ON THE NATURE OF THE IONS IN AIR

By Henry A. Erikson

Abstract

Production and ageing of the initial positive ion in dried air and nitrogen. Effect of water vapor.—Results are given showing the production and ageing of the initial positive ion in dried air and dried nitrogen. Results are also given showing that when the final positive air ion of mobility 1.36 is passed into moist air the final ions disappear and a swifter 1.87 ion appears. Results are also given showing that these in turn change back into a 1.36 ion. The interpretation given of the above is that a neutral H_2O molecule gives up an electron to the final 1.36 two molecule positive ion thus giving a one molecule positive ion which has a higher mobility. This H_2O^+ ion ages by attaching itself to another molecule forming a slower 1.36 ion. The article closes with a statement of the reasons for the author's view that the initial and final positive ions are respectively one and two molecules large.

IN EARLIER papers[1] results have been published which indicate that an H_2O molecule transfers an electron to the final positive air ion (mobility 1.36 cm/sec per volt/cm) thus forming an H_2O^+ ion which has the same mobility as the initial positive or the negative air ions namely 1.87 cm/sec per volt/cm.

In this paper are given the results of a closer examination of this transition. A diagram of the apparatus is given in Fig. 1. A and B are two brass

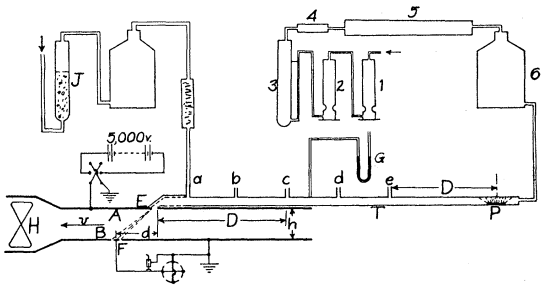

Fig. 1. Diagram showing arrangement of apparatus.

plates which form the top and bottom of a tube about 70 cm long and of rectangular cross-section. The distance between the plates A and B is 3.5 cm. Air from the room passes through the tube AB as a result of the action of a fan H, 12 cm in diameter, and driven at a speed of 5000 R.P.M. by a synchronous motor connected by a silent link-belt to a cream-separator worm. By this means an air speed of about 3500 cm/sec is obtained.

The ions are produced by placing a polonium plate at P in the auxiliary tube PE, Fig. 1 (100 cm long and 4 cm in diameter). The air passes from P to E carrying the ions with it. The air velocity in this auxiliary tube was

[1] Erikson, Phys. Rev. **30**, 344 (1927); **31**, 311 (1928); **32**, 791 (1928).

about 165 cm/sec. At E the ions pass into the main stream. Plate A was kept at a potential of about 5000 volts with reference to B which is connected to earth. In case A is positive with respect to B, the positive ions are driven across the air stream to the plate B. Because of the motion of the air they are also carried down-stream a distance d. When the electrode F is at the proper down-stream distance an ionic current is obtained which is registered by the electrometer. By plotting the currents against the distances d the ionic spectrum is obtained, the distance d for the maximum of which is proportional to the reciprocal of the ionic mobility in accordance with the relation

$$k = h^2 v / Vd$$

where h is the distance between the plates A and B, V their difference of potential, v the speed of the air, and k the mobility of the ions.

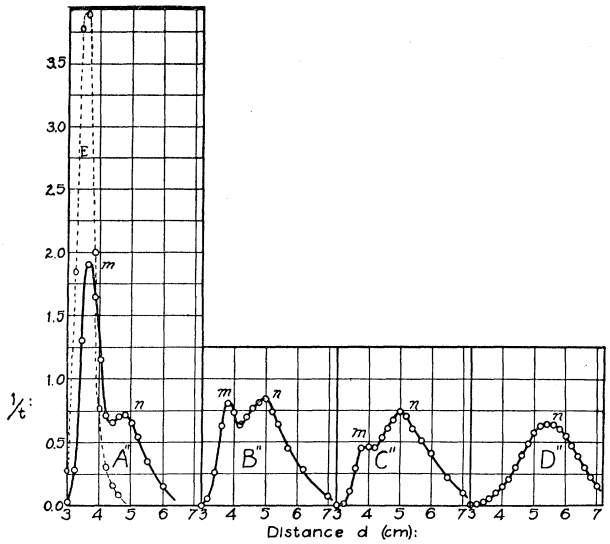

Fig. 2. Curves showing change with age of initial positive ion into final ion in dried air.

As the effect of moisture is quite marked, it is necessary to dry the air which passes through the auxiliary tube in which the ions are produced. In this work the air passed through the calcium chloride towers 1 and 2. It was then bubbled through a sulphuric acid column 3. After passing through glass wool in 4, it passed through a tube 5, 6 cm diameter and 1.2 meters long, containing P_2O_5 and glass wool. From this tube it passed into the glass chamber 6 and from there into the auxiliary tube.

In order to show what ions are formed in air dried in this manner the following observations were made. In Fig. 2, curve A'' is for the positive ion and was obtained when the polonium plate was placed at a. In this case the ions are obtained very soon after their formation. The maximum m is for the initial positive ion of mobility 1.87, the same as that of the

negative ion shown by the dotted curve *E*. Maximum *n* is for the final positive ion, mobility 1.36. Curve *B''*, Fig. 2, was obtained when the polonium was at *b*, thus giving ions a little older. It is seen how the final ion *n* is formed at the expense of the initial ions *m*. Curve *C''*, Fig. 2, was obtained when the polonium was at *c*. Practically all of the initial ions *m* have changed over to the final 1.36 ion *n*.

Curve *D''*, Fig. 2, was obtained with the polonium plate sufficiently far up stream, distance *D*, so that all the initial 1.87 ions have had time to change over. On the writer's view the initial 1.87 ion is a single molecule which has lost an electron in the ionizing process. This initial positive one molecule ion shares an electron with a neutral molecule, thus forming the final positive 1.36 ion which is therefore an ion complex two molecules large. It is this transition which is observed above.

Ions Produced in Dried Nitrogen

In order to reduce still further the chance of being misled it was decided to use nitrogen. The nitrogen was procured from the Kansas City Oxygen

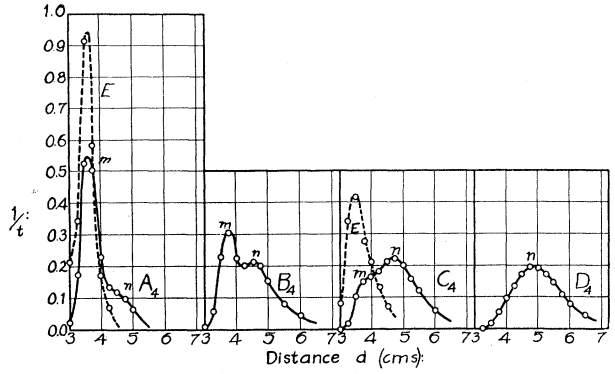

Fig. 3. Curves showing change with age of initial positive ion into final ion in dried nitrogen.

Gas Company. This nitrogen according to the Company's test has a purity of 99.7 percent or better. The gas was delivered in the usual commercial cylinders at a pressure of 1500 lbs/sq. in. The gas in the filling container is saturated. The nitrogen in the cylinders delivered is therefore somewhat below saturation.

In order to dry the nitrogen a cylinder of the same size was opened and 0.7 lb. of phosphorous pentoxide was introduced. The cylinder was then evacuated after which it was connected to the supply cylinder and the pressure allowed to equalize. The cylinder containing the nitrogen and the P_2O_5 was then allowed to stand for one week. The nitrogen was then passed directly into the auxiliary tube at *P*. The stream being adjusted by means of the reducing valve so that the surfaces of the H_2SO_4 in the gauge *G* were on the same level thus securing atmospheric pressure in the auxiliary tube.

Fig. 3 gives the results obtained. Curve A_4 is for the positive ion and was obtained with the polonium close to E, Fig. 1, all the side tubes being closed. This shows that practically all the ions are initial 1.87 ions. A trace of the final 1.36 ion is seen at n. Curve E is for the negative ion. Curve B_4 was obtained with the polonium moved up stream to b, Fig. 1, the nitrogen used having been dried for 24 hours instead of one week as in A_4. Here it is seen that more of the initial ions m have had time to change over into the final ions n.

Curve C_4 was obtained with the polonium at c, Fig. 1, the nitrogen having been dried for 24 hours. Here the initial ions m are practically gone. Curve E is for the negative ion and shows that it is unaffected. Curve D_4 was obtained with the polonium at e, the nitrogen having been dried for 24 hours. Here it is seen that all the ions are final 1.36 ions.

The conclusion from the above is that the formation of the initial ion and its transition into the final ion is a characteristic process in both air and nitrogen.

The Effect of H_2O on the Final Ion

It is seen above that when the polonium is placed up stream a distance D, all the initial ions have had time to change into the final ion. In order to examine the effect of H_2O, side tubes a, b, c, d, e were inserted in the

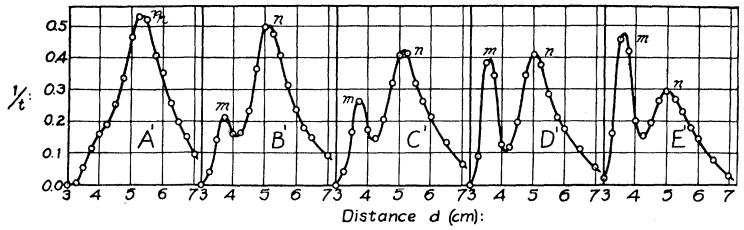

Fig. 4. Curves showing the increase in the number of initial ions with increase in amount of moisture.

auxiliary tube EP, and the polonium was placed a distance equal to D on the up stream side of the side tube e. Only the final positive ions are therefore present when they reach the tube e.

Air which had bubbled through water in the tower J, Fig. 1, was passed into the auxiliary tube at the points a, b, etc. In Fig. 4 are shown the results obtained when the moist air was admitted through the side tube a only. Curve A' was obtained with no moist air admitted. The air passing through the auxiliary tube EP, Fig. 1, was dried in this case by passing through two calcium chloride towers then through a glass tube 8 cm in diameter and 1.2 meters long containing glass wool and P_2O_5, then through two similar tubes in parallel, also containing P_2O_5 and glass wool. Curve A' shows that the positive ions present are the final 1.36 ions, n.

A small amount of moist air was then admitted through the side tube a, and the curve B', Fig. 4, was obtained. Here it is seen that the initial 1.87

ion, *m*, is appearing. Curve *C'* was obtained when more moist air was admitted at *a*. A greater number of initial ions *m* are present and less of the final. Curve *D'* was obtained with more moist air admitted at *a* and curve *E'* with still an additional amount. It is thus seen, as reported earlier, that the addition of water causes the transition of the final 1.36 ion into the initial 1.87 ion.

The writer's view is that a neutral H_2O molecule, having an ionization potential of about 13, gives up an electron to the final two-molecule 1.36 positive ion which, if it is an air ion, has an ionizing potential of the order of 16. A one-molecule positive 1.87 H_2O ion is thus formed, the 1.36 ion being neutralized.

Fig. 5 shows the results obtained with conditions the same as for Fig. 4. Here, however, a stream of constant moisture was passed consecutively through the side tubes. Curve *A* is for air dried as described in the case of air above, and with no moist air entering. Only the final ion *n* is present. Curve *B* was obtained when the moist air was admitted through the side

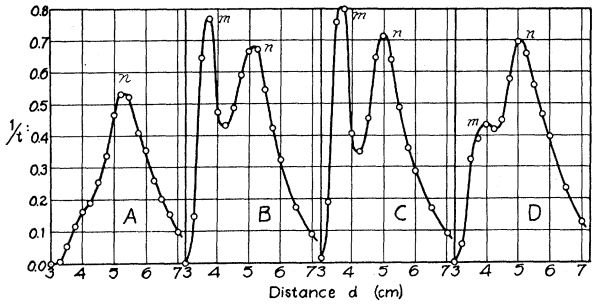

Fig. 5. Curves showing the increase, then decrease in number of initial positive ions with time in moist air.

tube *a*. It is here seen that the initial 1.87 ion *m* has formed, whereas without the moisture only the final positive ion *n* is present. Curve *C* was obtained when the moist air was admitted through the side tube *c*. It is here seen that there has been no appreciable increase in the number of initial 1.87 ions. The reason for this is that the initial 1.87 water ion formed is ageing, that is, it is attaching itself to neutral molecules and is thus again forming a final 1.36 ion. Curve *D* was obtained when the moist air was admitted through the side tube *e*. Here it is seen that the initial 1.87 water ions have quite completely changed into the 1.36 ions *n*. It is thus evident that the 1.87 positive ion formed due to the action of water attaches itself to another molecule. A point of interest here is that a higher resolving power is obtained than in the case of the corresponding air ions. This would mean that water ions are more stable. These results also indicate that the final ion represented by curve *A* is not a water ion. When the ion *n*, curve *D*, is formed its mobility should be independent of the moisture content. When

Tyndall, Starr and Powell[2] found that additional moisture did not alter the mobility of the final ion in a closed vessel they were no doubt measuring in terms of the final water ion.

In two interesting articles[2,3] which appeared recently it is found that in closed vessels the initial ions do not appear. Mahoney finds, however, that the initial ion is present in a closed vessel when moist air is used and that this initial ion changes with age into the final ion. Tyndall, Starr and Powell also find only a slight indication of the presence of the intial ion in a closed vessel and suggest that the reason may be that something very favorable to the rapid transmission of the initial ion accumulates in a closed vessel. They suggest that it may be ozone formed by the ionizing rays.

Tyndall, Grindley and Sheppard[4] find that in using a blast method like the above the initial ion appears normally as found by the writer. In introducing ozone they find that the formation of the final ion is enhanced.

The experience of the writer leads him to favor this view. For example, when room air which has been heavily ionized by means of beta-rays, but from which the ions have been removed by means of a field, is passed through the auxiliary tube, Fig. 1, where it is again ionized by the polonium, a greater proportion of final ions is obtained. In a closed vessel these products accumulate and an increased effect may be expected.

Since the results given in this paper were obtained, the writer has remodeled the apparatus so that the air through the auxiliary tube, after passing through $CaCl_2$ and P_2O_5, passes through copper coils immersed in liquid air, care being taken to have the air also pass through glass wool while cold. It is then found that only the initial ion is obtained at short age and also that the rate of transition of the initial into the final ion is very greatly reduced. It is also found that passing the air through $CaCl_2$ and P_2O_5 only, without the liquid air cooling, favors greatly the formation of the final ion. When air which has bubbled through H_2SO_4 is used the negative ion is also affected. These results will appear in a later publication.

Discussion of Results

The question of interest is:—Are the above ions clusters of several molecules or are they of a simple one or two-molecule structure? It is accepted that the ionizing process consists in an electron leaving a molecule under the action of the ionizing ray. On the basis of no appreciable dissociation by the rays one is forced to assume that the positive ion formed as a consequence of the ionizing process is initially one molecule large provided of course that the medium ionized is in the molecular state. In the permanent gases such as nitrogen, oxygen, CO_2, argon, etc., at normal temperature, this is conceded to be the state. There is furthermore evidence that in the ionizing process only one electron is emitted from each body ionized. To this helium seems to be a slight exception.

[2] Tyndall, Starr and Powell, Proc. Roy. Soc. **A121,** 172 (1928).
[3] Mahoney, Phys. Rev. **33,** 217 (1929).
[4] Tyndall, Grindley and Sheppard, Proc. Roy. Soc. **A121,** 185 (1928).

The conclusion therefore is inevitable that the initial positive ion formed in the permanent gases is one molecule large. There is evidence that the electron emitted in the ionizing process remains free but a very short time. The only possibility the electron has for terminating its free state is initially to attach itself to a neutral molecule of the medium. It is thus seen that initially, one is forced to think in terms of a one molecule positive ion and a one molecule negative ion.

By using the blast method described above, the writer[5] was able, as is also shown above, to evaluate the ions very soon after their formation in air. It was then found that in air the positive ion has the same mobility as the negative ion. The value of this common mobility is 1.87 cm/sec per volt/cm. This value of 1.87 is the highest value observed in air at normal temperature and pressure neglecting small variations depending upon the degree of purity of the medium. Since the mobility value 1.87 is the same for both the initial positive and negative ions they must have the same charge and the same complexity of structure as to molecular grouping. The most obvious conclusion therefore is that these two 1.87 bodies are the initial one molecule positive and negative ions referred to above. Were they clusters of several molecules a time interval for their formation would be necessary which should be detectable in the measurements. No evidence of this has been obtained. Furthermore were these two 1.87 ions clusters of several molecules it is not likely that the equilibrium value for the mobility would be the same for the positive as for the negative since their natures are different. The positive is deficient in electrons and therefore has an electron affinity, the negative on the other hand has an excess of electrons and is surrounded by neutral molecules which have their electron affinity already satisfied. In this reasoning one does not include gases of the character of chlorine which have an electron affinity. As is observed above and as was observed by the writer several years ago, the initial positive 1.87 ion soon changes into an ion of mobility 1.36 cm/sec per volt/cm which is the final positive ion and which is a fairly stable structure. It is possible to obtain a resolving power sufficiently high so that the final positive ion may be separated from the initial ion. Fig. 6 shows what is possible in the way of resolution. The maximum m is for the initial (1.87) ion and the maximum n is for the final (1.36) ion. In this process of separation there is no evidence of intermediate ions. As seen above in Fig. 2 it is possible by increasing the time to observe the formation of the final ions at the expense of the initial ions. If the initial and the final positive ions were clusters of several molecules the above clear cut observations would not be thinkable. Intermediate bodies would be inevitable in the process of formation which would preclude a clear cut resolution such as is found possible. The conclusion seems inevitable that the 1.36 ion is due to the initial one molecule, 1.87 ion,

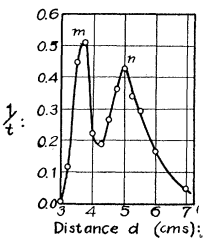

Fig. 6. Curve showing degree of possible separation between initial and final positive ions.

[5] Erikson, Phys. Rev. **20**, 117 (1922).

attaching itself to a neutral molecule thus forming a two molecule ion complex the characteristic mobility of which is 1.36. If, furthermore, the two positive ions are clusters it is difficult to see why these two would be stable and other groupings unstable.

It is seen above that when H_2O is added to the air the final 1.36 ion disappears and a 1.87 ion is formed. As stated above the writer believes that the H_2O molecule having a lower ionizing potential gives up an electron to the final 1.36 ion thus neutralizing it and giving in its place a one molecule H_2O positive ion which since it is one molecule large and carries a single charge has the mobility 1.87, the same as the negative ion, and which is characteristic of a one molecule ion. Were the ions clusters it is hardly to be expected that the 1.87 value would result from an alteration of this character.

In earlier papers it was shown that the same two characteristic values are obtained when argon, CO_2 and hydrogen are passed through the auxiliary tube.

The values 1.87 and 1.36 are so different and so distinctive that it is difficult to avoid the conclusion that they represent the first and second steps in molecular aggregation. In other words that the value 1.87 is characteristic of a one molecule ion and the value 1.36 characteristic of a two molecule ion.

Air, argon, CO_2, hydrogen and actinium, thorium and radium active deposits have ions of comparable mobilities in air. This means that the mobility is practically independent of the mass of the ion. Apparently the mobility depends almost wholly upon the charge carried by the ion, the resistance to motion being determined by the polarizing action on the adjacent molecules of the medium. Apparently also the mobility is independent of the structure of the molecule, for example atomic argon and CO_2.

As soon, however, as an artificial attachment between two or more molecules takes place the mobility changes. It seems necessary to distinguish in mobility work between an artificial grouping forming complexes and the natural atomic grouping in the molecule. For example, suppose two molecules a and b, one of which has a positive charge, become attached to each other. They form a complex of two molecules which has a mobility value which is less than 1.87, the characteristic value being 1.36. If then the n atoms in a and the n atoms in b rearrange themselves so as to form a natural one molecule structure, the mobility immediately changes to 1.87, the value which is characteristic of a one molecule ion.

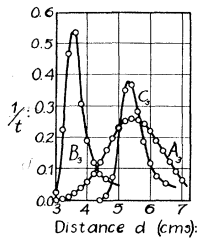

Fig. 7. Curves showing that the final positive ion curve is wider than the negative ion curve for the same diagonal path.

The final 1.36 positive ion is not a completely stable body. The widths of the curves for the final positive ions is indicative of this. That the greater width of the final positive ion curve is not due to the greater obliquity at which the ions come to the electrode is shown by the curves in Fig. 7. Curve A_3 is for the final positive 1.36 ions. Curve B_3 is for the negative ion, mobility 1.87, obtained at the same voltage and air velocity as Curve A_3.

Curve C_3 is for the negative ion when the voltage was reduced so that the negative maximum comes at the same down stream distance as the maximum of the final positive ion.

It is thus seen that the width of the curve C_3 is not comparable to that of A_3. This must mean that the final 1.36 positive ion is not highly stable. In passing between the plates AB, Fig. 1, it may simplify back to a one molecule initial ion thus reaching plate B farther up stream or the final 1.36 ion may attach itself temporarily to a third molecule and therefore pass farther down stream. Both of these effects cause a widening of the curve.

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