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Mobilities, Diffusion Coefficients, and Reaction Rates of Mass-Indentified Nitrogen Ions in Nitrogen*†

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Measurements at room temperature of the drift velocity, the longitudinal diffusion coefficient, and the transverse diffusion coefficient have been made for low-energy mass-identified nitrogen ions in nitrogen gas in a drift-tube mass spectrometer. These parameters were evaluated using an analysis described in the article immediately preceding this one. The mobilities of N^+ and $N_2{}^+$ were obtained over the E/N range from 7 to 700×10^{-17} V cm^2, yielding zero-field reduced mobility values of 2.97 and 1.87 cm^2/V sec, respectively. The mobilities of $N_3{}^+$ and $N_4{}^+$ were obtained over the E/N range from 2 to 40×10^{-17} V cm^2, yielding zero-field reduced mobility values of 2.26 and 2.33 cm^2/V sec, respectively. For N^+ and $N_2{}^+$, the longitudinal diffusion coefficients were determined from the widths of the experimental arrival time spectra, and the transverse diffusion coefficients were determined from the attenuation of the ion count rate as the drift distance was increased. For both ions the two diffusion coefficients were observed to be equal and in agreement with the Einstein relation at low E/N, but to behave quite differently as E/N was increased. It has previously been reported that the longitudinal diffusion coefficients of both ions increase rapidly by more than an order of magnitude; the transverse diffusion coefficient of N^+ has been found to increase in a similar fashion, although much less rapidly, while that of $N_2{}^+$ remains nearly constant. Measurements were made up to an E/N of 700×10^{-17} V cm^2. The rates of the two ion-molecule reactions, $N^+ + 2N_2 \rightarrow N_3{}^+ + N_2$ and $N_2{}^+ + 2N_2 \rightarrow N_4{}^+ + N_2$, were also measured by an attenuation technique over the E/N range from thermal to 100×10^{-17} V cm^2. The reaction rates at thermal energy were determined to be 1.8×10^{-29} cm^6/sec and 5.0×10^{-29} cm^6/sec, respectively, and both rates were observed to decrease as E/N was increased.

I. INTRODUCTION

This article presents the results of an extensive investigation of the drift, diffusion, and reaction of low-energy nitrogen ions in nitrogen gas at room temperature. The data were obtained with a drift-tube mass spectrometer of ultra-high-vacuum construction. Using an analysis discussed in the preceding paper,[1] the mobilities of N^+, $N_2{}^+$, $N_3{}^+$, and $N_4{}^+$ ions in nitrogen gas have been determined, both the longitudinal (D_L) and the transverse (D_T) diffusion coefficients of N^+ and $N_2{}^+$ have been measured,[2] and the reaction-rate coefficients for the three-body ion-molecule reactions

$$N^+ + 2N_2 \rightarrow N_3{}^+ + N_2 \qquad (1)$$

and

$$N_2{}^+ + 2N_2 \rightarrow N_4{}^+ + N_2 \qquad (2)$$

have been evaluated.

The *mobility* K is defined[3] as the ratio of the drift velocity v_d to the electric field strength E, and is inversely proportional to the gas number density N. To facilitate comparisons of data obtained at different gas number densities, we shall make use of the "reduced mobility" K_0, defined by the equation

$$K_0 = K(p/760)(273.16/T),$$

where p and T are the gas pressure and temperature, in Torr and deg Kelvin, respectively, at which the measurement of K was made. At a given temperature T, the parameter E/N determines the average energy and the transport properties of the ions. Hence the data are presented as a function of E/N. As E/N is decreased toward zero, the reduced mobility K_0 approaches a constant value known as the "zero-field reduced mobility." In each of the cases investigated here, mobilities were measured to sufficiently low E/N that accurate values of the zero-field mobility could be obtained.

In accordance with the suggestion made by Huxley *et al.*,[4] the units of E/N will be denoted by the "Townsend" or "Td," where 1 Td $= 10^{-17}$ V cm^2.

Brief historical sketches of nitrogen ion swarm research have been published[5,6] recently, and a more detailed review has also been made.[7] The consensus is that much of the existing nitrogen mobility data are seriously affected by reactions of the ions with nitrogen molecules or impurities, and in most of the experiments mass-spectrometric analysis of the ions was not performed. In addition, the accuracy of many ion-molecule reaction-rate measurements has been questioned[8] because the analysis of the data did not take into account the effect of transverse diffusion. In the present research, the ions are mass analyzed, and the effects of reactions and diffusion are carefully considered in the reduction of the data.

II. APPARATUS

The drift-tube mass-spectrometer apparatus employed in these measurements is, except for certain improvements to be discussed below, the same as that described by Albritton *et al.*[9] The essential internal components are shown in Fig. 1. Nitrogen gas is admitted to the drift tube through a servo-controlled leak, and continuously flows from the tube through the 0.08-cm-diam exit aperture in the endplate. The pressure in the drift tube is held constant during operation at some desired value in the range 0.02 to 1 Torr.

A pulsed electron-impact ion source is used to create, repetitively, short bursts of primary ions at a selected source position on the drift-tube axis. A portion of each burst of ions is gated into the drift region by a double-grid electric shutter in the ion entrance aperture, and migrates down the axis of the drift tube under the influence of a weak electric field produced by the drift field guard rings. When the burst reaches the end of the drift tube, a sample of the ions present are swept out through the exit aperture located on the axis. The core of the emerging jet of ions and gas molecules is cut out by the conical skimmer and allowed to pass into the rf quadrupole mass spectrometer. Ions of only a selected charge-to-mass ratio traverse the length of the spectrometer, and are then detected individually by the electron multiplier. This detector is operated as a pulse counter, and its output pulses are sorted electronically as to their arrival time by a 256 channel time-of-flight analyzer. A spectrum of arrival times is built up by superimposing the data from about 10^5 ion bursts for a given source position, and then the procedure is repeated for various other positions of the source. Following this, the mass spectrometer is tuned successively to other ionic masses, and arrival time spectra are acquired for each other type of ion present in the drift tube.

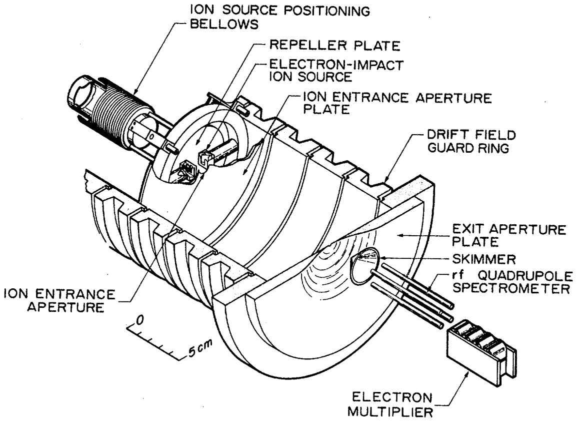

FIG. 1. Basic components of the drift-tube mass spectrometer.

As already mentioned, a number of modifications have been incorporated in the original apparatus for the present research. A double-grid electric shutter[7] was mounted in the 1.9-cm hole in the ion entrance aperture plate. This shutter allowed more precise definition of both the initial spatial extent and the time of entry into the drift tube of the ion swarm. Provision was made to permit the opening of the shutter at a variable time after the creation of the ions in the source. A small focusing electric field was applied to guide the ions exiting the drift tube through the skimmer. The magnitude of this field was restricted to values such that no resulting dissociation of N_2^+, N_3^+, or N_4^+ could be observed. Improved baking and the use of gold gaskets has reduced the equilibrium background pressure in the drift tube to 2×10^{-8} Torr, when the main pumpout line is closed so that the drift tube is being pumped through only the 0.08-cm-diam exit aperture.

The nitrogen gas used for this work was supplied with an impurity level of less than 10 parts per million. Use of this gas combined with the low equilibrium pressure of the drift tube allowed operation with no detectable impurity ions.

III. ANALYSIS

The analysis used to reduce the data has been described in the article immediately preceding this one,[1] and is discussed in detail in Ref. 7. For the case of an ion species formed only in the ion source, this analysis leads to an expression describing the flux Φ of ions leaving the drift tube through the exit aperture as a function of the drift distance z and the time t:

$$\begin{aligned}\Phi(0,z,t) = {} & [As\, e^{-\alpha t}/4(\pi D_L t)^{\frac{1}{2}}] \\ & \times (v_d + z/t)(1 - e^{-r_0^2/4D_T t}) \\ & \times \exp[-(z - v_d t)^2/4D_L t] \,. \qquad (3)\end{aligned}$$

In Eq. (3), D_L and D_T are, respectively, the longitudinal and transverse diffusion coefficients, α is the frequency for a reaction which results only in the depletion of the ion species under consideration, r_0 is the initial radius of the entering disk-shaped ion pulse, s is its initial surface density, and A is the area of the exit aperture.

Comparison of the experimental arrival-time spectra with this analytical expression allows evaluation of the drift velocity, the diffusion coefficients and ion-molecule reaction rates. Figure 2 shows a comparison of Eq. (3) (the solid curve) with experimental data (the histogram), for N^+

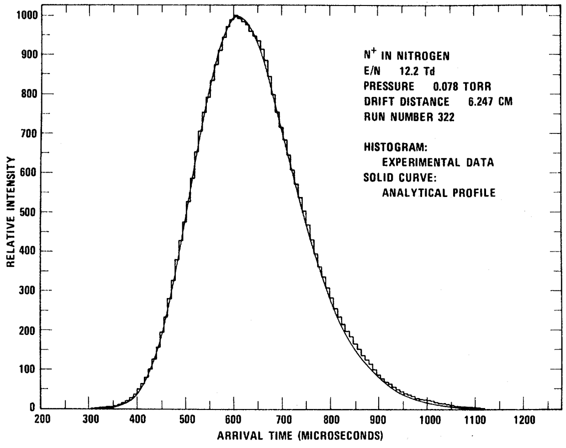

FIG. 2. Comparison of an experimental histogram with the corresponding analytical profile for N^+ in N_2.

ions in N_2, at low E/N and at a pressure sufficiently low that reactions occurred at a negligible rate. In making this plot of Eq. (3), the value of v_d was obtained from the experimental value of $\bar{t}$ for the histogram. Then, since the data presented were obtained at low E/N where the Einstein relation

$$D_L = D_T = K(\kappa T/e) \qquad (4)$$

is expected to be valid, the values of D_L and D_T were obtained from v_d through this relation. Finally, the analytical expression was normalized to agree with the data points at the peak, since the absolute source density s and other multiplicative efficiency factors were not known.

It is evident from Fig. 2 that Eq. (3), with the parameters determined in this manner, quite accurately reproduces all of the features of the experimental histogram. The location of the peak is determined by the value of v_d. The width and shape of the spectrum are determined by the longitudinal diffusion coefficient, D_L. The decrease in the relative total number of ions composing the spectrum as the drift distance is increased is governed, in the absence of a depleting reaction, by the transverse diffusion coefficient D_T. [It is demonstrated in the preceding paper[1] that a set of such experimental spectra obtained for different values of the drift distance, but under otherwise identical conditions, can all be fitted by Eq. (3) with only one arbitrary normalization to some one spectrum of the set.]

When a depleting reaction is occurring, as is the one for N^+ in N_2 at higher pressures, the reaction will also affect the relative intensity of the spectrum as the drift distance is varied. Further, at high E/N Eq. (4) is not expected to be valid, so that D_L and D_T become unknowns to be evaluated from the data. The application of the analysis to the determination of D_L and D_T at high E/N will be discussed in Sec. V. The measurement of α will be discussed in Sec. VI.

As already mentioned, the analysis described here strictly applies only to the case of an ion species that is formed only in the ion source, before the ion burst is admitted into the drift space. Of the four ion species observed in nitrogen, only N^+ and $N_2{}^+$ are true primary ions formed directly by electron bombardment; $N_3{}^+$ and $N_4{}^+$ are secondary ions which will be created continuously during the drift by Reactions (1) and (2), as long as there are any appreciable numbers of the parent species N^+ and $N_2{}^+$ present. ($N_3{}^+$ and/or $N_4{}^+$ may also be formed in or near the ion source by other processes such as chemi-ionization, but this fact is not of direct interest at the moment.) An additional complication arises from the fact that Reaction (2) can also occur in the reverse direction[6]; very clearcut evidence is seen in the present work, under some conditions, of the formation of $N_2{}^+$ in the drift space from the dissociation of $N_4{}^+$. The relative importance of each of the many processes in determining the features of the arrival-time spectra is, however, an often sensitive function of such factors as E/N, the gas pressure, the drift distance z, and the length of time the ion burst is "aged" in the source before it is gated into the drift space. Because of the wide variation in all of these factors that is available with the present apparatus, it has proved possible to apply at least some parts of this simple analysis, although sometimes over only a restricted range of E/N, to all four of the ions seen in nitrogen. The particulars for each case are discussed in the context of the following sections; we wish however to emphasize here the general statement that all of the results given in this paper are of the nature of the nearly independent, one-at-a-time determinations described above and in the preceding paper,[1] with rather well-defined bounds of possible error. This approach contrasts with that of McKnight *et al.*[6] whose data required a more complex analysis involving the simultaneous fitting of several parameters.

IV. MOBILITIES

The reduced mobilities obtained for N^+ and $N_3{}^+$ in N_2 are shown in Fig. 3; those for $N_2{}^+$ and $N_4{}^+$ in Fig. 4. These mobilities were determined from the mean arrival time of the ions by the method discussed in the preceding paper[1] and in Ref. 7.

The primary ions N^+ and $N_2{}^+$ are subject to the depleting reactions given by Eqs. (1) and (2). As discussed in Ref. 7, such a reaction preferentially depletes the late side of the arrival time distribution, reducing the mean drift time $\bar{t}$, so that a correction becomes necessary in the determination of v_d. This correction was kept negligible for these ions by restricting the measure-

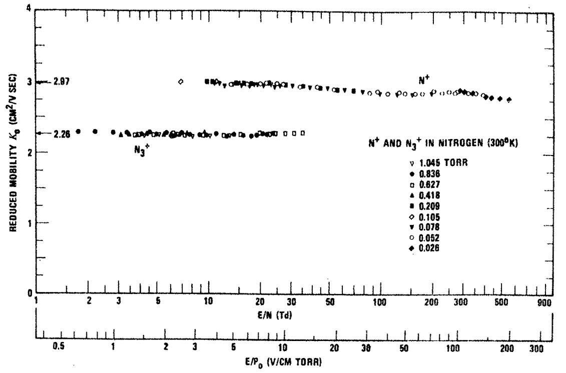

FIG. 3. Mobility results for N^+ and N_3^+ ions in nitrogen.

ments to sufficiently low pressures (below about 0.2 Torr for N^+ and 0.1 Torr for N_2^+) that the reaction frequencies were small. Verification that the reaction error was negligible was provided by comparing a plot of Eq. (3), using the value of v_d obtained from the mean drift time, with the experimental spectrum. Figure 2 shows such a comparison for the case of N^+. It is this pressure restriction that sets the lower bound of about 6 Td on the E/N range of the K_0 measurements for these two ions; it is evident from the figures that this range extends low enough that K_0 has become constant and equal to the zero-field reduced mobility.

For the case of N_2^+, a combination of the low pressures and an additional restriction of the measurements to short drift distances limits the total production of N_4^+ in the swarm, by reaction (2), and hence limits the formation of N_2^+ ions in the drift space by N_4^+ dissociation. For E/N above 40 Td a small amount of such secondary N_2^+ ions are seen in the arrival time spectrum, but they are relatively distinct from the primary N_2^+ ions, and an approximate correction for them can be made. A more detailed discussion can be found in Ref. 7.

N_3^+ and N_4^+ ions are formed from the primary N^+ and N_2^+ ions by the three-body reactions described by Eqs. (1) and (2). Each of these reactions is reversible, the forward reactions being favored by high pressures and low E/N and the reverse reactions favored by high E/N. By making measurements on the N_3^+ and N_4^+ ions with long drift distances and high pressures, it is possible to drive the reactions essentially to completion in the forward direction either in the ion source or at least before the ions have drifted a significant distance from the ion source, and by restricting the measurements to fairly low E/N, breakup of the N_3^+ and N_4^+ ions into N^+ and N_2^+ by the reverse reactions is prevented. Thus it was possible to obtain true drift velocities for both N_3^+ and N_4^+ over a restricted range of E/N, even though both of these ions are secondary ions formed by reactions.

The zero field, reduced mobilities obtained in these measurements are 2.97 cm^2/V sec for N^+, 1.87 for N_2^+, 2.26 for N_3^+, and 2.33 for N_4^+. These results are believed to be correct to within ±4%. A detailed error analysis is presented in Ref. 7.

Comparison of the data of the present experiment with the results of previous mass-analyzed experiments in nitrogen are presented in Figs. 5 and 6. It can be seen that the present work is in excellent agreement with the results of McKnight *et al.*[6] The agreement with the results of Martin *et al.*,[10] which were also obtained in this laboratory but on an entirely different apparatus, is fair. However, it is recognized that the Martin data were subject to significantly larger possible errors than are the present results. The disagreement between the present results and those of Saporoschenko[11] is more substantial. The N_3^+ results of Saporoschenko were not obtained over an E/N range that overlaps that of the present work. However, it appears unlikely that his data, if extended to lower E/N, would join smooth-

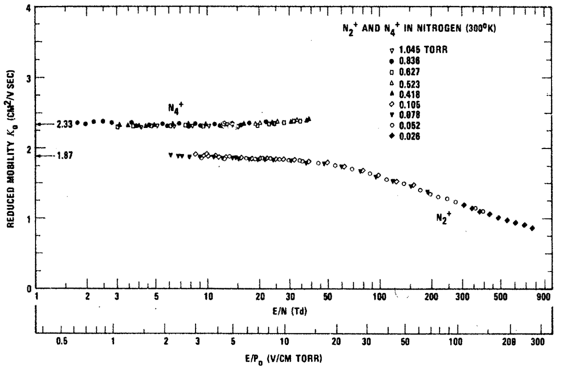

FIG. 4. Mobility results for N_2^+ and N_4^+ ions in nitrogen.

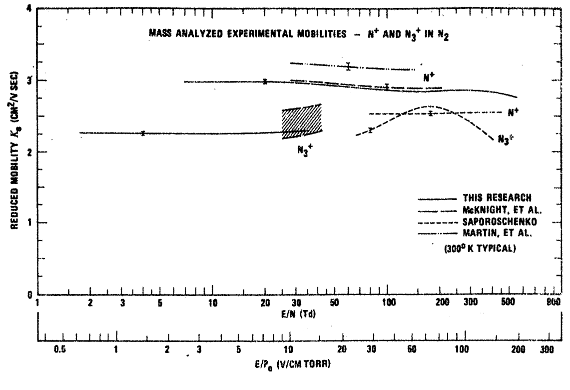

FIG. 5. Comparison of N^+ and N_3^+ mobility data with the results of other mass-analyzed experiments.

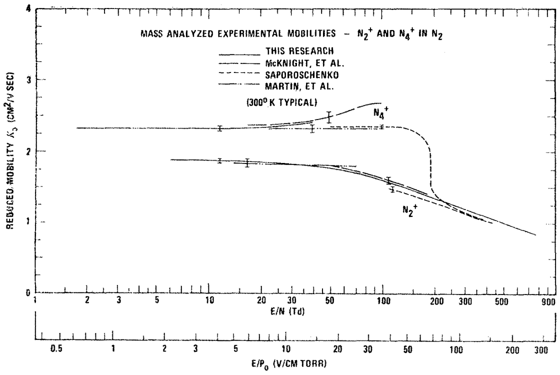

FIG. 6. Comparison of $N_2{}^+$ and $N_4{}^+$ mobility data with the results of other mass-analyzed experiments.

ly with those of the present work. If his N^+ data were raised to agree with the present data, and his $N_3{}^+$ data raised by the same amount, it seems more likely that the two experiments would produce similar results in the intermediate region between the existing sets of data. It is indicated that the N^+ and $N_3{}^+$ data of Saporoschenko do apparently confirm the existence of a hump in the $N_3{}^+$ mobility curve similar to those[12] for $H_3{}^+$ in H_2 and $D_3{}^+$ in D_2. It is also consistent with an observation by McKnight *et al.* that on the E/N range from 140 to 170 Td the mobility of $N_3{}^+$ was at least as great as that of N^+. It also appears possible that the $N_4{}^+$ results of Saporoschenko, particularly at high E/N, are strongly influenced by the reaction (2). The results of Keller *et al.*[5] are not included in the present comparison since it has now been concluded[7] that the Keller data must suffer from a systematic error of approximately 20%.

The values of the zero-field reduced mobility obtained here are compared with the Langevin polarization limit prediction[3] in Table I. The K^+ values[1] are included for comparison. Note that $N_2{}^+$ exhibits the greatest discrepancy, with an experimental mobility much smaller than the Langevin prediction. This can be attributed to the existence of resonant charge transfer between $N_2{}^+$ and the N_2 molecules. Dalgarno[13] has estimated that the value 1.5 cm²/V sec is reasonable for the mobility of $N_2{}^+$ in N_2 if resonant charge transfer is the main interaction.

TABLE I. Experimental and Langevin polarization limit mobilities for nitrogen and potassium ions in nitrogen.

	N^+	$N_2{}^+$	$N_3{}^+$	$N_4{}^+$	K^+
Experimental value	2.97	1.87	2.26	2.33	2.55
Langevin polarization limit value	3.42	2.80	2.55	2.42	2.60

V. DIFFUSION COEFFICIENTS

It is shown in Ref. 7 that even though only estimates of the transverse diffusion coefficient and the reaction rate might be available, the longitudinal diffusion coefficient D_L can be determined with good accuracy from the shape of the experimental arrival-time spectra. The technique is to adjust D_L in the analytical expression for the flux, Eq. (3), until the analytical profile and the experimental data best correspond when normalized to agree at their points of maximum intensity. The longitudinal diffusion coefficient results have been published elsewhere,[2,7] and appear on Fig. 4 of the preceding article,[1] and so will not be repeated here.

The total intensity of a given species of primary ion which reaches the detector of the apparatus will depend on the position of the ion source. As the drift distance is increased, the increased effect of transverse diffusion will cause a smaller fraction of the ions to reach the exit aperture. Furthermore, any depleting reactions with the gas molecules will produce an attenuation of the primary ion population as it drifts through the gas. The method used to determine the transverse diffusion coefficient, D_T, consists of comparing the total number of ions composing the experimental spectra at various drift distances $I'(z_j)$ with the integrated intensity on the axis

$$I(z)=\int_0^\infty \Phi(0,z,t)\,dt \tag{5}$$

calculated for corresponding E/N and pressure conditions. As has been mentioned previously above $I(z)$ must be normalized to agree with $I'(z_j)$ for one value of z_j, normally for the shortest drift distance used ($z_j=6.25$ cm). It is shown in Ref. 7 that only a reasonable estimate of D_L is actually needed in Eq. (5) in order to determine D_T, but for the present cases accurate values of D_L were available from previous work.[2] The drift velocities are also known independently. Hence $I(z)$ can be calculated and D_T varied until a best fit with $I'(z_j)$ is obtained, if the reaction frequency α is known or is small. Such an analysis depends on the ion species under consideration being produced entirely in the ion source, as is the case with the N^+ and $N_2{}^+$ ions.

At low E/N, D_T can be calculated with confidence from the Einstein relation, Eq. (4). Hence at low E/N, the comparison of $I(z)$ with $I'(z_j)$, with D_T given by the Einstein relation, can be used to determine the reaction frequency α. This value of $\alpha=\alpha_t$ can then be used in $I(z)$ to determine D_T at higher E/N. Of course, α is not necessarily expected to equal α_t at higher E/N, but it is expected to vary fairly slowly. In addition, since D_T depends on $1/N$ while α depends on N^2, data taken at low pressures (less than 0.1 Torr) will emphasize the effects of diffusion and minimize the effects of the reaction. All of the transverse diffusion-coefficient data were taken at pressures less than 0.08 Torr.

The following procedure was used. The reaction frequency α was assumed to equal its thermal value α_t. Values of D_T were determined by comparing experimental $I'(z_j)$ data with a series of curves representing $I(z)$ calculated for various D_T. These values of D_T were used to determine values of α at higher E/N (see Sec. VI). Then these higher E/N values of α were used to recalculate the $I(z)$ curves, and a second comparison with the $I'(z_j)$ data was made. However, the use of more accurate values for α caused only a negligible change in the various $I(z)$ curves at the low pressures used to determine D_T, and no change in D_T from the values determined by assuming $\alpha = \alpha_t$ was required.

The results obtained for N^+ and N_2^+ ions in nitrogen are shown in Fig. 7. The above restriction to low pressures determined the lower bound of the E/N region of the D_T measurements. Although in retrospect it appeared that a further iteration of the procedure above might have permitted some downward extension of the range, it is clear that in both cases, the data approach the ND_T values predicted by the Einstein relation at low E/N. No other data are available for comparison with the results presented here.

No similar analysis to evaluate the diffusion coefficients of the secondary ions N_3^+ and N_4^+ has been attempted.

VI. REACTION-RATE COEFFICIENTS

Rate coefficients were determined for the Reactions (1) and (2), which lead to the production of N_3^+ from N^+ and N_4^+ from N_2^+, respectively. The intermediate pressure range, 0.1 to 0.4 Torr was chosen for operation. At lower pressures the reaction frequencies are small and the effect of the reactions is masked by transverse diffusion. At higher pressures, the reactions go essentially to completion before the required observations can be made.

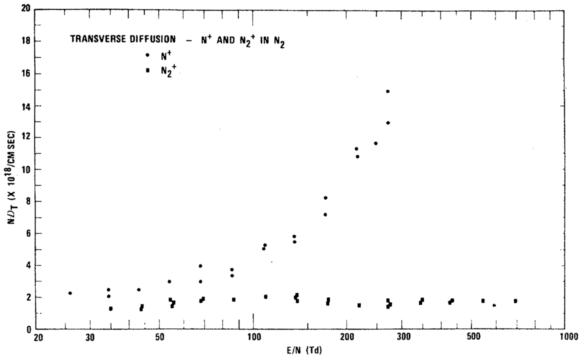

FIG. 7. Transverse diffusion coefficients for N^+ and N_2^+ ions in nitrogen.

The basic method used is the same as that used for the determination of D_T (see Sec. V). A comparison is made between the total number of N^+ or N_2^+ ions composing the experimental spectra at various drift distances, $I'(z_j)$, and the integrated intensity on the axis, $I(z)$. If this comparison is to yield values of the reaction frequency α, then the transverse diffusion coefficient must be known. D_L is known from the results of Ref. 2, and v_d is known from Sec. IV.

The requirement that D_T be known divides the determination of α into three E/N regions. In the low E/N region (below 30 Td), D_T can be calculated from the Einstein relation and can thus be considered to be known to within the accuracy that the zero-field mobility is known. In the intermediate E/N region (20 to 100 Td), D_T can be considered known on the basis of the determination discussed in Sec. V, but is not known as accurately as in the low E/N region. In the high E/N region (above 100 Td), the reaction rate was not determined because to obtain data in this region, it would have been necessary to operate at such low pressures that the effects of the reaction would have been over shadowed by diffusion.

We may note from Eq. (3) that in the limit of small D_L and D_T (i.e., high gas pressures) and/or large α, the reaction will entirely dominate the spectra intensities and $I(z)$ may be written

$$I(z) \approx I_0 e^{-\alpha z/v_d}. \tag{6}$$

Under these conditions, there is an approximately exponential decrease in the total number of detected primary ions as the drift distance z is increased. This fact is used to obtain a first approximation to α before a detailed comparison between $I(z)$ and $I'(z_j)$ is made.

The reaction frequencies were first determined in the low E/N region, and the resulting values of α_t were used in the measurement of the D_T values reported in Sec. V. Then these values of D_T were used in the determination of α in the intermediate E/N region.

The order of both reactions was ascertained by measuring α at various gas pressures. For a three-body reaction, α is related to the reaction-rate coefficient k and the gas number density N by the equation $\alpha = kN^2$, and in each case, the data could be fitted by an equation of this form. Hence we are justified in saying that N_3^+ and N_4^+ are formed in the reactions $N^+ + 2N_2 \rightarrow N_3^+ + N_2$ and $N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$. Figure 8 shows two examples of comparisons of $I'(z_j)$ and $I(z)$ for N^+ in N_2 at the same low E/N (17 Td), but at two different pressures. The uppermost curve in each case is calculated for $k=0$, i.e., for diffusion only. The lower curves are calculated under the assumption that $\alpha = kN^2$, for selected values of k near the expected rate. From the points which represent $I'(z_j)$ it can be seen that for both pressures the rate constant is near 1.8×10^{-29} cm^6/sec. Clearly the most accurate evaluation of k can be made at the higher pressure, where the contribution to the attenuation of the reaction, relative to diffusion, is greatly enhanced. However, demonstration of the constancy of k over a suitable pressure range (in every case at least the factor of 2 illustrated here) is necessary to verify the assumed three-body nature of the reaction. Figure 9 shows similar data for N_2^+ but at an intermediate E/N (87 Td). Again the order of the reaction is verified.

At thermal energies the rate coefficient for the reaction (1) is determined to be $(1.8\pm0.2)\times10^{-29}$ cm^6/sec. For the Reaction (2) the thermal rate is $[5.0(+0.9, -0.6)]\times10^{-29}$ cm^6/sec. Values of k for the complete range of E/N covered are presented in Fig. 10.

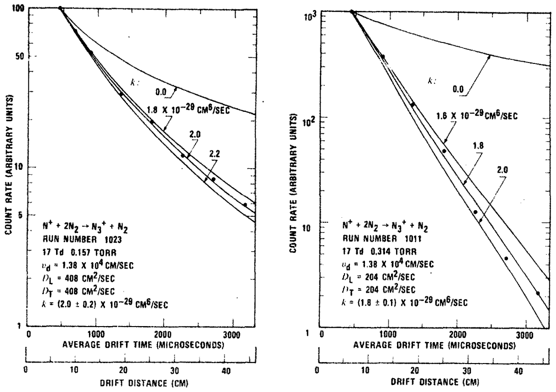

FIG. 8. Typical comparisons of data with the analytical expression [Eq. (5)] to determine the rate of the reaction $N^+ + 2N_2 \rightarrow N_3^+ + N_2$ at low E/N.

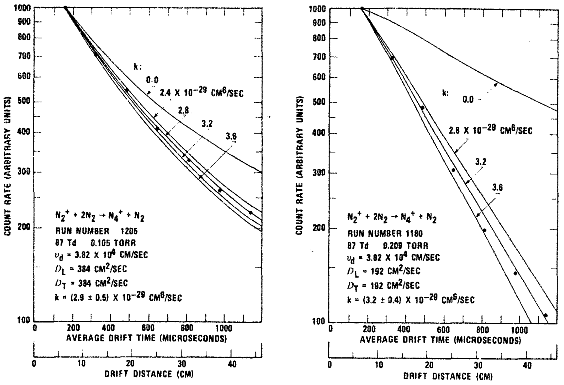

FIG. 9. Typical comparisons of data with the analytical expression [Eq. (5)] to determine the rate of the reaction $N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$ at an intermediate E/N.

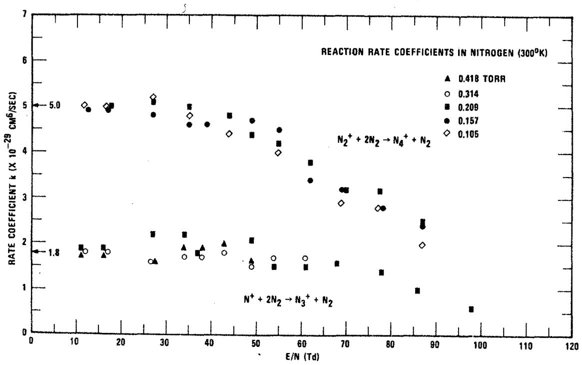

FIG. 10. Reaction-rate coefficients for the depletion of N^+ and N_2^+ in nitrogen over the E/N range from 12 to 100 Td.

Table II compares the thermal reaction rate obtained for the depletion of N_2^+ by this research with the results of other workers. The agreement is reasonably good for measurements of this type, although most of the reported results lie somewhat above the present value. However, the possible error in most of these results is quoted to be quite high, and hence the apparent "agreement" of four of the experiments on a value for k of about 8×10^{-29} cm^6/sec may be simply fortuitous. The error bounds quoted for the value of k reported in this research are believed to be realistic,[7] and this measurement is believed to be the most accurate of those performed on this reaction rate to date.

Information on the E/N behavior of this reaction rate was given by Woo[14] and McKnight *et al.*[6] Both reported a decrease in k as E/N was increased, and the rate of this decrease is in general agreement with the decrease reported here.

Note added in proof: R. N. Varney [Phys. Rev. 174, 165 (1968)] reports measurements of the rate constants of both Reaction (2) and the reverse dissociation reaction (Varney's k_{-2} and k_{+1}, respectively), at the four E/N values 113, 142, 170, and 198 Td ($E/p_0 = 40$, 50, 60, and 70 V/cm Torr; the conversion factor between these units is 1 Td = 2.83 V/cm Torr). His values for k_{-2} lie on a straight line on a semilogarithmic plot ($\log k_{-2}$ versus E/p_0). See Fig. 8 of Varney's paper. The straight-line extrapolation of Varney's data to lower E/p_0 is in excellent agreement with the present results for Reaction (2) for $E/N > 50$ Td (for E/p_0 from 17 to 30 V/cm Torr). In his Fig. 8, Varney shows a "Probable Thermal Cutoff," his estimate of how k_{-2} would break off from the straight line and tend toward a constant value, as E/p_0 is decreased below 20 V/cm Torr. This es-

TABLE II. Comparison of existing results for the N_2^+ depletion reaction [Eq. (2)] at lowest E/N values reported.

Investigator	k (10^{-29} cm^6/sec)	E/N (Td)	Type of experiment
This research	5.0 (+0.9, −0.6)	12 to 27	Drift tube
Fite *et al.*[a]	3[b]	Undetermined, but probably low	Afterglow
Woo (Ref. 14)	9[b]	56	Drift tube
Warneck[c]	8.5[b]	Undetermined, but probably low	Mass spectrometer
Knewstubb[d]	8.0 ± 0.4[e]	No electric field	Flowing gas
McKnight *et al.* (Ref. 6)	7 (± a factor of 2)	50	Drift tube

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

[b] No error estimates stated.

[c] P. Warneck, J. Chem. Phys. 46, 1251 (1965).

[d] P. F. Knewstubb, in "Proceedings of the International Conference on Mass Spectrometry," Berlin, 1967 (unpublished).

[e] Possible systematic error of up to 30% not included.

timate is in fact in excellent agreement with the present results in the region $E/N < 50$ Td.

The only available result for comparison with the rate for the depletion of N^+ [Eq. (1)] is that of McKnight *et al.*[6] They reported a rate of 3×10^{-29} cm^6/sec at an E/N of 50 Td for an assumed three-body reaction. The data were taken at only one pressure, and hence the pressure dependence was not determined. When the possible error of a factor of 2 or 4 in this rate is considered, it must be assumed to be in agreement with the value of about 1.6×10^{-29} cm^6/sec reported here (see Fig. 10).

No evaluation of the rates of the reverse reactions to Eqs. (1) and (2) appears to be possible with the present restricted analysis. As mentioned above, the reverse reaction to Eq. (2) is very definitely seen to occur. The observed behavior would be consistent with a rate that increases very rapidly with increasing E/N, as reported by McKnight *et al.*[6], and in agreement with recent findings of Varney.[15] No definite evidence for the reverse reaction to Eq. (1) has been found in the present study.

VII. CONCLUSIONS

The zero-field reduced mobilities of N^+, N_2^+, N_3^+, and N_4^+ in N_2 were found to be 2.97 ± 0.12, 1.87 ± 0.08, 2.26 ± 0.08, and 2.33 ± 0.08 cm^2/V sec, respectively. The longitudinal and transverse diffusion coefficients for N^+ and N_2^+ in N_2 were obtained on the E/N range from thermal to several hundred townsends. At low E/N, all coefficients were in agreement with the prediction of the Einstein relation. As E/N was increased, D_T for N^+ increased quite rapidly (although not as rapidly as does D_L for the same ion), while the D_T of N_2^+ increased only slightly; for both ions it can be stated that, for all values of E/N investigated, $D_T \leq D_L$. The three-body reaction-rate coefficients for the reactions $N^+ + 2N_2 \rightarrow N_3^+ + N_2$ and $N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$ were determined to be $(1.8 \pm 0.2) \times 10^{-29}$ cm^6/sec and $[5.0(+0.9, -0.6)] \times 10^{-29}$ cm^6/sec, respectively, at thermal energies. Both rates decreased as E/N was increased.

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Electron-Transfer Cross Sections of 5 to 70-keV Hydrogen Atoms and Ions in Magnesium Vapor*

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Experimental electron-capture and loss cross sections of 5- to 70-keV hydrogen atoms and ions in magnesium vapor are reported for the processes

$$H^+ \rightarrow H^0,\ H^0 \rightarrow H^+,\ H^0 \rightarrow H^-, \text{ and } H^- \rightarrow H^0.$$

The cross sections for these processes are compared with measurements by other groups. Results for the $H^+ \rightarrow H^0$ capture process in magnesium are compared with the semiclassical formulation by Bates and Mapleton and with Born-approximation [Brinkman-Kramers (BK)] calculations by Hiskes adjusted according to prescriptions by Mapleton and Nikolaev. The adjusted BK capture cross sections are in satisfactory agreement with the measurements.

I. INTRODUCTION

At proton energies between about 5 and 30 keV, cross sections for electron capture from metal vapors are much larger than from common gases. This is true of total capture cross sections and for capture into highly excited levels. Capture from magnesium vapor into the level with principal quantum number $n = 6$ is the subject of a separate paper.[1] Here we report measurements of total cross sections for electron capture and loss by 5 to 70-keV hydrogen atoms and ions in Mg for the following processes:

$$\sigma_{10}:\ H^+ + Mg \rightarrow H^0 + \cdots, \tag{1}$$

$$\sigma_{01}:\ H^0 + Mg \rightarrow H^+ + \cdots, \tag{2}$$

$$\sigma_{0\bar{1}}:\ H^0 + Mg \rightarrow H^- + \cdots, \tag{3}$$

$$\sigma_{\bar{1}0}:\ H^- + Mg \rightarrow H^0 + \cdots. \tag{4}$$

At present exact cross-section calculations for electron capture from heavy atoms are essentially impossible in the energy range considered here. As a result, there is considerable interest in classical approximations[2] and in semiempirical methods of adjusting results of the relatively easily evaluated Brinkman-Kramers (BK) approximation.[3,4] Both approaches have given good results for the common gases; we shall see that the adjusted BK results give reasonably good agreement with magnesium experiments.

II. APPARATUS AND PROCEDURE

The experimental arrangement is shown schematically in Fig. 1. A collimated, momentum-analyzed beam of hydrogen atoms or ions, chopped

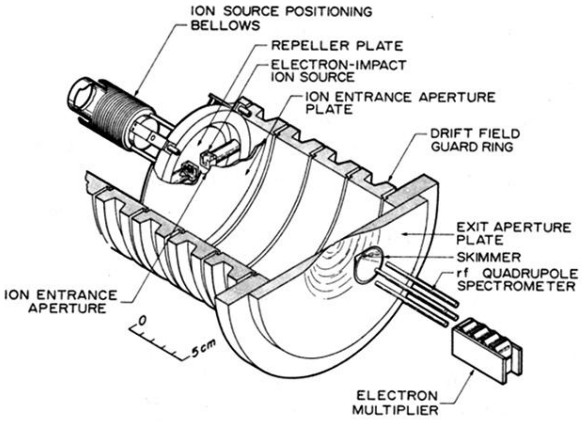

FIG. 1. Basic components of the drift-tube mass spectrometer.