THE MASS OF POSITIVE IONS IN A GLOW DISCHARGE

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Abstract

Preliminary results are presented here in an attempt to determine directly the mass of gas ions in air, N_2, O_2, and SO_2. The ions were formed in a glow discharge, allowed to drift at low velocity through a distance of 2.5 cm, and passed as a molecular beam through a slit 0.01 mm by 5.0 mm where the mass spectrum was analyzed with a positive ray analysis apparatus of the Dempster type. The pressure in the discharge and drift spaces was maintained at 0.1 to 0.5 mm of mercury. The following ions appeared in relatively large quantities: N^+, N_3^+, O^+, N_2^+, O_2^+, O_3^+, SO_2^+, and $H_2SO_3^+$. In addition a smear of heavier ions appeared in smaller numbers, though the intensity was greater in air than in the pure gases and, in air, became relatively larger at high pressures. Peaks corresponding to molecular weights of 56–64, 76, 80, 96, 108, 138, 140, 168 and 200 were the most prominent indicating the presence of such ions as $2N_2^+$, $N_2O_2^+$, $2O_2^+$, $N_2O_3^+$ and heavier combinations. N_3^+ and O_3^+ ions apparently play an important role in gas ion phenomena though the N_3^+ is relatively unstable since it breaks up in the magnetic field into $N_2^+ + N$. In view of the results it seems likely that air ions aged over a considerable period of time are of a complex and heterogeneous nature, due probably to the formation of nitric oxides, while the ions in pure gases remain monatomic, diatomic and triatomic except for attachment to impurities.

Introduction

THE most perplexing problem in the field of gas ions to-day concerns the nature of the ions. As a result of extensive and thorough measurements of such quantities as mobility, coefficient of recombination, and attachment coefficient of electrons the behaviour of ions under various conditions is fairly well known. However, it is often difficult to interpret this behaviour correctly as such measurements do not give any direct or definite answer to the question of the mass and composition of the ions. In some cases gas ions may consist of single atoms and molecules, but it seems likely that in most gases as the ions age they become more complex in nature. This supposition is born out by many mobility experiments such as those of Erickson on the aging of the positive ion, those of Loeb on mobility in mixtures, and more recently the work of Loeb[1] on Na positive ions in H_2 and N_2, and that of Bradbury[2] on aging. Such investigators as Zeleny and Fontell in their recent work on the spread of mobilities have shown quite definitely that at any rate after aging about a second, there must be ions of various sizes and kinds present. The possibility that ions of a molecular weight of several hundred occur after aging a second or more was indicated by the recombination experiments of the writer.[3]

[1] L. B. Loeb, Phys. Rev. **38,** 549 (1931).
[2] N. E. Bradbury, Phys. Rev. **37,** 1311 (1931).
[3] O. Luhr, Phys. Rev. **35,** 1394 (1930); **36,** 24 (1930).

Since all angles of approach to the mobility problem have failed to determine definitely the real constitution of the ions it appears imperative that the mass be measured by a direct method. It occurred to Professor L. B. Loeb that the problem might be solved by forming the ions in a glow discharge and employing the Stern method to determine the velocity spectrum in a molecular beam. After consultation with Professor Stern on the feasibility of the method it was decided that accurate measurement with velocities of the order of a fortieth of a volt would be impossible owing to the presence of unknown contact potentials. Professor Stern suggested however, that the problem might be approached by forming a molecular beam as suggested by Professor Loeb and measuring the distribution of masses with a Dempster type of positive ray analysis apparatus. Since the chance of a collision in a molecular beam is very remote the ions should not break up in the analyzing chamber and the masses present could be determined directly. In all previous positive ray analyses the normal ions would be broken up by low pressures and high fields before entering the analyzing chamber. The conditions in a glow discharge cannot of course be strictly compared to those in a gas at high pressures where the ionization is produced by x-rays, polonium or some similar method. However, the intensity of ionization obtained by such means is entirely too small to be measured by a positive ray analysis method when one considers that the ion current must diffuse through a slit of the order of 0.01 by 5.0 mm in size. Normal gas ion conditions can be approximated in the glow discharge if the pressure is kept as high as possible and the ions after formation are allowed to drift through some cm of gas with a velocity so small that any aggregates which might be formed would not be likely to break up on collision with neutral molecules; that is, the result would be the same as though the ions were formed by any other method at high pressures and aged over a very short period of time. It was felt in undertaking the experiment that even if normal gas ion conditions could not be attained useful knowledge would result from the determination of the ionization products formed in a discharge tube operating between 0.1 and 1.0 mm of mercury pressure.

The present results are preliminary in nature and probably give a better idea of the ionization products as formed in the discharge than the nature of normal gas ions. However, particularly at the higher pressures where the effective aging is greater, positive ions of mass larger than a single molecule begin to appear in quantities comparable with the number of charged atoms and molecules. So far no negative ions have been observed even in gases such as oxygen and sulfur dioxide which have considerable electron affinity; but this is not surprising considering the low pressures and hence relatively few collisions which the electrons would make with neutral molecules before being swept out of the volume.

Apparatus and Method

The form of apparatus finally adopted after considerable experiment is shown in Fig. 1. A discharge was maintained between the electrodes A by means of a sixty cycle neon sign transformer with a potential of about 4000

volts or as high as could be employed without overheating the tube. About 2.5 cm below the electrodes was a nickel cap G with a tungsten wire grid in the center through which some of the ions formed in the discharge could pass. The grid G and the first slit of the analyzing chamber S_1 were separated a distance of 2.5 cm, the ions drifting through the gas in this space with a field of five volts per cm. The slit S_1 was 0.01 mm wide and 5.0 mm long; so the pressure in the discharge and drift spaces could be maintained at 0.1 to 0.5 mm of mercury while the pressure in the analyzing chamber could be kept down to 10^{-4} mm by continuous pumping.

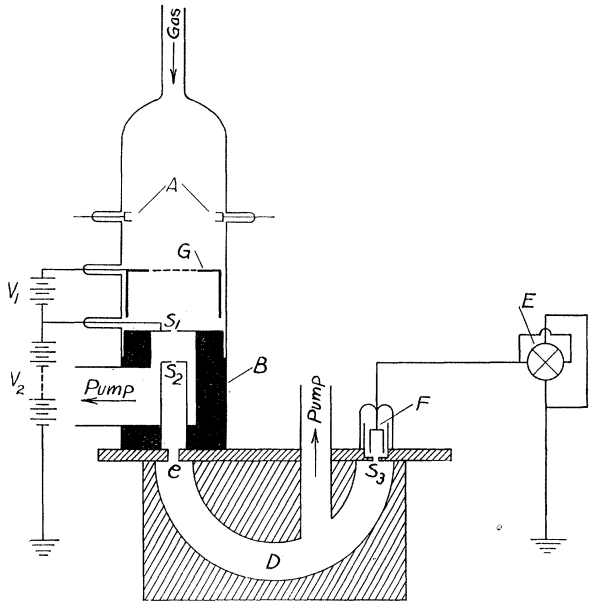

Fig. 1. Diagram of apparatus.

The analyzing chamber, made of brass, was of the standard Dempster type kindly loaned to the writer by Dr. R. E. Holzer and recently described by him.[4] The ions passed through the slit S_1 with a velocity of only a small fraction of a volt, were accelerated by the potential V_2 (100 to 200 volts), bent into a semicircle of 5.0 cm radius by a magnetic field at the point C and collected in the Faraday cylinder F where the charge was measured by the electrometer E. S_1 was insulated from the grounded analyzing chamber by mica and picein wax. B was a soft iron cylinder for magnetic shielding. The slit S_2 was 0.5 mm wide and S_3 about 1.5 mm wide.

The first attempts at measurement were made with an all glass apparatus having the inside walls silvered for electrostatic shielding. The metal cap and grid G were omitted and although some ion current was obtained through the slits S_1 and S_2, the velocities were so heterogeneous due to the high potential discharge that no appreciable current was obtained through the slit S_3. The

[4] R. E. Holzer, Phys. Rev. **36,** 1204 (1930).

glass apparatus was finally abandoned in favor of the metal chamber and a brass plate with a cm hole in the center was used in place of the grid and cap *G*. Still no ions were obtained in the Faraday cylinder as the metal plate did not sufficiently shield the drift space from the high potential discharge. Large ion currents were later obtained by placing a single electrode above the brass plate, the plate itself acting as the other electrode; but in this case the ions were projected through the slit S_1 with a velocity of about 300 volts and the conditions of drift were obviously not fulfilled. Next a filament and grid of the type employed by Smyth,[5] Hogness and Lunn[6] and others was tried and worked very well at pressures up to 0.05 mm, but above that the intensity of ionization dropped to a negligible amount. As it was necessary to work at pressures of at least 0.1 mm and preferably near 1.0 mm this method had to be abandoned. Finally the apparatus shown in Fig. 1 and described above was adopted and gave satisfactory results at pressures of 0.1 to 0.5 mm, though the ion current, especially at higher pressures was relatively small. It is hoped by means of a more intense discharge, faster pumping (hence a wider slit S_1) and more sensitive methods of detection that in the future much higher pressures, longer aging and at the same time larger currents may be attained. Negative ion currents of sufficient intensity to be measured should also be obtained under such favorable conditions.

The gases employed in the experiment were purified by passage through tubes of $CaCl_2$, NaOH, and P_2O_5; and in addition in the case of pure nitrogen through a tube of hot copper to remove the oxygen. The gas then flowed through a capillary, passed through two liquid air traps and into the discharge tube. The liquid air traps precluded the possibility of the presence of any large amount of mercury, water vapor or organic material from stopcock grease, gauges and walls of the tube.

In taking measurements it was found most satisfactory in view of the large range of masses to be covered, to keep the accelerating potential V_2 constant and vary the magnetic field by changing the current through the coils of the electromagnet. The electromagnet was calibrated by means of a flipcoil and Grassot fluxmeter, and the calibration later checked with ions of known mass. A rate of deflection method was employed in measuring the ion currents to the electrometer.

Results

Results were obtained in a number of pure gases and mixtures including N_2, O_2, SO_2, air, SO_2-N_2 mixtures and N_2-ether mixtures. The intensity of ionization in pure SO_2 and N_2-ether mixtures was too small to be measured satisfactorily. Typical results obtained for the other gases are shown in Figs. 2 to 7 inclusive. As the relative intensities of the various ions were extremely sensitive to small changes in the pressure of the discharge it was difficult to check the curves accurately, especially at higher pressures. There was such a smear of ions or larger mass and the intensity was so small that it was difficult

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

[6] T. R. Hogness and E. G. Lunn, Proc. Nat. Acad. Sci. **10,** 398 (1924).

even to check the position of many of the peaks. However, peaks corresponding to certain of the masses appeared so consistently that there can be no doubt of their existence.

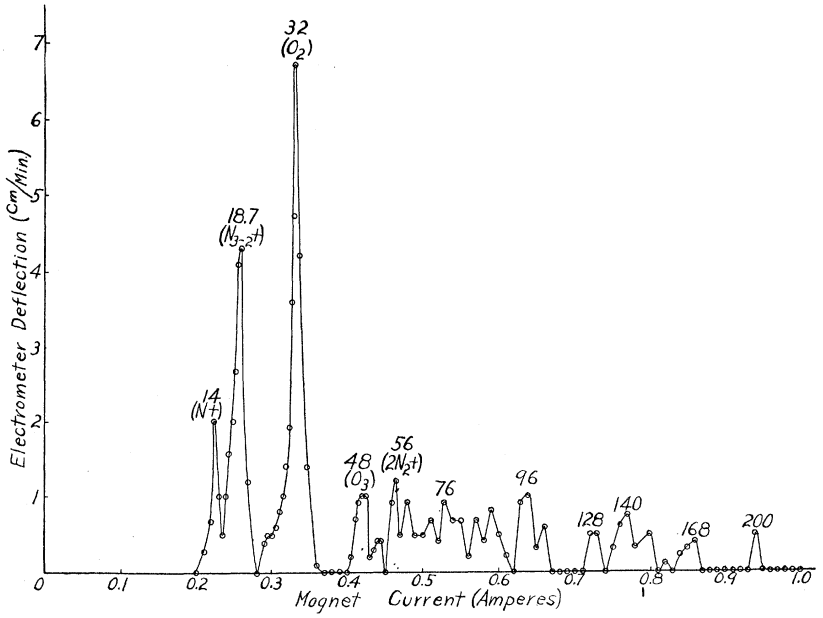

Fig. 2. Results in air with pressure in the discharge tube of 0.075 mm of mercury and accelerating potential V_2 of 150 volts. Numbers above the peaks indicate the molecular weights of the ions.

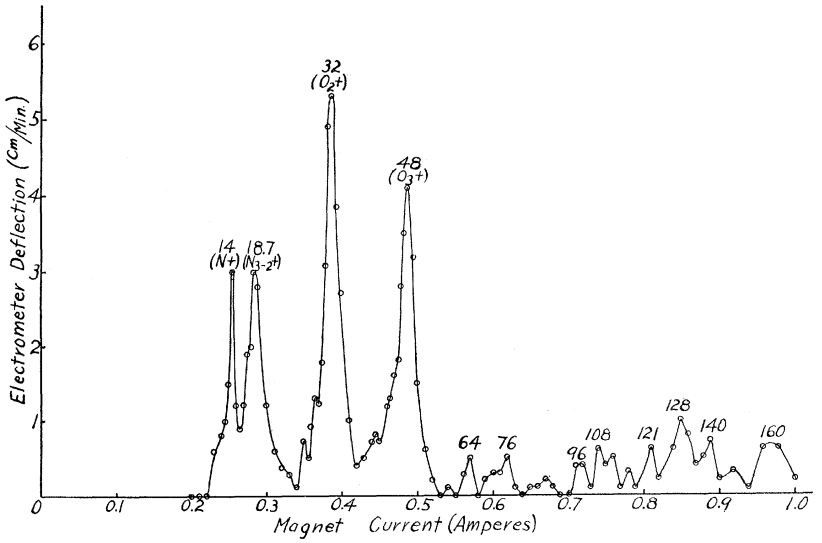

Fig. 3. Results in air with pressure in the discharge tube of 0.10 mm and accelerating potential V_2 of 150 volts. Numbers above the peaks indicate the molecular weights of the ions.

Fig. 2 shows a curve taken in air at 0.075 mm pressure in the discharge tube with an accelerating potential V_2 of 150 volts. The first mass which appears is 14.0 corresponding to N^+. O^+ is absent in measurable quantities, but a strong peak appears at a mass of about 18.7 which can only be accounted for by assuming an N_{3-2}^+ ion which is accelerated in the electric field as N_3^+ and

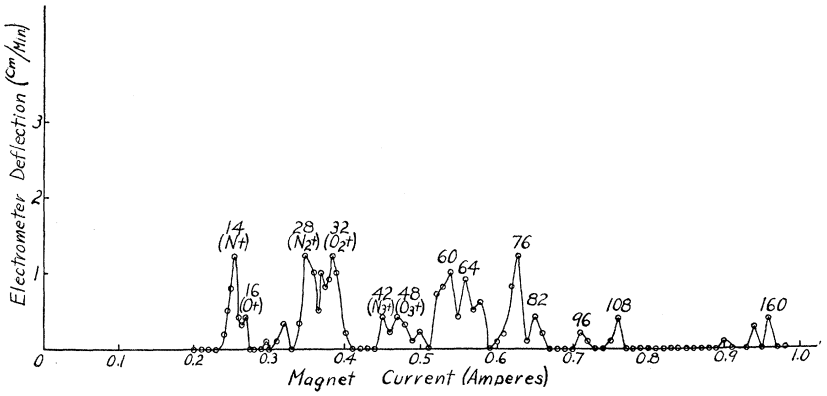

Fig. 4. Results in air with pressure in the discharge tube of 0.400 mm and accelerating potential V_2 of 191 volts. Numbers above the peaks indicate the molecular weights of the ions.

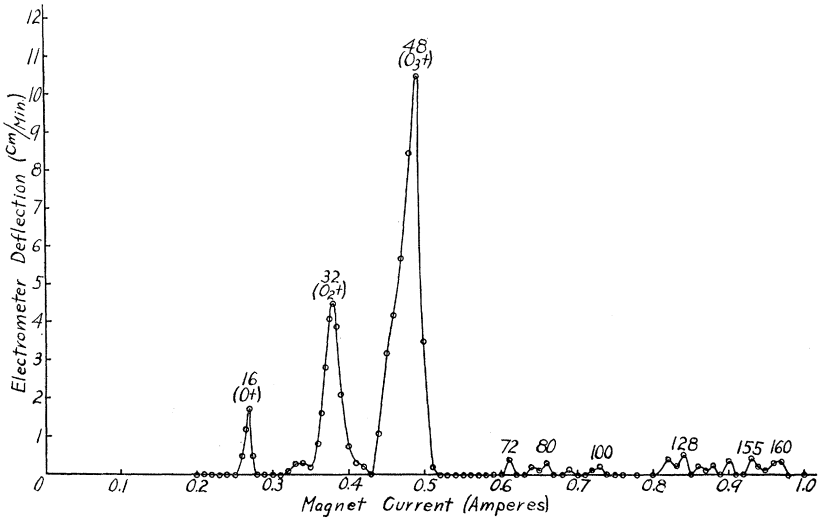

Fig. 5. Results in pure oxygen with pressure in the discharge tube of 0.10 mm and accelerating potential V_2 of 193 volts. Numbers above the peaks indicate the molecular weights of the ions.

breaks up in the magnetic field into N_2^+. This ion may have been observed by Smyth[7] working at low pressures but he attributed the corresponding peak to an impurity, presumably water. In the present work however, the peak occurs at a point corresponding to a mass which is consistently greater than 18. It disappears completely in pure O_2 or other pure gases but is always rela-

[7] H. D. Smyth, Proc. Roy. Soc. **104A**, 121 (1923)

tively strong in pure N_2 or in nitrogen mixtures. In view of the careful drying of the gases and the presence of the liquid air traps there could hardly be suffi-

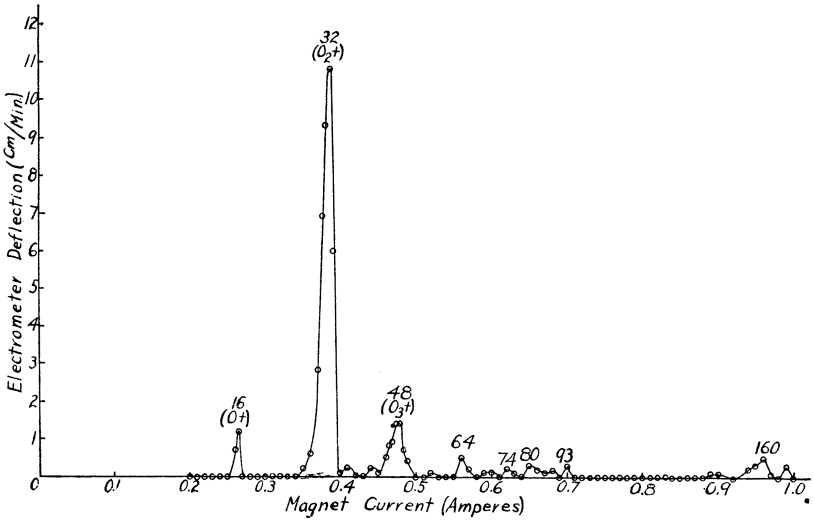

Fig. 6. Results in pure oxygen with pressure in the discharge tube of 0.30 mm and accelerating potential of 193 volts. Numbers above the peaks indicate the molecular weights of the ions.

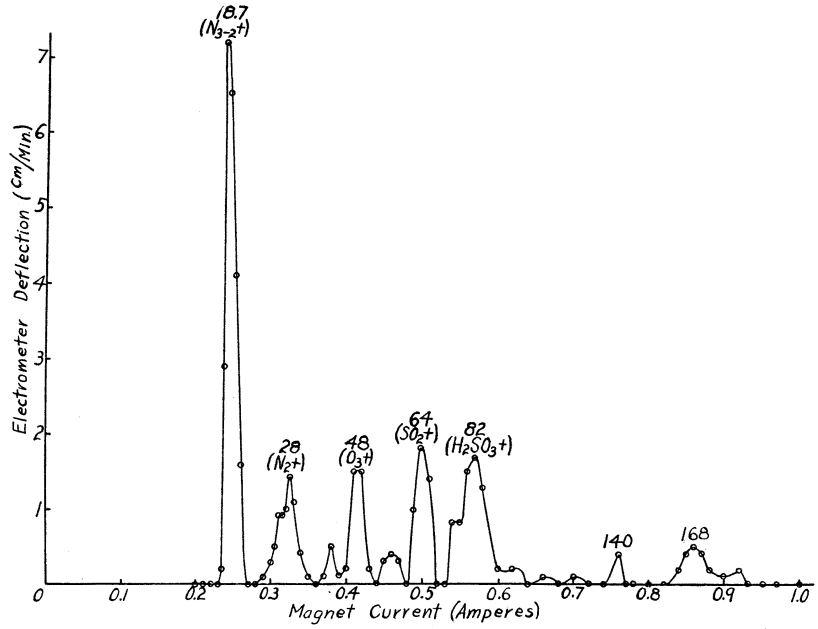

Fig. 7. Results in mixture of fifty percent N_2 and fifty percent SO_2 at a pressure of 0.30 mm and accelerating potential of 150 volts.

cient water vapor remaining to give such intense ionization. The next peak is due to O_2^+, N_2^+ being absent or too weak to measure. O_3^+ appears next as

a definite peak, with masses of approximately 56, 60, 76, 96, 128, 140, 168, and 200 following. These peaks do not stand out very definitely against a smear of ionization in the background, but peaks corresponding to these masses have a tendency to appear again and again in air.

Fig. 3 shows another curve taken in air at slightly higher pressure (0.10 mm). In this case O_3^+ is very pronounced with O_2^+ still the strongest, N^+ and N_{3-2}^+ quite strong and a smear of heavier ions.

Fig. 4 is a typical curve taken in air at higher pressures (0.40 mm). As the pressure increases the intensity of the ions of smaller mass decreases markedly while the intensity of the heavier ions, particularly of masses around 60 and 76 tends to increase. This is of course to be expected as the ions are now aged somewhat longer having made about 400 collisions with neutral molecules before entering the analyzing chamber.

Figs. 5 and 6 show two runs in pure oxygen taken at 0.10 and 0.30 mm pressure respectively. In both cases the number of heavy ions is relatively small, but it is interesting to note that at the lower pressure the O_3^+ peak is much the strongest while at the higher pressure O_2^+ appears to be the principle product of ionization.

Fig. 7 shows the results for a mixture of fifty percent N_2 and fifty percent SO_2. N_{3-2}^+ appears the most intense while N_2^+, O_3^+, SO_2^+ and $H_2SO_3^+$ show up as definite peaks of relatively large intensity. In this case the SO_2 was taken directly from a tank without drying or purifying; so water vapor was undoubtedly present in considerable quantity and may have contributed partially to the N_{3-2}^+ peak.

Measurements in pure N_2 showed N_{3-2}^+ to be the most intense with considerable N^+ and N_2^+ but no appreciable number of heavier ions. As has been indicated previously, no negative ions could be found in any of the gases but this is not surprising since even at the higher pressures of about 0.5 mm the electrons would make only about five hundred collisions in the drift space and only a negligible number could attach to neutral molecules. Small quantities of negative ions formed in the discharge at lower pressures have been observed by J. J. Thomson and Smyth but would probably escape detection in the present experiments due to the relatively low intensity of ionization. No multiply charged ions were found in the work reported here, but it was to be expected that the few doubly charged ions formed in the discharge would lose one of their charges to a neutral molecule while passing through the drift space.

Summary and Conclusions

The results may be summed up as follows: (1) In air, N_2, O_2, and SO_2 the following positive ions give strong definite peaks varying in intensity under varying conditions of pressure of the gases but easily obtainable from a glow discharge of the kind employed in this experiment: N^+, N_{3-2}^+, O^+, N_2^+, O_2^+, O_3^+, SO_2^+ and $H_2SO_3^+$. (2) In addition to the simple ions noted above there appears a smear of complex ions of larger mass up to a molecular weight of 200. The number of these heavy ions is small but is greater in air than in the pure gases and becomes relatively larger at higher pressures where the ions

make several hundred collisions with neutral molecules in the drift space. The peaks which appear most often and most prominently correspond to ions of the following molecular weights: 56–64, 76, 80, 96, 108, 128, 140, 160, 168 and 200. (3) Negative ions do not appear in measureable quantities.

It seems likely that the heavier ions consist of such combinations of atoms and molecules as $2N_2^+$, $N_2O_2^+$, $2O_2^+$, $N_2O_3^+$, $O_2O_3^+$, $N_2O_5^+$ etc. The preliminary results obtained in these experiments do not definitely answer the question of the nature of gaseous ions. However, the fact that in air at higher pressures the heavier ions become nearly equal in number to the lighter ions indicates that after some aging air ions at least do not consist of simple atoms and molecules of nitrogen and oxygen, or even of ozone and N_3. In particular, nitric oxides probably play an important role in the formation of the heavier molecular aggregates. On the other hand, in pure oxygen and nitrogen, the relative number of heavy ions is much smaller even at high pressures and it is probable that aside from attachment to impurities the ions remain essentially of a simple nature. Undoubtedly O_3^+ and N_3^+ ions play considerable role in gas ion phenomena and apparently the O_3^+ ion is very stable while N_3^+ is less stable since it breaks up into $N_2^+ + N$ in the magnetic field. It is interesting to compare the behaviour of nitrogen and hydrogen. The writer as well as other observers employing a filament at low pressures (the order of 0.01 mm) has observed a considerable quantity of H_{3-1}^+ as well as H^+, H_2^+ and H_3^+. Apparently H_3^+ breaks up in the magnetic field into $H^+ + H_2$ while N_3^+ breaks up into $N_2^+ + N$.

There remains a point to be discussed regarding the possibility that certain heavy ions, if formed, would break up in the analyzing chamber where they are rapidly accelerated in electric and magnetic fields. If the ions are relatively stable it should be impossible for a breakup to occur as long as there is no collision with neutral molecules or other ions. Since this condition is fulfilled in a molecular beam of the type employed in these experiments, and a certain number of heavy ions have actually been observed, some of the ions at least are able apparently to withstand the shock of acceleration in the fields. On the other hand a breakup in the magnetic field is certainly observed in the case of N_3^+ and H_3^+. It seems doubtful however that this effect is due directly to the magnetic forces. An ion of this sort may be stable only when in an excited state and if radiation takes place a breakup may follow. The possibility remains that other less stable heavy ions may be present which have not been observed owing to a change of mass in the analyzing chamber. Perhaps the more or less irregular smear of heavy ions observed is due in part to an effect of this sort; but the important fact remains that ions up to a molecular weight of 200 have been observed, indicating that aged ions in air are of a complex and probably heterogeneous nature.

In conclusion, the writer wishes to take this opportunity for expressing his gratitude to Professor L. B. Loeb whose advice and help have been an inspiration throughout the course of these and previous experiments at the University of California. He also wishes to thank Professor Otto Stern of Hamburg for valuable suggestions in regard to the technique of molecular beams, and Commander T. Lucci of the Italian Navy, retired, who aided in taking some of the readings.