The Nature of Gas Ions

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The mass of gas ions formed in a glow discharge and aged up to 10^5 impacts was determined by a Dempster type of mass-spectrograph. In hydrogen it is found that the primary ion, H_2^+, changes within a few thousand collisions to H_3^+, together with small quantities of H^+. The nitrogen primary ions, N^+ and N_2^+, attach to neutral molecules in about 10^5 impacts to form N_3^+ and N_4^+. In pure oxygen the ions consist almost entirely of O_2^+ with small quantities of O^+. Air ions include all possible nitrogen and oxygen ions, the aged air ions consisting principally of N_3^+, N_4^+ and O_2^+ together with the oxides of nitrogen. Charges are transferred from O_2^+ to NO, NO_2 and N_2O. Water vapor is particularly active in acquiring a charge by transfer and H_2O^+ ions may be most numerous in apparatus not baked out. No heavier clusters than N_4^+ were observed. No negative ions were observed. Some conclusions published in earlier work must be revised.

INTRODUCTION

IN an earlier paper[1] the writer reported some work in determining the mass of the "normal" gas ion. The method consists essentially in production of the ions in a glow discharge, aging by allowing them to drift at low velocity through some cm of gas, then formation of a molecular beam by passage of ions and gas molecules through a fine slit into a highly evacuated space where the ratio of charge to mass is determined in a Dempster type of mass-spectrograph. The rate of formation of secondary ions by attachment of neutral molecules or transfer of charge in the drift space may be studied qualitatively by varying the pressure or the drift field and distance.

With a new and improved apparatus results have been obtained which require revision of some of the former conclusions, and indicate certain definite trends in the aging process for relatively new ions.

APPARATUS

The form of apparatus employed during most of the experiment is shown in Fig. 1. A discharge was maintained between the water-cooled aluminum electrodes A. A few ions passed through the grid G where they drifted under the action of a field, usually of the order of a volt per cm, to the slit S_1 which was made very narrow (about 0.01 mm) in order that the pressure in the analyzing chamber could be kept down to 10^{-4} mm for pressures above the slit varying from 0.1 to 0.5 mm. The drift space could be varied from 2.5 to 5.0 cm. Except for minor improvements the analyzing chamber was similar to the one previously described.

Wax was eliminated by the use of ground joints throughout, together with an annular ring C of pressed amber for insulation of the slit S_1 from the remainder of the apparatus. The present apparatus also has narrower slits S_2 and S_3 than the older apparatus, and is connected to an electrometer of higher sensitivity. Water cooling of the electrodes allowing a more intense discharge,

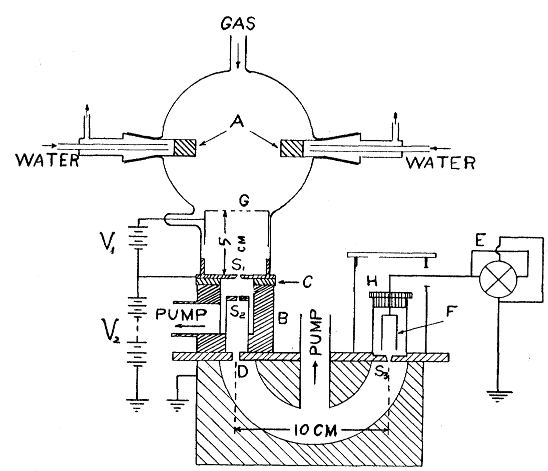

FIG. 1. Diagram of apparatus.

[1] O. Luhr, Phys. Rev. 38, 1730 (1931).

together with faster pumping, and increase of the drift space to 5.0 cm made it possible to more than double the age of the ions.

Results

1. Hydrogen

In hydrogen H^+, H_2^+ and H_3^+ were found. The H_2^+ and H_3^+ did not appear to break up into simpler ions in the analyzing chamber. At a pressure of 0.3 mm, and with a field of 0.8 volt per cm in the 2.5 cm drift space, 80 percent of the ions were H_3^+ and the remainder about equally divided between H_2^+ and H^+. At lower pressures the percentage of H_2^+ increased relative to the other two, indicating H_2^+ is the primary ion.

2. Nitrogen

Results for nitrogen are shown in Figs. 2 and 3.[2] When the higher pressures and longer drift space were used, N_3^+ and N_4^+ ions appeared. These are apparently formed by the attachment of N^+ and N_2^+ to neutral molecules after a large number of collisions. The curve of Fig. 3 was taken with a discharge between a hot filament and a grid of the type used by Smyth[3] instead of a glow discharge. The tube had been operated too short a time to remove all the water vapor. It appears that the N_{3-2}^+ ions (mass 18.6) previously reported were water vapor ions.

3. Oxygen

The curves obtained with tank oxygen and that prepared from potassium permanganate and potassium chlorate were puzzling at first. The interpretations given in the Figs. 4, 5 and 6 were finally adopted. A nitrogen discharge was passed through the tube before the oxygen was admitted. It seems that nitrogen occluded in the surfaces of the apparatus was sufficient to yield the NO^+ and NO_2^+ for many hours operation of the tube. When a new tube was used with oxygen, the NO^+ and NO_2^+ ions disappeared very soon. After air was used in this tube the ions having masses of 30 and 46 reappeared as shown in Fig. 5, dotted curve. No quantitative correlation between the relative numbers of the various oxides of nitrogen was obtained. There was a tendency for NO^+ to predominate with the larger quantities of nitrogen.

4. Air

All possible oxygen and nitrogen ions occur in air, with the addition of the nitric oxides, water vapor if the tube is not thoroughly dried, and Hg^+ if mercury is not carefully removed by liquid air traps. Typical results are shown in Fig. 7 for relatively new ions. As expected the quantity of N_3^+ and N_4^+ becomes greater with increasing age. Traces of an ion of molecular weight 68 have been found but it disappears after the discharge has been operating a short time. Contrary to results previously reported other heavier ions, probably due to wax vapors, are absent in the present apparatus.

5. Water vapor

Water ions appear to be largely secondary in nature, being readily formed by transfer of charge from other ions, as their number is relatively increased when the aging is greater. Since a small amount of water vapor gives a large H_2O^+ ion current, the probability of transfer of charge to the water molecule is evidently large. In Fig. 3 two peaks appear. One is attributed to HO^+. Sometimes the H_2O^+ peak is displaced toward the heavier ions. It is suggested that this may be caused by the kinetic energy given to the ion when it acquired its charge. This effect may have been responsible for the consistent appearance of 18.6 ions in the earlier experiment which were attributed to N_{3-2}^+.

6. Negative ions

No negative ions were found in any gas. The arrangement of the apparatus is such that the probability of attachment of electrons to molecules in the drift space is small even in oxygen and the few negative ions formed in the discharge could not be observed with the extremely narrow slit S_1, necessary in this experiment.

[2] It should be noted here that the ordinate scale of the curves is arbitrary, and the actual electrometer deflections in the case of the dotted curve have been divided by ten to show the relative numbers of light and heavy ions. The total intensity of ionization depends on the width of the slit S_1 (Fig. 1) and decreases rapidly with increasing pressure, becoming practically zero above 0.5 mm. The scale of electrometer deflections in Figs. 3, 4 and 5 have likewise been adjusted to show approximately equal quantities of the primary ions.

[3] H. D. Smyth, Phys. Rev. **25**, 452 (1925).

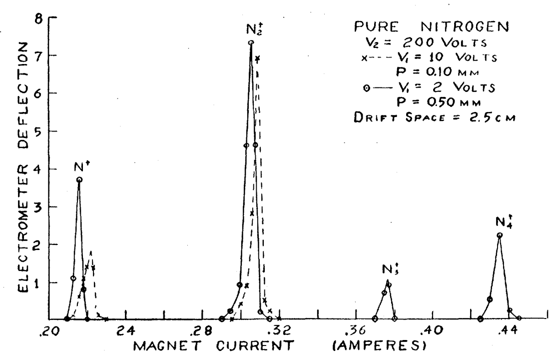

FIG. 2. Ions in nitrogen showing relative intensities with variation of age in a drift space of 2.5 cm.

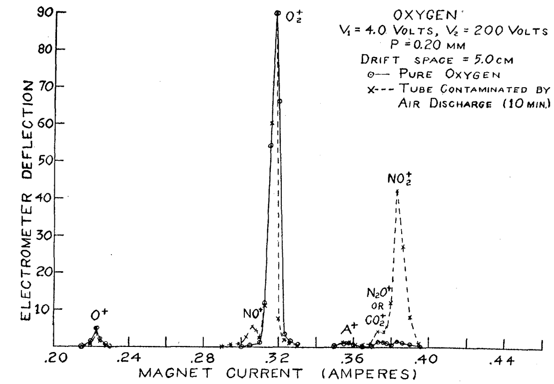

FIG. 5. Ions in pure oxygen and in the same tube after contamination by nitrogen resulting from nitrogen discharge.

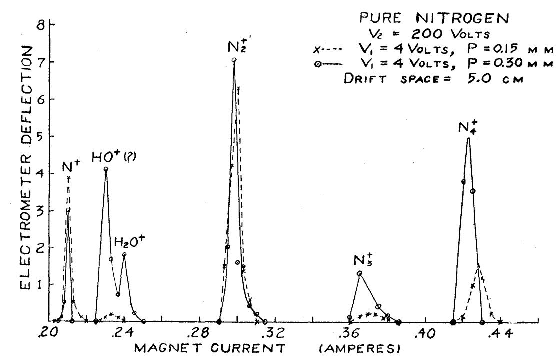

FIG. 3. Ions produced by a filament and grid in nitrogen, showing effect of varying the pressure in the drift space.

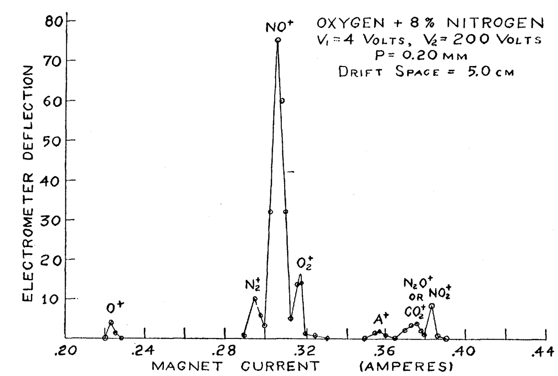

FIG. 6. Nitric oxide ions produced by transfer of charge in the drift space predominate where a small percentage of nitrogen is added to oxygen.

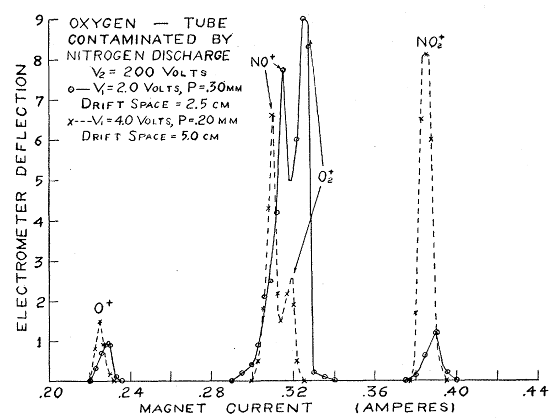

FIG. 4. Ions in oxygen showing the effect of varying the age when nitrogen contamination is present.

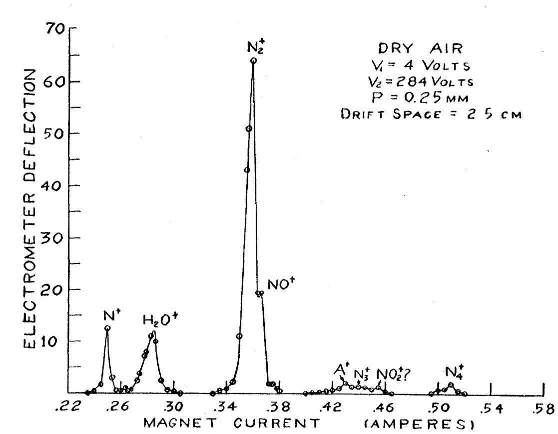

FIG. 7. Relatively new ions in air.

Discussion of Results

Assuming the usual relations between mobility of ions, pressure, and field strength the number of collisions for an ion in crossing the 5 cm drift space under a drift field of 0.8 volt per cm at a pressure of 0.5 mm is 10^5. This corresponds to an age of 4×10^{-6} seconds at atmospheric pressure. The age of ions usually measured in mobility experiments is 0.001 to 1.0 second. Hence the results here are of value only in determining the phenomena occurring in the earlier stages of the aging process.

In hydrogen, the normal positive ion under some conditions may be H_3^+ as that ion appears to form from H_2^+ after a few thousand collisions.

In nitrogen N^+ and N_2^+ appear to be primary products of ionization. The complexes N_3^+ and H_4^+ form after 10^5 collisions or a time of 4×10^{-6} seconds at atmospheric pressure. This result was calculated by a procedure similar to that used by Loeb[4] in determining the attachment coefficient of electrons.

The only ions observed in pure oxygen were O_2^+ with traces of O^+. When the oxygen is contaminated with nitrogen, the oxides NO, NO_2 and N_2O are formed and receive charges by transfer from the O_2^+ ions.

In air all possible nitrogen and oxygen ions were found. After the maximum aging possible in this experiment the ions in air chiefly O_2^+, N_3^+, and N_4^+.

Finally it has been established that up to 10^{-5} seconds at atmospheric pressure no complex ions except H_3^+, N_3^+ and N_4^+ are formed and that the ions H_2O^+, NO^+ and NO_2^+ are formed by transfer of charge. Transfer processes are probably more important under the usual conditions of purity than are the formations of complexes, and it is certain that such phenomena play an important rôle in any aging process.

The writer wishes to express his thanks to Mr. Edwin Kass, who assisted in taking some of the measurements, and to Professor L. B. Loeb, of the University of California, who has read the manuscript critically.

[4] L. B. Loeb, *Kinetic Theory of Gases*, p. 507, New York (1927). The available data must be extrapolated somewhat for these low pressures but should be correct at least in order of magnitude.