ON THE MOBILITIES OF GAS IONS IN HIGH ELECTRIC FIELDS.

By Leonard B. Loeb.

I.

Introduction and Statement of Problem.

THE earliest experiments on the diffusion of the ordinary gaseous ion revealed the fact that the diffusion coefficients of the ions into a gas were about a tenth as great as the diffusion coefficients of similar uncharged molecules into the same gas. This low diffusion coefficient also manifests itself in the comparatively low order of magnitude of the values of the mobilities of the gaseous ions (*i. e.*, the comparatively low velocities of the ions in unit electric field). An attempted explanation of this was made as early as 1897[23] through the assumption that the ions were not single charged molecules, but rather groups of molecules clustered around an electron or a positive atomion. One of the early mathematical derivations of the "cluster" theory was due to Langevin[1] and estimated that the cluster consisted of about ten molecules. An attempt was made in 1909 by Wellisch,[2] and also by Sutherland,[3] to account for the low mobilities of the ions by assuming that they consisted of single charged molecules. The lowering of the mobility coefficients was on this view ascribed to a retardation of the ion in its path through the gas in virtue of its charge. The charge on the ion would cause it to exert attractive forces on the uncharged gas molecules. Thus the ion in traversing unit distance through the gas would encounter more collisions with the gas molecules than would an uncharged molecule. The retardation of this "small ion" in its path through the gas due to the charge would be equivalent to that caused by the increase in the size of the ion assumed by the "cluster" theory. Both the "cluster" and the "small ion" theories explain a number of phenomena exhibited by the ions about equally well. There are however radical differences between the consequences of the two theories which should, if investigated experimentally, lead to the adoption of one to the exclusion of the other.

On the assumption of a "cluster" ion we should expect, under circumstances where the cluster acquires a high kinetic energy, that it might suffer disintegration upon impact. Such a disintegration, or breaking up of ions, would obviously manifest itself by an abnormal increase of the mobility. The kinetic energy might be gained by the ion if it fell through a sufficiently high potential difference in traversing a mean free path. The value of the kinetic energy at which the disintegration should occur would depend on the potential energy of the ion cluster. The breaking up, or the abnormal increase in mobility of the ion cluster, should take place at approximately the same value of field strength times mean free path for both the positive and the negative ion clusters.

The "small ion" theory would naturally not lead one to expect any such result. The mobility of the ions should remain approximately constant with possibly only slight variations in its value until fields were reached near which ionization by collision could take place. In fields of such strength it is conceivable that the negative ion might acquire sufficient energy to knock off its electron. The positive ion would undergo no such change, retaining an approximately constant mobility.

This predicted difference in the behavior of the positive ion, from the standpoint of the two theories, would enable one to distinguish definitely between them, were the actual behavior of the positive ion known. If the positive ion were conclusively shown to acquire an abnormally high mobility in fields in which it would experience high values of the product of field strength times the mean free path, the "cluster" theory would be established. The proof, however, would not be so certain, were such an abnormality discovered in the case of the negative ion: For this abnormality might be interpreted in the light of the "small ion" theory as being due to the fact that under certain circumstances the highly mobile negative electron existed in a free state, *i. e.*, unattached to a molecule. Consequently experiments which could lead to a determination of the mobility of the positive ion under such circumstances are absolutely necessary to distinguish between these two theories.

Attempts in this general direction were made by numerous observers (Kovarick,[4] Lattey,[5] Todd,[6, 7] Townsend[8]). For reasons which will become obvious later, most of their work was done by allowing the ions to acquire kinetic energy by falling through long mean free paths at comparatively low potentials. In other words, these experimenters worked with small electric fields, at low gas pressures. The positive ions showed abnormal mobilities only in the results of Todd,[6, 7] who worked at extremely low pressures. To the writer's knowledge it is only in the study of the discharge of electricity from points that an attempt has been made to estimate the mobilities of the ions under conditions in which they were subjected to high fields at high pressures. Chattock,[9] in fields estimated as high as 3,000 volts per cm., found perfectly normal values of the mobility for both ions by this method. Franck,[10, 18] Moore,[22] and others, using this method in fields of about 10,000 volts per cm., found the mobilities of both ions to be abnormally high. Not much confidence should be placed on these results as a means of differentiation between the two theories, for the results of the various observers do not agree. Furthermore, the field strength at which these mobilities were determined can merely be guessed at, for the nature of the field is absolutely unknown.

Since no work has been done in this field before, and since it offered possibilities of investigating the mobilities of the positive and negative ions under conditions which might lead to a differentiation between the two theories, it was considered of interest to determine the mobilities under high electric fields at higher pressures. Accordingly, at the suggestion of Professor Millikan, this problem was undertaken by the writer.

II.

Modes of Attack Attempted in This Work.

The method of measurement decided upon as being the most suitable for these purposes was the Franck[10, 19] modification of the Rutherford[17] alternating current method. Even with this comparatively simple method the problem becomes one of considerable technical difficulty. Since the velocity of the ion varies directly with the field strength, the velocity of the ion will be high. In order to be able to catch the ions between the gauze and the plate when the distance between them is small enough so that the field between them is approximately uniform, the period over which the accelerating field acts on the ions must be very short. In other words, the frequency of the alternations must be very high. The problem is then to obtain an alternating potential difference whose value is high, and whose frequency of alternation is great enough to enable small plate distances to be used. The difficulties of this task were the chief factor which limited the determinations of the other observers to low fields and low pressures.

The first attempt was made to obtain such an alternating potential difference by means of a commutator scheme. For this purpose a commutator was built of ebonite 25.5 cm. in diameter with 20 brass segments, 2.6 cm. long. It was fastened to the shaft of a well balanced motor which was capable of giving a speed of 2,200 revolutions per minute. The potential difference was obtained from a bank of small lead storage cells. Work with this apparatus was carried on for about four months in the winter of 1914. Field strengths up to 1,000 volts per cm. were worked with. With the maximum frequency of alternation obtainable, these fields of 1,000 volts per cm. formed the upper limit of fields that could be handled with any degree of certainty. Furthermore, at the potential difference of 2,000 volts which were necessary to give these field strengths, serious sparking around the commutator occurred. This sparking finally became so bad that the brushes used burnt out several times during a three-hour determination, and this commutator was discarded. The results indicated no marked increase in the mobility of either ion. As this was near the limit of frequency of alternation which could be obtained at these potentials by any commutator scheme obtainable at the Ryerson laboratory, the commutator method was abandoned.

Through the courtesy of Director Stratton of the Bureau of Standards, for which the writer wishes to express his gratitude, an attempt was made during the summer of 1913 to utilize the high frequency sine wave generator belonging to the Bureau. The generator has a range of frequencies extending from 10,000 to 100,000 cycles per second. The potential delivered by it was approximately 100 volts at 30,000 cycles. The high voltage then had to be obtained by tuning a resonance circuit containing capacity and inductance to resonance with the generator. In this manner 4,000 volts were obtained at 30,000 cycles. This frequency, however, was too high for these experiments with the potentials obtainable. Accordingly, after a trial this method was also abandoned.

It was finally decided to attempt to utilize the resonance circuit of the Chaffee[11] Arc for obtaining the high frequency oscillation. This arc gives a nearly undamped sine wave and is quite simple to operate. The principle upon which the arc operates is described in detail in Professor Chaffee's original paper. It is an arc between copper and aluminum terminals in an atmosphere of hydrogen. The arc is operated in parallel with a condenser across a direct-current power main giving a potential difference of 530 volts. The discharge of the condenser across this arc results in unidirectional current surges through a primary coupling coil in series with the arc. The frequency of the surges is primarily determined by the capacity of the condenser and the current supply. This surge, acting upon the coupling coil of a secondary circuit, sets the latter into oscillation in its own period, as demanded by the nature of the constants of the secondary circuit. If the two circuits are tuned so that the primary discharge occurs regularly just in time to add its impulse to an oscillation of the secondary circuit in the proper phase to reinforce it, the resulting oscillations in the secondary circuit consist of a practically undamped train of waves. In practice, the discharges of the primary are generally so arranged that they occur once for every three or four oscillations in the secondary. The effect of the secondary on the primary when they are in tune is in the nature of a trigger action tending to make the impulses come at the proper time.

III.

Method of Obtaining High Fields at High Frequencies.

The frequency desired in the arc circuit was in the neighborhood of 5,000 cycles per second with a potential of from 5,000 to 10,000 volts. The circuit perfected for this purpose is represented in Fig. 1. Because the energy output of the arc is small, and because as little damping as possible was desired, special precautions had to be taken to reduce dielectric absorption and resistance in the secondary circuit. R in the figure was a variable lamp bank resistance placed in the direct-current circuit. With it the current could be varied almost continuously from .2 to 2.5 amperes. C_1 is the primary discharge condenser, the magnitude of whose capacity regulated the frequency of the discharge through the arc. In this work it consisted of two 1 microfarad Western Electric telephone condensers, insulated to stand 1,000 volts alternating potential. L_1 was the primary of a small coupling coil wound with the wires of the primary and secondary in parallel. It was approximately 70 cm. long, 20 cm. in diameter, and had 110 turns of wire. The secondary of this coil is designated by L_2 in the diagram. L_2' consisted of a single large coil of 97 turns of No. 8 hard-drawn copper wire, wound on a hexagonal frame 95 cm. in diameter and 74 cm. long. The insulation on L_2' was ebonite throughout. The inductance of L_2 and L_2' together amounted very closely to 8×10^6 cm. C_2, the secondary condenser, was an air condenser having 150 galvanized iron plates 38 by 38 cm. square, each separated by about 3 mm. of air. The capacity of the condenser on measurement turned out to be 0.0863 microfarad. L_3 consisted of three large coils wound on dry sugar barrels covered with paraffined paper. In the winding No. 18 double cotton-covered wire was used. The coils when wound were thoroughly saturated with molten paraffine. The dimensions are given below. These were connected in series, end for end, and loosely coupled to the large secondary coil L_2'.

Coil.	Length.	Mean Diam.	No. Turns per Cm.
1............	53 cm.	51 cm.	5.6 No. 16 wire.
2............	54 cm.	53 cm.	8.0 No. 18 wire.
3............	65 cm.	56 cm.	7.5 No. 18 wire.

The capacity of the tertiary condenser C_3 was .0042 microfarad and consisted of two "Navy" jars in parallel. The capacity of the tertiary circuit also included the distributed capacity of the large coils, the capacity of a Braun electrostatic voltmeter, the capacity of a small variable tuning condenser, and the capacity of the ionization chamber. The tuning was accomplished by varying the current in the primary arc circuit, by varying the primary condenser, and by varying the inductance picked off the secondary inductance coil. The frequency of alternation used was found to be 7,666 cycles per second when the ionization chamber was in the circuit.

The frequency of the alternating potential was determined by photographing the image of the spark in a revolving mirror. The speed of the mirror was varied from 2.5 to 10 revolutions per second. Two different cameras were used, one being a camera with a Cooke anastigmat. lens, $f = 3.5$. The distance between the sparks was determined by photographing a 10 cm. steel scale in the spark gap on the same plate with the sparks. The distance between the mirror and gap was varied from 158 cm. to 212 cm. and the distance between the camera and the mirror was also varied. The mean of fifteen different plates gave the frequency as being 7,666 cycles per second.

The potential was read on a Braun static voltmeter while the determinations were being made. The potentials varied from 4,150 volts to 4,650 volts. The voltmeter had a range of 10,000 volts, so that the readings were taken right at the center of the scale where they were most accurate. The voltmeter was calibrated.

IV.

Apparatus and Mobility Measurements.

The apparatus used in the mobility determinations was essentially the same as that of other observers who used this method. It had, however, some slight changes that were necessitated by the fact that neither the potential nor the frequency of the alternating potential could be varied through sufficiently wide limits. The determinations were accordingly made by varying the distance between the gauze and the plates, keeping the potential and frequency constant. The essential features of the apparatus, as well as the dimensions, are included in the diagram, Fig. 1. The ions were generated by means of a film of ionium on the brass plate I fastened beneath the gauze. The gauze was mounted on ring G, which was supported by a tripod set in a well-paraffined wooden block. Above the gauze the collecting plate K, surrounded by an earthed guard ring E was suspended parallel to it from an insulated brass tube set in the supporting disc, P. The plate could be raised or lowered by means of a nut, N, which rotating against the collar C, engaged with a thread in the vertical rod of the collecting plate. To facilitate the lowering of the plate, a spiral steel spring S was fastened to the lower part of the collar and to the shoulder of the collecting plate. This pressed the nut firmly against the top of the collar. The pitch of the thread allowed the plate to be moved half a mm. for each complete turn of the nut. A bell-jar silvered inside covered the whole apparatus, making a close contact with the flat iron disc which served as a base. Through two amber plugs in the base, the wires to the accelerating fields were led in. The lower plate F of the accelerating field was placed three cm. below the gauze, and parallel to it. To enable the nut to be rotated with the bell-jar over it, a steel tube was set into the neck of the bell-jar. This had a hole in the center into which was ground a brass plug. At the lower end of the latter a prong projected that engaged with an amber cylinder projecting from the side of the nut N. The brass plug A could be rotated by means of a handle from the outside. Contact between the electrometer lead and collecting plate was made through an amber tube set in the brass plug A by means of a fine steel wire. This wire projected into a deep mercury cup drilled out of the center of the rod of the collecting plate. On top of the disc P were placed several small cups containing P_2O_5, which were carefully grounded. The orifice O in the base allowed the air to be withdrawn. All air that was admitted to the apparatus passed through a long drying train containing P_2O_5, H_2SO_4, and $CaCl_2$. The lead wires from the chamber went to a small ebonite commutator Z carefully insulated on paraffine. On the same base with the commutator were three small "flash light" batteries B' which gave a potential of 9 volts, and furnished an accelerating field for the ions of 3 volts per cm. The quadrant electrometer Y used in this work had a fine quartz suspension, and a sensibility of 1,500 mm. per volt.

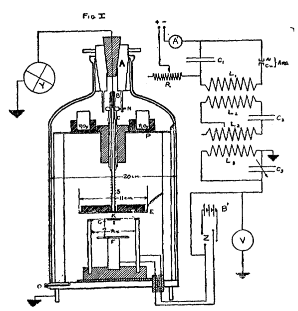

Fig. 1.

In making a determination the potential and the frequency of the alternating current were kept constant, and the distance between the plates was varied. The deflections of the electrometer corresponding to readings taken at various distances between the gauze and the plate were recorded. The deflections were due to the ions which had accumulated on the upper or collecting plate during the interval in which the alternating potential was allowed to act on the ions. This period of collection varied for various determinations being usually about 15 or 30 seconds. If all the ions had a constant mobility, the theory would lead us to expect, on plotting these results with the deflections as ordinates and the distances as abscissae, that we should get a curve parallel to the X axis until the critical distance is reached which the ions are just able to traverse in the time of one half alternation of the field. At this

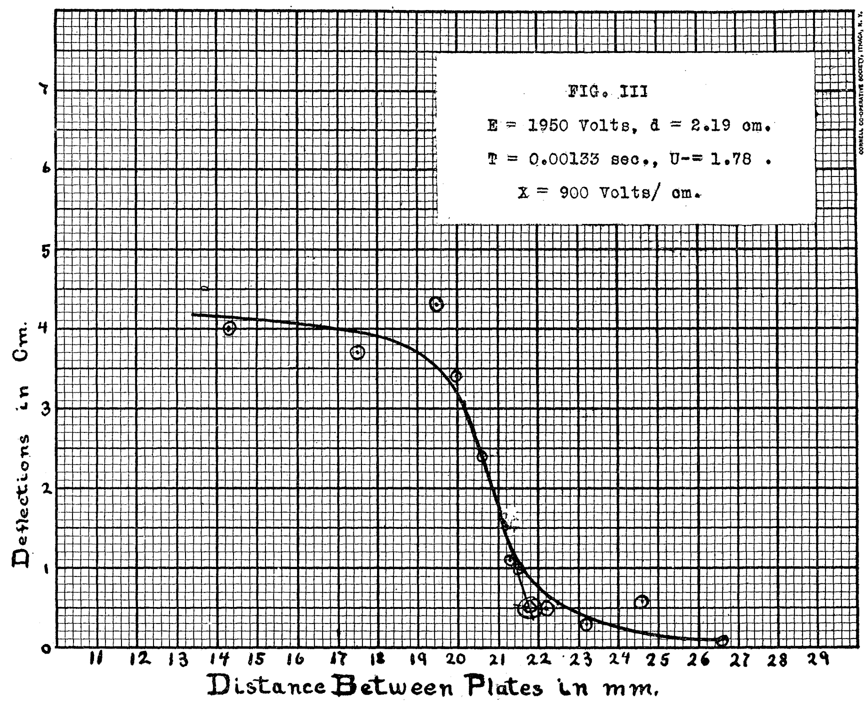

Fig. 3.

point the curve should drop abruptly to O parallel to the Y axis. In practice this is never actually the case, since first, the ions do not all start from exactly the same point in the meshes of the gauze. Further, the plate and the gauze are never exactly parallel. With the changing distance between the plates the distortion of the field due to outside influences might also change the value of the field strength. Finally, in plotting the deflections for the same time of charging of the plate, the assumption is made that the capacity of the electrometer and the collecting system is constant. This is actually not the case, for the capacity varies slightly with the distance between the gauze and plate. Thus, the deflections observed are not quite strictly proportional to the number of the ions. All these factors round off the corners of the curves and cause the otherwise vertical line to be inclined at a slight angle with the vertical. A typical curve for one of the determinations for the commutator work is given in Fig. 3. The intercept of the curve with the X axis was chosen as the critical distance. This gives the

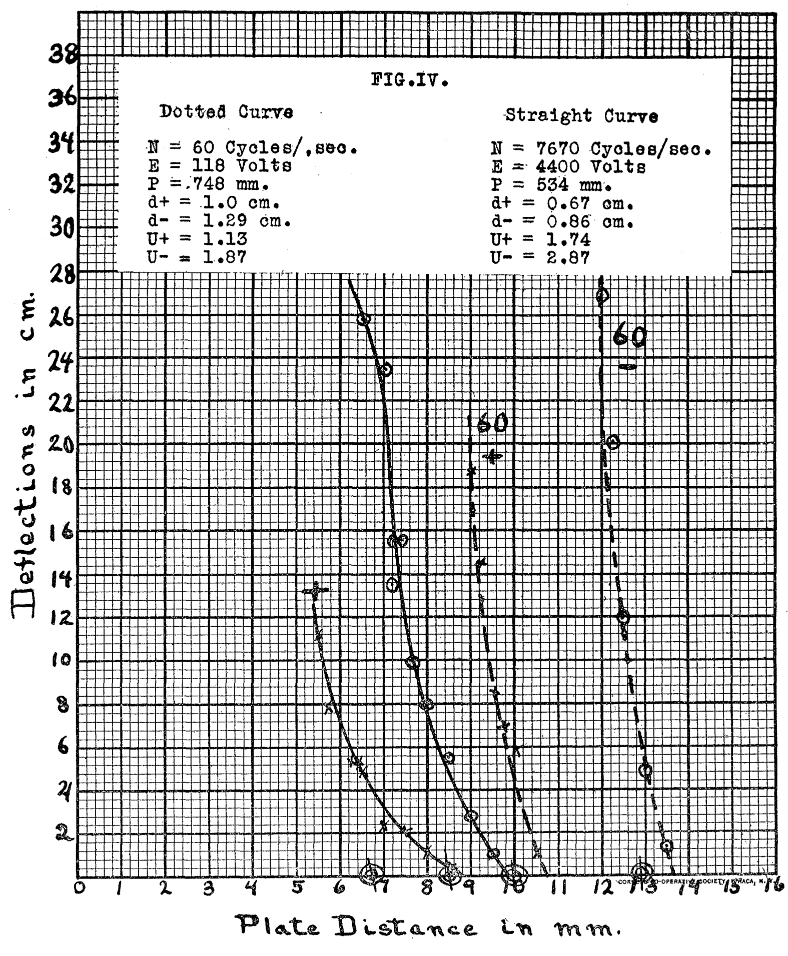

Fig. 4.

critical distance traversed by the ions that have been subjected to the most intense field, and which have come from the nearest point of the gauze. A typical set of curves for the determinations using the arc as a source of alternating potential, are given in Fig. 4. One pair was taken at the high potential with the high frequency alternating current, and correspond to the deflections of the positive and negative ions. The curves marked 60 correspond to determinations on the positive and negative ions using the 120-volt 60-cycle city power alternating current. The only difference between these curves and the curves taken with the commutator is that the former show only the vertical element of the curve. This is due to the fact that in the work with the arc a greater sensitiveness was attained through the use of a more sensitive detecting instrument, and through the use of coarser gauze (10 meshes to the cm.). The time of collection of the ions with the arc was 15 seconds. The increased sensitiveness also caused the increase in prominence of the tails of the curves in these measurements.

V.

Sources of Error.

The errors to which these measurements are subject may be classified under three heads. The first class may be designated as instrumental errors, which are due to the form of the ionization chamber. To this class belongs the lack of parallelism between the plate and the gauze, with its attendant distortion of the field, as well as the distortion of the field due to outside influences. The effects of these were, however, shown to be practically negligible in these determinations for reasons to be given later.

The distances between the plate and the gauze were measured by means of a cathetometer which gave them with an accuracy of 0.1 mm. This was more accurate than the determination of the critical distances from the curves, which could only be obtained within 0.3 mm. This amount of uncertainty was due to the tailing off of the curves near the X axis. In determining the critical distances from the curves these tails were ignored, the intercept being taken as the point where the continuation of the straight, downward part of the curve intercepted the axis of abscissae. To preclude the possibility of the existence of serious errors of the first class in the measurements of the mobilities, check determinations were made with the chamber using the 60-cycle 120-volt alternating potential from the city power mains. The mobilities thus obtained were found to be strictly normal, their values lying close to the mean of the best determinations by other observers, thus showing these uncertainties to be negligible.

The second class of errors is due to inaccuracies entering into the values of various constants of the alternating potential. The frequency of the oscillations was determined as previously described, with an accuracy of two per cent. either way.

A second source of uncertainty of this class lay in the fact that the form factor of the alternating current from the arc was not determined. The mobilities were computed on the assumption that the alternating potential had the form of an undamped sine wave. The Chaffee arc is supposed to give such a wave. However, there exists the possibility of the presence of higher harmonics. These might change the form of the wave which would necessitate an alteration in the constant factor $\pi/\sqrt{2}$ in the mobility equation. This alteration for the extreme case of the transition from a sine wave of frequency N, to a square wave of the same frequency, measuring the potential with a static voltmeter, might lower the factor above by as much as ten per cent.

Possibly the greatest source of inaccuracy in the second class might arise through the variation of the potential given by the arc. This fluctuated nearly continually between the values 4,150 volts and 4,650 volts, as indicated by the static voltmeter. Each point of the curves between plate distance and deflection corresponds to a mean of from five to ten separate readings taken over an interval of 15 minutes. The curves through the points plotted were drawn so as to be as near the mean as possible. Consequently, the intercept of the curve with the axis of abscissæ, which determined the critical distance, corresponds to a potential difference which was very near the mean of 4,400 volts.

The last class of errors are those due to the improper drying of the air used in the determinations. The effect of careful drying was distinctly noticeable, and was in all probability the greatest cause of variation of the experimental results recorded. In the first experiments with the arc circuit the air was not carefully dried, the air being passed through only a short drying train. The later determinations were made on air that had passed through a long drying train containing $CaCl_2$, H_2SO_4, and P_2O_5. In some of the later determinations notably those at about 430 mm. pressure (see Table II.), the air had stood over P_2O_5 for several days before being used. In general it may be stated that the lower values of the mobilities recorded in the table, pertain to measurements made with imperfect drying.

VI.

RESULTS.

The results obtained by the commutator method are given in Table I.

In the first column are the frequencies of alternation; in the second are the critical distances. In the third and fourth columns the mobilities of the positive and the negative ions are calculated from the formula $U = d^2N/V$; in which d = critical distance, N = frequency of alternation in one half cycles per second, V = potential. The last column gives the values of the field strengths at the critical distances in volts per

TABLE I.

Ionic Mobilities Obtained with the Commutator, Winter 1914.

N.	*d.*	*U+.*	*U—.*	*X.*
60	1.12	1.38		96.0
428	0.86	1.45		257.0
747	0.87	1.26		514.0
625	1.42	1.39		698.0
740	1.82	1.50		990.0
60	1.26		1.780	94.0
650	1.56		1.795	618.0
706	2.12		1.960	720.0
725	2.17		1.880	900.0

cm. The pressures were in all cases the atmospheric pressures at the time the measurements were taken. No precautions as to drying the air were taken in these early commutator experiments.

The results show that for fields ranging from 90 volts per cm. to 900 volts per cm. there is no certain abnormal increase of the mobility of either ion. Further, it should be noted that in these determinations there is no tendency for the negative ion to increase its mobility relative to the positive ion, as would be expected should the negative ion begin to break up at the highest potential used.

The results obtained with the arc are tabulated in Table II.

TABLE II.

Ionic Mobilities Obtained with Chaffee Arc, Winter 1916.

N.	*d+.*	*d—.*	*u+.*	*u—.*	*P.*	*U+.*	*U—.*	*X+.*	*X—.*
60	0.99	1.38	1.10	2.12	760 mm.	1.10	2.12	121	87
60	1.00	1.26	1.13	1.78	756 mm.	1.12	1.76	120	96
60[1]	1.00	1.28	1.13	1.85	748 mm.	1.12	1.84	118	93
60	1.33	1.56	1.95	2.70	578 mm.	1.48	2.05	91	77
		Mean mobilities at			760 mm.	1.21	1.94		
7,670	0.50		0.97		750 mm.	0.98		12,450	
7,670	0.55	0.64	1.17	1.59	746 mm.	1.19	1.62	11,450	9,750
7,670	0.54	0.61	1.07	1.37	747 mm.	1.09	1.40	11,550	10,000
7,670	0.50	0.65	1.25	1.80	735 mm.	1.28	1.86	12,450	9,600
7,670	0.66	0.84	1.70	2.74	534 mm.	1.27	1.95	9,580	7,430
7,670[1]	0.78	1.02	2.36	4.04	436 mm.	1.36	2.32	8,000	6,000
7,670[1]	0.85	1.01	2.72	3.88	430 mm.	1.54	2.18	7,346	6,160
7,670	0.82	1.10	2.58	4.29	416 mm.	1.41	2.29	7,610	5,670
7,670	0.85	0.90	2.67	3.07	384 mm.	1.35	1.53	7,340	6,910
7,670	0.80	0.86	2.51	2.90	382 mm.	1.26	1.46	7,800	7,260
7,670[2]	1.11	1.22	4.78	5.80	304 mm.	1.96	2.32	5,610	5,160
		Mean mobilities at 760 mm.				1.33	1.89		

[1] These readings were taken with very dry air.

[2] The value of the positive mobility only estimated here, not determined.

The determinations of the positive and negative mobilities were made simultaneously by changing the commutator of the accelerating field. In the first column are the frequencies of alternation. In the second, the critical distances, and in the fourth, the pressures in mm. of mercury are given. The third column contains the mobilities of the ions as calculated from the formula for a sine wave alternating current, *i. e.*, $U = \pi Nd^2/\sqrt{2}E$, where E is the potential given by the electrostatic voltmeter, N the frequency, and d the critical distance. The fifth column contains the mobilities of both ions reduced to 760 mm. pressure. In the last column the field strengths under which the determination was made, are given in volts per cm. for the maximum value of the alternating field.

The range of pressures worked with extended from 750 mm. to 300 mm. of mercury. The work could not be carried to higher field strengths at this frequency with the arc, for at a distance of about 4 mm. at atmospheric pressure occasional sparking began between the plates. The potential difference between the plate and the gauze as registered by the electrostatic voltmeter was but 4,400 volts, when sparking began at a distance of 4 mm. According to all results obtained on the sparking potentials at atmospheric pressure by the various observers, the potential difference which a static voltmeter would read, when sparking took place at 4 mm., should, with the alternating potentials, be about 10,000 volts. This sparking was therefore in all probability due to occasional momentary irregularities in the operation of the arc, which would allow the potential to reach a value as high as 10,000 volts. This effect would not invalidate the mobility determinations, for the number of ions driven to the plate through such an occasional irregularity would not be great enough to sensibly affect the electrometer. They might, however, possibly augment the tails of the curves. This sparking limited the pressures to which the experiments could be pushed for the following reason: The point where the positive ions could just be detected was just 1.5 mm. away from this sparking point, *i. e.*, at about 5.5 or so mm. Now the distance over which a spark will pass varies inversely with the pressure, voltage being constant. The distance at which the ions can just be detected varies as the square root of the mobility. But the mobility varies inversely as the pressure, and, therefore, the distance at which the ions may just be detected varies inversely as the square root of the pressure. The result is that the pressure was not far distant, with the frequency used, at which the sparking began to encroach on the distance at which the ions might be detected. This occurred at about 300 mm., the mobilities of the positive ions measured at this pressure being quite unreliable due to the sparking. The mean of the determinations are 1.33 for the positive ions and 1.89 for the negative ions. The field strengths corresponding to the maximum value of the potentials used range from 12,450 volts per cm. down to 5,160 volts per cm. They all agree in showing that *neither the mobility of the positive nor of the negative ion shows any tendency to abnormal increase* for the pressures and field strengths worked with. Further, it can be seen that the *negative ion shows no tendency to increase in mobility over the positive ion*, as it should do, did it start to break up.

VII.

Discussion of Results.

The results on the positive ions obtained in high fields at high pressures in air seem on the basis of the "cluster" theory to be in direct contradiction with the results of Todd[6, 7] who worked with positive ions at very low pressures and low voltages. The "cluster" theory demands that for a sufficiently high value of the product, mean free path times field strength, the positive ion should show an abnormal increase in mobility. This apparently occurred in the case of Todd's experiments at a value of $X/p = 2.6$, where for the sake of convenience we represent the value of field strength times mean free path by the ratio of X/p to which it is proportional, letting X be the field strengths in volts per cm. and p the pressure in mm. of mercury. The writer worked on positive ions with pressures as low as 300 mm. and with ratios of $X/p = 18.0$ and yet found no abnormal increase in the mobilities. This means that with these values of X/p, ranging from 0.1 to 18.0, the cluster, if it exists, shows no tendency whatever to break up. Beyond the range of these experiments, which was limited by the irregularities in the operation of the arc, the ion cluster might conceivably break up.[1] The range of X/p where this might occur extends from $X/p = 18.0$ to $X/p = 39.6$. At the latter point sparking occurs between parallel plates at a pressure of 760 mm. Ionization by collision must take place somewhere between these limits. The exact point where this occurs for the positive ions has not been determined to the best of the writer's knowledge. Since it is obvious that the positive ion cluster must begin to disintegrate before the value of ionization by collision by positive ions can occur, it is also obvious that the values of X/p worked with are close to the threshold of the value where the ions must begin to disintegrate, if they disintegrate at all. One may consequently assert that at atmospheric pressures in air the ions show no tendency to abnormal mobilities in fields which should be great enough to cause a cluster ion to break up. This con-

[1] The premature sparking is presumably not to be attributed to the behavior of the ions, since the irregularities in the operation of the arc are entirely sufficient to explain this action.

clusion is in excellent accord with the recent results of Wellisch[13, 14] obtained on the mobilities of positive ions at very low pressures, *i. e.*, 0.05 mm., with low potentials. He found that at values of X/p as high as 34.5 and higher, the mobility of the positive ions was constant, and very nearly equal to that found by all observers at high pressures. This value of X/p was very nearly equal to that causing ionization by collision to begin for the negative ions at those pressures, according to Townsend's data.

The results of the writer on the negative ions taken at high pressures and with high fields appear at first sight to be at variance with the results of the observations at low pressures. On the basis of the results at low pressures and the cluster theory Townsend[12] in his recent book (Electricity in Gases), comes to the conclusion that the breaking up of the negative cluster takes place at values of $X/p = 0.1$. He further asserts on the basis of some results of Lattey[5] that this break-up point for lower pressures at least is a function of X/p. It is true that the apparent break-up point in the results of most observers at pressures below 10 cm. of mercury does occur at a value of X/p about equal to 0.1. However, such a break-up point is not in any sense a function of X/p alone. This became at once evident to the writer when, in view of his results, he worked over the data of Kovarick[4] on the breaking up of negative ions at low pressures. The break-up point was found to be more nearly a function of p alone than of X/p. This may be seen from Table III., which gives the values of X/p of some observers, and the results obtained by them as regards the mobilities of the ions.

Table III.

Observer.	X/p.	Pressure.	Mobility.
Lattey[5]	.06	28.0 mm.	Abnormal − ion.
Kovarick[4]	.15	510.0 mm.	Normal − ion.
Kovarick[4]	.053	11.4 mm.	Abnormal − ion.
Todd[6]	2.6	.79 mm.	Abnormal + ion.
Writer	.128	750.0 mm.	Normal − and + ions.
Writer	1.2	750.0 mm.	Normal − and + ions.
Chattock[9]	4.0	760.0 mm.	Normal − and + ions.
Writer	13.0	746.0 mm.	Normal − ions.
Frank[10, 18]	13.0	760.0 mm.	Abnormal − and + ions.
Writer	16.6	750.0 mm.	Normal + ions.
Writer	17.0	304.0 mm.	Normal − ions.
Writer	18.3	304.0 mm.	Normal + ions.
Wellisch[13]	34.6	.87 mm.	Normal + and − ions.
Townsend[12]	38.0	4.1 mm.	Beginning of ionization
Bishop[15]	40.0	100.0 mm.	by collision.
	39.5	760.0 mm.	Sparking potential in air.

Besides the values of X/p and the names of the observers, the pressures in mm. of mercury are given at which the determinations were made. The table also includes the values of X/p for ionization by collision, and for sparking at atmospheric pressure. The conclusions of Townsend are further shown to be at variance with the results of the writer who determined the negative mobilities at pressures as low as 300 mm. and at values of X/p as high as 17 without finding the least indication of an abnormal increase in the absolute value of the mobility of the negative ion. Even if these results as to the absolute values of the mobilities were quite inaccurate, the fact that the negative ions show no increase in mobility relative to the positive ions would indicate the absence of the disintegration of a negative cluster. One must conclude that the apparent breaking up of a negative cluster observed at the low pressures by the other observers is in reality not a breaking up of the cluster at all, for it does not obey the laws which such a breaking up should obey. The explanation of the abnormally high mobilities at low pressures must then be looked for elsewhere. It was stated in the introduction that it is conceivable that the very mobile negative electron might under certain circumstances exist in a free state and enter into the determinations of the mobilities. That this actually occurs at very low pressures has been shown by Townsend and Tizard.[20] If the free electron exists at intermediate pressures, the following statements may be made concerning it. It did not appear in appreciable numbers in the results of the writer at the pressures with which he worked. Further, it must be concluded that the appearance of the free electron is not primarily a function of X/p. Finally, its appearance seems to depend on the pressure alone. The pressure where it appears in a gas might also depend on the chemical nature of the gas. The existence of free negative electrons was ascertained for the pure gases, helium by Franck[20, 18] and nitrogen and hydrogen by Haines,[16] at atmospheric pressure. Wellisch[13] found that for air the free electrons make their appearance below 8 cm. of mercury in quantities great enough to detect. The conclusions stated above again agree in a striking manner with those arrived at by Wellisch from his experiments on the mobilities at very low pressures, and low potentials. Besides the free negative electrons which he detected at the lower pressures, Wellisch found perfectly normal negative ions down to pressures as low as 0.15 mm. mercury. These negative ions had mobilities strictly inversely proportional to the pressure, even though the value of X/p was as high as 34.5. He found that as the pressure was reduced, the relative number of the free electrons to the normal ions increased. No ions of intermediate mobility were detected. The apparent increase of the mobility of the negative ions at pressures of about 10 cm. and below observed by most workers may therefore be ascribed to the fact that their methods were not sensitive enough to detect the free electrons as such. They thus obtained as mobilities a sort of fictitious mean mobility between the mobilities of the normal negative ions and the free electrons. These fictitious mobilities increased with decreasing pressure due to the greater proportion of free electrons present.

The results obtained by the writer on the mobilities of the positive and the negative gas ions at atmospheric pressures with high fields, lead to the conclusion that over a considerable range of field strengths the ions in air at high pressures show no tendency to break up. Considering the extent of the range worked with, and also considering the results of Wellisch over an equally great field at low pressures and low potentials, with which these results are in excellent agreement, one is forced to question the validity in the "cluster" theory, which until now has been that most generaly accepted.

In conclusion the writer wishes to express his great appreciation for the advice and encouragement given him by Professor R. A. Millikan, at whose suggestion the problem was undertaken. The writer's thanks are due to Professor E. Leon Chaffee for his kind suggestions concerning the operation of the arc, and to Mr. Kia Lok Yen for his valuable assistance in surmounting the considerable technical difficulties encountered in the latter part of the work.

Summary.

1. Utilizing the resonance circuit of the Chaffee arc as a source of alternating potential difference, and utilizing the Rutherford alternating current method of measuring mobilities, the mobilities of the positive ion were measured in fields nearly powerful enough to cause ionization by collision in air at atmospheric pressure. The mobilities were found to be perfectly normal within the limits of experimental error.

2. The mobilities of the negative ions were measured under the same conditions. No change in the absolute value of the mobilities of the negative ions could be detected, nor could any change in the mobilities of the negative ions relative to the positive ions be detected.

3. The results are in agreement with the recent results of Wellisch obtained at low field strengths and very low pressures, in leading one to the conclusion that the "cluster" theory of the ion is no longer tenable.

REFERENCES.

1. M. Langevin. Thesis, 1902.
2. E. M. Wellisch. Trans. Roy. Soc., *A*, 209, 1909.
3. W. Sutherland. Phil. Mag., 18, 341, 1909.
4. A. F. Kovarick. PHYS. REV., 30, 415, 1910.
5. R. F. Lattey. Proc. Roy. Soc., *A*, 84, 1910.
6. Todd. Phil. Mag., Ser. 6, Vol. 22, p. 791, 1911.
7. Todd. Phil. Mag., June, 1913.
8. J. S. Townsend. Proc. Roy. Soc., *A*, 85, 1911.
9. Chattock. Phil. Mag., 48, 401, 1899.
10. J. Franck. Ann. der Physik., 21, 972, 1906.
11. E. L. Chaffee. Proc. Am. Acad. Arts & Sc., Nov., 1911.
12. J. S. Townsend. Electricity in Gases, Oxford, 1914.
13. E. M. Wellisch. Am. Jour. Science, May, 1915.
14. E. M. Wellisch. Phil. Mag., March, 1916.
15. Bishop. PHYS. REV., December, 1911.
16. Haines. Phil. Mag., November, 1915.
17. Rutherford. Proc. Camb. Phil. Soc., IX., 1898.
18. Franck. Jahrb. d. Rad. u. Elect., IX., No. 2, May, 1912.
19. Franck and Pohl. Verh. d. Deutsch. Phys. Ges., 9, 69, 1907.
20. Townsend and Tizard. Proc. Roy. Soc., *A*, 87, 1912; *A*, 88, 1913.
21. Franck. Ver. d. Deutsch. Phys. Ges., 12, 1910.
22. Moore. PHYS. REV., 1912.
23. Rutherford. Radioactive Substances and their Radiations, p. 56.