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Low-Field Drift Velocities and Reactions of Nitrogen Ions in Nitrogen

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Drift velocities and reactions of nitrogen ions have been investigated at 300°K at values of E/N (the ratios of electric field to number density) between 1.5 and 20×10^{-16} V cm^2, and at pressures between 0.5 and 1 Torr. Ions were produced in a glow discharge and were gated into a drift cell, withdrawn through a slit, and their mass and intensity were determined as a function of the drift time by a mass analyzer. Comparison of experimental results with theoretical calculations allowed the determination of true drift velocities and reaction rates for ions undergoing reaction during the drift time. The ions in nitrogen were found to occur in two groups, N_2^+-N_4^+ and N^+-N_3^+, such that interactions within the groups are much faster than any interactions between the groups. Rate constants for the reaction $N_2^++N_2+N_2 \rightarrow N_4^++N_2$ were found to vary from 7×10^{-29} to 2×10^{-29} cm^6/sec between E/N of 5×10^{-16} and 18×10^{-16} V cm^2, while for the reverse reaction the rates varied from 0.3×10^{-13} to 110×10^{-13} cm^3/sec. The pressure dependences of the reaction rates were consistent with a three-body forward reaction and a two-body reverse reaction over our limited pressure range. For the N^+-N_3^+ system, the interaction of N^+ with the neutral gas to produce N_3^+ was observed at $E/N=5\times10^{-16}$ V cm^2 with a rate constant of 3×10^{-29} cm^6/sec. No reactions could be positively identified which produced N^+ over the range of our experimental parameters.

I. INTRODUCTION

The determination of drift velocities of nitrogen ions in nitrogen has been the subject of a large number of investigations in recent years.[1] The wide divergence of the published mobilities resulting from these investigations is due to the presence of four distinct nitrogen ion species in nitrogen, and to interactions within the gas which convert ions from one species to another. This, combined with the presence of possible impurities and the usual experimental errors, has made the interpretation of the available information extremely difficult. Under these conditions the simultaneous mass analysis of the ion species with the determination of ion drift velocities was the only method by which the difficult relations between the nitrogen ions could be further resolved, and even experiments with mass-analyzed currents need careful interpretation before true mobilities can be determined.

The first mobility measurements made on nitrogen ions in nitrogen were made by Tyndall and Powell,[2] (1930) using Tyndall's "four-gauze" method. Measurements were made by Bradbury[3] (1932) and by Mitchell and Ridler[4] (1934). In 1953 Varney,[5] using a pulsed Townsend discharge, extended the range of these measurements to higher E/N. To explain his observations he concluded that in his pressure range (1–35 Torr) the ions were largely N_4^+ at low E/N, that they were N_2^+ at high E/N, and that in the intermediate region each ion changed many times back and forth between N_2^+ and N_4^+. The essential correctness of Varney's conclusion was indicated by later experiments of Kovar, Beaty, and Varney[6] (1957) on the temperature dependence of the mobility of nitrogen ions in nitrogen. Further work by Dahlquist[7] (1963), by Davies, Dutton, and Llewellyn-Jones[8] (1964), by Woo[9] (1965) by Samson and Weissler[10] (1965), and by Bloomfield and Hasted[11] (1966) was hampered by the difficulty of interpreting the total current in a gas containing four different positive ions.

The first published reports on mobility experiments in which the ions were mass analyzed while their drift velocities were measured were made at the Sixth International Conference on Ionization Phenomena in Gases (Paris, 1963). At this meeting, preliminary data by Martin, Barnes, Keller, Harmer, and McDaniel[12] and the data of McAfee and Edelson[13] were presented.

McAfee and Edelson used a 0.1-μsec spark source to initiate a Townsend discharge in a mobility tube coupled to a mass analyzer. The discharge was confined to a region 1 cm long containing nitrogen at pressures up to 10 Torr. All of the data, except for four points for N_4^+ refer to E/N between 18 and 260×10^{-16} V cm^2.

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[1] For a recent review of the theory and the relevant experimental literature, see Ref. 14.

[2] A. M. Tyndall and C. F. Powell, Proc. Roy. Soc. (London) **A129**, 162 (1930).

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

[4] J. H. Mitchell and K. E. W. Ridler, Proc. Roy. Soc. (London) **A146**, 911 (1934).

[5] R. N. Varney, Phys. Rev. **89**, 708 (1953).

[6] F. R. Kovar, E. C. Beaty, and R. N. Varney, Phys. Rev. **107**, 1490 (1957).

[7] J. A. Dahlquist, J. Chem. Phys. **39**, 1203 (1963).

[8] P. G. Davies, J. Dutton, and F. Llewellyn-Jones, in *Atomic Collision Processes*, edited by M. R. C. McDowell (North-Holland Publishing Company, Amsterdam, 1964), p. 950.

[9] S. B. Woo, J. Chem. Phys. **42**, 1251 (1965).

[10] J. A. R. Samson and G. L. Weissler, Phys. Rev. **137**, A381 (1965).

[11] C. H. Bloomfield and J. B. Hasted, Brit. J. Appl. Phys. **17**, 449 (1966).

[12] D. W. Martin, W. S. Barnes, G. E. Keller, D. S. Harmer, and E. W. McDaniel, in *Proceedings of the Sixth International Conference on Ionization Phenomena in Gases* (Société d'Edition et de la Recherche Publicitaire Imprimeurs, Paris, 1963), Vol. I, p. 295.

[13] K. B. McAfee and D. Edelson, in *Proceedings of the Sixth International Conference on Ionization Phenomena in Gases* (Société d'Edition et de la Recherche Publicitaire Imprimeurs, Paris, 1963), Vol. I, p. 299. For experimental details and mathematical analysis see J. A. Morrison and D. Edelson, J. Appl. Phys. **33**, 1714 (1962); D. Edelson, J. A. Morrison, and K. B. McAfee, *ibid.* **35**, 1682 (1964); D. Edelson and K. B. McAfee, Rev. Sci. Instr. **35**, 187 (1964).

The preliminary report by Martin *et al.*,[12] has been superseded by the work of Keller, Martin, and McDaniel.[14] The apparatus used was a 50-cm drift tube with a movable electron beam ion source operating up to pressures of about 1 Torr. Data were obtained at E/N values between 2 and 20×10^{-16} V cm². Drift velocities were determined by measuring drift times at two different distances and dividing the difference in the distances by the difference in the mean arrival times for each distance.

Recently Saporoschenko[15] attached a mass spectrometer to the drift tube that had been used by Sinnott[16] for studies of hydrogen. In this tube, ions were produced in a glow discharge and the drift times measured using Tyndall double-grid shutters at the beginning and end of a 1-cm drift space. He used pressures from 0.5 to 1.5 Torr in the drift space and obtained data for E/N values from 5 to 50×10^{-16} V cm². Drift velocities were measured by determining the drift time which was associated with the peak ion intensity and dividing this into the drift distance. His data, with the apparent drift velocity data of Keller, Martin, and McDaniel and the data of McAfee and Edelson are shown in Figs. 9 and 10.

As will be shown, differences in experimental conditions and in the method of interpreting the data have led to widely diverging values for the drift velocities of the nitrogen ions as reported by these investigators. This paper will present data obtained with a newly constructed apparatus which, with a recently developed analysis, yield true drift velocities, and in addition, give ion-molecule reaction rates.

II. EXPERIMENTAL PROCEDURE

A. Apparatus

The apparatus used in the experiments reported in this paper was developed in this laboratory and permits time resolution of the current arriving at the end of the drift space for each of the ion species in the gas. A schematic diagram of the apparatus is shown in Fig. 1.

Electrodes in the source and drift space were of stainless steel supported on high-purity alumina rods. The ions were produced by a continuous 1.2-MHz, 200–300-V (peak to peak) glow discharge in the source, and were extracted by a constant dc field into the ion cooling region. The ion cooling region was 5.5 cm long and the E/N in the region was maintained between 4 and 10×10^{-16} V cm² so that the drift times for ions to cross the cooling region were between 60 and 270 μsec. Two fine grids spaced 1 mm apart act as the gate at the entrance to the drift space. Gate times were usually 1 μsec but were increased to 4 μsec in a few of the very low-field measurements. Guard rings were provided to maintain the uniform electric field in the drift space, which was 3.00 cm long and 1.9 cm in diameter. Potentials on the guard rings were maintained by resistors outside of the vacuum system. Potentials on the other electrodes were maintained by individually regulated power supplies. The exit aperture was a 0.0035-cm slit, 1.6 cm long, made by cutting a 120° V-shaped groove in a 0.25-cm stainless-steel plate and then grinding down the opposite face of the plate to produce the slit. In this way an aperture was produced which presented a flat surface to the drift cell and could withstand transient pressure differentials when the system was pumped down. The aperture opened up very rapidly on the side away from the drift cell to facilitate pumping the gas emerging through the aperture. Pressures (P_0) in the drift space were between 0.5 and 1 Torr in the experiments reported here, and data were obtained at 300°K for E/N values from 1.5 to 19×10^{-16} V cm².

Ions reaching the slit were extracted and focused into the source of a Bendix time-of-flight mass analyzer by a 70-V potential applied to the first section of the ion lens. Examination of the ion current transients indicated that some conversion of complex ions to simpler ion species took place during the acceleration by the ion lens but the mass analyzer discriminated sharply against ions which lost energy in this region, and the amount of N_2^+ formed by collision breakup of N_4^+ and reaching the collector was always less than 5% of the complex ion current. The source of the mass analyzer was maintained at a pressure of less than 2×10^{-4} Torr by a separate mercury-diffusion pump with a capacity of 300 liters/sec. Experiments showed that increasing the pressure in the lens and source regions by reducing the source pumping rate did not change the relative intensity of the ions. Ions entered the source, which was held at a potential of 35 V negative to the slit, and continued across to the opposite wall, where they were collected unless the draw-out pulse was applied. The draw-out pulse was applied to an electrode at one side of the source and swept all the ions in the source at the time the pulse was applied into the field-free drift space, where they were accelerated to 3 kV and allowed to drift. Horizontal

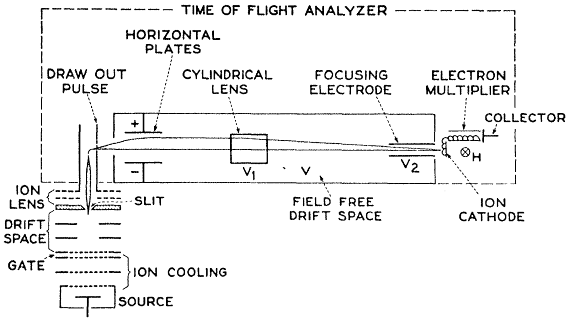

FIG. 1. Schematic view of the apparatus. The slit, through which the ions are extracted, separates the drift tube from the mass analyzer. The drift tube contains nitrogen at pressures between 0.5 and 1 Torr. A diffusion pump maintains the mass-analyzer source at pressures below 2×10^{-4} Torr. The field-free drift space is differentially pumped to below 5×10^{-5} Torr.

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[14] G. E. Keller, D. W. Martin, and E. W. McDaniel, Phys. Rev. **140**, A1535 (1965).

[15] M. Saporoschenko, Phys. Rev. **139**, A352 (1965).

[16] G. Sinnott, Phys. Rev. **136**, A370 (1964).

deflection plates were set to compensate for the transverse velocity component of the ions (which enter the source and the flight tube with 35 eV of energy perpendicular to the direction of flight) and thus strongly discriminate against ions which lost energy through collisions in the region between the slit and the source. Note that the use of a pulsed mass analyzer made it unnecessary to use a second Tyndall gate for drift velocity timing, the equivalent of a second gate being supplied by the draw-out pulse whose effective width was about 1 μsec for N_4^+ and $\frac{1}{2}$ μsec for N^+.

All of the ions entered the field-free drift tube at the same time and with the same energy, and the ion mass resolution was accomplished by the time separation during flight. Ions were focused by a cylindrical lens onto the ion cathode of a Bendix magnetic particle multiplier with a current gain of 10^6 to 10^7. The ion mass was determined by measuring the time between the draw-out pulse and the ion arrival at the multiplier. Accurate delay circuits apply a gate pulse to the particle multiplier which diverted the current in the multipler from a single ion species into the collector. This current was then read on an electrometer.

The ion current emerging from the slit was determined as a function of the drift time in the drift cell by measuring the current of a given ion species as a function of the time between the opening of the double grid gate and the leading edge of the draw-out pulse. Delay times ranged from 5 to 200 μsec and were produced by a digital delay generator. A correction was applied to allow for the delay between the time the ions leave the slit and the time they arrive in the source of the mass analyzer. This correction, which was both calculated and experimentally determined (with good agreement), did not exceed 6 μsec for the heaviest ion. The experiment was cycled at about 5 kHz except at the longest delay times when the rate was reduced to about 3 kHz. The time necessary to record the ion transients for all the ions for a given set of parameters did not exceed 30 min. Figure 2 shows typical ion current transients for the four ions in nitrogen.

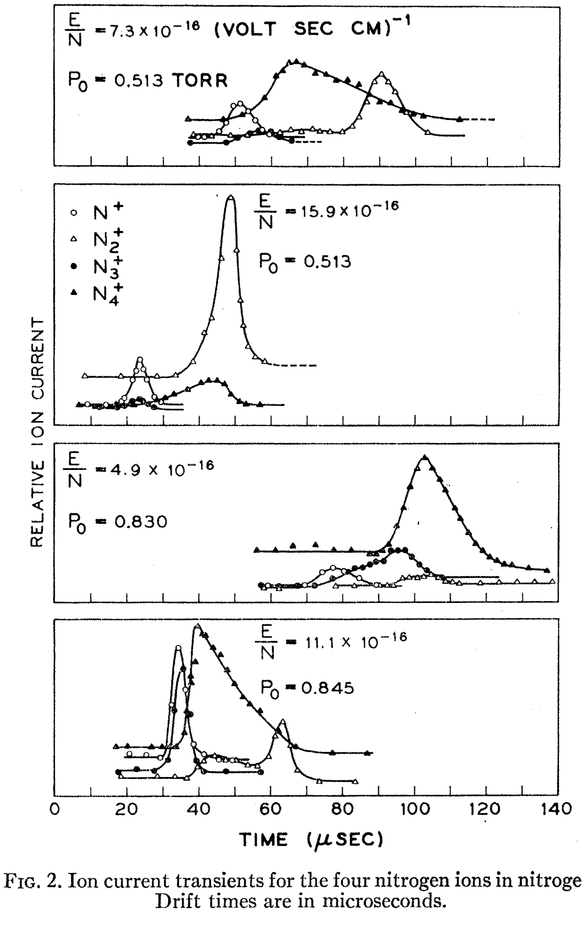

FIG. 2. Ion current transients for the four nitrogen ions in nitrogen. Drift times are in microseconds.

B. Gas Handling Apparatus

All of the pressures reported here were made with nitrogen pressures between 0.5 and 1 Torr using cylinder nitrogen of the prepurified variety obtained from the Air Reduction Company. The nitrogen was dried by passing it through two liquid-nitrogen traps in tandem before it was admitted to the drift cell. A Granville-Phillips automatic pressure controller and capacitance manometer combination maintained a constant pressure. Actual pressures were measured by a McLeod gauge attached directly to the gas handling line. The pressure measurement was checked by attaching a specially calibrated McLeod gauge directly to the drift cell.

Investigation of the observed ion spectra showed that the principal contaminating ions were due to evolution of water vapor within the drift cell itself and that running the discharge for an hour reduced the impurity ions to barely detectable amounts.

III. RESULTS

A. Drift Velocities

Ion drift velocities are obtained as a function of E/N, the ratio of the electric field to neutral molecule number density, by dividing the average drift time of the molecule into the drift distance. Ideally the ions enter the drift space through the Tyndall gate in a single pulse, and move across it under the influence of the electric field, arriving at the end as a single ion peak of approximately Gaussian distribution. In this ideal case the arrival time of the peak ion current marks the average drift time for the particular ion species. In practice, however, the presence of ion-molecule reactions may complicate the picture by converting ions of one species into another. Under these conditions the problem of interpretation becomes more difficult, since ions arrive at the end of the drift space having traversed part of the distance as one ion at one velocity and part as another ion with another velocity. The presence of a current pulse markedly different from a slightly skewed Gaussian shape as predicted by theoretical analysis is sufficient evidence of such ionic conversion during the drift time, and ion drift times determined under these conditions must be treated with great care if true drift velocities are to be obtained.

Typical ion current transients derived from our experiments for the four nitrogen ions in nitrogen are shown in Fig. 2 and the drift velocities obtained from the data are shown in Fig. 3. For two of the ions, N^+ and N_2^+, we were able to determine drift velocities by using peak current intensities in the ion current transients. Comparison of the data with computed ion current transients showed that the current peaks could be distorted by interionic reactions, but that under our experimental conditions the distortion for these ions was small enough to be ignored. When N_2^+ current transients showed two peaks, a study of the pressure dependence of the two peaks always revealed which peak represented the true drift velocity.

The situation with N_4^+ was more difficult. Examination of the current shapes showed that almost none of this ion was admitted to the drift space through the Tyndall gate and that virtually all of the observed N_4^+ ions had been formed from N_2^+ during the drift time. Under these conditions the N_4^+ peak current arrival time was found to give drift velocities somewhat slower than the true drift velocities. Only a complete analysis of the ion current transients could determine true drift velocities from the data.

Such an analysis was carried out and is described in the following paper.[17] Briefly, ion current transients for the N_2^+–N_4^+ system were generated on a digital computer using known input parameters. By comparing the data with the computer-generated current transients, two drift velocities and two reaction rates are simultaneously determined. Such a comparison of data with the computer solution is shown in Figs. 4, 5, and 6 where data gathered at various pressures and at various values of E/N are shown and compared with computer solutions. The parameters for the computer solutions are shown under each solution. $V_{N_4^+}$ and $V_{N_2^+}$ are the drift velocities of the two ions and $\lambda_{N_2^+}$ and $\lambda_{N_4^+}$ are the reaction time constants defined in Sec. III B. Physically these reaction time constants correspond to the time for a given quantity of ions (N_2^+ or N_4^+, respectively) to decay to $1/e$ of the original concentration in the absence of reverse reactions. The ratio of the amounts of the two ions admitted to the drift cell is given by $I^0_{N_4^+}/I^0_{N_2^+}$, and $D_{N_2^+}$ and $D_{N_4^+}$ are the two diffusion constants. The drift velocities are then obtained, not from the arrival time of the peak ion current, but from the drift velocity used to generate the computer solution which best fits the data. Drift velocities determined in this way are independent of apparatus factors. The expected times of the current peaks for nonreacting ions crossing the drift space at the stated velocities are shown by the short lines at the top of the figures. Evidently for N_2^+ the current peak corresponds closely to the true drift time. For N_4^+ the distortion is serious: In all cases the peak ion current is considerably displaced from the true drift time, and at E/N equal to 18×10^{-16} V cm^2 the expected arrival time for an ion drifting at the velocity of N_4^+ shows no N_4^+ current at all (see Fig. 6). Examination shows that above E/N about 15×10^{-16} V cm^2 the reaction rate for the conversion of N_4^+ to N_2^+ becomes very rapid and under these circumstances any N_4^+ which entered the drift space had reacted to form N_2^+ during the drift time, and the N_4^+ appearing in the extracted current was produced from N_2^+ very close to the end of the drift space. The N_4^+ peak then occurred at a time which depended on the drift velocities and on the rates of formation and breakup of the ions. The peak does lie between the expected arrival times for the two ions but does not represent the true drift velocity of the ion, since it is affected by the experimental pressure and various apparatus parameters. The actual N_4^+ drift velocity is found by comparison of the computed curve with the experimental data, and the drift velocity continues to be consistent with the smooth curve shown by the dashed line in Fig. 3. The N_4^+ drift velocity point at $E/N=18\times10^{-16}$ shown in that figure represents the N_4^+ velocity used to generate the computed curve shown in Fig. 6. No abrupt change in N_4^+ drift velocity takes place.

In the range of E/N below about 11×10^{-16} V cm^2 the true N_4^+ drift time is best determined from the inflection point on the leading edge of the current transient, as can be seen in Figs. 4 and 5. Most of the data

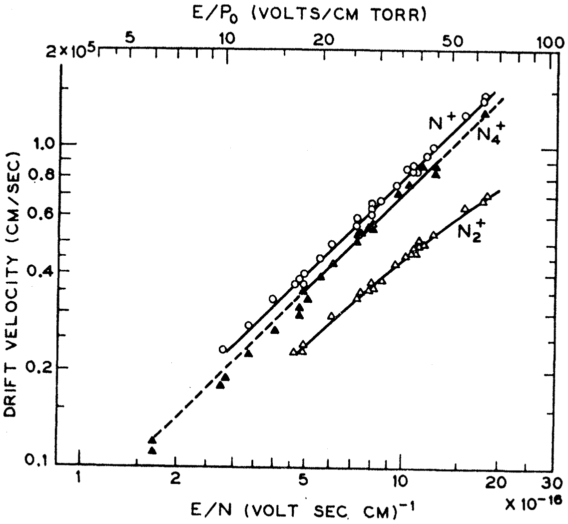

FIG. 3. True drift-velocity data for nitrogen ions in nitrogen. The straight lines shown through the points for N^+ and N_4^+ have unit slope. The line shown through the points for N_2^+ has unit slope at low E/N and a slope slightly greater than $\frac{1}{2}$ at high E/N. N_3^+ is not shown since the true drift velocity could not be determined from our data. The dashed line for N_4^+ at high E/N represents the drift velocity for N_4^+ obtained by comparison with the computer-generated curves. At low E/N the data for N_4^+ become less certain and the curve is shown dashed to indicate that the true drift velocity may deviate slightly from the straight line.

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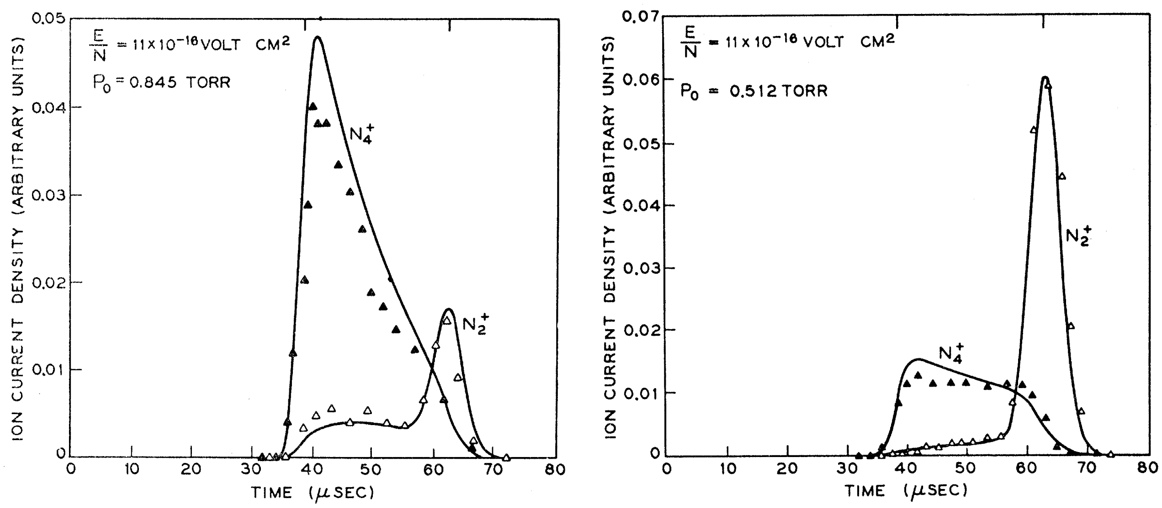
[17] D. Edelson, J. A. Morrison, L. G. McKnight, and D. P. Sipler, following paper, Phys. Rev. **164**, 71 (1967).



(a) (b)

FIG. 4. A comparison of computed ion current transients (solid lines) with experimental points for the N_2^+-N_4^+ system at $E/N = 11\times10^{-16}$ V cm² ($E/P_0 = 39$ V cm^{-1} Torr^{-1}) and at two different pressures. The parameters used to generate the computed solution are given for each curve. The reaction time constants used are consistent with a second-order nitrogen pressure dependence for the forward reaction: $N_2^+ + N_2 + N_2 \rightleftarrows N_4^+ + N_2$ and a linear nitrogen pressure dependence for the reverse. The short lines at the top of the figure show the expected peak position for ions admitted to the drift space and drifting with the drift velocities of N_2^+ and N_4^+ without reaction. Note that almost all of the N_4^+ ion observed was formed within the drift space. Parameters used in the computed solution: (a) $V_{N_2^+} = 4.8\times10^4$ cm/sec; $V_{N_4^+} = 7.8\times10^4$ cm/sec; $\lambda_{N_2^+} = 30$ μsec; $\lambda_{N_4^+} = 160$ μsec; $D_{N_2^+} = 87$ cm²/sec; $D_{N_4^+} = 141$ cm²/sec; $I^0_{N_4^+}/I^0_{N_2^+} = 0.04$. The indicated fit includes the conversion of about 4% of the N_4^+ current to N_2^+ to simulate the effect of collisions during the ion-extraction process. (b) $V_{N_2^+} = 4.8\times10^4$ cm/sec; $V_{N_4^+} = 7.8\times10^4$ cm/sec; $\lambda_{N_2^+} = 82$ μsec; $\lambda_{N_4^+} = 264$ μsec; $D_{N_2^+} = 87$ cm²/sec; $D_{N_4^+} = 141$ cm²/sec; $I^0_{N_4^+}/I^0_{N_2^+} = 0.01$. The computed currents include the conversion of 2.6% of the N_4^+ current to N_2^+ to simulate the effect of collisions during the ion-extraction process. The relative intensity of the N_2^+ ion in the computer solution has been increased by $\frac{1}{3}$ to give the indicated fit.

for N_4^+ shown in Fig. 3 have been determined from the time measured to this point. At low E/N ($<5\times10^{-16}$ V cm²) the problem becomes more difficult since the long diffusion time tends to obscure all the features of the current shape and this makes the inflection point more difficult to find. In addition it may conceal the effects of slow reactions of the ion. The drift velocities at low E/N are then somewhat less precise than those of E/N greater than about 5×10^{-16} V cm² and are shown as dashed lines in Fig. 3.

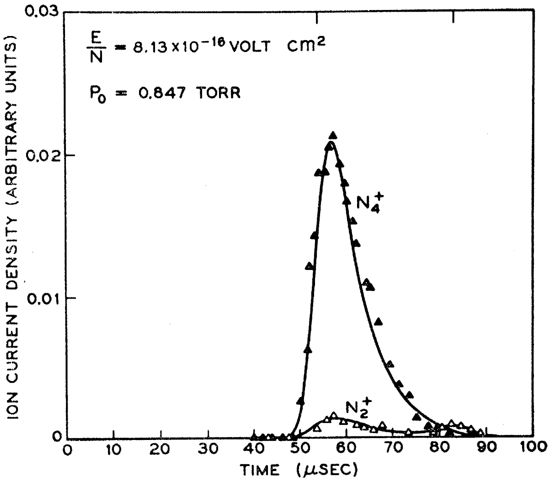


FIG. 5. A comparison of computed ion current transients (solid lines) with experimental points for the $N_2^+ - N_4^+$ system at $E/N = 8.13\times10^{-16}$ V cm² ($E/P_0 = 28.8$ V/cm Torr). The small peak at 84 μsec gives the true drift velocity of the ion. Data taken at the same E/N at increased pressure show no peak at 84 μsec. Parameters used in the computed solution: $V_{N_2^+} = 3.6\times10^4$ cm/sec; $V_{N_4^+} = 5.6\times10^4$ cm/sec; $\lambda_{N_2^+} = 20$ μsec; $\lambda_{N_4^+} = 1000$ μsec. $D_{N_2^+} = 94$ cm²/sec; $D_{N_4^+} = 145$ cm²/sec; $I^0_{N_4^+}/I^0_{N_2^+} = 0.0$. The indicated fit includes the conversion of about 4% of the N_4^+ current to N_2^+ to simulate the effect of collisions during the ion-extraction process. Most of the N_2^+ peak at 58 μsec is the result of this ion conversion.

The situation with regard to N_3^+ is less satisfactory. The drift velocities determined from peak current intensities are affected by changes in pressure at constant E/N and, as can be seen in Fig. 7, the μN values determined from these peak current transit times, when plotted against E/N, depart from the constant or slowly decreasing values predicted by mobility theory. In addition to these indications, the shapes of the ion current transients show evidence of distortion due to interaction with other ions. Under these conditions true drift velocities can be found only by analyzing the ion current shapes and taking ionic interconversion into account. In the case of N_4^+ such an analysis is feasible and gives true drift velocities, but N_3^+ is present in considerably smaller amounts under our experimental conditions and in addition it may undergo interaction with more than one other ion. This combination of a small signal and the possibility of a complex interaction makes such an analysis impracticable under our experimental conditions, and the information available on true drift velocities of N_3^+ is less precise than for the other three ions. For purposes of comparison, however, we have calculated the range of μN values for N_3^+

using the drift times determined from the ion current peak and this range is shown in Fig. 7, along with the data of earlier investigators. The range shown does not imply any severe restriction on the true drift velocities of the ion, and the true μN values for N_3^+ may lie outside of this range, though they are unlikely to depart radically from the values shown.

Despite the uncertainty in the true drift velocities for N_3^+, one observation can be made: The peak position for N_3^+ in the region $14<E/N<17\times10^{-16}$ V cm² makes N_3^+ as fast or faster than the other three nitrogen ions. In this region the drift velocity must be at least as great as that determined from the peak current, since interaction with the other ions could not produce a peak arriving before the fastest ion involved.

A plot of μN against E/N for the other three ions, shown in Fig. 8, illustrates graphically the relationship of the experimental drift velocities to the theoretical predictions. With the possible exception of N_4^+ at low E/N (where the uncertainty in the drift velocity increases) the ions are seen to be well behaved over the range of N and E/N used in our experiments, and all show the expected constant or slowly decreasing μN with increasing E/N. On the other hand, the μN values obtained are not in very good agreement with those predicted by the Langevin theory in the polarization limit. Values of μN in the limit are 9.20, 7.54, 6.86, and 6.51×10^{19} V^{-1} cm^{-1} sec^{-1} for N^+, N_2^+, N_3^+, and N_4^+, respectively, and these values are marked on the left side of Fig. 8. Also shown is the μN value of 4.04×10^{19} estimated for N_2^+ by Dalgarno[18] making allowance for the resonance charge transfer of N_2^+ ions in nitrogen. We have made no attempt to extrapolate our values and obtain "the reduced mobility" for the ions but it is obvious that a considerable change in the behavior of the ions would have to take place at very low E/N to produce an intersection at the theoretical values. At present we know of no theory which would lead us to expect such behavior.

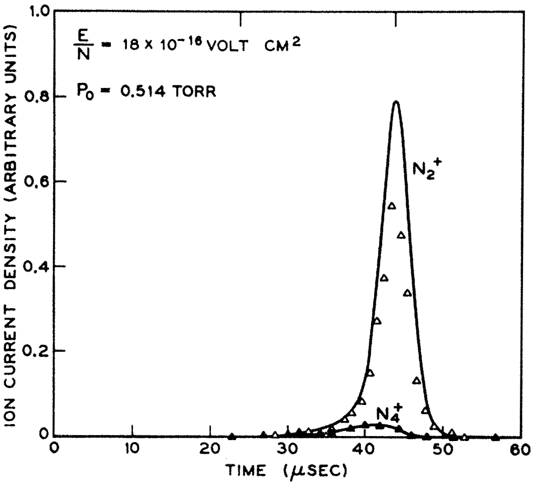


FIG. 6. A comparison of computed ion current transients (solid lines) with experimental points for the $N_2^+-N_4^+$ system at $E/N=18\times10^{-16}$ V cm² ($E/P_0=64$ V cm^{-1} $Torr^{-1}$). The N_4^+ peak at about 42 μsec represents N_4^+ ions formed from N_2^+ late in the drift space. The short lines at the top of the figure show the expected peak positions for ions entering the drift space and crossing with the true drift velocities of N_4^+ and N_2^+ without reaction. The rapid breakup of N_4^+ at this high E/N makes N_2^+ the most abundant ion. Parameters used in the computed solution: $V_{N_2^+}=6.9\times10^4$ cm/sec; $V_{N_4^+}=12.6\times10^4$ cm/sec; $\lambda_{N_2^+}=150$ μsec; $\lambda_{N_4^+}=5$ μsec; $D_{N_2^+}=89$ cm²/sec; $D_{N_4^+}=163$ cm²/sec; $I^0_{N_4^+}/I^0_{N_2^+}=0.0$. The effect of ion conversion in the extraction process was not included since with N_2^+ the dominant ion the effect would be negligible.

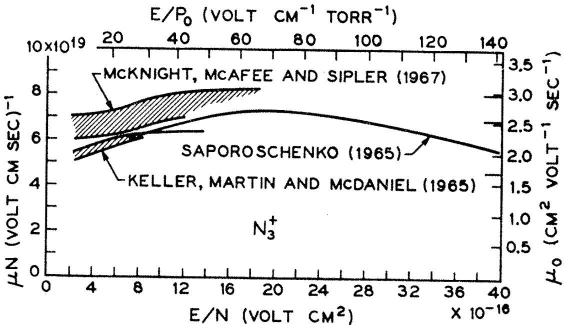


FIG. 7. A comparison of μN data for N_3^+ at various values of E/N. True N_3^+ drift velocities could not be obtained from our data and the range shown represents the *apparent* μN values derived from peak ion current intensity. The cross-hatched area represents the variation in apparent velocity (obtained from the ion intensity peak) with changing pressure. True μN values for this ion may lie outside this range but they are unlikely to differ radically from the values shown here. The long marks on the right-hand side of the drawing indicate the μN values for N^+ and N_4^+ and the maximum (lowest field) value for N_2^+ derived from our data.

A comparison of our data with that of other workers is shown in Figs. 9 and 10. Note that Keller, Martin, and McDaniel[14] determined drift velocities using the differences in *mean* drift times obtained from a drift tube with a variable drift distance. This makes the effect of interionic conversion on their data for N_2^+, N_3^+, and N_4^+ difficult to evaluate, but it is certain that the different reaction times at the different distances will introduce distortions from the true drift velocity for these

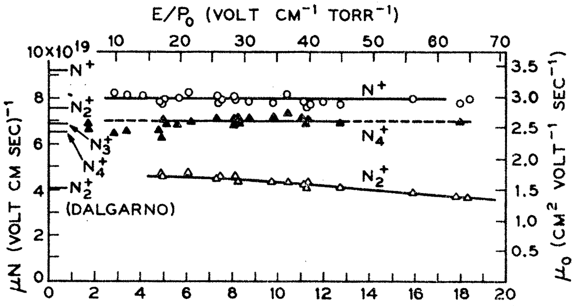


FIG. 8. A plot of μN against E/N for three of the nitrogen ions in nitrogen. On the left are shown the polarization limit values for the ions from the Langevin theory and the value for N_2^+ suggested by Dalgarno.

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[18] A. Dalgarno, M. R. C. McDowell, and A. Williams, Phil. Trans. Roy. Soc. (London) **A250**, 411 (1958); A. Dalgarno, *ibid.* **A250**, 426 (1958).

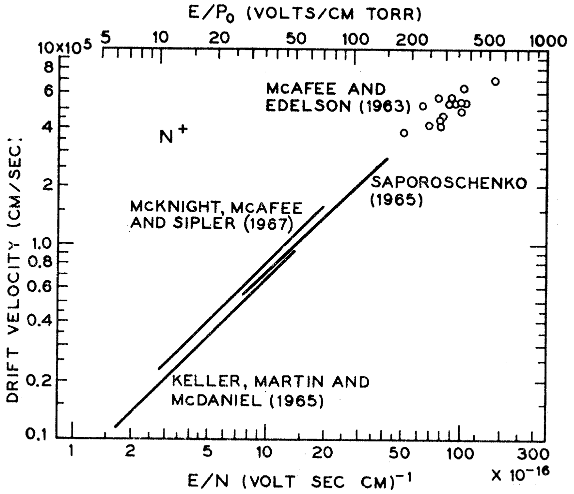

FIG. 9. A comparison of mass-analyzed drift-velocity data for N^+. The data for N^+ from the various investigators are strictly comparable and the small differences must be ascribed to experimental factors.

ions. Recognizing the problems involved in interpreting the data, they presented their results for these ions as *apparent* drift velocities, emphasizing in the word *apparent* that their data might be displaced from true drift velocities. In fact their drift velocities for N_4^+ were so strongly affected by interaction with N_2^+ that they are not shown in Fig. 10. For N^+ however, the method used should produce the true drift velocity of the ion.

Saporoschenko[15] determined drift velocities from the ion current peaks and here again the drift velocities for N_3^+ and N_4^+ may be displaced from the true drift velocity by reaction in the drift space. For N^+ and N_2^+, however, the reactions should not distort the peak position in his experiments and the drift velocities for these ions should represent true drift velocities. The data for N^+ shown in Fig. 9 should then be strictly comparable, and the small differences must be attributed to experimental effects.

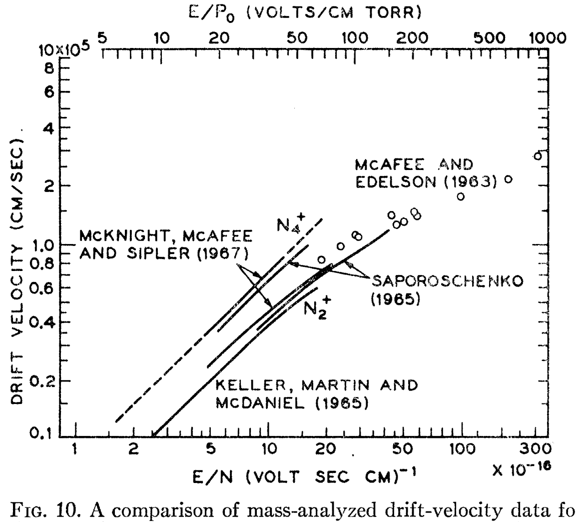

FIG. 10. A comparison of mass-analyzed drift-velocity data for N_2^+ and N_4^+. The circles show the drift velocities for N_2^+ determined by McAfee and Edelson (Ref. 13). Only the N_2^+ data of Saporoschenko are strictly comparable to our data since in all other cases the apparent drift velocity may differ from the true drift velocity. We have eliminated the most obvious examples of such a discrepancy and have not plotted the N_4^+ apparent drift velocities when they were strongly affected by interconversion with N_2^+.

B. Reaction Rates

The presence of interconversion between nitrogen ions has been the principal complicating factor in the interpretation of drift velocity data obtained from nitrogen. Such interconversion in nitrogen was first suggested by Varney[5] to explain a sudden break in the slope of his measured ion drift velocities in that gas. He proposed that at low E/N ($<11\times10^{-16}$ V cm^2) the ions are largely N_4^+; at higher E/N ($>25\times10^{-16}$ V cm^2) they are N_2^+, and in the intermediate region each ion changes many times from N_2^+ to N_4^+ and back. This is borne out by our results and his drift velocities correspond closely with the drift velocities for these two ions determined in the present investigation.

In order to more closely examine this reaction, reaction rates were determined by comparison of the experimental points with curves generated using the numerical analysis described in the accompanying paper.[17] The interaction time intervals used were between 0.3 and 0.7 μsec, and variations of this time by a factor of 2 did not seem to affect the shapes of the computed current transients. Figures 4, 5, and 6 show a comparison of the experimental and the calculated ion current transients for the N_2^+–N_4^+ system under various conditions, and the values of the parameters used to generate the computer solutions are given. The fits are seen to be sufficiently close for the parameters to be estimated in this way. It is not possible, however, in this type of estimation by curve comparison, to establish an exact measure of confidence for these estimates.

The reaction rates of the ions are defined in terms of the parameter λ, the time constant for the reaction. For the two-body reactions:

$$\text{reaction rate} = d\rho/dt = -KN\rho = -\rho/\lambda \qquad (1)$$

and for three-body reactions:

$$\text{reaction rate} = d\rho/dt = -KN^2\rho = -\rho/\lambda, \qquad (2)$$

where ρ is the number density of the ions, K is the rate constant, and N is the number density of the neutral nitrogen molecules. From the pressure dependence of the time constants of the ion transients determined at $E/N = 11.1\times10^{-16}$ V cm^2, the forward and reverse reactions

$$N_2^+ + N_2 + N_2 \rightleftarrows N_4^+ + N_2, \qquad (3)$$

were found to be best viewed as three- and two-body reactions, respectively. The pressure variation of the forward reaction rate, that is, for the formation of N_4^+, showed clearly that the pressure dependence was greater than linear though the uncertainty in the time constants does not allow us to completely rule out the possibility the the reaction might be of some intermediate order. We assumed that this reaction is indeed a three-body reaction and rate constants at other E/N were then determined from the reaction time constants and the number density of the neutral N_2 molecules. The use of these rate constants at pressures radically different from 1 Torr would be most unwise before the reaction rates have been investigated over a greater range of pressures. For the two-body reaction

$$N_4^+ + N_2 \rightarrow N_2^+ + N_2 + N_2, \tag{4}$$

the reaction constant ($\mathrm{cm^3\ sec^{-1}}$) is then given by

$$K_{N_4^+\rightarrow N_2^+} = 1/\lambda_{N_4^+} N. \tag{5}$$

For the three-body reaction

$$N_2^+ + N_2 + N_2 \rightarrow N_4^+ + N_2, \tag{6}$$

the reaction rate constant ($\mathrm{cm^6\ sec^{-1}}$) is given by

$$K_{N_2^+\rightarrow N_4^+} = 1/\lambda_{N_2^+} N^2. \tag{7}$$

The reaction rates derived from the data are shown in Table I. The effect of collisions converting ions from one species to another in the region between the exit slit of the drift cell and the source of the mass analyzer is not large, but it does introduce some uncertainty into the reaction rates determined for N_4^+ going to N_2^+ at low E/N where the reaction has a long time constant and produces correspondingly small amounts of N_2^+.

The over-all errors in the drift velocities of N^+, N_2^+, and N_4^+ are estimated to be only a few percent in the best cases, and less than 20% in all. The reaction rates are much more sensitive to the exact curve shapes as well as to the particular value of E/N; the uncertainty in the best cases is probably less than a factor of 2 and in the worst cases probably no more than a factor of 4. Uncertainty in the diffusion constants is probably a factor of 2.

A somewhat insensitive check on some of the reaction rates determined from the ion current transient shapes is given by the fraction of the total charge of a given ion which reacted during the drift time. By estimating the shapes of the ion current transients admitted to the drift space and assuming that the particle multiplier is equally sensitive to the two ions, the total amount of charge of one ion converted to the other during the drift time can be approximately determined, and from this the reaction rate can be derived. Reaction rates based on an analysis of this kind were reported previously[19] and are also shown in Table I. The uncertainty in the reaction rate constants obtained in this way is greater than for the values obtained by comparison with theoretical curves, and the agreement to within a factor of 2 or 3 is as good as could be expected.

TABLE I. Reaction rates for the N_2^+-N_4^+ ion conversion as a function of E/N.

Reaction:	$N_2^++N_2+N_2\rightarrow N_4^++N_2$		$N_4^++N_2\rightarrow N_2^++N_2+N_2$	
E/N ($\mathrm{V\ cm^2}$)	Rate from ion transient shape ($\mathrm{cm^6/sec}$)	Rate from charge conversion ($\mathrm{cm^6/sec}$)	Rate from ion transient shape ($\mathrm{cm^3/sec}$)	Rate from charge conversion ($\mathrm{cm^3/sec}$)
5×10^{-16}	$7\ \times10^{-29}$	5×10^{-29}		
8×10^{-16}	5.5×10^{-29}	2×10^{-29}	0.3×10^{-13}	1×10^{-13}
11×10^{-16}	$4\ \times10^{-29}$	2×10^{-29}	$2\ \times10^{-13}$	4×10^{-13}
18×10^{-16}	$2\ \times10^{-29}$		$110\ \times10^{-13}$	

The reaction rates given in Table I for the three-body association of N_2^+ with neutral nitrogen to produce N_4^+ agree in general with the reaction rates determined by Woo[9] for what was undoubtedly this reaction although he was unable to positively identify the ions in his experiment. His values correspond to rates of 9, 4.5, and 0.9×10^{-29} $\mathrm{cm^6/sec}$ at E/N values of 5.6, 9.3, and 16×10^{-16} $\mathrm{V\ cm^2}$. This rate has also been measured by Warneck,[20] who found a three-body pressure dependence, and obtained a rate of 8.5×10^{-29} $\mathrm{cm^6/sec}$ at low E/N. It is interesting to note that Fite *et al.*[21] working in afterglows with an undetermined (probably low) E/N deduced the rate 5×10^{-13} $\mathrm{cm^2\ sec^{-1}}$ for reaction (6) which corresponds to a rate of 3×10^{-29} $\mathrm{cm^6\ sec^{-1}}$ at their pressure of 0.5 Torr.

In addition to the interaction between N_2^+ and N_4^+, the time constant for the reaction

$$N^+ + N_2 + N_2 \rightarrow N_3^+ + N_2 \tag{8}$$

was determined although the pressure dependence and the order of reaction were not determined. Equation (8) does not, then, indicate a known reaction mechanism, but merely the association of N^+ ions with neutral nitrogen molecules to form N_3^+ with the measured time constants. The time constants for this reaction at $E/N = 4.9\times10^{-16}$ $\mathrm{V\ cm^2}$ are consistent with reaction rate of 3×10^{-29} $\mathrm{cm^6\ sec^{-1}}$ (or 9×10^{-13} $\mathrm{cm^3\ sec^{-1}}$) at a pressure of 0.9 Torr. The uncertainty in these values is probably less than a factor of 4. The corresponding value derived from total charge conversion, which has been reported previously,[19] is about 1×10^{-29} $\mathrm{cm^6/sec}$. The reaction producing N_3^+ from N^+ is not in itself

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[19] L. G. McKnight, K. B. McAfee, and D. P. Sipler, at the 16th Annual Gaseous Electronic Conference, Minneapolis, Minnesota, October, 1965 (unpublished); Bull. Am. Phys. Soc. **11**, 498 (1966). The rate constants reported at this meeting were all given for a second-order reaction, i.e., a two-body process. Where necessary, they have been converted to the three-body rate constants given in Table I by dividing through by the average gas number density for our experimental conditions.

[20] P. Warneck, J. Chem. Phys. **46**, 502 (1967).

[21] W. L. Fite, J. A. Rutherford, W. R. Snow, and V. A. J. van Lint, Discussions Faraday Soc. **33**, 264 (1962).

sufficient to explain the shape of the observed N_3^+ ion current transients if we assume a constant μN for that ion. The chief complicating factor is the appearance of the N_3^+ ion peak at a time in advance of (or very closely coincident with) the N^+ peak at $E/N \sim 15\times10^{-16}$ V cm^2 and at a time considerably behind the N^+ peak at $E/N<10\times10^{-16}$ V cm^2. Since the peak ion current must occur somewhere between the expected arrival times of the two ions involved in a reaction, this behavior indicates that either there are complex interactions with the other ion species, or that μN for N_3^+ actually decreases at low E/N. We have suggested[19] that some of the phenomenon might be explained by a rapidly reversible reaction converting N_3^+ to N^+ and back again, and there is some evidence that the reaction

$$N_3^+ + N_2 \rightarrow N^+ + N_2 + N_2 \qquad (9)$$

does take place, especially at higher E/N ($>30\times10^{-16}$ V cm^2) but reaction (9) certainly does not take place at $E/N<10\times10^{-16}$ V cm^2 and the observed formation of N_3^+ from N^+ in this region is still not sufficient to produce the observed ion current transients if we assume constant μN for N_3^+. The possibility of a complex interaction of N_3^+ with more than one ion could, in theory, be determined by an extension of our numerical analysis to include more than one interaction, but under our experimental conditions N_3^+ is present only in small amounts, and the combination of a small signal and a complex interaction makes such an analysis impracticable. If additional reactions do take place, however, they must be considerably slower than the reactions reported here.

C. Diffusion Constants

The computer-generated curves showed that the current shapes were insensitive to the exact diffusion constant chosen and this leads to considerable uncertainty in the determined values of this constant. The diffusion constants used to fit the data at $E/N = 11\times10^{-16}$ V cm^2 are between 1.5 and 3 times those which would be derived from the Einstein relationship between the diffusion constant D and the ion mobility μ:

$$\mu/D = e/kT \qquad (10)$$

if the temperature T is set to the ambient temperature of the experiment (300°K), e is the ionic charge, and k is the Boltzmann constant.

IV. CONCLUSIONS

The following conclusions can be drawn concerning the behavior of nitrogen ions in nitrogen: The ions in nitrogen occur in two groups: N^+–N_3^+ and N_2^+–N_4^+, where the interactions within the groups are large compared with possible interactions between groups. N_3^+ and N_4^+ are the favored ions at low E/N ($<11\times10^{-16}$) and N^+ and N_2^+ are not stable at low E/N except in the presence of high temperature and low pressure. Interactions between the groups must be very slow with reaction-time constants greater than 500 μsec, if they exist at all under our experimental conditions. The formation of N_3^+ from excited N_2^+ observed in mass-spectrographic investigations[22–24] was not observed, but this reaction and others involving excited states of the ions may have been suppressed in our experiments by the ion-cooling region, where ions were allowed to drift for some time before entering the drift space.

N^+ enters the drift space and crosses in a single well-defined peak. At low E/N ($<5\times10^{-16}$ V cm^2) it interacts to produce N_3^+ with a time constant of about 40 μsec at $N=2.9\times10^{16}$ molecules/cm^3 which corresponds to a reaction rate of 3×10^{-29} cm^6/sec. This reaction probably takes place at lower E/N as well but this cannot be established from our data with certainty. No reactions were observed which definitely produced N^+.

The drift velocity variation of N_3^+ can only be explained by a real variation of μN with E/N or as a slow interaction with the N_2^+–N_4^+ system or both. The observed formation of N_3^+ from N^+ is not alone sufficient to produce the observed results. The reverse reaction, that is the formation of N^+ from N_3^+, does not take place with any speed at $E/N<10\times10^{-16}$ V cm^2. N_2^+ and N_4^+ are closely related through a reversible reaction and the rapid variations in reaction rates with E/N are shown in Table I. N_2^+–N_4^+ were the principal ions obtained from the discharge and the total ion intensity was great enough so that the formation of ions in the N^+–N_3^+ system from those in the N_2^+–N_4^+ system should have been easily observed. No obvious indications of such an interaction were found, and only the anomalous behavior of the N_3^+ ion velocity derived from the intensity peak prevents us from being absolutely certain of the separation of the two ion systems, at least on a time scale comparable with the reactions within the ion groups.

ACKNOWLEDGMENTS

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[22] M. Saporoschenko, Phys. Rev. **111**, 1150 (1958).

[23] M. S. B. Munson, F. H. Field, and J. L. Franklin, J. Chem. Phys. **37**, 1790 (1962).

[24] V. Cermák and Z. Herman, Collection Czech. Chem. Commun. **27**, 1493 (1962).