THE DISTRIBUTION OF MOBILITIES OF IONS IN MOIST AIR*

By John Zeleny
Sloane Physics Laboratory, Yale University

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Abstract

A search was made in undried air for groups of ions having different mobilities and no such distinct groups were found among ions two or more seconds after their formation. A critical study was made of the effects of diffusion upon the distribution of ions moving in an electric field. Experimental results obtained for N, the volume density of ions which after a time t are located at a distance r from the origin agree fairly well with the theoretical formula

$$N=\frac{N_0}{(4\pi Dt)^{3/2}}e^{-r^2/4Dt},$$

where D is the coefficient of diffusion. The mobilities and the spreading of the ions were measured by a modification of the author's method in which ions passing between two concentric cylinders under an electric field are simultaneously carried axially by a slow, non-turbulent current of air of known velocity. The ions entered the air stream through small openings in the walls of the outer cylinder and their distribution at the central cylinder was measured by catching them on a narrow insulated section of that cylinder which was connected to an electrometer. The ions were found to be confined to one group covering a range of mobilities in which the fastest ions have mobilities about 45 percent larger than the slowest for positive ions and about 30 percent larger for negative ions. The distribution would be explained if a number of unresolved permanent distinct groups exist, but a more probable explanation rests on the assumption that the ions are clusters which change in size under the influence of molecular bombardment, the life of each stage being sufficiently long so that the number of changes occurring during the time of passage of the ions is not very great. No certain change in the distribution was noted for changes of the time of passage of the ions between 0.05 sec. and 0.67 sec. The mobilities of the ions were determined under widely different conditions in air ranging in water content between 1.5 mg/liter and 7.6 mg/liter. Without weighting the observations, the average mobility found for the negative ions is 2.00 cm/sec·volt/cm for an average water content of 3.2 mg per liter of air, and the average for the positive ions is 1.22 cm/sec·volt/cm for an average water content of 2.7 mg per liter of air, the most probable error in each case being about one percent.

SOME observers have in recent years reported results on the mobility of ions in air which point to the existence of several distinct types of ions of each sign.

Nolan[1] using the blast method found indications in moist air of eight unique mobilities for both positive and negative ions. Later he and Harris[2] using both the blast method and the alternating field method found still

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[1] J. J. Nolan, Proc. Roy. Irish Acad. **35,** 38 (1920).

[2] J. J. Nolan and J. T. Harris, Proc. Roy. Irish Acad. **36,** 31 (1922).

more types of ions both in saturated air and in dried air. The interpretation of the observations was questioned by Blackwood[3] and Loeb[4] who in attempts to verify the results found no positive evidence of more than one unique mobility for ions of each sign. Nolan[5] repeated the observations taken with the alternating field method and obtained now about 20 groups of ions which according to a computation are progressively made up of 15 to 36 molecules each. C. T. R. Wilson[6] found by his cloud method that ions formed by an alpha-ray were separated by an electric field into four groups.

Erikson[7] discovered that the positive ion in air soon after formation has the same mobility as the negative ion but in a very short time undergoes changes so that its mobility assumes the lower value which has usually been assigned to it. No other types of ions were found. This result was verified by Wahlin[8] and by Tyndall and Grindley.[9] After aging the ions for a longer time Wahlin[10] later found six distinct types of positive ions in air.

Busse[11] interprets results he obtained by a blowing method as showing that the ions produced in air by rays from radioactive substances have mobilities spread over a wide range whose magnitude depends on the sign and age of the ions and on the humidity of the air. Laporte[12] in an extensive research by a new method involving the passage of ions between two rotating disks obtains well defined distribution curves which he also interprets as showing that the ions of each sign are not all alike but that they differ among themselves by such small steps that their mobilities appear to cover continuously a large range of values whose limits differing by more than 100 percent depend upon the sign of the ions and upon the humidity of the air.

Briggs[13] obtained a similar though less extended band of mobilities in air for recoil atoms of radioactive substances, the largest value being 50 percent larger than the smallest.

Schilling[14] using extreme precautions for getting pure air not only confirmed the large effect of traces of impurities but also showed that "aging" of ions does not occur in pure or in saturated air but only for intermediate states, when the mobilities of both kinds of ions diminish with age, between 0.05 sec. and 1.2 sec.

Mahoney[15] found only the final ions in dry or fairly dry air. These showed no change in mobility for ions of either sign for a range of age from

[3] O. Blackwood, Phys. Rev. **20,** 499 (1922).
[4] L. B. Loeb, Jour. Franklin Inst. **196,** 537 (1923).
[5] J. J. Nolan, Phys. Rev. **24,** 16 (1924).
[6] C. T. R. Wilson, Proc. Camb. Phil. Soc. **21,** 408 (1922–23).
[7] H. A. Erikson, Phys. Rev. **20,** 117 (1922).
[8] H. B. Wahlin, Phys. Rev. **20,** 267 (1922).
[9] A. M. Tyndall and G. C. Grindley, Proc. Roy. Soc. **A110,** 358 (1926).
[10] H. B. Wahlin, Phil. Mag. **49,** 566 (1925).
[11] W. Busse, Ann. d. Physik. **81,** 277 (1926).
[12] Marcel Laporte, Ann. de Physique **8,** 466 (1927).
[13] G. H. Briggs, Proc. Camb. Phil. Soc. **23,** 73 (1926).
[14] H. Schilling, Ann. d. Physik **8,** 23 (1927).
[15] J. J. Mahoney, Phys. Rev. **33,** 217 (1928).

0.001 sec. to 0.03 sec. He considers the ions of each sign all to have the same mobility. In moist air of 60 percent or 90 percent relative humidity the results of Erikson on aging of the positive ions were confirmed, only that the rate of transformation was found to be somewhat slower than that reported by Erikson.

These various results bear rather conflicting testimony on the structure of gaseous ions and in connection with them must be borne in mind the very large number of other researches on mobilities whose results have been interpreted in terms of a unique mobility for each sign of ion. It seemed highly desirable that more work be done to throw added light on the problem of the distribution of ionic mobilities under conditions where disagreement as to the facts still exists.

A blast method, although more laborious and in some respects of more restricted use than the alternating field method, was chosen for the work being reported because it has the great merit that in its use a steady state exists during the procedure of making a measurement, and this state makes a detailed analysis of results more certain. Moreover in the form used by Erikson and by Tyndall and Grindley different types of ions should indicate themselves by separate peaks in a curve, evidence which for measurements of this kind is generally regarded as more convincing than that given by "breaks" in a curve.

For measurements of the absolute mobilities of ions, and for investigations on the distribution of mobilities within an apparent group it is essential that the air streams used in the experiments be free from all turbulence. In order to eliminate the turbulent motion of the air stream which was doubtless present in researches where high velocity streams were used in tubes of rectangular cross section, I adopted as best suited for the purpose a modified form of the apparatus I used in my early mobility measurements.[16]

METHOD

In this method a steady stream of gas of known mean velocity is blown through the space between two coaxial cylinders, and the distance measured that the ions are carried down stream by the gas while they are moving the distance between the two cylinders under the influence of the radial electric field. The ions were produced in an outer chamber and introduced into the stream by means of auxiliary air jets passing through small holes in the outer cylinder. The charge carried by those which are caught on a narrow, insulated portion of the inner cylinder was measured. At any point a distance r from the common axis of the cylinders the radial velocity of the ions is given by $[kV/r \log (b/a)]$, k being the mobility of the ions, V the potential of the outer cylinder, b the inner radius of the outer cylinder, and a the outer radius of the inner cylinder. The down stream velocity of the ions at the same point due to the air stream is given by

[16] J. Zeleny, London Phil. Trans. **A195**, 193 (1900).

$$v=\frac{p}{4\mu \log (b/a)}\left[(b^2-r^2)\log\frac{r}{a}-(r^2-a^2)\log\frac{b}{r}\right],^{17} \quad (1)$$

where p is the pressure difference per unit length of the cylinders and μ is the coefficient of viscosity of the gas. The actual path of the ions is a compound curve each terminus of which is normal to one of the cylinders. (See curve A of Fig. 9.)

If U is the mean velocity of the gas stream and X is the distance the ions are carried down stream in crossing between the cylinders, the mobility

$$k=\frac{U(b^2-a^2)}{2VX}\log\frac{b}{a}\cdot \quad (2)$$

The present paper will be confined to an account of the work done on the mobility of old ions in filtered air having its normal water content. It was thought that the presence of water and carbonic acid might be propitious for the formation of ions of different types if such types exist.

Apparatus

The apparatus used is shown diagrammatically in Fig. 1 and consists of two concentric brass cylinders the outer of which is 123 cm long and has

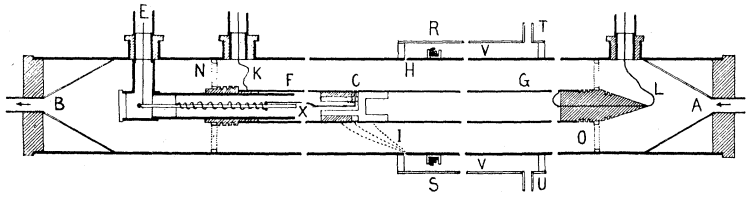

Fig. 1. Diagram of apparatus.

an inner diameter of 7.297 cm while the inner cylinder has an outer diameter of 2.538 cm. The inner cylinder is divided into three main sections, which are insulated from one another. The narrow section, C, to be called the collecting ring, is 1.5 mm wide and is separated from F (15.9 cm long) and from G (70 cm long) by air gaps, 0.38 mm wide. The central cylinder is supported in an exactly coaxial position with the outer cylinder by two wheel supports N and O, each of which has four narrow spokes connecting its hub with its rim. The hubs are insulated from the inner cylinder. The wires K and L permit F and G respectively to be connected either to ground or to an electrometer. The collecting ring, C, is joined by the wire X and a flexible spring and rod arrangement to the wire E leading to the electrometer. This arrangement permits the central electrode to be moved parallel to its axis for changing the position of C relative to the ion inlet openings in the outer cylinder, without disturbing the connections to the electrometer. The quadrant electrometer was used at sensitivities between 1500 and 3000 scale divisions

[17] Leigh Page, Theoretical Physics, p. 231.

per volt, and permitted work with small ion densities to minimize the effects of space charges and of mutual repulsion of the ions.

Distributed uniformly around the circumference of a right section through H of the outer cylinder are 102 holes each 1 mm in diameter, which permit ions produced in the ionization chamber VV, by radioactive material in the tubes RS, to be blown into the space between the two cylinders by a slow auxiliary air stream entering at T and U.

The ions were produced in VV by beta-rays coming from forty small glass tubes (old radon tubes) containing Ra D, E, F. The tubes were fastened around the circumference of a movable metal ring RS and were partially surrounded by a lead collar shield to prevent direct beta-rays striking the chamber walls near the openings at H, in order to reduce to a negligible amount the number of scattered beta-particles entering the main gas stream through these holes. The ring RS was usually placed 1.5 cm from the openings H and with streams of the magnitude used to carry ions into the main apparatus the age of the ions when they entered at H was more than 2.5 sec.

The auxiliary air stream by which the ions were carried into the main stream was supplied by a device which forced a constant measurable volume of air per sec. into the chamber VV. This was done by displacing air in a fixed gasometer by water entering through a pipe under a constant pressure head. Before entering the ionization chamber the air was dried by passage through a tower of calcium chloride[18] and filtered by passage through a cotton filter.

The main gas stream entered the space between the cylinders through a funnel A, provided with a number of gauzes of fine mesh (not shown in Fig. 1) for equalizing the stream as it enters. The air was supplied by the laboratory compressed air system and was filtered by passage through a large cotton filter. Its water content was determined periodically by chemical means. The rate of flow of the air was measured by means of a water manometer placed in parallel with a fixed length of tubing that carried the flow; the arrangement having first been calibrated by aid of a precision gasometer for whose use I am indebted to Professor Yandell Henderson.

Notwithstanding the fact that the stream velocities to be used were well below the limits for which turbulent motion sets in as given by Osborne Reynolds,[19] the steadiness of the gas flow between the two cylinders under the experimental conditions used was investigated by aid of smoke jets. A full size duplicate apparatus was made in which a brass tube was used for the upstream portion of the outer cylinder while the remaining portion was made of a piece of glass tubing of nearly the same diameter to permit observation of the smoke jets. The brass portion was provided with inlet holes around a circumference similar to those used in the actual apparatus for admitting ions.

[18] This might have been omitted to advantage in view of recent work of Erikson (Phys. Rev. **32,** 791 (1928)) showing that some of the final positive ions in dry air are changed to the initial type on entering moist air. [Added in proof. Recent measurements made on positive ions gave the same distribution of mobilities when the calcium chloride tower was removed from the ion bearing air current as was obtained when the tower was present.]

[19] Osborne Reynolds, London Phil. Trans. **A174,** 935 (1883).

Forcing air through these holes at the same rate as was done during the measurements in the original apparatus had no effect on the stability of the main air stream between the concentric cylinders. When smoke was admitted with the air entering these holes the glass part of the system presented the beautiful appearance of a hundred narrow stationary white streaks running the full length of the tube without the slightest mingling, although in such very close proximity to one another. The smoke streamers remained close to the wall of the outer cylinder. Measurements made with a bent wire gauge placed in one of these streamers at a distance of about 5 cm from its point of entrance showed a maximum penetration of but 1.5 mm into the main stream when the velocity of the air entering the inlet holes was 17 cm/sec. and the mean velocity of the main stream was 8.6 cm/sec. In the actual experiments the inlet jet velocities used were somewhat smaller than that given above but due correction will be made for the penetration of these jets into the main streams between the cylinders.

A single smoke jet was used for testing the stability of the central portion of the air stream. The jet entered from the up-stream side of the apparatus through a long narrow glass tube having an opening about 1 mm in diameter. It is essential to have the jet stream enter very slowly. For average stream velocities up to 12 cm/sec. the stream lines remained very steady. Above this velocity the smoke jet began to show a slow irregular side wabble, the excursions of which were larger at right angles to a radius than along it. At a mean velocity of 14.5 cm/sec. the maximum excursions were at times as much as 1 mm and at a velocity of 20 cm/sec. the excursions covered several millimeters at some distance down stream from the jet inlet.

Two methods of procedure were followed in making measurements. In the first, the collecting ring was kept at a fixed distance down stream from where the ions entered, and readings were taken of the charge received by the ring as the potential of the outer cylinder was varied. In the second method the potential of the outer cylinder was kept at a fixed value and the central cylinder was moved so that the collecting ring occupied different positions relative to the ion-inlet openings.

Experiments with Stationary Collecting Ring and Variable Voltage

An example of the results obtained when the center of the collecting ring was kept at a fixed distance of 4 cm from the plane through the centers of the ion inlet holes is given in Fig. 2. The positive ion currents received by the collecting ring are represented in the curves by ordinates corresponding to voltages on the outside cylinder given as abscissas. In curve *A* the average velocity of the air stream was 9.7 cm/sec. and in curve *B* it was 14.7 cm/sec. The auxiliary stream by which the ions were carried into the main stream through the inlet holes delivered 20 cc of air per sec. Allowance for this air volume has been made in the above values of the average air stream velocities. Each curve has considerable breadth but only one peak. The largest voltage for which ions reached the collector in each case is approximately three times

as large as the lowest voltage. This means that for any one voltage the ions reach the central electrode spread over a rather large distance along its length. A part of this spread arises from the physical widths of the ion entrance holes and of the ion collecting ring, the whole distance thus involved being 2.9 mm. This does not account for as much as ten percent of the spread observed. Another part of the spreading arises from the diffusion and mutual repulsion of the ions in their passage between the two cylinders. The magnitude of this effect has been determined experimentally and will be considered in detail in connection with the second method of procedure where the voltage is kept fixed and the collector ring moved, since in that method the correction can be applied more directly. It need only be stated here that when the requisite transformations are made to permit the correc-

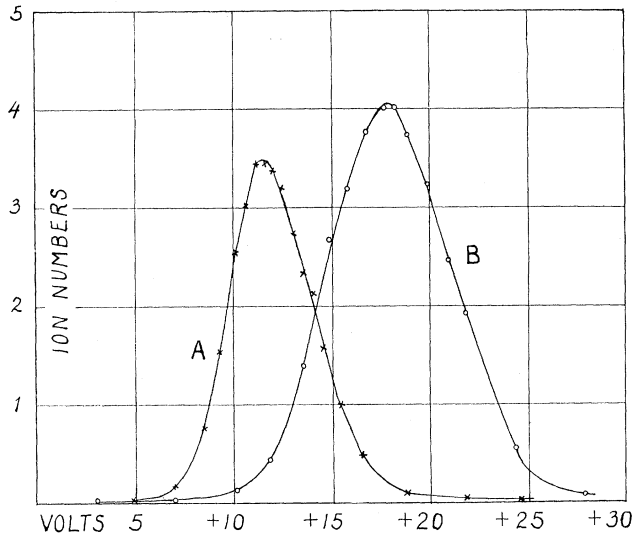

Fig. 2. Positive ion currents for different voltages. Collecting ring distance, $X=4$ cm. Air pressure = 76.9 cm of Hg. Temperature = 23°C. Water content of air = 2.4 mg/liter. Air stream velocity, for curve $A=9.7$ cm/sec; for curve $B=14.7$ cm/sec.

tion to be applied to the results obtained by the procedure now under consideration, the computation shows that a portion of the observed spreading of the ions remains unexplained unless we assume that all of the ions do not have the same mobility. Making this assumption, the continuous nature of the curves points to the conclusion that the ions are not comprised in a few distinct groups having definite but quite different mobilities. More probably, as assumed by Busse[11] and by Laporte,[12] the ions form one statistical group in which the mobility changes more or less gradually from one portion of the ions to the next. If there are permanent groups of ions within the range observed, which differ in mobility among themselves, these have not been resolved. The many curves obtained both with positive and negative ions show no evidence of more than one peak.

The observations recorded in Fig. 3 were made primarily to find electrons or negative ions of high mobility if present. For this purpose the collecting ring was placed only 0.49 cm down stream from the holes through which the ions enter. The gas stream velocity used was 21.4 cm/sec., and the auxiliary ion stream delivered 22.9 cc/sec. Fast ions or electrons should be detected if present with small voltages on the outer cylinder. The many readings taken in this region at small voltage intervals give no indication of the presence of any ions of this character as numerous as one-tenth of a percent of those represented by the peak of the curve.

The whole evidence of all of the experiments both with positive and negative ions is against the existence in moist air of more than one general group of ions of each sign, two or more seconds after the formation of the ions.

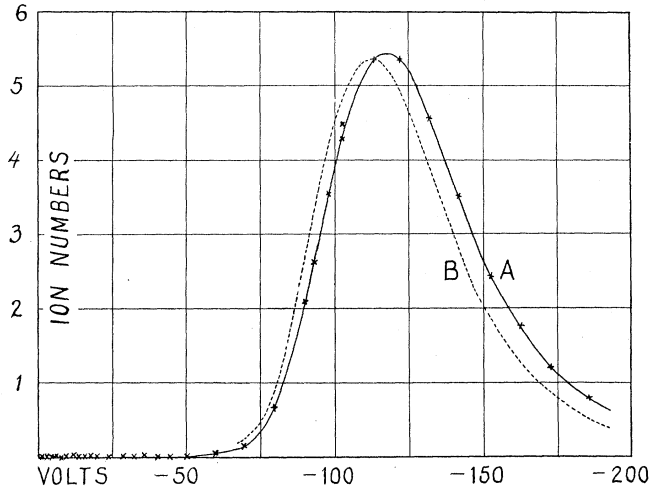

Fig. 3. Negative ion currents for different voltages. Collecting ring distance, $X=0.49$ cm. Air pressure = 76.1 cm of Hg. Temperature = 21°C. Water content of air = 2.38 mg/liter. Air stream velocity = 19.9 cm/sec. Curve B is corrected for variation of spreading with voltage.

The present method of procedure lends itself to the determination of absolute values of mobilities for the ions corresponding to the peaks of the curves. Two correction factors which are involved will first be considered.

Owing to the fact that the collecting ring has a definite width while the total linear spread of the ions received along the length of the central cylinder depends in an inverse manner upon the potential difference between the two cylinders, the curves shown do not give the exact distribution of the ions. When a large voltage is applied and the ions cover but a short length of the inner cylinder those striking the fixed width of the collector ring form a larger fraction of the whole than would have been the case had a smaller voltage been used and the ions been spread over a greater distance along the cylinder. To correct for this variation of dispersion with voltage, the distribution for some one voltage is taken as a standard and the readings for other voltages are adjusted to the scale for the standard voltage by taking the readings to

be inversely proportional to the two voltages concerned. The dotted curve in Fig. 3 is a corrected curve obtained in this way from the main curve, the standard voltage taken being the one for which the two curves cross each other. The peak of the curve is shifted by this correction toward the smaller voltages, usually by about 2 to 3 percent.

The second correction to be considered arises from the fact that the air laden with ions has an appreciable radial velocity as it enters the main gas stream through the small openings in the outer cylinder. The actual distance these jets of ionized air penetrated into the gas stream was determined, as already noted, by aid of smoke, for a case where the jets had a somewhat larger velocity than that used in most of the experiments. For velocities differing from this the distance of penetration of the jets was found by assuming that this distance is directly proportional to the entering velocity of the jets. During nearly all of the measurements made the penetration distance of the jets was approximately 1 mm. In this portion of their path the ions move under the combined action of the electric field and of the jet stream. The contribution which the jet stream makes to the inward displacement of the ions is the part of the penetration distance given by the ratio of the mean velocity of the jet stream to the sum of this mean velocity and the velocity of the ions under the electric field alone. The mean velocity of the jets was taken as one half of their velocity on entrance. The computed distance the ions were carried inward by the action of the jets of air was found for the different cases to be between one and three percent of the total distance between the cylinders. This percentage of the distance thus computed for each case was applied as a first approximation correction to the mobility value obtained by Eq. (2). The effect of the correction was to diminish the mobility values given by the formula.

The contact difference of potential between the collector ring and the outside cylinder was found by experiment to be but 0.05 volt, the ring being negative with respect to the cylinder.

The mobility thus found for the negative ions from the corrected peak of the curve in Fig. 3, when reduced to air under a pressure of 76 cm of mercury and to a temperature of 20°C on the assumption that mobilities vary inversely as gas densities, was 2.10 cm/sec · volt/cm. The water content of the air was 2.38 mg per liter of air. The values obtained similarly for positive ions from the curves of Fig. 2 were in each case 1.21 cm/sec · volt/cm.

A summary of all of the results obtained by this method of procedure for the mobilities of those positive and negative ions which reached the central electrode at the peaks of the corresponding distribution curves is given in Table I. X is the distance the collecting ring was situated down stream from the ion inlet openings, U is the mean velocity of the main stream and S the volume of air entering per sec through the ion inlet holes. The fourth column gives the water content of the air used, in mg per liter, and the last two columns give the mobilities. Owing to the varying water content the results are not directly comparable. The average of the mobilities found by this first procedure is 1.20 cm/sec for the positive ions and 2.00 cm/sec for

the negative ions, corresponding to an average water content of about 3 mg per liter of air. Corrections have been made in all cases for the variation of dispersion with voltage and for the effect of the ion inlet streams as has been explained, and the results have been reduced to normal air pressure and a temperature of 20°C. The average ratio of the voltages marking the beginning and end of each distribution curve (compare Fig. 2) was 2.7 for positive ions and 2.4 for negative ions. These numbers do not indicate the range

TABLE I. *Summary of mobility results; fixed collecting ring method.*

X Down stream distance cm	*U* Velocity main air stream cm/sec	*S* Ionized air vol. cc/sec	Water content mg/liter	Mobility of positive ions cm/sec · volt/cm	Mobility of negative ions cm/sec · volt/cm
3.00	7.43	16.	—	—	1.94
3.00	7.43	16.	—	1.20	—
3.00	7.43	16.	—	—	1.98
3.00	7.43	16.	—	—	2.12
3.00	13.6	17.	4.67	—	2.02
3.00	13.6	16.6	4.07	—	1.94
3.00	13.6	16.	—	1.22	—
3.00	13.5	13.5	1.87	1.19	—
4.00	13.5	12.	5.32	—	2.00
4.00	13.9	27.	5.32	1.20	—
4.00	13.4	20.5	2.51	1.22	—
4.00	13.4	20.	2.51	—	1.97
4.00	5.42	16.	2.40	1.20	—
4.00	15.2	20.	2.35	1.21	—
4.00	9.91	20.	2.35	1.21	—
8.00	11.7	20.	2.35	1.22	—
8.00	11.7	18.	2.14	—	2.03
1.12	11.7	18.	2.38	1.13	—
1.12	11.4	5.5	2.38	1.14	—
1.12	11.4	5.5	2.38	—	1.99
1.12	11.7	20.2	2.38	—	1.97
1.12	11.8	20.3	2.38	—	1.94
1.12	11.9	25.	2.38	—	1.93
.49	21.7	23.	2.39	—	2.10
			Average	1.20	2.00

of mobilities included in each set of ions, but are given to show that the spreading of the positive ions was somewhat greater than that of the negative ions.

A modification of the experimental arrangement may be made by connecting the down stream portion *F* of the inner cylinder as well as the collecting ring *C* to the electrometer. The arrangement is then similar to that which I used originally[16] for mobility measurements except that at that time the ions were produced by x-rays in a narrow section transverse to the cylinders. Curve *A* in Fig. 4 represents the results of an experiment done with this modified arrangement, the ordinates representing in arbitrary units the number of ions carried past the gap *C* for different voltages on the outer cylinder.

For very small values of the voltage the ions are blown out of the apparatus except such as are caught by the wire K. As the voltage is increased the ions eventually all reach the section F of the inner cylinder and the curve remains horizontal until the voltage is sufficiently high for some of the ions to be pulled across to G. This latter number increases with increase of field until none of the ions get past C and the ordinates of curve A vanish. Curve B of the same figure was obtained with the collecting ring C alone connected to the electrometer, the ordinates being on twice the scale of those of curve A. It is seen that with increasing voltages on the outer cylinder, B begins to rise where A begins to fall, it reaches its maximum height where the slope of A is the greatest and the two reach the zero axis at approximately the same voltage. If any unique mobility is to be obtained by use of

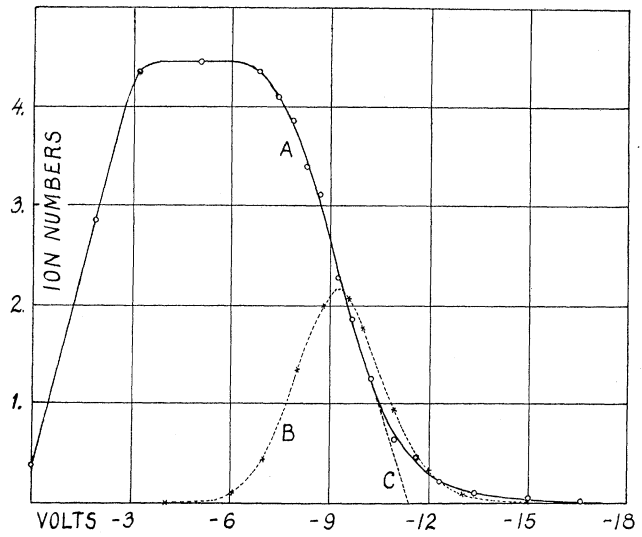

Fig. 4. Negative ion currents for different voltages. Curve B gives currents reaching collecting ring at $X=4$ cm; curve A gives currents from all ions carried down stream 4 cm or more. Air pressure = 74.45 cm of Hg. Temperature = 22.5°C. Water content of air = 5.32 mg/liter. Air stream velocity = 13.0 cm/sec.

a curve like A it should be found from a voltage corresponding to the maximum of curve B, i.e., where curve A has the greatest slope. What was actually done in the early mobility experiments,[16] in which however the ions were introduced differently as already described, was to prolong the slope of a curve similar to A, until it intersected the axis of abscissas and use the intercept voltage thus found for computing the mobility. It is now seen that the mobility so obtained was not that which here corresponds to that of the maximum slope. In the example given in Fig. 4, the mobility obtained from the voltage at the maximum slope is 20 percent higher than that got from the C intercept voltage. Owing to the different way in which the ions were initially distributed this correction may not be applied directly to the old mobility values.

Spread of Ions by Diffusion

It seemed highly important to determine as accurately as possible whether all and if not all what part of the spreading of the ions along the central electrode, shown by the experiments described above, may be explained by the diffusion and mutual repulsion of the ions in their motion between the cylinders. For this purpose it was found advantageous to change the procedure to a more laborious one in which a constant potential difference was maintained between the cylinders and the ion distribution reaching the central one was obtained by moving the collecting ring, C, to different distances down stream from where the ions enter the air stream.[20]

The ion distribution was first found in this way in each experiment with no air stream flowing between the electrodes. Examples of the distributions

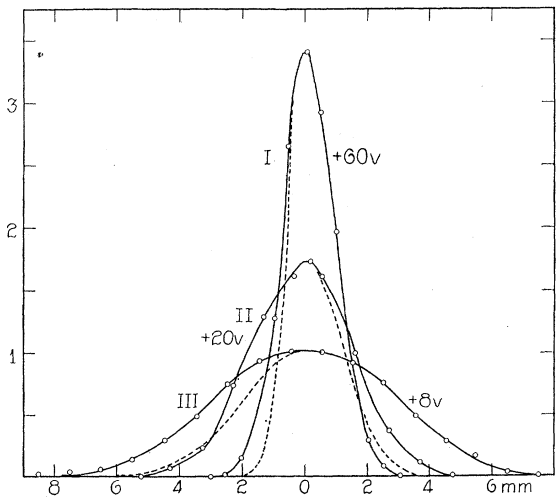

Fig. 5. Distribution of ions along central cylinder for specified positive voltages on outer cylinder when no air stream is flowing. Atmospheric pressure. Broken line curves give theoretical distributions.

of positive ions for three different voltages on the outside cylinder are shown by the full line curves in Fig. 5. Curve I should be slightly displaced to the left of the position shown. A portion of the spreading having a width of 2.9 mm is due to the dimensions of the collecting ring and of the openings through which the ions enter. The remainder arises from the combined effects of lateral diffusion and of mutual repulsion of the ions. It was thought that an appreciable part of the spreading of the ions might be due to the slowing up of the air jets which carry the ions into the space between the two cylinders, but a comparison experiment done in which no jets were used, the ions being produced by alpha-rays entering directly the openings in the outer cylinder, showed that such spreading is negligible in amount.

[20] A similar procedure was used by Erikson and by Tyndall and Grindley in some of their experiments.

It is of some importance to determine whether a considerable part of the observed spreading arises from the mutual repulsion of the ions, even though small ion densities were used with the object of minimizing this effect; since, when the ions are carried down stream in an oblique path, mutual repulsion acts to spread the ions at right angles to this path.

The amount of spreading due to diffusion of the ions alone may be computed as follows. Einstein[21] has shown that the probability of a particle being between two planes dx apart which are a normal distance x from the location of the particle at a time t seconds previously is given by

$$[1/(4\pi Dt)^{1/2}]e^{-x^2/4Dt}dx$$

where D is the coefficient of diffusion of particles of the kind in question. From this expression it may be deduced that if N_0 is the ion density in an elementary volume at any moment the ions from this volume will be so spread by diffusion after a time t that at a distance r from the initial position the ion density will be

$$N=\frac{N_0}{(4\pi Dt)^{3/2}}e^{-r^2/4Dt}. \tag{3}$$

For purposes of comparison it is only necessary to use the numerical values of the exponential term for different values of r.

Since the value of D is intimately connected with the value of the ionic mobility it seemed best to compute the coefficient of diffusion from the mobility k here obtained, by the relation

$$D=\frac{3\times 10^8 k}{1.23\times 10^{10}}. \tag{4}$$

Using for the mobility of the positive ions the value 1.22 cm/sec, the coefficient of diffusion is found to be 0.0298. This value is considerably smaller than the values given by Townsend[22] for positive ions produced by Becquerel rays, these being 0.032 for dry air and 0.036 for moist air.

To compare the values obtained by Eq. (3) with the experimental results shown in Fig. 5 it is only necessary to use for each case the time taken by the ions to cross the space between the two cylinders. It is evident that the lateral spreading of the ions is not influenced by the motion imparted to them by the electric field which is normal to this direction.

The time required for the ions to traverse the distance between the two cylinders is given by

$$t=\frac{(b^2-a^2)}{2Vk}\log_e\frac{b}{a}=\frac{6.18}{Vk} \tag{5}$$

V, being as before the potential difference between the two cylinders and k the ionic mobility. The times of passage of the ions are thus found to be 0.053

[21] A. Einstein, Ann. d. Physik **17**, 558 (1905).

[22] J. S. Townsend, Phil. Trans. **A195**, 259 (1900).

sec for the case represented by curve I, 0.25 sec for curve II, and 0.63 sec for curve III. The dotted curves, Fig. 5, show in each case the theoretical spreading of the ions as computed by Eq. (3). These dotted curves fall in each case inside of the experimental ones. It must be remembered however that to make a direct comparison possible it would be necessary to have the ions start from a region of negligible width and to have their distribution measured by an equally narrow collector. In the experimental procedure the ions originated in an area of 1 mm width and the collector gathered ions from a region almost 1 mm to either side of its middle point. Both of these considerations tend to make the experimental curves broader than the theoretical ones. If full allowance of 1.45 mm is made of half the widths of the ion streams and the collector, the experimental curve III agrees almost exactly at its lower end with the theoretical one, whereas the discrepancy now shown is more than corrected for in the other two curves. Had Townsend's value of the coefficient of diffusion been used for computing the spreading of the ions, the dotted curves would have been still farther from the axis than they now are. It will suffice to say without more detailed dis-

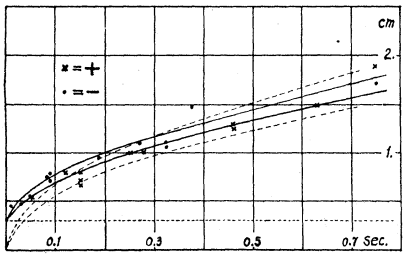

Fig. 6. Variation with time of crossing of total spread of ions in both directions, when no air stream is flowing. Atmospheric pressure.

cussion that diffusion is sufficient to account for all or nearly all of the spreading observed and that therefore mutual repulsion of the ions had at best but little effect. Even if an appreciable amount of the spreading results from mutual repulsion, the method of correction to be used will correct for it in large part.

It is of interest to note that diffusion should be taken into account in making mobility measurements by methods like the Rutherford alternating field method. If the passage of the positive ions should take 0.1 sec, then because of diffusion as computed by Eq. (3), ions of a density of one-quarter of a percent of the maximum density would be found 2.68 mm ahead of the main body of ions. For a time of passage of 0.01 sec. the corresponding distance would be 0.85 mm.

It is seen from Eqs. (4) and (5) that the product Dt of Eq. (3) will for a given voltage have the same values for both positive and negative ions, and that accordingly the ions should be equally spread out on reaching the central electrode. This was found experimentally to be the case. For the same time of passage however the negative ions spread more than do the positive ones.

The experimental values obtained for this spread taken between the extreme limits of the two limbs of each distribution curve (like A of Fig. 2) are given in Fig. 6 for both positive and negative ions, since use is to be made of these values later on. The points on the curves represent all of the values obtained even though in some of the cases the number of observations made on the distribution was not sufficient to determine the limits with much precision. The curves are projected back so that at $t=0$ the ordinate intercept has a value of 2.9 mm, the sum of the widths of the ion inlet holes and of the collecting ring. The ordinates above the horizontal dotted line thus represent the total spreading in both directions. The broken curves in Fig. 6 show the spreading in both directions as computed by Eq. (3) for limits where the ions have a density of one-quarter of a percent of the density at the maximum. For the coefficient of diffusion of the negative ions the value 0.0488 was used as computed from the mobility, 2.00 cm/sec. The upper curve is for negative ions, the lower for positive. These curves are separated by a greater distance than are the experimental curves. If Townsend's values for the coefficients of diffusion are used in Eq. (3) the separation of the two theoretical curves is reduced to about the same amount as that shown for the experimental results. If the experimental curves are lowered to allow for the widths of the ion inlet holes and the collector, the experimental curves do not show as much spreading as do the theoretical ones computed on the supposition that all of the spreading arises from diffusion. Perhaps the full allowance should not be made for the sum of the widths of the inlet holes and collector. Some of the discrepancy remains to be explained but it is quite evident that no effects of mutual repulsion of the ions are discernible.

Experiments with Constant Voltage and Variable Position of Collecting Ring

The actual measurements made with a gas stream flowing and where the distribution of the ions received by the inner cylinder was determined by moving the collecting ring, will now be considered in detail. Two examples of the results are shown in Figs. 7 and 8. In Fig. 7 the applied potential on the outer cylinder was $+20$ volts. Curve A gives the distribution of the ions along the inner cylinder when no gas was flowing through the apparatus. The ions here are spread over a length of approximately 10.0 mm. Curve B shows the distribution when an air stream of average velocity 6.52 cm/sec was carrying the ions down stream during their passage between the two cylinders. The peak of this curve is displaced 16.5 mm down stream from that of Curve A and the ions are now spread over approximately 17.2 mm, instead of 10.0 mm. This increase of 7.2 mm in the spreading of the ions along the inner cylinder indicates that the ions did not all take the same time in their passage and it remains to find whether this difference of mobility arises from an actual difference among the ions themselves or whether it can be accounted for by some effect which is not included in the allowance of 10.0 mm already made for the spreading of the ions when no air stream was passing through the apparatus.

Any separation of the ions by diffusion which is parallel to the axis of the cylinders does not affect the time taken for the ions to cross between the cylinders nor is this time affected by the motion of the air down stream.

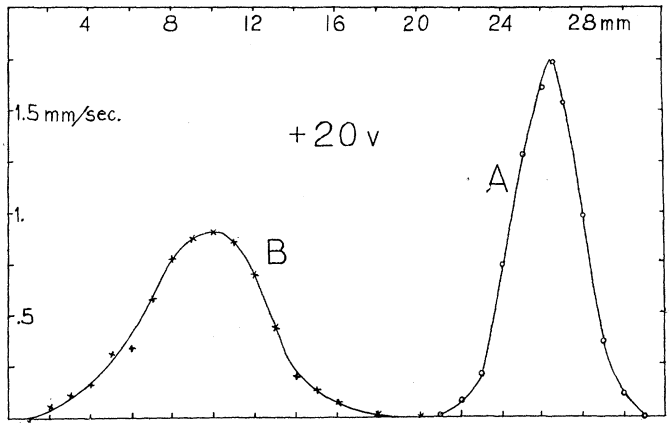

Fig. 7. Distribution of ions along central cylinder with +20 volts on outer cylinder. *A*, without air stream. *B*, with air stream velocity = 6.52 cm/sec. Air pressure = 75.2 cm of Hg. Temperature = 21.3 °C. Water content of air = 1.46 mg/liter.

Were this the whole effect of diffusion the spreading along the cylinders of ions having a unique mobility would be the same with the air stream as without. Diffusion however spreads the ions in all directions, and the time of passage of those diffusing against the field is lengthened while for those

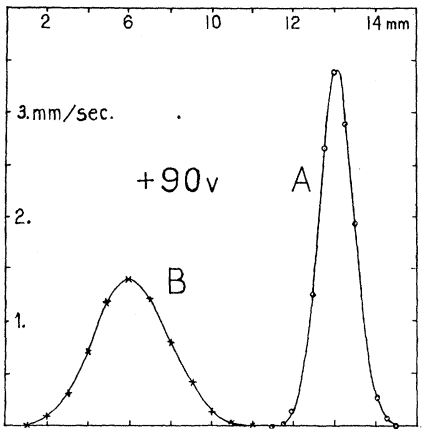

Fig. 8. Distribution of ions along central cylinder with +90 volts on outer cylinder. *A*, without air stream. *B*, with air stream = 18.95 cm/sec. Air pressure = 75.5 cm of Hg. Temperature = 22.4 °C. Water content of air = 3.08 mg/liter.

diffusing with the field the time is shortened. This change in the time of passage produces no effect upon the location of the place where the ions will reach the inner electrode when no gas stream is flowing between the cylinders

but in case such a stream is flowing it will do so. It remains to show in any special case how much if any this radial diffusion will carry ions, when they arrive at the inner cylinder, beyond the limits of the axial diffusion observed when no air stream is used.

In considering the results of diffusion of ions from an extended volume of gas it suffices to find the distribution of the ions after a given time from a small element of volume, and then superimposing the distributions from all of the volume elements in question. The final distribution of the ions originating in one volume element is not affected by the presence of other ions from other elements since in diffusion the ions are supposed to have no mutual interaction but to have their wanderings governed solely by chance. In the present arrangement where the ions enter the stream through small openings, a small element of one stream may be followed in its passage and the distribution of its ions on arrival at the central electrode will represent the distribution of all of the other elements.

The ions starting from the outer cylinder in an elementary volume are spread over a larger and larger volume as they approach the inner cylinder. Owing to the radial nature of the electric field, the volume throughout which these ions are distributed as they approach the inner cylinder with increasing speed is not spherical. Its section made by a plane passing through the cylinder axis will be more or less elliptical with the minor axis parallel to the axis of the cylinders and equal in length to the spread of the ions along this axis as determined experimentally when no gas stream is flowing. Moreover owing to the variable velocity of the gas stream through which the ions pass, the major axis of the diffusion volume undergoes a tilt, the forward half of the volume being carried down stream faster than the rear half during the first part of its journey and slower than the rear half during the last part of the passage. A step by step analysis of two examples showed that this tilt which is never large compensates itself almost completely when the volume reaches the inner cylinder so that at that time its major axis is essentially normal to the axis of the cylinder.

The procedure which was followed to find how far beyond the limits of the minor axis of the diffusion ellipsoid any of those ions reached the inner cylinder which had diffused with or against the motion due to the electric field will be illustrated by considering the example represented by Curve *B* of Fig. 7. Without an air stream the ions showed a spread in either direction of one half of 10.0 mm or 5.0 mm. This spread does not all arise from diffusion since without any diffusion owing to the width of the ion stream and of the collecting ring a spread of 1.45 mm in each direction would have been indicated. The net spread due to diffusion alone is thus $5.0-1.45=3.55$ mm. If in a uniform field therefore the central ion of the diffusion volume would have moved 2.38 cm, the distance between the two cylinders of our apparatus, the most forward ion would have gone $2.38+0.355=2.735$ cm while the rearmost ion would have moved but 2.025 cm. The apparent mobilities of these ions would accordingly be respectively 1.40 cm/sec and 1.04 cm/sec, taking 1.22 cm/sec for the mobility of the central ion.

The time taken for the central ion to cross as given by Eq. (5) is 0.253 sec. The distance r from the axis that the slowest ion is situated at this instant is given by

$$t=\frac{b^2-r^2}{2Vk}\log_e\frac{b}{a}=\frac{0.528}{20\times 1.04}(13.31-r^2)=0.253\ ;\ \text{whence}\ r=1.83\ \text{cm}.$$

The ion is therefore still $1.83-1.27=0.56$ cm from the surface of the central cylinder. The elliptical section of the diffusion volume at the moment when the central ion reaches the inner cylinder would have a semi-minor axis of 0.355 cm and a semi-major axis of 0.56 cm. A part of an ellipse B with these values as axes is now constructed (see Fig. 9) with the major axis passing

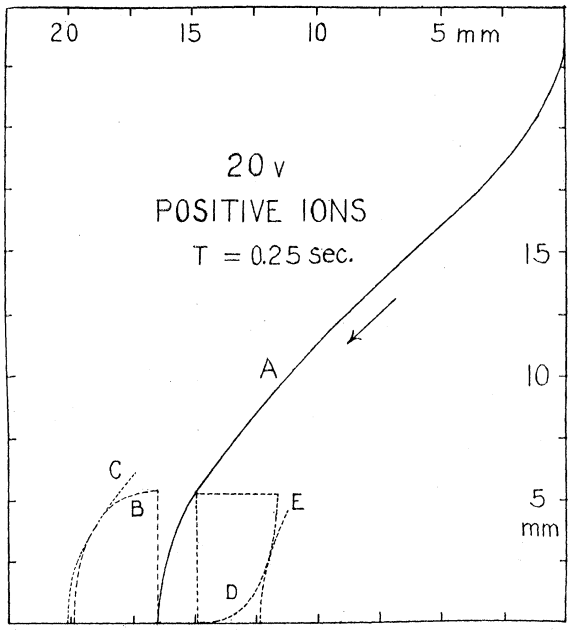

Fig. 9. Curve A shows path of positive ion taking 0.25 sec. to cross. Air stream velocity = 6.52 cm/sec. $BCDE$ illustrate method of correcting spread of ions for upward and downward diffusion. See text.

through the point where the central ion of path A reached the cylinder, in this case, 1.65 cm down stream from the point of entry of the ions into the air stream. Of all the possible ion paths starting from the place of entry the one, C, that is tangent to this ellipse B will give the farthest down stream point that can be reached by any ion in the diffusion volume. This point is obtained most easily by trial on a large scale drawing. To do this the equation of the path of an ion must first be found and this is obtained as follows: The down stream velocity of the ion due to the air current, at a distance r from the axis, is

$$\frac{dx}{dt}=\frac{p}{4\mu\log(b/a)}\left[b^2\log\frac{r}{a}+a^2\log\frac{b}{r}-r^2\log\frac{b}{a}\right]$$

and its radial velocity due to the electric field at the same place is

$$\frac{dr}{dt} = -\frac{kV}{r \log (b/a)}$$

whence the equation of the path becomes

$$x = \frac{p}{16 k V \mu} \left[(b^4 + r^4) \log \frac{b}{a} - 2b^2 r^2 \log \frac{r}{a} - 2a^2 r^2 \log \frac{b}{r} - (a^2 - b^2)(r^2 - b^2) \right]. \quad (6)$$

The value of p/μ is readily determined for any special case by the equation giving the volume of gas passing per second through the apparatus, i.e.,

$$\text{volume/sec} = \frac{\pi (b^2 - a^2) p}{\mu} \left[(b^2 + a^2) - \frac{b^2 - a^2}{\log (b/a)} \right].$$

The actual value of p in the experiment was quite small being of the order of one bar per cm.

After one path curve is drawn on a large scale it becomes comparatively simple to draw from this others which are more or less elongated replicas of it.

It is seen that in this case the tangential path C reaches the cylinder at 2.01 cm which is only a trifle beyond the limits of the diffusion volume and the correction sought is here very small. When the ions are carried much farther down stream and the time of their passage between the cylinders is longer than was the case in this example the correction may assume large values and experimental errors make its exact determination difficult. The correction is doubtless overestimated by this method because as the diffusion volume becomes elliptical fewer ions diffuse to the extreme end of the major axis of this volume than reach the ends of the minor axis.

The up-stream limit on the central cylinder that may be reached by ions which have diffused in the direction of the electric field may be obtained in a manner quite similar to that used above for determining the down stream limit. Thus in the above example the foremost ions of the diffusion volume take 0.22 sec. to traverse the distance between the two cylinders, and at that instant the central ions of the volume are found to be still 0.54 cm from the inner cylinder and the minor axis of the diffusion volume is 0.32 cm, as given by the curve for positive ions in Fig. 6. We next construct the quadrant of the ellipse, D, Fig. 9 and find the ion path which will be tangent to this ellipse. This path reaches the cylinder at 1.22 cm. The limits thus found between which ions all having one mobility should arrive at the central cylinder for the case under consideration are 2.01 cm and 1.22 cm down stream from the ion inlet openings. Owing to the widths of the collecting ring and of the ion inlet openings these limits should be extended in each direction by 0.145 cm, giving 2.15 cm and 1.08 cm as the extreme limits. These distances are to be compared with the observed distances in Fig. 7 between the limbs of curve B and the center of the undisplaced curve A, which are 2.55 cm and 0.83 cm. The observed spreading of the ions is thus seen to be 0.65 cm greater than is accounted for by diffusion on the supposi-

tion of a unique mobility. Assuming that the remnant spread arises from the presence of ions of different mobilities, the values of these mobilities at the two extreme limits are 1.44 cm/ sec. and 0.985 cm/sec., the larger being 46 percent greater than the smaller. A similar analysis of the results shown in Fig. 8 gives for the peak mobility 1.30 cm/sec. and for the two extreme values 1.72 cm/sec. and 1.07 cm/sec., the water content of the air being in this case twice as large as in the preceding one.

A simple consideration shows that the peak of each distribution curve represents very closely the place reached by the central ion of the diffusion volume.

TABLE II. *Results for positive ions.*

1	2	3	4	5	6	7	8	9	10	11	12
Volts on A	Air velocity cm/sec	Water content mg/liter	Crossing time sec	Largest X cm	Largest X corrected	Peak X cm	Smallest X cm	Smallest X corrected	Peak mobility cm/sec	Lowest mobility	Highest mobility
30.15	18.95	3.63	0.16	—	—	2.84	—	—	1.32	—	—
30.1	18.95	—	·16	4.22	3.82	2.94	1.72	2.23	1.29	.98	1.68
15.0	18.95	3.63	.32	7.75	6.82	5.65	3.81	4.68	1.34	1.10	1.60
90.0	18.95	3.08	.05	1.49	1.22	1.00	0.48	0.76	1.27	1.05	1.69
7.0	11.42	4.00	.75	—	—	7.18	—	—	1.27	—	—
9.0	11.11	3.22	.54	7.84	6.29	5.64	3.34	4.50	1.30	1.17	1.61
40.0	12.74	1.65	.13	2.32	1.96	1.57	.90	1.29	1.23	.99	1.49
20.0	6.52	1.46	.27	2.55	2.06	1.65	.83	1.37	1.18	.95	1.42
10.0	3.40	1.99	.58	2.72	1.86	1.85	1.07	1.86	1.09	1.09	1.09
30.0	10.14	1.87	.17	2.52	2.12	1.63	.97	1.40	1.24	.96	1.45
10.0	10.14	1.87	.51	7.05	5.75	4.92	2.77	4.00	1.21	1.04	1.50
8.0	3.40	2.37	.67	3.65	2.69	2.18	1.10	2.06	1.15	.95	1.25
							Averages		1.24	1.03	1.48

TABLE III. *Results for negative ions.*

1	2	3	4	5	6	7	8	9	10	11	12
Volts on A	Air velocity cm/sec	Water content mg/liter	Crossing time sec	Largest X cm	Largest X corrected	Peak X cm	Smallest X cm	Smallest X corrected	Peak mobility cm/sec	Lowest mobility	Highest mobility
30.1	18.95	3.63	0.10	—	—	1.79	—	—	2.12	—	—
30.1	18.95	4.42	.10	—	—	1.93	—	—	1.96	—	—
30.	18.95	—	.10	2.55	2.19	1.94	1.20	1.60	1.97	1.74	2.40
30.	18.95	2.94	.10	2.65	2.29	1.93	1.25	1.65	2.03	1.67	2.33
15.	18.95	3.63	.20	5.15	4.61	3.70	2.55	3.16	2.05	1.63	2.38
9.	11.11	3.22	.34	5.00	4.09	3.62	2.54	3.43	2.04	1.80	2.15
90.	18.95	3.53	.03	1.01	0.78	0.62	0.31	0.56	2.04	1.60	2.25
10.	3.40	1.50	.34	1.83	1.27	1.13	0.53	1.15	1.79	1.58	1.75
30.	10.14	1.50	.10	1.54	1.17	0.97	0.56	0.94	2.10	1.73	2.16
10.	10.14	1.50	.30	4.22	3.52	2.90	1.82	2.56	2.07	1.71	2.35
10.	3.40	7.63	.33	1.74	1.19	1.09	.44	1.07	1.86	1.71	1.90
8.	3.40	2.19	.40	2.29	1.55	1.32	.49	1.22	1.94	1.65	2.10
							Averages		2.00	1.68	2.18

In order to test the method and find the best working conditions, determinations were made with largely different values of the quantities involved. The voltage applied to the cylinder A was varied in the ratio of 1 to 13, the time taken for the ions to cross being thus varied over the same range. The velocity of the air stream was varied in a ratio of about 1 to 6. The distances that the ions were carried down stream in crossing between the cylinders were altered in the ratio of about 1 to 7. The ion density was varied several fold. Some of the extreme conditions used were not suitable for high accuracy. Nevertheless the results are all recorded in Tables II and III.

In both tables, column 7 gives the displaced distances of the peaks of the distribution curves and column 10 gives the mobilities computed from these distances, reduced to a pressure of 76 cm of mercury and a temperature of 20°C after correction has been made for the effect of the ion inlet jets discussed in a previous section. In column 6 are given the values of the farthest distance ions were carried down stream after the values of column 5 were corrected for diffusion, etc. as explained on the preceding pages. Column 9 gives similarly corrected values of the shortest distance ions were carried down stream. Columns 11 and 12 give values of mobilities corresponding respectively to the distances in columns 6 and 9, after being reduced and corrected as were those of column 10. The values of the mobilities which correspond to the peaks of the ion-distribution curves are not strictly comparable among themselves owing to the variations in the water content of the air, although these variations did not cover a large range. Those mobilities given in column 10 of Tables II and III for which the water content of the air was determined, are plotted as ordinates in Fig. 10 as disks against the water content of the air as abscissas. Similar values taken from Table I are plotted with crosses.

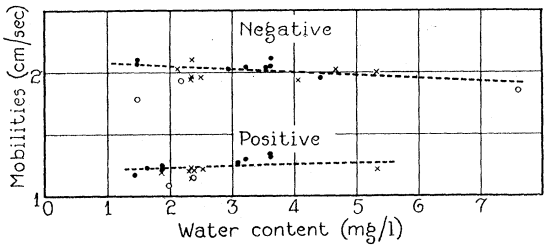

Fig. 10. Mobilities plotted against water content of air.

It must be remembered as was stated above that these results include some observations which were taken to test out the method under extreme experimental conditions where high accuracy was not attainable. Especially noticeable is the somewhat erratic position of the points marked by triangles which represent results obtained with a stream velocity of only 3.4 cm/sec., the lowest that was used. These differ greatly among themselves also as regards the limits of spread of the ions. One of the results for negative ions for a water content of 1.5 mg/liter is so low that some unusual error is suspected. [Added in proof. This has been traced to reading 191 on a scale as 189.] There is some question whether these readings should be considered of equal value with the others. Their omission certainly removes the most discordant of the results.

Most of the values are crowded into so small a range of water content of the air that a very accurate curve of relation cannot be drawn. The negative mobilities show a decrease with increase of water content of the air, the rate being somewhat less than that given by Tyndall and Grindley.[23] The mobili-

[23] A. M. Tyndall and G. C. Grindley, Roy. Soc. Proc. **A110**, 341 (1926).

ties of the positive ions, appear on the whole to increase with increase of water content of the air. The average of the mobilities of the positive ions given in column 10 of Table 2 is 1.24 cm/sec. · volt/cmf or an average water content of 2.7 mg per liter of air. For the negative ions the average of the values given in column 10 of Table III is 2.00 cm/sec. · volt/cm for an average water content of 3.2 mg per liter of air. The results are reduced to a pressure of 76 cm of mercury and a temperature of 20°C. The value for the negative ions is identical with that found by the stationary collecting ring method as given in Table I. The value for the positive ions is here three percent larger.

The determinations of the limits of spread of the ions are necessarily subject to much more error than the location of the peaks of the distribution curves. The limits were taken at points where the ordinates of the curves were about one-quarter of a percent of the maximum ordinate. In a few of the earlier measurements these limits of spread were not determined, as shown by blanks in the Tables. The distance between the limits given in columns 6 and 9 is the spread of the ions along the inner cylinder which is left unaccounted for, after the corrections have been applied for diffusion and for the other causes which have been considered, on the supposition of a unique mobility for all of the ions of each sign. Assuming that this remnant spread of the ions is indicative of the presence of ions of different mobilities, the limiting values of these mobilities have been computed and are given in columns 11 and 12 of the Tables. For the positive ions the mobilities at the upper limit are on the average 45 percent larger than those of the lower limit while for the negative ions they are 30 percent larger. Within the rather large experimental errors of these quantities, there appears to be no systematic change of the relative values of the limiting mobilities with the time of crossing of the ions nor with the water content of the air over the ranges used. It should be pointed out, because the fact may have some significance, that for the positive ions the "peak" mobility is very closely midway between the values of the extreme limits whereas for the negative ions the "peak" value is markedly closer to the higher limit. Laporte's curves for the negative ions in moist air show rather the opposite of this.

Discussion

The only previous results on distribution of mobilities that can be compared directly with those obtained here are those of Laporte,[12] who did not use a blast method. The total spread of mobilities in air as shown by his curves is approximately the same as that given by my curves. Moreover he also finds the spread of the positive ions greater than that of the negative ions. He does not give numerical values for the relative values of the maximum and minimum mobilities but as he estimates the effect of diffusion in his experiments to be much less than that found by me, his ratios should be larger than those given above.

Other observers, who have employed blast methods for measuring mobilities, have used such large stream velocities that owing to the turbulence of the motion it was not possible to ascribe the observed spreading of the

ions definitely to the presence of ions of different mobilities. Nearly all such observers have however remarked upon the breadth of the positive ion distribution curves being greater than that of the negative. There was a question in those cases whether the greater breadth of the positive ion curves did not arise either from the turbulence of the gas stream since these ions for the same field take longer to cross or from the fact that the positive ions are carried down stream farther than are the negative ions. Erikson[24] avoided this dilemma by using different fields for the two ions so that the time taken to cross was the same for both ions. Using old ions, he still finds the spread of the positive ion curve very much greater than that of the negative. Mahoney[15] also used this procedure but he states that the feet of the positive ion curves he obtained are only a little wider than those of the negative curves. However, in his figures, the central portions of the positive ion curves appear much broader than do those of the negative curves. Briggs,[13] as stated, estimates that the mobilities of the recoil atoms of radioactive substances are distributed continuously over a range of values, of which the largest are 50 percent greater than the smallest.

The evidence seems therefore fairly conclusive that the ions under consideration, whether positive or negative, do not all have the same average mobility; it is overwhelmingly so for the positive ions. Two different explanations present themselves to account for the distribution of mobilities which has been found. We may suppose that among aged ions there is present a number of more or less permanent groups of ions which differ in mobility by such small amounts that they have not been resolved by the methods used. Or, what seems more plausible, we may think of the ions as molecular clusters whose size is undergoing changes owing to the continuous bombardment of the molecules of the circumambient gas. The changes in size of the clusters must be considered as taking place at sufficiently long intervals so that in the time of crossing the number of changes is not very great. Busse[25] supposes water molecules alone cluster about the original ion and Laporte[12] postulates further that after the original ion has become surrounded by one layer of water molecules it is possible for molecules of the surrounding gas to become attached also. These hypotheses were both based on the supposed finding by Busse of what he thought were monomolecular ions having a mobility of 14–15 cm/sec. Busse[26] has since withdrawn this result, because the more extensive and more refined experiments of Schilling[14] failed to detect ions of such high mobility. It is therefore not necessary to consider water molecules as essential for cluster building, although other experiments indicate that such molecules occupy a preferential position.

Erikson[7,24] has presented the attractively simple and strongly supported hypothesis that the negative ions and the "initial" positive ions are monomolecular whereas the "final" positive ions consist of two molecules. Recent work has however greatly weakened the full force of the arguments adduced for this view.

[24] H. A. Erikson, Phys. Rev. **33**, 403 (1929).
[25] W. Busse, Ann. d. Physik **81**, 587 (1926).
[26] W. Busse Ann. d. Physik **84**, 327 (1927).

The first argument given by Erikson is that since the ions must initially have been monomolecular we should be able to detect the transition stages if clusters are formed. That this need not be the case is shown by the work of Mahoney[15] who found that in dry air, cleared of condensable vapors by liquid air traps, the final positive ion was fully formed 0.0014 sec. after its creation. This time is too short for the detection of any intermediate stage or stages and hence also a negative cluster may be formed too quickly for the detection of any stage earlier than the final one.

Erikson's most powerful argument for his hypothesis centers about the two distinct peaks obtained during the transition period of the positive ion, and he argues that if several molecules were involved intermediate stages should appear between the initial and final ions. The time involved in this transition period runs into hundredths of seconds whereas Mahoney found the time required for the full formation of the final positive ion in dry air to be less than 0.0014 sec.; it may have been much less. The comparatively long period discovered by Erikson that the "initial" ion takes to transform into the final form may therefore measure something quite different from the time required for the occurrence of a propitious encounter during which a charged molecule may attach itself to a neutral one. According to Valasek[27] and Tyndall and Grindley[9] increase of humidity of the air increases the transformation period of the positive ions, and Mahoney only found this period sufficiently long for measurement in the presence of water vapor. Molecules of water or molecules of some other impurity,[28] are therefore in some way involved in retarding the formation of the final positive ion, and this must arise from a change produced in the nature of the ion first formed by the ionizing process. The ion thus transformed must later undergo another drastic change in some comparatively rare encounter which makes possible the formation of the final ion cluster. This view is essentially the same as that held by Tyndall, Grindley and Sheppard.[26]

The experimental evidence presented in this communication shows that the final ions in moist air, both positive and negative, consist in each case of a group of which the members do not all have the same mobility. As the "initial" positive ions have the same mobility as the negative ions, they too must consist of a group whose individuals are not all alike.

Since Erikson[24] also found the distribution curve for the final positive ions to be much broader than a similar curve for negative ions under a like displacement, he too is forced to assume that the final positive ion is a changing aggregation, varying according to his view between one, two and three molecules.

The changes produced in the mobility especially of the negative ions in air by the addition of small amounts of impurities seem much too large to be accounted for by supposing them due to a diminution of the free paths of the ions caused by the polarization of the molecules of the impurity being greater than that of the molecules of the gas itself. It is therefore natural to

[27] Leila M. Valasek, Phys. Rev. **29**, 542 (1927).

[28] A. M. Tyndall, G. C. Grindley and P. A. Sheppard, Roy. Soc. Proc. **A 121**, 185 (1928).

suppose that the impurity produces the observed changes because it becomes more readily attached to an ion than do the main constituent molecules of the gas.

The method used in these experiments has proved itself well adapted for measuring the absolute values of the mobilities corresponding to the peaks of the distribution curves. Steady motion of the gas stream is realized, the quantities involved can all be obtained accurately, and the effects of diffusion, mutual repulsion of the ions, and effects of space charge can be eliminated. Some improvement on the accuracy of the results reported could be obtained by using only the most favorable values of the quantities measured.

It should be noted that some observers using high fields reduce their results directly by proportion to values for lower fields whereas theory shows that for such high fields the velocities of the ions are not proportional to the fields.

The value of 1.22 cm/sec. obtained for the mobility of the positive ions is considerably smaller than that usually given. The reason for this may be the fact that the positive ions decrease in mobility with age and the ions I used were all over two seconds old. The value given is only a little below 1.24 cm/sec., the value recently obtained by Tyndall, Starr and Powell[29] by a relative method for positive ions 0.25 sec. old.

It is proposed to make measurments with the apparatus described in very dry air and under other conditions. Ions may be produced directly in the main gas stream by allowing alpha-rays to enter for a short distance through the ion inlet openings *H*. Some preliminary measurements already done in this way where the time taken for the ions to cross the space between the cylinders was 0.01 sec., gave almost but not quite identical single peaked distribution curves for both positive and negative ions.

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[29] A. M. Tyndall, L. R. Starr and C. F. Powell, Roy. Soc. Proc. **A121**, 172 (1928).