is if $2\rho_0 = a(1+f/(l'-g))$, the rays of different velocity will enter the magnetic field at the proper points to be united at P. In this way the velocity dispersion produced by the electric field is counterbalanced by the dispersion in the magnetic field, and a divergent beam entering at S containing particles of slightly different velocities is brought to a focus at P. For example, if $a=8.48$ cm, $\phi=90°$, and $l'=1$ cm, then $f=7.55$ cm, $g=-4.57$ cm and ρ_0 must be 10 cm giving $l''=5.66$ cm.

This focusing condition can be filled exactly only by one radius of curvature ρ_0. If different ions of the same energy are used, the curvature in the electrostatic field will be the same for all, but in the magnetic field the paths will have different radii of curvature. For ions that do not follow the path for perfect focus, the image width dc increases with their distance from P. A simple geometrical computation shows that $dc/DC = PP'/PC$. Thus with a diaphragm at C of 2 mm opening the image width of an infinitely narrow slit would be increased to 0.1 mm at a distance of 1 cm from P. For the qualitative analysis of elements this widening of the image is not disturbing, and for exact comparisons of atomic weights by the method of doublets, the doublets may be always brought to the position of exact focus.

The observations made with an apparatus constructed on these principles will be described in a later paper.

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Electron and Negative Ion Mobilities in Oxygen, Air, Nitrous Oxide and Ammonia

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The electrical shutter method for measuring electron mobilities in gases has been extended to include experiments in oxygen, air, nitrous oxide and ammonia. The experimental data support the hypothesis that collisions of low energy electrons with molecules of these gases may be inelastic. Such collisions cause excitation of vibrational levels, electronic levels, or dissociation of the molecule. The results are compared with experiments reported elsewhere on negative ion formation in these gases. In general the onset of negative ion formation is accompanied by inelastic collisions which result in a marked increase in the electron drift velocity. Negative ion mobilities in these gases have been measured in the same apparatus by an adaptation of the Rutherford alternating current method. The ions were formed by electron attachment in an auxiliary field and their mobility determined at various ages. The probable character of the ions is discussed after comparing the experimental results with those predicted by the Langevin theory.

A. Electron Mobilities

An electrical shutter method for measuring the drift velocities of electrons in gases has been described in previous communications.[1, 2] The results heretofore obtained have been restricted to gases in which the electrons remained free. By working at somewhat reduced pressures, however, it is possible to extend the method to take data in gases in which negative ions are formed by electron attachment. Under these circumstances there appears a negative ion background current upon which is superimposed the electron current to be measured. For gases in which the probability of electron attachment at a collision is of the order of 10^{-4} to 10^{-6}, the background current can be reduced sufficiently to permit accurate measurement of the electron current maxima by restricting the pressure to values between 2 and 10 mm. In the present experiments the electrons were emitted from a photoelectric surface in the same apparatus employed in the measurements on hydrogen[1] using, however, the constant potential and varying frequency method of measurement.[2]

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[1] N. E. Bradbury and R. A. Nielsen, Phys. Rev. **49**, 388 (1936).

[2] R. A. Nielsen, Phys. Rev. **50**, 950 (1936).

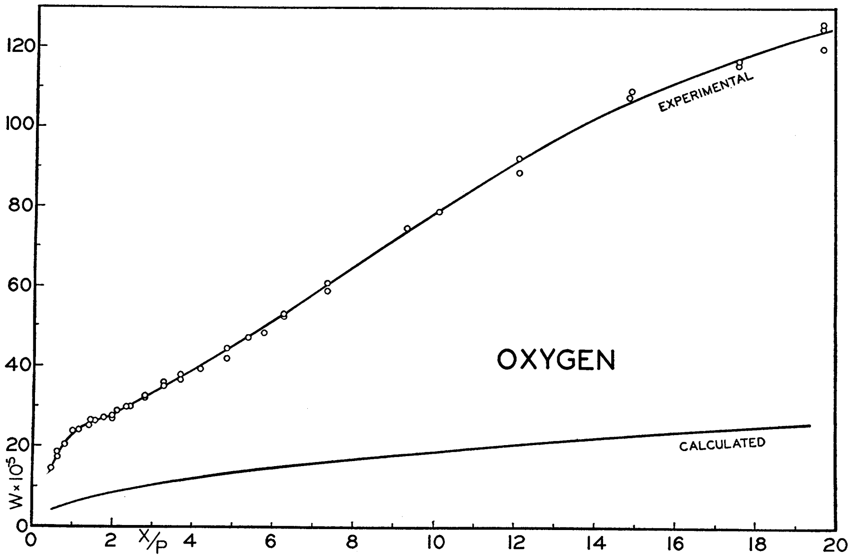

FIG. 1. Electron drift velocity in oxygen as a function of X/p.

Oxygen

Oxygen was obtained from a commercial tank of the gas and all condensable impurities were removed by passage through traps immersed in liquid nitrogen. The experimental data are reproduced in Fig. 1, together with a curve calculated on the basis of Brüche's[3] values for the collision cross section and Townsend and Bailey's[4] values for the mean energy of the electrons. It is seen that the experimental values are considerably greater than the theoretical and, as in the case of hydrogen and nitrogen, this may be ascribed to the presence of inelastic collisions. For values of $X/p<2$, where the average electron energy is less than one volt, these inelastic collisions occur in the excitation of vibrational levels. At an X/p of about 2, a marked point of inflection is observed in the experimental curve. This is undoubtedly due to the increased possibility of excitation of the $^1\Sigma$ state of O_2 whose energy is 1.62 volts above the ground state. Electrons of this energy are available in consequence of their distribution about their mean energy of one volt. Support for this hypothesis is to be found in the experiments on negative ion formation in oxygen.[5] The probability of electron attachment at a collision in this gas, at first decreases with X/p and then undergoes a rapid rise beginning at approximately an X/p of 2. This rise as well as the increase in drift velocity at this point may be ascribed to the increase in number of low energy electrons following collisions in which the $^1\Sigma$ state is excited.

Air

Samples of air employed in these measurements were purified by passage through traps immersed in liquid air. The experimental results are shown in Fig. 2. It is of interest to note that Blanc's law[6] is obeyed for the drift velocity of electrons in air inasmuch as values calculated from the experimental drift velocities in nitrogen and oxygen agree closely with those found experimentally. This is, of course, true only in this instance because the mean energy as a function of X/p as well as the distribution function of electron velocities, appear to be nearly the same for the two gases. The strong inflection at $X/p=2$ in oxygen may also be noticed in the curve for air.

Nitrous oxide

Nitrous oxide was obtained from a commercial cylinder of the gas stated to be of high purity.

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[3] E. Brüche, Ergeb. d. exakt. Naturwiss. **8**, 185 (1929).

[4] J. S. Townsend and V. A. Bailey, Phil. Mag. **42**, 873 (1921).

[5] N. E. Bradbury, Phys. Rev. **44**, 883 (1933).

[6] L. B. Loeb, Phys. Rev. **32**, 81 (1928).

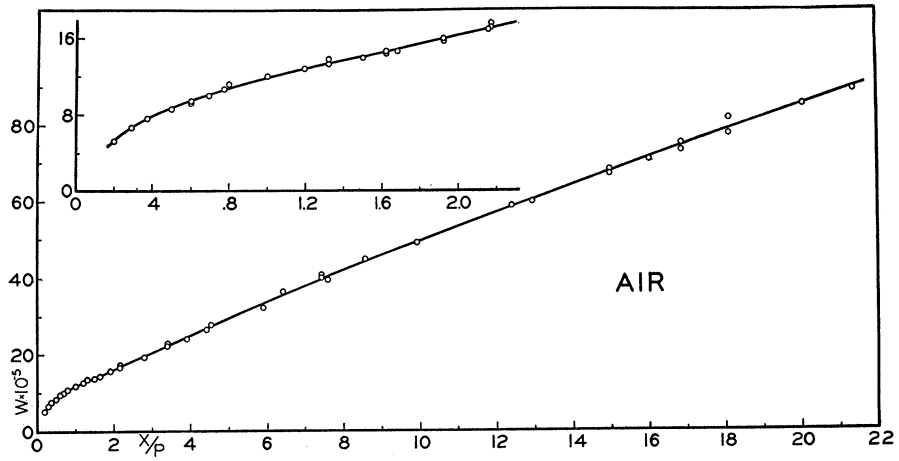

FIG. 2. Electron drift velocity in air as a function of X/p.

The gas was subjected to fractional distillation at reduced pressure at liquid-air temperatures, and the middle fractions only retained for use. The experimental data are presented in Fig. 3. While measurements have been made of the cross section of N_2O as a function of electron energy,[7] the results do not extend to sufficiently low energies to permit the calculation of a theoretical curve. It is of interest to compare the curve of Fig. 3 with what is known of negative ion formation in this gas.[8] Negative ions are not formed in N_2O by low energy electrons. At an X/p of 2, however, negative ions begin to appear which are ascribed to the dissociation reaction

$$N_2O+e\rightarrow N_2+O^-.$$

It is thus not surprising to find evidence of the dissociation in the drift velocity curve where it takes the form of an increasingly rapid rise at an $X/p\sim 0.6$.

Ammonia

Ammonia was obtained from a commercial cylinder of the anhydrous gas. The gas was liquefied over metallic sodium and fractionated at low pressure with liquid air and solid CO_2. The experimental data are shown in Fig. 4. At $X/p\sim 8$, a rapid increase in drift velocity is observed. This is without doubt to be ascribed to the same process which causes the onset of negative ion formation[9] in this gas at approximately this same value of X/p. This process has been suggested to be one of dissociation of NH_3 by electron impact with the initial formation of NH^-. The behavior of the drift velocity at lower values of X/p is remarkable for its linearity. Inasmuch as the variation of drift velocity with X/p for constant cross section and in the absence of inelastic collisions, is as $(X/p)^{\frac{1}{2}}$, this must mean a cross section for collision in NH_3 which increases at least as rapidly as the inverse square root of the electron energy.

B. NEGATIVE ION MOBILITIES

In order to measure negative ion mobilities, the electrical connections to the experimental apparatus were changed so as to permit the use of

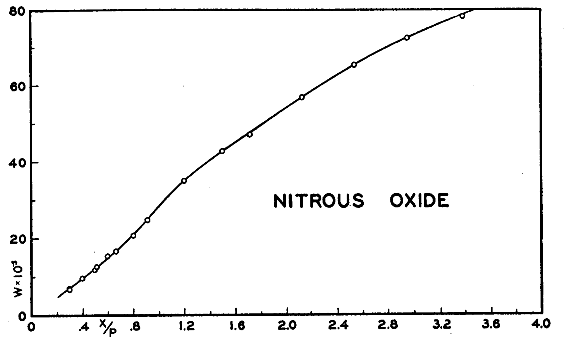

FIG. 3. Electron drift velocity in nitrous oxide as a function of X/p.

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[7] V. A. Bailey and J. B. Rudd, Phil. Mag. **14**, 1033 (1932).

[8] N. E. Bradbury and H. E. Tatel, J. Chem. Phys. 2, 835 (1934).

[9] N. E. Bradbury, J. Chem. Phys. 2, 827 (1934).

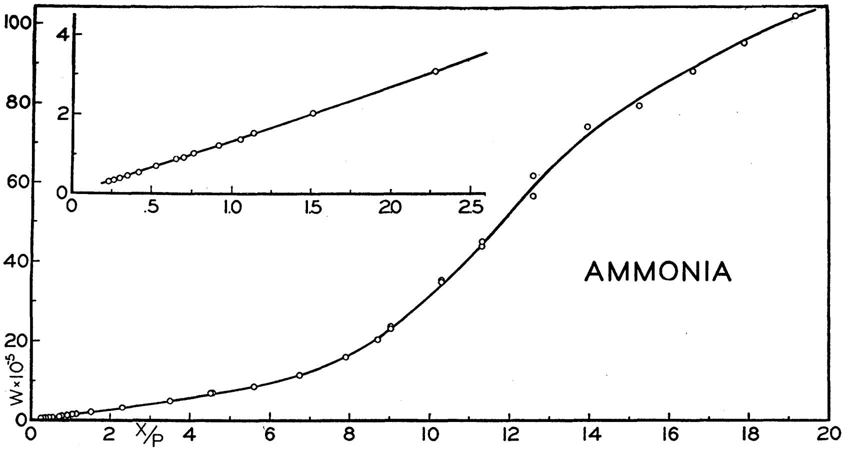

FIG. 4. Electron drift velocity in ammonia as a function of X/p.

the Franck and Pohl modification of the Rutherford alternating current method.[10] This was done in the following way: a steady auxiliary field was applied between the emitting surface and the lower grid which was of sufficient strength to insure the formation of negative ions in NH_3 and N_2O. Between alternate wires of this grid was maintained a high frequency alternating field, the magnitude of whose potential was sufficiently high to sweep from the current stream all electrons, but to permit the passage of negative ions. A square wave alternating potential was applied between this grid and the collecting electrode. This square wave was produced by commutation and had a variable frequency between 20 and 400 cycles/second. The second grid had no function, and was kept at a potential appropriate to its position in the field by connecting it to the surrounding guard ring. The wave form and frequency were determined by a cathode-ray oscillograph permanently connected to the apparatus.

The precautions to be observed in the use of this method have been pointed out by Loeb.[11] In particular, if the strength of the auxiliary field in which the ions are formed is not equal to that of the measuring field, interpenetration of fields will result, and the distance actually traveled by the ions in the measured time will not be the distance between the grid and the collector. Accordingly, the higher the ratio of auxiliary to main field, the shorter the effective distance, and therefore the greater the *apparent* mobility. For this reason, measurements of the mobility must be made as a function of the ratio $R = F_a/F_m$, where F_a and F_m refer to the auxiliary and the main field strength, respectively. The actual value of the mobility is then obtained by extrapolation to unity. It may be pointed out that in the experiments reported here, the distance between grid and collector was 80 mm and the grid spacing 1 mm. The use of such a relatively long distance tends to decrease the effect of field interpenetration on the measured value of the mobility.

The character of the experimental data obtained is shown in Fig. 5 in which the current is plotted as a function of frequency. Although the intercept of the current curve with the axis is not perfectly sharp, the extrapolation of the curve to the axis may be carried out with difficulty and is theoretically justified by the form of the current curve. The mobility may then be calculated from the expression $k = d^2/VT$, where V is the potential carrying ions across the field, d the distance through which the ions move, and T the time of application of V. The mobility may then be reduced to standard conditions by the expression $k_{20^\circ} = k(p/760)(293/T)$.

As, expected, the experimental values of k are dependent upon the ratio R of the field strengths on both sides of the grid. The values of the mobility obtained in oxygen as a function of R are plotted in Fig. 6. The variation is seen to be

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[10] Franck and Pohl, Ver. der Deut. Phys. Ges. **9**, 69 (1907).

[11] L. B. Loeb, J. Frank. Inst. **196**, 771 (1923).

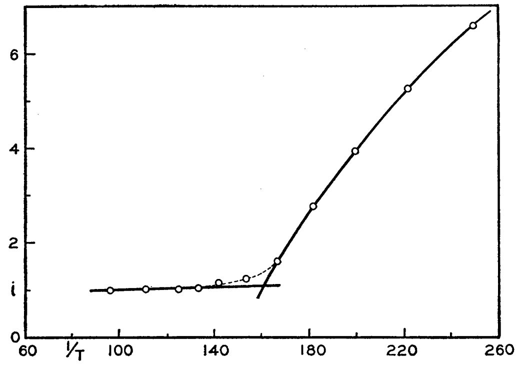

FIG. 5. Electrometer current as a function of the frequency of the square wave alternating potential.

linear and may be extrapolated to $R=1$ to obtain the true value of the mobility. Actually, since the mobility of the ion may vary with its age, this procedure must be justified. In O_2, ions of the same age were measured with R varying from 10 to 40. It will be noticed that these lie on a straight line which may be extrapolated to $R=1$ as well as to higher values. It will also be noticed that the point for $R=104$ lies on this line, although this ion is considerably older. Furthermore, points below $R=10$ which correspond to very short ion ages also lie upon a straight line whose slope is substantially the same as the first. From this data alone, however, it cannot be said that the actual variation of k with R is linear from $40<R<100$, for within this age range a decrease in mobility with age may occur. In these experiments, in general, an increase in R may be associated with an increase in the age of the ion. If the mobility of the negative ion in oxygen remained approximately constant between the ages 0.0002 to 0.0007 second, corresponding to $20<R<104$, then the linear extrapolation to high R is obviously justified. If, however, at the *oldest* age ($R=104$) the true mobility has decreased below that corresponding to $R\sim 20$, the actual mobility *vs.* R curve must be concave upwards. In the particular case of negative ions in air the ion of shortest age corresponds to the highest value of R. If the extrapolated curve deviated from linearity by being only very slightly concave upwards, one would be led to a value for the mobility of the negative ion in *air* which *increases* with age. Inasmuch as such a behavior is contrary to all previous experience, linear extrapolation in the reduction of data taken by this method seems justified.

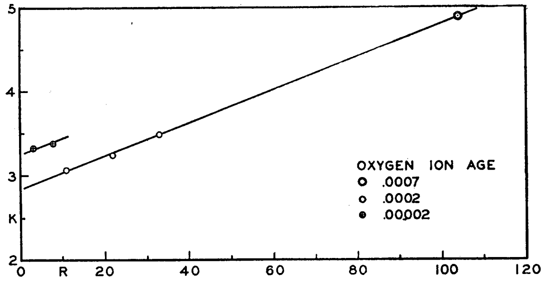

FIG. 6. Mobility of negative ions in oxygen as a function of the ratio of auxiliary to main field strength.

Oxygen

The experimental results for the mobility of the negative ion in O_2 are presented in Fig. 7. The mobility is seen to be a function of ion age with a value of 3.3 cm^2/volt sec. for the fastest ion, and to decrease with age to a value of 2.85 for the oldest ion measured. In order to provide a uniform age scale, which can be compared with other experiments, the actual ion ages in the gas at the pressure of the experiment have been recomputed to ages corresponding to atmospheric pressure and 20°C. The values for k obtained in this experiment are much higher than those ordinarily given, and undoubtedly do not refer to the so-called "normal" mobility in this gas. However, ions with a mobility greater than the "normal" have been reported by one of the authors,[12] who found that in oxygen of high purity but at atmospheric pressure and ion ages of 0.05″, a transient mobility of 2.65 was observed which shortly decreased to 2.47 and lower. The older ion in the present experiments probably corresponds to an earlier phase of the 2.65 mobility ion previously reported. The meaning of these values with regard to the character of the ion will be considered separately

Air

The results for the mobility of the negative ion in air are presented in Fig. 7. Due to the low coefficient at attachment in this gas it was impossible to obtain sufficient ion currents under conditions which simultaneously gave short ion ages. Consequently the fastest ion observed had a mobility of 2.8 which appeared to decrease

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[12] N. E. Bradbury, Phys. Rev. **40**, 508 (1932).

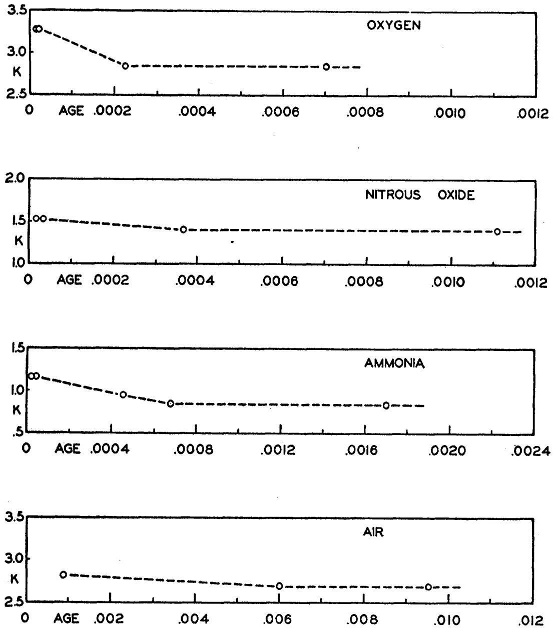

FIG. 7. Negative ion mobilities in oxygen, nitrous oxide, ammonia, and air, as a function of ion age, in seconds.

slowly with age up to 0.01″. This ion is probably of the same character as the ion of similar mobility and age in O_2 since it is known that nitrogen molecules do not attach electrons.

Nitrous oxide

The mobility of negative ions in N_2O are presented in Fig. 7. Since negative ions in this gas are apparently not formed by direct attachment, the ions measured were those formed in an auxiliary field with $X/p>2$. It is seen that the mobility decreases with age from a value of 1.5 to 1.4. This older value is almost exactly the same as that obtained by Loeb.[13]

Ammonia

The mobility of negative ions in NH_3 decrease rapidly with age for short ages, dropping from a value of 1.15 to 0.85 in less than 0.001 second. The value for the older ion is in good agreement with that of 0.87 given by Loeb.[14]

DISCUSSION OF RESULTS

Various theories have been presented giving the dependence of ion mobility upon the physical constants of the ion and the gas through which it moves. The Langevin[15] theory assumes hard spherical ions of diameter σ, which experience an inverse 5th power law of attraction with neutral molecules resulting from dielectric forces. Hassé and Cook[16] have presented a theory which supposes an inverse 5th power law of attraction superimposed upon the dielectric forces together with an inverse 9th power law of repulsion. This latter equation does not require the use of an ion-molecule collision radius. However, since the coefficients of the inverse powers are not known with accuracy, and furthermore, since calculations by the two theories lead to substantially the same results, the Langevin theory will be used in this discussion. This theory has been used very successfully by Powell and Brata[17] to explain the mobility of positive alkali ions in the rare gases.

The Langevin theory gives the mobility to be of the form

$$k=\frac{A}{[\rho(D-1)]^{\frac{1}{2}}}\left(\frac{m+M}{M}\right)^{\frac{1}{2}},$$

where M is the mass of the ion, m the mass of the gas molecule, ρ the gas density, and D the dielectric constant of the gas, A is a function of a quantity λ where

$$\lambda^2=(8\pi p\sigma^4)/((D-1)e^2),$$

in which p is the pressure, σ the sum of the radii of ion and molecule, and e the electronic charge. A as a function of λ may be obtained from a table given by Hassé.[18] The values of σ used in these calculations will be those taken from viscosity measurements.

If values are substituted in the above equation corresponding to a *monomolecular* ion in O_2 using the value of σ given by Jeans[19] of 3.6×10^{-8} cm, one obtains a value of 3.46 for the mobility at 20°C. This corresponds remarkably well with the experimental value of 3.3 and serves to suggest the hypothesis that the *ion actually measured at these short times is O_2^-*. If, instead of the ion

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[13] L. B. Loeb, Phil. Mag. **43**, 229 (1922).

[14] L. B. Loeb, Proc. Nat. Acad. Sci. **12**, 617 (1926).

[15] W. P. Langevin, Ann. chim. phys. **8**, 238 (1905).

[16] H. R. Hassé and W. R. Cook, Phil. Mag. **12**, 554 (1931).

[17] C. F. Powell and L. Brata, Proc. Roy. Soc. **A138**, 117 (1932).

[18] H. R. Hassé, Phil. Mag. **1**, 139 (1926).

[19] J. H. Jeans, *Dynamical Theory of Gases* (Cambridge University Press, London, 1925), p. 327.

O_2^-, the mass and approximate radius corresponding to a bimolecular oxygen ion is substituted, the value of 2.94 is obtained for the mobility. In this calculation, the value of A is relatively insensitive to changes in σ and the factor $((m+M)/M)^{\frac{1}{2}}$ plays the important role. The relative difference between this value and that calculated for a monomolecular ion is nearly the same difference as observed experimentally. Thus it is suggested from this data that within the first 2×10^{-4} second, *the addition product to the initial monomolecular negative ion in O_2 is a molecule whose molecular weight is between 15 and 35.* This suggests either H_2O or O_2. Subsequent ions have lower mobilities due either to the attachment of further molecules of impurity or the transfer of charge to some bulky impurity molecule inevitably present in the most stringently purified gas. Under such circumstances the factor A plays an increasingly important role, and the mass factor a lesser one.

Similar calculations may be carried out for air. If an ion be assumed of the same mass and radius which leads to a value of 2.94 in O_2, a value of 2.88 is obtained for the mobility of such an ion in air. This is slightly lower than its mobility in O_2 and is in accord with the experimental results of 2.85 in O_2 compared to 2.8 in air. It is therefore suggested that the same ion was observed in both cases, and that the failure to observe a faster ion in air was due to the greater ion ages studied.

In N_2O the original ion formed may be O^-. Assuming this to be so, the calculated value for the mobility is 2.73. This is much higher than the experimental value for the shortest ion ages measured, and therefore such an ion must lose its identity within 10^{-5} second. Using the molecular weight corresponding to the ion $(NO)_2^-$, a value for the mobility of 1.85 is obtained. It must be pointed out that the value of σ for this ion is very uncertain; great reliance cannot therefore be placed upon the calculated value for the mobility. It may be said, however, that the ion at an age of 10^{-5} second apparently has a mass at least that of $(NO)_2$, and increases its mass and diameter but little thereafter.

It has been suggested that in the process of negative ion formation in NH_3 the initial process is the dissociation of the molecule with the formation of NH^-. Although values of σ are not available for this molecule, the high value of the dielectric constant makes A insensitive to variations in σ, and the mass factor plays the dominant role. If an approximate value of 5×10^{-8} cm can be assigned to σ, one finds the mobility of an hypothetical NH^- ion to be 1.25. This is not substantially higher than the fastest mobility observed. If one employs a mass corresponding to $(NH+NH_3)^-$ one calculates a mobility of 1.06 which is obtained experimentally at an age of approximately 2×10^{-4} second. From the shape of the graph, a mobility of 1.25 for extremely short times seems probable. This ion apparently rapidly picks up an additional molecule and in less than 0.001″ reaches a stable value of 0.85 which is characteristic of ions in even impure ammonia.

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The Development and Performance of an Electrostatic Generator Operating Under High Air Pressure

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A belt type electrostatic generator has been developed which operates in a steel tank, $5\frac{1}{2}$ feet in diameter and 20 feet long, under an air pressure of 100 lb./in.^{2}. The generator is provided with a high potential electrode system of a new design which serves both to give a high breakdown potential and to furnish a satisfactory potential distribution along the charging belts and the accelerating tube. The maximum potential of the generator is about 2500 kv and the highest steady potential at which reliable data have been obtained is 2160 kv. An evacuated tube for acceleration of ions has been developed which withstands the highest generator potential. The apparatus has been successfully used in experiments on atomic disintegration.