THE MOBILITIES OF IONS IN DRY AND MOIST AIR

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Abstract

With the method recently described the distribution of mobilities of aged ions in dry air has been determined and the values for moist air remeasured because of a neglected correction in the previous results. In air dried by passage through metal tubes and filters immersed in liquid air the negative ions were found to consist of two main groups of which the less numerous group comprises about one third of the total number of ions and has a peak mobility only about 60 percent of that of the main group. The number of ions in the lesser group was relatively smaller in air dried by calcium chloride alone and their presence in still smaller numbers in air having a water content of 2 mg per liter accounts for the dissymmetry in the distribution curves of negative ions in moist air reported in the previous paper. The distribution curves for positive ions in dry air also show some indications of two groups of ions only here the ions of the less numerous group, which does not appear in moist air, have a peak mobility about 40 percent higher than those of the main group. The absolute values of the peak mobilities found for the main group of negative ions in the driest air used for a pressure of 76 cm and a temperature of 20°C was 2.45 cm/sec. This diminished to 2.37 cm/sec for air dried by calcium chloride, and to 2.08 cm/sec for air containing 2 mg of water per liter. Under the same conditions the mobilities of the positive ions increased in succession from 1.05 cm/sec to 1.10 cm/sec to 1.36 cm/sec. These large opposite changes produced by a small fraction of one percent of water molecules can only be explained on the supposition that aged ions in air consist of molecular clusters whose structure is affected by the presence of water molecules. The second group of negative ions cannot consist of ions having multiple electronic charges, because the mobility of these ions is smaller than that of the main ion group. It cannot arise from the presence of impurities condensable at liquid air temperatures. Since electrons do not readily become attached to nitrogen molecules, the central molecule of each of these ions is probably an oxygen molecule and the two cluster groups may arise either from a difference caused by a different point of attachment of the electron to the central molecule or from the nature of the molecule that first becomes attached to this central molecule in the process of cluster formation.

In a recent paper[1] I reported some results on the mobilities of well-aged ions in moist air which showed that the ions of each sign are not all alike. No distinct groups were resolved but the mobilities in each case were found to be spread continuously over a range of values. Within this range, the positive ions as regards numbers present were distributed quite symmetrically about a most numerous kind, while the negative ions had mobility values extending much farther in the direction of lower mobilities than in the direction of higher mobilities.

[1] J. Zeleny, Phys. Rev. **34**, 310 (1929).

The method employed in the mobility measurements has some distinct advantages over other methods which have been used, and the work with it has now been extended to dry air.

The new results disclose for negative ions in very dry air a second group of ions comprising about one-third of the total number and having a mobility only about six-tenths of that of the ions in the main group. Indications of this new group in smaller numbers are well marked in air dried by passage through calcium chloride alone, and the presence of these ions in still smaller numbers also accounts for the lack of symmetry mentioned above in the distribution curves for negative ions in moist air.

Some indication too was found that among positive ions in very dry air a second group of higher mobility than that of the main group is also present.

The peak mobility of the main group of positive ions was found to decrease quite markedly when the air was dried, while that of the main group of negative ions increases with removal of moisture.

The method used consists in blowing a nonturbulent stream of air between two concentric cylinders, admitting ionized air into this stream through small openings in the outer cylinder, and measuring the distance the ions are carried down stream while they are crossing the space between the two cylinders under the action of an applied field.

The average velocity of the main air stream with which the velocity of the ions was compared was maintained throughout these measurements at approximately 8 cm/sec. This low velocity is well within the limits of nonturbulent motion in the apparatus used. The potentials used on the outer cylinder were such as allowed the ions in crossing to be carried down stream only far enough to permit an accurate determination of the distance, in order to keep the correction for ion diffusion as small as possible.

Reference should be made to the previous paper[1] for details regarding the apparatus and for the procedure used in reducing the observations, as well as for references to the work of other observers.

A few modifications were made in the apparatus. The connecting tubes were all made of metal or glass. The openings in the outer cylinder through which the ionized air is admitted into the main gas stream were enlarged and now consist of 20 slots along a circumference, each slot being 1 mm wide and 9 mm long. The total area of these openings is now such that with a stream of ionized air delivering 9.8 cc per sec. as was used throughout these measurements the correction which has to be applied to mobility determinations to allow for the penetration of this ion stream into the main air current is on the average less than one-half of one percent.

The movement of the inner cylinder with its insulated ion collector ring is now effected by a threaded micrometer head working on a rod extending from the system to be moved to the outside of the apparatus. This improvement makes possible more rapid and more accurate settings of the ion collector ring.

The radioactive material used for producing ions in the auxiliary chamber during these measurements consisted of a deposit of polonium on a nickel strip which was wound around the outside of the outer cylinder a short distance up stream from the openings through which the ions entered the main gas stream. The polonium coating was sealed gas tight by a covering of thin condenser paper.

The age of the ions as they entered the main gas stream was on the average about 3 sec. although some of the ions were only about 1 sec. old.

The air for the main gas stream was supplied by the pressure system of the laboratory. To dry the air, it was passed in succession through a large filter, through a 16 cm wide bottle containing granulated calcium chloride, through a second filter, through a long copper coil of small diameter immersed in liquid air, and finally through a second copper coil immersed in a water bath maintained at room temperature. The air for the auxiliary ion bearing stream was passed through a similar, separate drying system. In some of the last measurements, additional filters immersed in liquid air were added to the drying system. These contained first a section filled with coarse metal filings to ensure a closer contact between the cold surfaces and the air, and then closely packed glass wool to remove any crystals of ice which might be blown along by the stream and later be changed to vapor.[2]

Measurements of the mobilities of both positive and negative ions were made not only in air dried as has just been described, but also in air dried much less thoroughly by calcium chloride alone, and in undried air of low but determined humidity. These last measurements are included because the absolute values given in my last paper for the mobilities in moist air are somewhat low owing to the fact that the air pressure at the gauge used for measuring the stream velocity was unwittingly allowed to exceed the limit within which no correction for this pressure had to be made. A mercury manometer, previously removed to avoid the presence of mercury vapor, was now kept at this gauge and the gauge was recalibrated for the same gas pressures as were used in the measurements.

Air Dried by Aid of Liquid Air

Curve A of Fig. 1 gives an example of the way in which negative ions were found distributed along the inner cylinder, when the air used was dried as described above by passage through calcium chloride and through a long helical tube immersed in liquid air. The abscissas give the down stream distances from the place of entry of the ions into the air stream and the ordinates give the corresponding ion numbers. The difference of potential between the two cylinders was 12 volts. The curve of distribution is a compound one, and by drawing the two branches c and d, the sum of whose ordinates for any abscissa is equal to the corresponding ordinate of the experimental curve, the compound curve may be resolved into two simple curves having peaks at a and b. The observed distribution thus shows the presence of two distinct groups of ions, of which those of higher mobility are about twice as numerous as those of lower mobility. Some of the other

[2] H. A. Erikson, Phys. Rev. **34**, 642 (1929).

similar observations show a small number of ions carried even farther down stream than is here apparent, indicating ions of still lower mobility. The mobility corresponding to the peak of the less numerous group of ions was found to be on the average 1.45 cm/sec. which is about six-tenths of the value for the main group.

Curve *B* of Fig. 1 is an example of corresponding results obtained for positive ions. The difference of potential between the cylinders was 15 volts. The main air stream and the ion bearing stream as well were passed in this case through calcium chloride and tubes immersed in liquid air and subsequently through a cylindrical metal box, also immersed in liquid air, which contained a layer of fine metal turnings and closely packed glass wool.

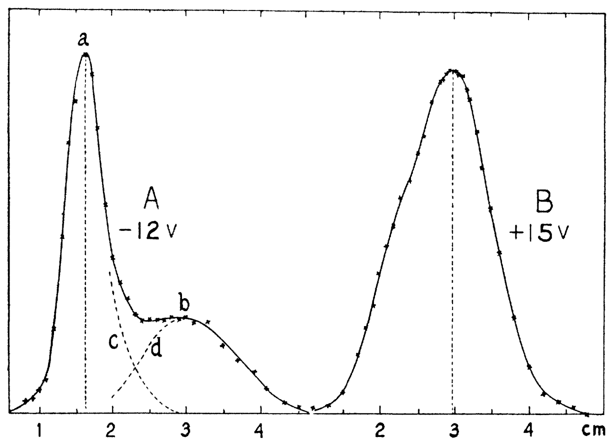

Fig. 1. Distribution of ions in dry air. Ordinates represent number of ions corresponding to down stream distances given as abscissas. Curve *A* is for negative ions in air dried by passage through tubes immersed in liquid air. Curve *B* is for positive ions where a filter immersed in liquid air was added to the drying system.

Curve *B* shows an entirely different distribution of ions than that found for negative ions. The dotted ordinate drawn through the peak of the curve shows that now the number of ions on the upstream side of the peak is greater than on the downstream side. There is a bulge in the curve near the abscissa distance 2.2 cm which appears also in all of the other similar observations, indicating the possible presence of an unresolved group of ions having a peak mobility of about 1.5 cm/sec., the mobility of the ions at the main distribution peak being here only 1.06 cm/sec.

A summary of the mobilities found for the peak of the distribution curves of the main group of ions in air dried by use of liquid air is given in Table I. The uncorrected potential of the outer cylinder relative to the inner one is indicated in each case. These results, as well as all others to be given, have been reduced to a temperature of 20°C and a pressure of 76 cm of mercury.

The unusually large difference between the positive and negative mobilities is to be noted. This difference is much larger than can be accounted for according to prevailing theories by a difference of mass alone. Linear dimen-

TABLE I. *Peak mobilities of predominant group of ions in very dry air.*

(a) Air dried by $CaCl_2$ and tubes in liquid air.			
+12 volts	1.10 cm/sec.	−12 volts	2.40 cm/sec.
+15 "	1.06 "	−15 "	2.38 "
+20 "	1.07 "	−10 "	2.41 "
Positive ions	1.08 cm/sec.	Negative ions	2.40 cm/sec.
(b) Air dried by $CaCl_2$ and tubes and filters in liquid air.			
+15 volts	1.04 cm/sec.	−15 volts	2.45 cm/sec.
+15 "	1.05 "	−15 "	2.44 "
+15 "	1.06 "		
+15 "	1.04 "	Negative ions	2.45 cm/sec.
Positive ions	1.05 cm/sec.		

sions of the ions must be invoked as a prominent factor in determining such variation in mobility.

The presence of the extra filters immersed in liquid air appears to have resulted in a more complete drying of the air, since the positive ion mobilities in (b) the lower portion of the table are on the average a little smaller than in (a) the upper portion, and those of the negative ions are a little larger. The amount of water remaining in the air after the above treatment must be very small. The computed amount at −194°C given in the International Critical Tables is 1.6×10^{-23} mg per liter; naturally such a low value cannot be approximated in the apparatus used.

The total spread of ions when they arrive at the inner cylinder as shown by the curves of Fig. 1 does not represent altogether ions of different mobilities. A part of the spread arises from diffusion and mutual repulsion of the ions during their passage between the two cylinders. A method of correcting for these effects is fully described in my previous paper,[1] and when applied to the results for positive ions shows that ions are present ranging in mobility from 0.83 cm/sec. to 1.58 cm/sec., the two possible groups present being treated as one. Owing to the partial overlapping of the two groups of negative ions, the spread of mobilities in the main group having the faster ions can only be obtained for the upstream side of the peak. The fastest ions here were found to have a mobility 11 percent greater than the peak mobility. In the group of lower mobility the estimated spread on either side of the peak mobility is between two and three times the above value.

The high value of the peak mobility of negative ions here given is in agreement with that obtained by Schilling[3] likewise in very dry air but for ions of lesser age. The mobility of the positive ions here found for very dry air is lower than values hitherto reported. It must be remembered that this value corresponds to the peak of a distribution curve which shows strong indications of a less numerous group of higher mobility. Schilling makes note of the fact that the curves he obtained with positive ions, using the alter-

[3] H. Schilling, Ann. d. Physik **83**, 23 (1927).

nating field method, were of a form to be expected from a mixture of different ions.

Air Dried by Granulated Calcium Chloride

A number of measurements were made with air dried by passage through granulated anhydrous calcium chloride only, this being known as a rather poor drying agent and leaving in air water to an amount of about 0.2 mg per liter.[4]

Examples of the ion distribution curves obtained under these conditions are given in Fig. 2, where curve *A* represents negative ions and curve *B* positive ions, the voltage used being 15 volts in each case.

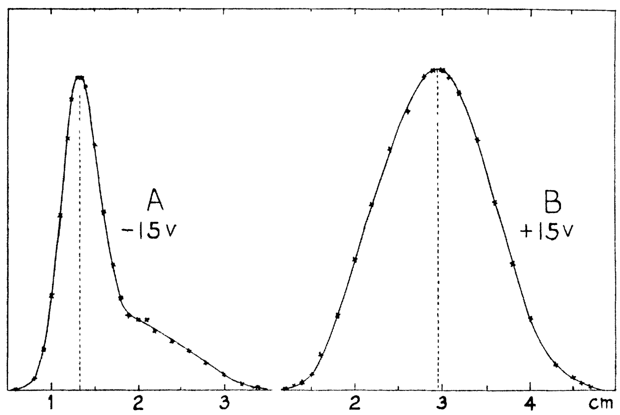

Fig. 2. Distribution of ions in air dried by calcium chloride. Curve A = negative ions. Curve B = positive ions.

The curve for the negative ions, in addition to the main group represented by the high peak, also shows the existence of ions of a smaller mobility but these are less numerous than was found to be the case (curve *A*, Fig. 1) with air more completely freed of water molecules.

The curve for the positive ions does not show the bulge seen on curve *B* of Fig. 1, although the dotted ordinate drawn through the middle of the peak helps to show the presence here also of a larger number of ions of mobility greater than the most numerous kind than there are of ions with a smaller mobility.

Table II. *Peak mobilities of ions in air dried by calcium chloride alone.*

+15 volts	1.10 cm/sec.	−12 volts	2.38 cm/sec.
+12 "	1.12 "	−20 "	2.33 "
+15 "	1.08 "	−10 "	2.35 "
+15 "	1.09 "	−15 "	2.41 "
+15 "	1.09 "		
+15 "	1.13 "	Negative ions	2.37 cm/sec.
Positive ions	1.10 cm/sec.		

[4] A. T. McPherson, Jour. Am. Chem. Soc. **39**, 1317 (1917).

Table II gives a summary of the results for the peak mobilities of ions in air of this degree of dryness.

The values for the positive ions are here a little larger and those for the negative ions somewhat smaller than those given in Table I.

The positive ion group was found to extend between the same limits as given above for positive ions in air dried by aid of liquid air. The main negative ion group extends from a peak mobility of 2.37 cm/sec. up to 2.54 cm/sec. The presence of a group or groups of negative ions of lower mobility here also prevents the getting of an estimate of the value of the lower limit of the mobilities in this main group.

Air with Average Water Content of 2 mg/liter

Fig. 3 gives examples of the distributions found for ions in filtered air drawn directly from the pressure system of the laboratory, and containing on the average 2 mg of water per liter. The air for the auxiliary stream in

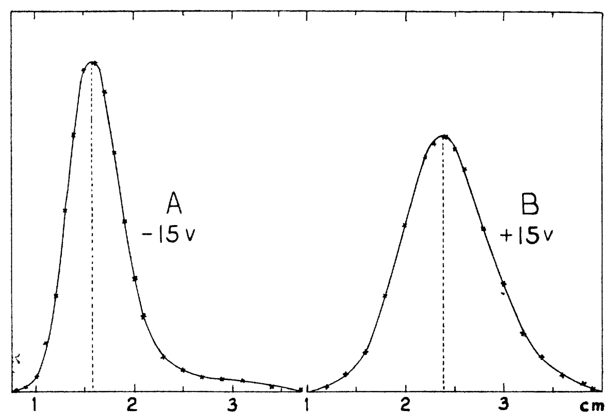

Fig. 3. Distribution of ions in air having a water content of 2 mg per liter. Curve *A* = negative ions. Curve *B* = positive ions.

which the ions were produced was supplied by a gasometer containing water and carried on the average 13.6 mg of water per liter. As this air did not mix with the main air stream, it is probable that the mobilities obtained are the same as would have been obtained had the ion bearing stream contained the same amount of water as was present in the main stream.

The positive ion distribution curve *B* shows the ions to be almost equally distributed on the two sides of the peak value. The negative ion curve *A* is again far from symmetrical but the group of ions of lower mobility, clearly indicated in Figs. 1 and 2, here shows only as an extended foot of the curve for the main ion group. It appears therefore that this low mobility group of ions forms a smaller and smaller portion of the whole number as the amount of water present in the air is increased. Its presence accounts for the lack of symmetry, reported in the previous paper, in the distribution curves for negative ions in moist air. The positive ions are spread over a somewhat smaller range of values here than is the case in dry air.

A summary of the results for moist air is given in Table III.

TABLE III. *Peak mobilities in moist air.*

Potential	Water content	Mobility	Potential	Water content	Mobility
+15 volts	1.90 mg/l	1.36 cm/sec.	−12 volts	1.45 mg/l	2.08 cm/sec.
+ 8 "	1.90 "	1.40 "	−15 "	1.98 "	2.05 "
+20 "	1.90 "	1.35 "	−12 "	1.98 "	2.07 "
+15 "	1.98 "	1.34 "	−12 "	1.74 "	2.12 "
+12 "	1.98 "	1.35 "			
+15 "	1.33 "	1.37 "		Negative ions	2.08 cm/sec.
+15 "	2.89 "	1.38 "			
	Positive ions	1.36 cm/sec.			

The water content of the air used in the main gas stream is given in milligrams per liter in the second and fifth columns. The water molecules in the stream formed only about one quarter of one percent of the total number and yet their effect on the mobilities of the ions is seen, by comparison with the values of Table I, to be quite marked, the positive ion mobilities being increased by about 30 percent and the negative ions decreased by about 18 percent relative to those obtained in the driest air used. It is not possible to account for these large opposite effects on the two ions by an increase in the resistance to their motion due to the presence of the water molecules. It is necessary therefore to postulate that aged ions consist of molecular clusters and that the water molecules produce a change in their structure, such that the size of the positive ion cluster is diminished and that of the negative ion increased.

The increase in the mobility of positive ions produced by the presence of water molecules as given above confirms my earlier results and is in agreement with the results of Blanc[5] and Laporte[6] for ions of lesser age. Several other observers have obtained an opposite effect of moisture upon the mobility of positive ions, but it must be noted that in general the ions used have been much less aged than was the case in the experiments being reported. Valta[7] using very young positive ions found their mobilities to decrease both with age and with water content of the air and has obtained in very dry air values as high as 6.8 cm/sec. Nolan and Nevin[8] found remarkable fluctuations in the values of the mobilities of ions of both signs as the water content of the air was increased. It is difficult to reconcile all of these different experimental results on the effect of moisture on ionic mobilities in air.

The results given above clearly show the presence of two groups of aged negative ions in very dry air. The group of lower mobility has about one-half as many ions as the one of higher mobility. The relative number of these slower ions is considerably smaller in air dried by calcium chloride alone, and is still less in air having a water content of 2 mg per liter.

[5] A. Blanc, Jour. de Physique **7,** 825 (1908).
[6] M. Laporte, Ann. de Physique **8,** 466 (1927).
[7] Z. F. Valta, Journal of Geophysics and Meteorology (Russian) **6,** 197 (1929).
[8] J. J. Nolan and T. E. Nevin, Proc. Roy. Soc. **A127,** 155 (1930).

It is of theoretical interest that among aged ions it is possible under any circumstances for two distinct groups of small ions to coexist. It is improbable that the new group consists of ions with multiple charges which tend to become reduced to unit charges in the presence of water molecules, since all of the evidence points either to an increase of mobility with increase of charge or to an independence of mobility of the ionic charge. The presence of some unusual impurity might be thought to give rise to the new ion group. If such an impurity consisted of vapors coming from the compression pump or elsewhere, we should expect its effect to be least pronounced or absent when the air was passed through tubes immersed in liquid air where such vapors would be condensed, whereas the opposite was found to be the case.

It is probable therefore that the two negative ion groups under discussion consist of clusters of molecules the center of each of which is a molecule of one of the chief constituents of the atmosphere, to which an electron has become attached. Since electrons do not attach themselves readily to nitrogen molecules the central molecules are probably oxygen molecules. The evidence available is not sufficient to account satisfactorily for the two negative ion groups, but we may suppose that the difference in cluster size arises either from a difference in place of attachment of the electron to the molecule or from a difference in the kind of molecules that by chance first become joined to the central charged molecules during the formation of the clusters.

I am indebted to Mr. R. S. Baldwin and to Mr. C. D. Bock for aid with the measurements.