ON THE NATURE OF THE IONS IN AIR AND IN CARBON DIOXIDE

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Abstract

Mobilities of ions of air and CO_2 in initial and final stages.—It has previously been shown that in air the positive ions have an initial mobility equal to that of negative ions, 1.87 cm/sec./volt/cm, which decreases in about 1/50 sec. on the average to 1.36 cm/sec./volt/cm. Using improved apparatus with an air speed of 20 m/sec. and fields of over 1000 volts/cm., curves were obtained showing clearly the presence of both initial and final ions. These are the same whether α or β rays are used to produce the ions. Negative ions show only one mobility. CO_2 ions gave curves which, within experimental error, agree with those for air, indicating one negative and two positive ions, but the time of transition to the final positive stage is somewhat shorter for CO_2. These results are best explained by assuming that in these cases ionization involves merely the detachment of an electron from a molecule, leaving a positive mono-molecular ion which soon attaches itself to a neutral molecule forming the final somewhat unstable bimolecular positive ion, while the electron almost immediately joins a neutral molecule forming a stable negative mono-molecular ion. Dissociation seems to play only a small part. It is concluded that single molecules singly charged, positively or negatively, all have about the same mobility which is independent of mass and molecular volume, and that a singly charged cluster of two or more molecules, not forming a single molecule, has a smaller mobility.

In earlier articles,[1] results were given showing the existence of an initial and final positive ion in air ionized by alpha rays. Evidence was also obtained showing that the initial ion transforms into the final ion. The half value transition period has recently been determined in this laboratory by Grummann and was found to be of the order of 1/50 sec. The mobility of the initial positive ion is the same as that of the negative ion, namely 1.87 cm/sec/volt/cm, and the final positive ion has a mobility the same as that normally found for the positive air ion namely 1.36 cm/sec/volt/cm.

The resolving power of the apparatus used was not sufficient to separate the two ions when present, for example, in the air at the same time. The reason for the low resolving power was evidently the transition which took place after the initial ion entered the electric field. To obviate this, it was necessary to reduce the time interval required by the ions to pass through the field.

[1] **Erikson,** (a) Phys. Rev. **17,** 400 (1921); (b) **Phys. Rev. 18,** 100 (1921); (c) Phys. Rev. **20, 117** (1922).

With this in view, the apparatus was reconstructed in accordance with Fig. 1. *A* and *B* are two plates 5×15 cm and are 3.5 cm apart. They are kept at a difference of potential by means of the battery *G*. In order to secure a uniform field, wires whose potentials vary in steps are placed at the sides of the space between *A* and *B*. These wires are connected at *C* to plates 2 cm wide, placed parallel and 0.5 cm apart.

The ions were produced by means of alpha rays from polonium placed at *D* and sufficiently far back to insure the presence of both the initial and final positive ions in about equal number at *E* where they enter the field between the plates *A* and *B*. When plate *A* is positive the positive

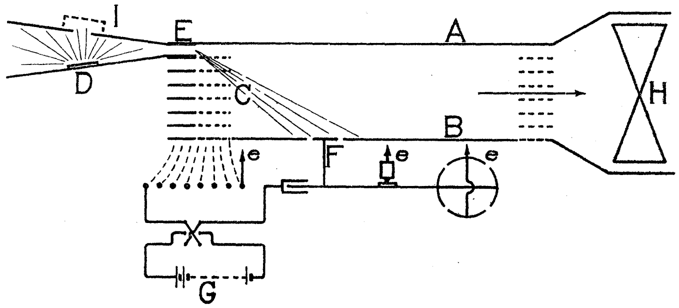

Fig. 1. Diagram of apparatus.

ions are repelled to plate *B* and at the same time are carried down stream with the air drawn through the apparatus by means of the fan *H*. The current received by the strip *F* for different values of the potential between *A* and *B* was determined. By plotting the current against potential the ionic spectrum is obtained.

In order to increase the resolving power it is necessary to make the time interval required by the ions to pass from *E* to *F* so short that the amount of transition of the initial ion into the final ion in this interval is negligibly small. This was accomplished by constructing a fan $4\frac{3}{4}$ inches in diameter, having eight blades set at angles of about 20°. The fan was given a speed of about 5000 r.p.m. by means of a belt, pulleys, and a 1/4 h.p synchronous motor having a speed of 1800 r.p.m. This gave an air velocity of about 2000 cm/sec. and therefore an interval of .002 sec. from *E* to *F*. In order to force the ions from plate *A* to plate *B* in this interval a correspondingly high difference of potential had to be used. The results obtained with ions due to alpha rays, are shown graphically in Fig. 2. *A* is the curve obtained for the negative ion and *B* the curve for the two positive ions. Part *C* of the positive curve is for the initial positive ion and part *D* is for the final positive ion.

It is seen that the maxima for the negative ion and initial positive ion correspond to about 3350 volts. This means that the negative and the initial positive ions have the same mobility. The maximum *D* for the final positive ion corresponds to about 4550 volts, giving a mobility ratio between the initial and final positive ions of 1.36 which corresponds to the mobility ratio normally found for the negative and positive air ions.

The widths of the curves for the negative and initial positive ions are such as may be accounted for by the fact that the measurements are made at an angle with the direction of motion of the ions, by the repulsion

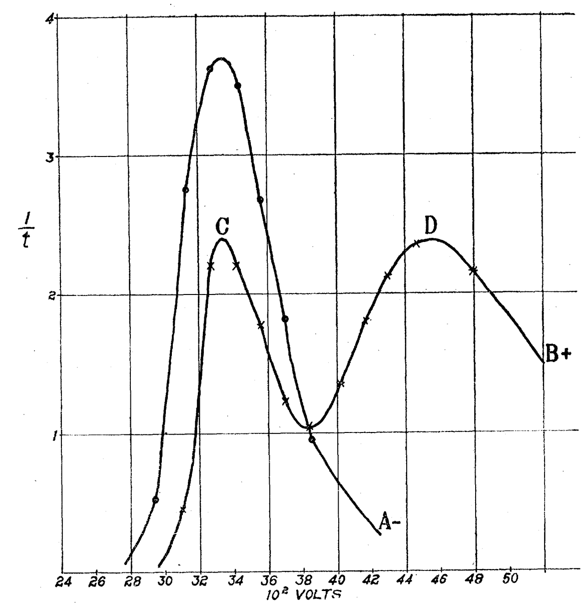

Fig. 2. Results with ions due to alpha rays.

between the ions, and by air turbulence. The width of the curve for the final positive ion cannot, however, be entirely accounted for in this manner. The effect in this case is as if a loading and unloading of the final ion is going on.

In order to determine whether the nature of the ions produced depends upon the ionizing agent, the above experiment was repeated using β rays. A source of β rays, obtained from decayed emanation tubes, was placed at *I*, Fig. 1. The funnel was surrounded by sheet lead so that the ionization was confined to the air passing into the apparatus at *E*. The distance between the plates *A* and *B* was somewhat smaller, hence the voltages required were lower than for the curves of Fig. 2. The results are shown by the curves in Fig. 3. The curves in Fig. 4 were obtained for ions produced by alpha rays from polonium as in the case of Fig. 2 but with conditions as identical as possible with those of Fig. 3. It is seen that the initial and final positive ions are present whether the ions are due to α or β rays and that their mobility ratio is normal. The average age of the ions in the case of the α rays, due to the position of the polonium plate, is a little less than in the case of the β rays, and therefore relatively more of the initial positive ions are present. But the similarity of the curves Figs. 3 and 4 indicates that there is no essential difference in the results of the ionizing process in the case of these two rays.

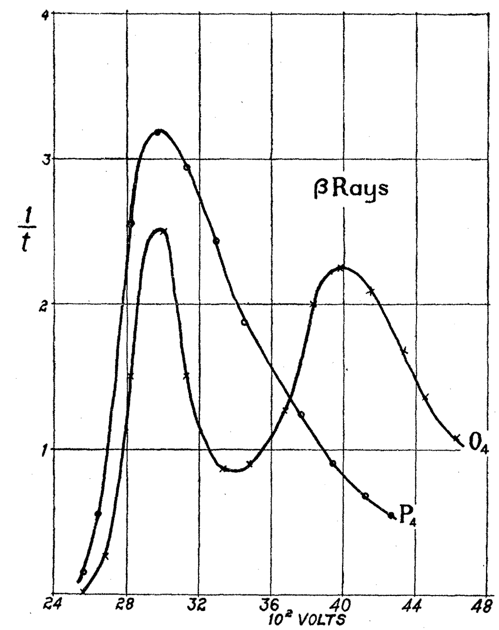

Fig. 3. Curves with ions due to beta rays.

As to the nature of the initial and final positive ions as well as the negative ion, an analysis may be made in terms of the following two assumptions:

(a) The ionizing process involves simply the removal of an electron from the molecule, otherwise leaving the molecule intact.

(b) The ionizing process consists in removing an electron as in (a) and in addition dissociating the molecule.

Assumption (a) leads to the following results. After the electron is removed from a molecule, it remains free for but a short time. This free state has been observed by Wellish, Loeb and others. The electron soon attaches itself to a neutral molecule forming a negative ion, one molecule large. The remainder of the molecule which lost an electron in the ionizing process forms a positive ion, one molecule large. This positive ion has the same mobility as the above negative ion since their charges and volumes are equal. This is, therefore, the initial positive ion. The transition consists in the initial ion attaching itself to another neutral molecule thus forming a positive ion two molecules in size. This constitutes the final positive ion.

Experiment indicates that a negative atom or molecule does not readily attach itself to another neutral atom or molecule of its own kind. In this work the constancy of the negative ion and its aversion to union with other bodies, have been very marked. This is perhaps to be expected as such a union would have to take place in the presence of an excess of electrons. The union of a positive atom or molecule with a neutral atom or molecule on the other hand means the sharing of a valency electron by two positive charges, a process which is probable and which is suggested by experimental results.

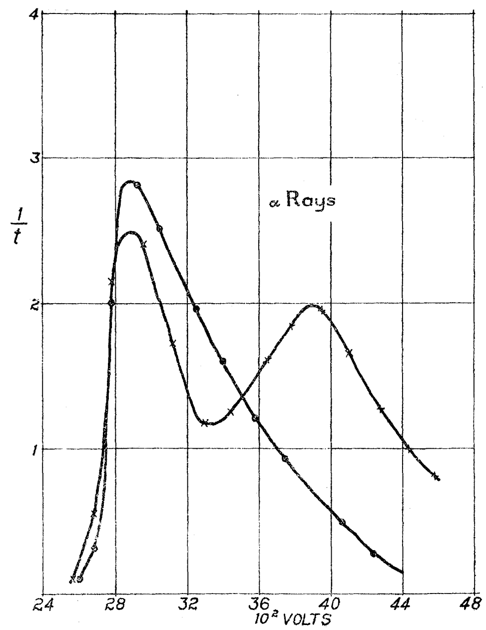

Fig. 4. Curves with ions due to alpha rays, obtained under the same conditions as those of Fig. 3.

Assumption (b) leads to the ions resulting from (a). In addition the dissociation may be assumed to result in $(O+O^{+}+e^{-})$ and $(N+N^{+}+e^{-})$ where e^{-} stands for an electron. If the electrons unite with some of the neutral atoms produced as well as with neutral molecules, two negative ions, one and two molecules large, will result from (b). The positive atoms may unite with neutral molecules and it is thus seen that assumption (b) may give rise to four positive ions, one, two, three and four atoms large.

Of the two assumptions, (b) is the less likely. If all the ions resulting from (b) were present in appreciable numbers, experiment would detect them. Furthermore, if dissociation takes place it would be reasonable to expect a difference in the results from α and β rays, whereas experiments show that no difference exists.

In an earlier article[1c] it was shown analytically that a mobility ratio such as exists between the initial and final positive ions means that the slower ion is twice as large as the other. This also favors assumption (a).

The writer, therefore, feels that (a) gives the best interpretation of the experimental results. On this basis the negative ion and the initial positive ion are each one molecule large and the final positive ion is two molecules large.

If it is further assumed that the final ion may attach itself to another molecule forming a cluster of three molecules the parts of which are so loosely tied together that they are quickly disintegrated through thermal impact, and if it is assumed that even the final two molecule ion is sometimes disintegrated by the more violent thermal impacts, an explanation of the greater spreading of the curve for the final positive ion is obtained.

There is, however, no justification for the complete rejection of (b). That dissociation to a certain extent takes place, especially in the case of the α ray, is experimentally established. The rejection of (b) must be in degree only. That the other ions predicted above and resulting from dissociation are present can hardly be denied. A sufficiently sensitive method should detect them.

The justification for the omission of double charges in the above analysis is based on results by Millikan, Gottschalk and Kelly[2] which showed that no double charged ions are produced in air by α rays.

The above results are for air taken from the room. In a separate experiment the apparatus was placed in a closed vessel. Results were obtained using dry and also saturated air. No effect due to moisture was observed. This, of course, is what should be expected as the above process is molecular. The heavy ions formed by the water vapor are carried down stream and do not enter into the measurements.

[2] Millikan, Phys. Rev. **15**, 157 (1920)

Carbon Dioxide Ions

To test the above conclusions, carbon dioxide gas was passed through the funnel *DE*, Fig. 1. The ions are then produced in CO_2 and enter at *E* where they are drawn out of the CO_2 sheet and pass, through the air entering at *C*, to the plate *B*. This gives an opportunity to determine the mobility of CO_2 ions in air. The CO_2 entered the apparatus from a large tank. This tank was filled from a commercial supply cylinder. No attempt was made to purify the gas.

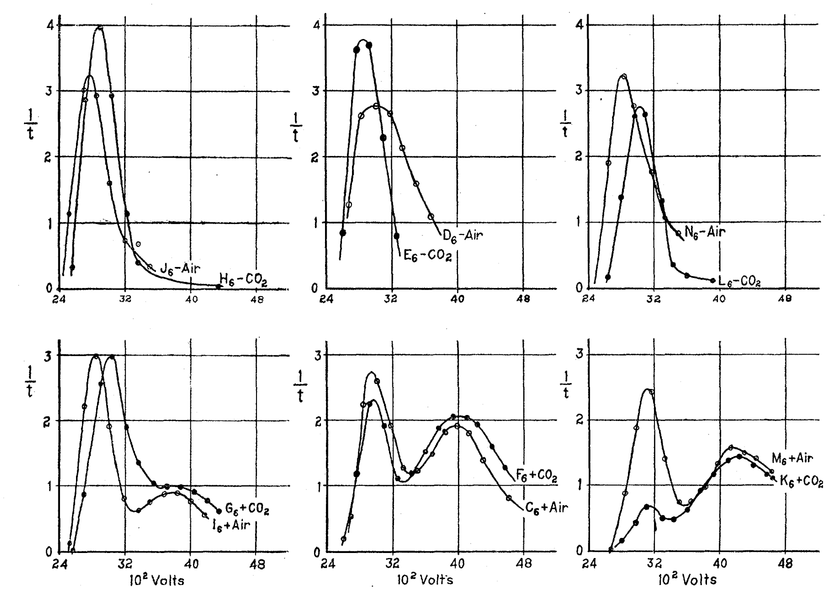

Fig. 5. Comparison of curves for CO_2 ions in air with those for air ions. Upper figures are for negative ions; lower figures for positive ions.

The results obtained are given in Fig. 5. The upper horizontal series is for the negative ions and the lower for the positive ions. The curves for the CO_2 ions have full dots. Accompanying each CO_2 curve is a curve showing the results obtained using air in place of CO_2, the conditions otherwise being as nearly identical as possible. The first vertical set from the left is for ions of an average age of about .005 sec. the second for .02 sec. and the third for about .06 sec.

It is thus seen that the negative CO_2 ion has the same mobility as the negative air ion, that only one ion is present, and that it undergoes no change with age. The lack of exact superposition is due to experimental variations such as slight changes in the air velocity. This is born out by repeated observations on the same ion.

This negative CO_2 ion is undoubtedly formed, as in air, by an electron, freed by the ionizing process, attaching itself to a molecule of CO_2, thus forming an ion one molecule large but containing three atoms. If this is correct then the fact that the negative air ion and the negative CO_2 ion have the same mobility means that the mobility of a natural structure such as a molecule is determined primarily by its charge and that the difference in the molecular volumes is not sufficient to give rise to a detectable difference in mobility. The difference in mass in this case is of small consequence, as is shown by the fact that heavy bodies such as actinium active deposit ions have very nearly the same mobility as the air ions.

A comparison of the curves in the lower series, Fig. 5, for the positive CO_2 ions and the positive air ions, also shows a close similarity. There is in CO_2 as in air, an initial positive ion and a final positive ion. The curves show however that the transition period of the initial to the final is less in the case of CO_2.

The interpretation in this case, on the basis of the above discussion, would be that the initial CO_2 ion is the remainder of a CO_2 molecule which lost an electron in the ionizing process and therefore is one molecule large. This ion being one molecule large has the same mobility as the negative air and CO_2 ions. This initial ion soon attaches itself to a neutral CO_2 molecule thus forming an ion two molecules large. The difference in volume of a positive air ion two molecules large and a positive CO_2 ion two molecules large is not sufficient to give rise to a detectable difference in mobility as is shown by the fact that the maxima correspond to the same voltage. If the above is a correct interpretation the situation may be summarized as follows: All single molecules having equal charges have approximately the same mobility. The mobility of an ion is not a function of its mass. However, any attachment which does not give rise to a natural molecular structure causes a change of mobility.

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