	24.4	153.9			
$G = \mathbf{24.57}$	24.7	39.4	7	36.03	5.147
	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 VII

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			
$G = \mathbf{23.58}$	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**			

identical. Similarly tables VI. and VII. 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 II., IV., V. and VI. or III., IV., V. and VII. show conclusively that the value of e_1 obtained in this way 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 drops the velocities of

[4] The readings 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 from the stop-watch readings 24.583.

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

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 tables VIII., IX., X. and XI. 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, Mr. Fletcher's and my own mean times on a given drop generally differ from each other by less than one one-hundredth 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 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 eleven parts and reading the *PD* of each part by means of a 900 volts Kelvin and White electrostatic voltmeter which we calibrated with an accuracy of one tenth of one per cent. by comparing it with a Weston voltmeter which had been standardized at the Bureau of Standards.

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 from the tables that even in the case of the largest drops, 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

TABLE VIII

Negative drop No. 20

Distance between cross hairs = 1.314 cm.
Temperature = 23.4° C.

	G (sec.)	F (sec.)	n	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
	M 84.87	114.7			
$V = 8431$	" 14.88	114.8	11	56.14	5.104
	" 14.87	115.3			
$F = 114.9$	" 14.90	64.2			
$G = \mathbf{14.857}$	" 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			
$v_1 = \mathbf{.08843}$				Mean e_1 =	**5.102**

TABLE IX

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	141.78	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			
$V = 8788$	" 7.92	32.7	30	151.69	5.056
$G = \mathbf{8.013}$	—	32.7			
	" 8.02	32.7			
$F = 24.67$	—	24.7			
$V = 8786$	—	24.6	32	161.41	5.044
	" 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			
$v_1 = \mathbf{.16436}$				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
141.78 — 131.58 =	10.20 ÷	2 =	5.10	1 per cent.
136.34 — 131.58 =	4.76 ÷	1 =	4.76	2 per cent.
151.69 — 136.34 =	15.35 ÷	3 =	5.12	2 per cent.
161.41 — 141.20 =	20.20 ÷	4 =	5.05	1 per cent.
141.20 — 136.17 =	5.03 ÷	1 =	5.03	2 per cent.

Weighted mean difference = 5.03.

TABLE X

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			
$F = 27.73$	" 4.66	27.7			
$V = 8843$	" 4.56	27.6	42	212.70	5.064
	" 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			
$F = 33.75$	" 4.68	33.8			
$V = 8841$	" 4.61	33.8			
	—	33.7	41	207.33	5.057
	" 4.64	33.7.			
	" 4.62	33.9			
$F = 42.55$	" 4.61	42.5			
$V = 8840$	" 4.61	42.6	40	202.28	5.057
	" 4.64	33.8			
$F = 34.05$	—	34.2			
$V = 8839$		34.2	41	207.30	5.055
	" 4.66	34.0			
	" 4.67	34.8			
	—	34.4	41		
$G = \mathbf{4.630}$	" 4.68	34.8			
	" 4.61	28.8	42		
	" 4.66	34.5			
$F = 34.67$	—	34.8	41	206.86	5.045
$V = 8837$	" 4.62	34.7			
Forced change with radium.					
$F = 59.50$	F 4.58	59.4			
$V = 8836$	" 4.63	59.6	39	196.75	5.045
	" 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			
$V = 8834$	" —	222.0	37	186.39	5.038
Forced change with radium.					
	F 4.64	35.0			
$F = 35.2$	" 4.60	35.2			
$V = 8833$	" 4.65	35.4	41	206.59	5.039
	" 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			
	—	19.2	45	226.21	
	—	19.7			
	—	19.6			
	—	19.3			
	—	19.2			
	—	19.7			
	—	19.5			
Forced change with radium.					
	—	64.0			
$F = 63.45$	—	66.4			
$V = 8827$	—	63.0	39	196.12	
	—	63.4			
$F = 100.2$	—	100.0			
$V = 8826$	—	100.3	38	191.11	
$v = .2175$				Mean $e_1 = \mathbf{5.046}$	

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

Differences

	e_n	n	e_1	error
$196.12 - 191.11 =$	$5.01 \div$	$1 =$	5.01	1 per cent.
$226.21 - 196.12 =$	$30.09 \div$	$6 =$	5.02	1 per cent.
$226.21 - 201.30 =$	$24.11 \div$	$5 =$	4.98	2 per cent.
$206.59 - 186.39 =$	$20.20 \div$	$4 =$	5.04	1 per cent.
$201.69 - 186.39 =$	$15.30 \div$	$3 =$	5.10	1 per cent.

Mean difference (weighted) = 5.035.

the bottoms of the tables. In fact, in general, even with the largest drops the relative value[5] 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 XII., which contains the final results of our observations upon all of the drops except three

[5] Since the same value of G is used in computing all of the e_ns the relative values of e_n or e_1 are practically independent of the error in G.

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. 1, which is the graph of the results contained in table XII. 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. 1, or

TABLE XI

Negative drop No. 32

Distance between cross hairs = 1.003 cm.
Temperature = 23.2° C.

	G (sec.)	F (sec.)	n	$e_n \times 10^{10}$	$e_1 \times 10^{10}$
$F = 8.5$	—	8.7			
$V = 8577$	—	8.3	123	622.40	
	—	8.5			
Changed without radium.					
	M 2.44	28.4			
	—	28.7			
	—	28.7			
$F = 28.70$	" 2.46	28.4	104	524.25	5.040
$V = 8573$	" 2.54	29.0			
	" 2.46	29.0			
	" 2.45	28.8			
	" 2.43	28.6			
Change forced with radium.					
$G = \mathbf{2.462}$	" 2.44	15.7			
	" 2.48	15.7			
$F = 15.72$	—	15.7	111	558.78	5.034
$V = 8568$	—	15.7			
	—	15.8			
Change forced with radium.					
$F = 59.1$	—	59.1	100	503.42	5.034
$V = 8565$	" 2.50	59.1			
$F = 60.0$	—	59.8	100	503.22	5.032
$V = 8563$	F 2.45	60.2			
Change forced with radium.					
$F = 81.5$	—	81.0	99	498.12	5.031
$V = 8561$	—	82.1			
Change forced with radium.					
	" 2.44	19.0			
$F = 20.0$	" 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
543.41 — 498.12 =	45.29 ÷	9 =	5.032	.5 per cent.
503.23 — 498.12 =	5.11 ÷	1 =	5.11	3.0 per cent.
558.78 — 503.42 =	55.36 ÷	11 =	5.035	.5 per cent.
558.78 — 524.25 =	34.53 ÷	7 =	4.94	3.0 per cent.

Mean difference (weighted) = 5.031.

and since further a sphere must have a higher rate of fall than a body of any other form whatever having the same mass and density, the hypothesis of binary drops to account for an occasional low value of e_1 is at least natural. After eliminating dust 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. 1. This is as large a departure from this curve as we have thus far obtained.

§ 6. *The Correction of Stokes's Law.*—The procedure actually adopted for correcting Stokes's law will be detailed elsewhere. The end result is this. An equation of the following form is made to replace Stokes's equation (2):

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

$$v_1 = \frac{2}{9}\,\frac{ga^2(\sigma - \rho)}{\mu}\left\{1 + A\frac{l}{a}\right\}, \qquad (6)$$

in which a is the radius of the drop, l the mean free path of the gas molecule, and A an undetermined constant which we obtain from our observations. It turns out that A is identical to within the limits of observational error (not more than 1 or 2 per cent.) with the value deduced by Cunningham[6] from the kinetic theory considerations, provided the f of his formula[7] is made equal to zero. This means that the value of A given by our observations is .815. The values of a in tables XII. and XIII. are computed from (6), in which a is now the only unknown.

§ 7. *The Absolute Value of e.*—Using now (6) instead of (4) to combine with (1) and denoting by e the absolute value of the elementary charge and by e_1, as heretofore, the value of this charge as obtained from the use of the usual form of Stokes's law, *i. e.,* from (4) there results at once

$$e\left(1 + A\frac{l}{a}\right)^{\frac{3}{2}} = e_1. \qquad (7)$$

[6] *Proc. Roy. Soc.,* 83, p. 360.

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

Table XIII. contains the values of e obtained from all of the observations recorded in table XII. except the first four and the last six. These are omitted not because their introduction would change the final value of e, for as a matter of fact this is not appreciably altered by including them, but solely because of the experimental errors involved in work upon either exceedingly slow or exceedingly fast drops. When the velocities are exceedingly slow residual convexion currents introduce errors, and when they are exceedingly fast the time determination becomes uncertain.

The final mean value of e is 4.9016×10^{-10}. The probable error computed from the number of observations shown in the last column and their average divergence should be about one tenth of one 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 obtained in the measurement of this constant. After a prolonged and very careful study of all the data available on the viscosity of air I have chosen as the most probable value of μ at 15°.0001785. For reasons which will be detailed elsewhere it is thought that the error in this value is less than one half of one per cent.

It is most interesting that the agreement between Cunningham's rational formula and our experimental results is so perfect. How perfect it is may be seen graphically from Fig. 2, in which the curve is computed from 7 under the assumption of $e = 4.9016$ and our experimentally determined values of e are plotted about this curve, every observation contained in Table XII. being shown in the figure. Nevertheless, it is to be particularly emphasized that the correctness of our 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. It is entirely possible that a series of experiments of this kind upon substances other than oil may lead to other values of A,

TABLE XII

No.	Velocity cm./sec.	Radius cm.	$e_1 \times 10^{10}$	Prob. Error.
1	.001315	.0000313	7.384	6.0
2	.001673	358	6.864	4.0
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	1.0
31	.3969	6047	5.060	1.0
32	.4074	6104	5.033	1.0
33	.4735	6581	4.911	1.5

TABLE XIII

No.	Velocity cm./sec.	Radius cm.	$e_1 \times 10^{10}$	Prob. Error.	$e \times 10^{10}$	Per Cent. Error.
5	.01085	.0000967	5.490	.5	4.892	.20
6	.01107	979	5.496	.7	4.889	.26
7	.01164	.0001004	5.483	.4	4.903	.03
8	.01176	1006	5.483	.4	4.916	.28
9	.01193	1016	5.458	.8	4.891	.22
10	.01339	1084	5.448	.5	4.908	.10
11	.01415	1109	5.448	.4	4.921	.42
12	.01868	1281	5.349	.5	4.900	.03
13	.02613	1521	5.293	.5	4.910	.17
14	.03337	1730	5.257	.5	4.918	.34
15	.04265	1954	5.208	.5	4.913	.21
16	.05360	2205	5.143	.4	4.884	.36
17	.05534	2234	5.145	.5	4.885	.34
18	.06800	2481	5.143	.7	4.912	.21
19	.07270	2562	5.139	.5	4.913	.01
20	.08843	2815	5.102	.3	4.901	.01
21	.09822	2985	5.107	.4	4.915	.27
22	.1102	3166	5.065	.4	4.884	.36
23	.1219	3344	5.042	.5	4.882	.40
24	.1224	3329	5.096	.5	4.923	.44
25	.1267	3393	5.061	.5	4.894	.15
26	.15145	3712	5.027	.5	4.880	.44
27	.1644	3876	5.050	.3	4.903	.03

Final mean $e = \mathbf{4.9016}$

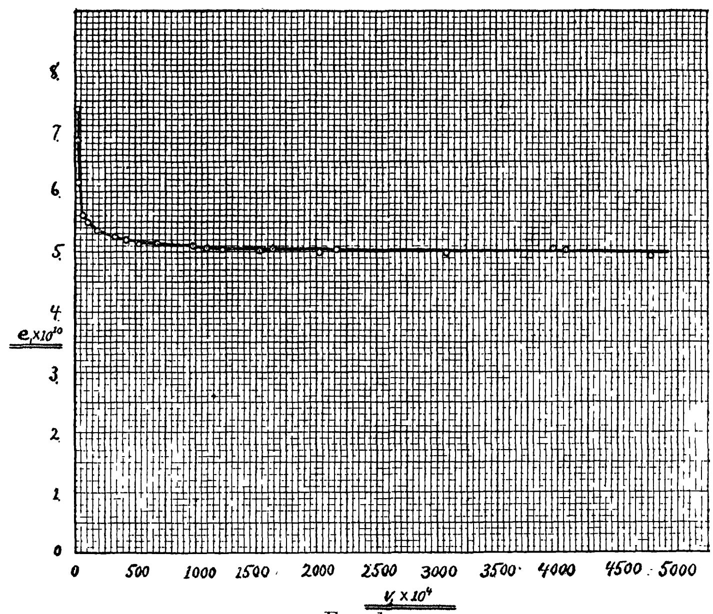

Fig. 1

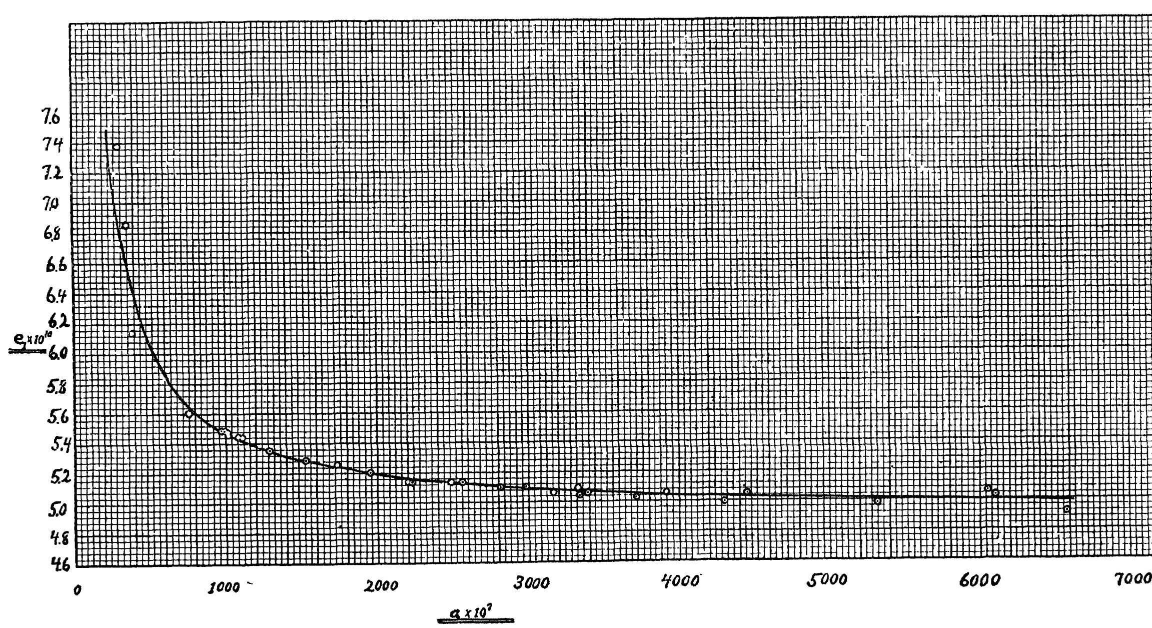

Fig. 2

but the value of e should in no way be affected thereby. It is of immense interest to know whether varying the mean free path by varying the pressure will affect the value of A in the way in which it ought according to Cunningham's theory, and we shall soon be in a position to settle this point and to make a further communication upon it.

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