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# ON THE NATURE OF THE NEGATIVE AND POSITIVE IONS IN AIR, OXYGEN AND NITROGEN.

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SYNOPSIS.

*Positive and Negative Ions in Air, Oxygen and Nitrogen.*—(1) *Mobilities just after formation* were measured by using a modified form of Zeleny's blast method. Ions produced in air by polonium rays were drawn immediately by a current of 470 cm./sec. into one side of a cross field of 130 volts/cm. and the distance they were carried along before they were dragged to the other side by the field was determined. When the average age of the ions was about 0.03 sec. the mobility was found to be the same for both positive and negative ions and equal to that for normal negative ions, about 1.89 cm./sec./volt/cm. As the age was increased to 0.5 sec., however, the positive mobility decreased to its normal value, about 1/1.40 times the negative mobility. The same results were obtained with dry commercial oxygen and nitrogen, except that the aging of the positive ion was more rapid in oxygen. (2) *Nature of the ions.* In explanation of the above results it is suggested that the negative ion and the initial positive ion are each one molecule in size and that the permanent positive ion is two molecules in size. This suggestion agrees with the view that when ionization occurs an electron is ejected from a molecule, leaving a positively charged molecule, an initial positive ion, which does not immediately acquire the second molecule needed to form a permanent positive ion. The electron attaches itself to a molecule and forms a permanent negative ion. It is also shown that the observed ratio of the mobilities for ions with one and two molecules respectively agrees with that computed according to the small ion theory of Wellisch.

THE nature of the positive and negative ions produced in air by an ionizing agent is a question of considerable interest. It has not been easy to obtain conclusive evidence.

In 1900 Zeleny[1] succeeded in determining the absolute values of the mobilities of the ions in question. The values found were, for the negative ion 1.87 cm./sec./volt/cm., and for the positive ion 1.36, giving the ratio of the negative mobility to the positive of 1.375.

Each of the above ions forms a stable unit. The ratio 1.375 shows that these units are not alike. To what this difference is due is a question of interest.

[1] Phil. Trans. A, Vol. 195, p. 193.

About two years ago[1] it occurred to the writer to try a modified form of Zeleny's blast method.

The experimental arrangement was as indicated in Fig. 1. *A* and *B*

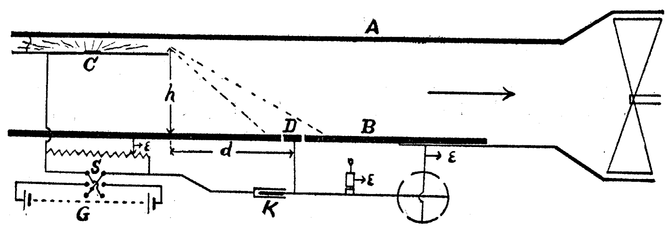


Fig. 1.

were two parallel plates 5 cm. wide, 40 cm. long and 4.5 cm. apart. *C* was a plate about 12 cm. long placed about 0.6 cm. below *A*. *A* and *C* were connected. *D* was a narrow insulated strip placed in the plane of *B* and connected to a quadrant electrometer. The plate *B* and strip *D* were movable so that the down stream distance of *D* could be altered. The sides of the apparatus were of glass.

Air from the room was drawn through this rectangular tube by means of a fan driven by a synchronous motor. Plate *B* was kept at zero potential while *A* was raised to the potential of the battery *G*. In order to compensate for any change in the voltage of the battery *G* during readings the air condenser *K* was introduced.

A polonium plate was placed at *C*, the rays from which ionized the air between plates *C* and *A*. As *A* and *C* were connected there was no field causing the ions to move to the plates. The ions were carried by the air to the mouth of this chamber where they entered the field between *A* and *B*. If *A* were positive the positive ions were driven to *B*, and negative to *A*.

By changing the down stream distance of the strip *D* the current at the different points on *B* could be measured. For each position of the strip *D* both the positive and negative currents were measured by reversing *S* leaving the conditions otherwise unchanged.

The velocity of the air was obtained by means of an anemometer. The times for a given deflection of the electrometer for the positive and negative currents at different positions of *D* were obtained. Upon plotting the reciprocals of these times against the down stream distances of *D* as abscissæ, the curves shown in Fig. 2 were obtained:

To the writer's surprise these two curves were found nearly to coincide, indicating equal mobilities of the positive and negative ions. The average age of the ions in this case was of the order of 0.03 second.

[1] PHYS. REV., (2) XVII., p. 400; (2) XVIII., p. 100.

The spreading of the curves is due primarily to the slant of the plate $B$ with reference to the direction of the ionic stream. By projecting on a plane at right angles to the ionic stream the spreading is of the order

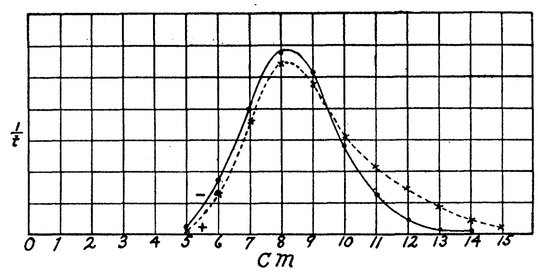


Fig. 2.

of 3 cm. instead of 8 cm. The amount of spreading due to the self repulsion of the ions is, on each side, of the order of 0.5 cm., about the thickness of the current sheet. Deducting this will reduce the spreading to about 1.5 cm. which is undoubtedly due mainly to air turbulence. Excessive air turbulence was however not present. This was determined by means of smoke streams. The factors given above are of an order such as to preclude the necessity of attributing the spreading to non-homogeneous ions.

The absolute value of the mobility may be determined as follows: Let $h$ be the average distance the ion travels at right angles to the stream of air and $d$ the distance it travels down stream in the same time $t$. Then

$$h = k\frac{V}{H}t,$$

but

$$t = \frac{d}{v};$$

$$\therefore \quad k = \frac{hHv}{Vd},$$

where $H$ = distance between the plates $A$, $B$,
$V$ = difference of potential between plates $A$, $B$,
$v$ = velocity of air,
$k$ = mobility of ion.

The mobility $k$ therefore varies inversely as the down stream distance $d$. The ratio of two mobilities therefore is

$$r = \frac{k_1}{k_2} = \frac{d_2}{d_1}.$$

If two ions have the same mobility their down stream distances $d$ are the same.

As the curves for the positive ion and the negative ion came superimposed, the conclusion must be that both ions had the same velocity.

The next question of interest was to determine if the mobility represented by the maxima of the curves was the normal mobility for the negative or for the positive ion.

The following values for the quantities necessary for the determination of the mobility were obtained:

$V$ = 535 volts,
$d$ = 8.2 cm. (using maximum of curve),
$h$ = 4.2 (using same average value for $H$),
$v$ = 470 cm./sec.

The above values gives for the mobility

$$k = 1.89 \text{ volt/cm.}$$

As this is of the order of the normal value for the mobility of the negative ion, the necessary conclusion is that the positive ion involved had the same mobility as the normal negative ion.

In order to determine if the age of the positive ion had any effect an extension was added as shown in Fig. 3. The polonium plate was placed

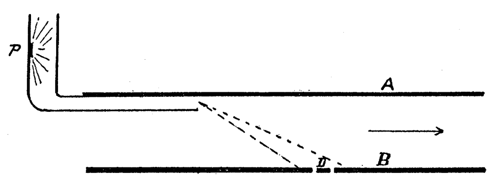


Fig. 3.

at $P$ so that the ions were of the order of 0.5 second old when they entered the field at $B$. The air velocity remained the same as before.

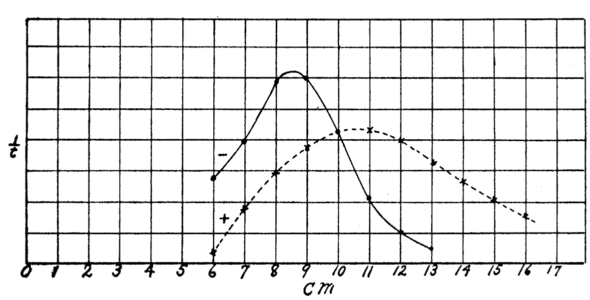


Fig. 4.

The curves obtained for the positive and negative ions are shown in Fig. 4. As the maximum for the negative ion remained unchanged it became evident that the poistive ion had undergone a change during the first fraction of a second of its life as its maximum had shifted down stream indicating a slower ion.

The same change was obtained when the ions were aged by reducing the velocity of the air, the polonium plate being at $C$, Fig. 1. The curves $A$ and $B$ in Fig. 5 were obtained in this manner. The ratio of the initial

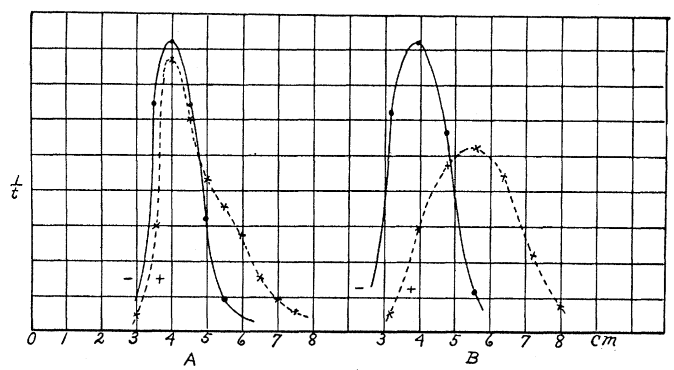


Fig. 5.

mobility to the final mobility is

$$\frac{k_1}{k_2} = \frac{5.5}{3.9} = 1.40$$

which is about the normal ratio for air.

The significance of the above must be that the negative and positive ions are initially alike in magnitude and that the positive ion soon increases to a larger stable unit.

In order to determine if this effect is peculiar to air the apparatus was enclosed so that oxygen and nitrogen could be investigated separately.

The gases were obtained from commercial supply tanks and were dried by passing through $CaCl_2$. The gases were not of a high degree of purity. The ions were aged by reducing the gas velocity.

The curves obtained are given in Fig. 6.

The results obtained show that in oxygen and nitrogen, of the purity involved, the negative ion does not change. The positive ion, however, does in each case undergo a change. It is also observed that the change in the mobility of the positive ion in oxygen is somewhat more rapid than in nitrogen.

*Statement of Hypothesis.*—In explanation of the above it seems most reasonable to take the molecule as the unit in terms of which the change takes place. On this basis the simplest hypothesis becomes as follows:

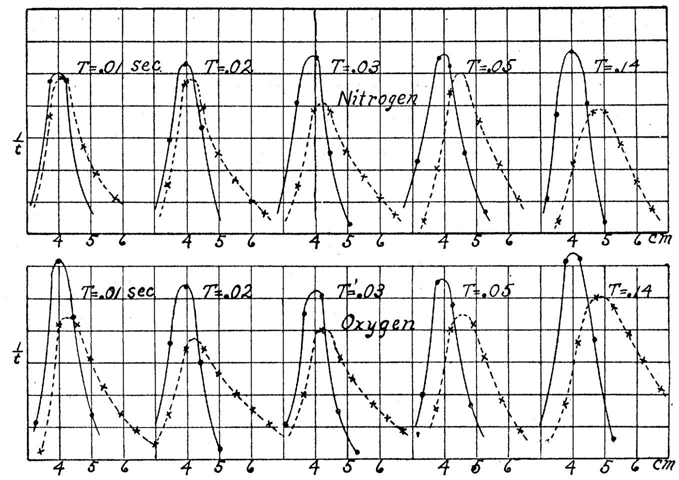


Fig. 6.

In the process of ionization of air one of the atoms of the nitrogen or oxygen molecules is caused to eject an electron, the molecule otherwise remaining intact. The electron remains free on the average a very small fraction of a second especially in the presence of oxygen. It soon attaches itself to a neutral molecule and this combination forms the negative ion. The positive remainder of the molecule which ejected the electron constitutes the initial positive ion. As the two above ions have the same mass and charge their mobilities are equal. The initial positive ion, however, soon attaches itself to a neutral molecule forming the permanent positive ion. Since its mass is twice as great as the initial positive ion or the negative ion, it has a smaller mobility.

*Evidence in Support of Hypothesis.*—It is of interest to consider the above hypothesis in connection with the small ion theory proposed and developed by Wellisch.[1] In this theory it was shown that the collision distance $\sigma$ existing between two uncharged molecules, changes to

$$\sigma[1 + 2R/mv^2]^{1/2}$$

when one of the molecules is charged. $R$ denotes the potential due to the polarization of the neutral molecule by the charge on the ion, and its value is shown to be

$$R = \frac{2(K - 1)e^2}{\pi n(S + S^1)^4},$$

[1] Phil. Trans. A, Vol. 209, p. 249.

where $S$ and $S^1$ are the diameters of the force spheres of the molecule and ion respectively, $K$ is the specific inductive capacity, and $e$ the charge.

The collision distance thus becomes

$$\sigma\left[1 + \frac{4(K-1)e^2}{\pi n m v^2 (S+S)^4}\right]^{1/2}.$$

The expression for the reciprocal of the mean free path is

$$L^{-1} = \pi n\left[1 + \frac{M}{m}\right]^{1/2}\sigma^2.$$

This when the new expression for $\sigma$ is introduced becomes

$$L^{-1} = \pi n\left(1 + \frac{M}{n}\right)^{1/2}\sigma^2\left[1 + \frac{4(K-1)e^2}{\pi n m v^2 (S+S^1)^4}\right].$$

Substituting this in Langevin's expression for the mobility, namely

$$k = \frac{eL}{MV}$$

gives on the basis of equipartition of energy

$$k = \frac{A\eta}{\rho p}4\sqrt{2}\left(\frac{m}{M}\right)^{1/2}\left(1 + \frac{M}{m}\right)^{-1/2}\left(1 + \frac{S^1}{S}\right)^{-2}\left[1 + \frac{4(K-1)e^2}{\pi n m v^2 (S+S^1)^4}\right]^{-1},$$

where $M$ = the mass of the ion,
$m$ = the mass of the molecule,
$S^1$ = diameter of force sphere of ion,
$S$ = diameter of force sphere of molecule.

The ratio of two mobilities becomes:

$$\frac{k_1}{k_2} = \frac{\left(\frac{m}{M_1}\right)^{1/2}\left(1 + \frac{M_1}{m}\right)^{-1/2}\left(1 + \frac{S_1}{S}\right)^{-2}\left[1 + \frac{4(K-1)e^2}{\pi n m v^2 (S+S_1)^4}\right]^{-1}}{\left(\frac{m}{M_2}\right)^{1/2}\left(1 + \frac{M_2}{m}\right)^{-1/2}\left(1 + \frac{S_2}{S}\right)^{-2}\left[1 + \frac{4(K-1)e^2}{\pi n m v^2 (S+S_2)^4}\right]^{-1}}.$$

Using Wellisch's values of

$$3.70 \text{ for } \frac{(K-1)e^2}{4\pi n m v^2 S^4}$$

and placing $S' = aS$ and $M = bm$, the above ratio becomes

$$\frac{k_1}{k_2} = \frac{\sqrt{b_2}\,\sqrt{1+b_2}\,(1+a_2)^2\left[1 + \frac{59.2}{(1+a)^4}\right]}{\sqrt{b_1}\,\sqrt{1+b_1}\,(1+a_1)^2\left[1 + \frac{59.2}{(1+a)^4}\right]}.$$

Let $k_1$ = mobility of ion of mass $m$, *i.e.*, $M_1 = m$, $S_1 = S$; then $a_1 = 1$, $b_1 = 1$ and

$$\frac{k_1}{k_2} = \frac{\sqrt{b_2}\,\sqrt{1 + b_2}(1 + a_2)^2\left[1 + \frac{59.2}{(1 + a_2)^4}\right]}{26.6}.$$

The above expression may be written

$$\frac{k_1}{k_2} = \frac{\sqrt{b_2}\,\sqrt{1 + b_2}\,J}{26.6},$$

where $J$ is a function of $a_2$. The function $J$ is a minimum for

$$a_2 = 1.77.$$

Using this value of $a_2$ in $J$, for the ion of mass $M_2 = 2m$, *i.e.*, $b = 2$, gives for the ratio

$$\frac{k_1}{k_2} = 1.418.$$

It is thus seen that the initial ion of $M_2 = m$ and final ion of $M = 2m$ of the hypothesis gives a mobility ratio of 1.418 when the diameter of the force sphere of the final ion is 1.77 times that of the molecule $m$. This is in satisfactory agreement with the observed ratio 1.40.

It is necessary to determine if other values of $b$ and $a$ will give the observed ratio 1.40.

Since $J$ is a minimum for $a = 1.77$ it is evident that values of $M_2$ greater than $2m$ will give ratios which for all values of $a_2$ will be too large. For values of the mass of the ion less than $2m$, only two cases are possible namely, $M_2 = m$ and $M_2 = 3/2m$ (three atoms). For each of these there are two values of $a_2$ either of which will give the observed mobility ratio as may be found by substituting 1.40 for the ratio and solving for $a_2$. These are

$$a_2 = 0.58 \text{ and } 3.87 \text{ for } M_2 = m$$

and

$$a_2 = 0.96 \text{ and } 2.92 \text{ for } M_2 = 3/2m.$$

As the change in size is of the nature of an addition to the solid kernel, the charge remaining the same, the above values are quite untenable. The observed ratio is therefore obtained only in the case of an ion two molecules in size.

Since $\sqrt{2m/m} = \sqrt{2} = 1.414$, is in fair agreement with the observed ratio of the mobilities, the above suggests that in any one gas the mobility is approximately proportional to the inverse square root of the mass of the ion.

The velocity in the direction of the field $X$, obtained by an ion in the time $t$, is

$$v = \frac{Xe}{M} t,$$

where $t$ is the mean free time between collisions. The average velocity of drift will therefore be

$$\bar{v} = \frac{Xe}{2M} t$$

and the mobility, which is the coefficient of $X$, is

$$k = \frac{e}{2M} t.$$

The value of $t$ is determined by the velocity of temperature agitation and the velocity, which is superimposed, due to the field. As the former is large compared to the latter, $t$ may be regarded as entirely determined by the velocity of temperature agitation $V$. We may consequently write

$$t = \frac{\lambda}{V},$$

where $\lambda$ is the mean free path ot the ion.

The mobility then is

$$k = \frac{e\lambda}{2MV}.$$

Substituting, on the basis of equipartition of energy, the value of $V$ obtained from the relation

$$1/2MV^2 = 3/2RT$$

gives the mobility

$$k = \frac{e\lambda}{2\sqrt{M}\sqrt{3RT}}.$$

The ratio for two sets of ions then becomes

$$\frac{k_1}{k_2} = \frac{\sqrt{M_2}\lambda_1}{\sqrt{M_1}\lambda_2}.$$

The statement that the ratio of the mobilities of two ions in any one gas is proportional to the inverse ratio of the square root of their masses, therefore requires that their mean free paths be the same. This would be the case if the mean free path is determined primarily by the charge.

The indication of all the above is that the final positive ion has a mass which is twice the mass of the initial positive ion.

The question then becomes: Is one justified in assuming that the initial positive ion is one molecule in size? It is evident that this question must be answered through a knowledge of the ionization process.

The strongest evidence at the present time is the existence of free electrons at the instant of ionization. The results obtained by Franck, Haines, Wellisch, Loeb and others are conclusive on this point. On the strength of this we would conclude that the ionization process consists in the ejection of an electron. The next obvious step is to assume that the electron attaches itself to a neutral molecule rather than an atom. The chance of the first must be very much greater than the second. If this takes place then the negative ion is one molecule in size. If it is larger than one molecule the early transition stages should be detectible experimentally. Different transition stages have not been observed in these experiments.

If the negative ion is one molecule in size then the initial positive ion must be one molecule in size, since their mobilities are the same.

As shown above the indications are that the final positive ion is two molecules in size. If it is larger than this the transition stages should be detectible experimentally. This in connection with the ion in question is not observed in this investigation.

It is of interest to note that on the basis of the above, the mobilities 1.32, 1.53, 1.87, 2.64 may be predicted corresponding respectively to the ions of masses, two molecules, three atoms, one molecule, one atom.

There has just come to my hands a paper by Nolan and Harris[1] in which results are given which are interpreted as indicating the presence of several mobilities. Among these for the positive as determined by a blast method are

$$(2.5),\ 2.04,\ \ 1.79\ \ 1.52\ \ 1.37.$$

Evidence of 2.5 was only obtained by an A.C. method. Of these five values four are predicted by the above.

I am glad to take this opportunity of expressing my indebtedness to Professor W. F. G. Swann and to Professor John T. Tate for their helpful suggestions and kind interest.

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UNIVERSITY OF MINNESOTA,
March 9, 1922.

[1] Proc. Roy. Irish Acad., XXXVI., A, 2, p. 31.