Reactions of H^+ in H_2 and D^+ in D_2; Mobilities of Hydrogen and Alkali Ions in H_2 and D_2 Gases*†

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Measurements of transport parameters of low-energy mass-identified ions in H_2 and D_2 gases have been made in a drift-tube mass spectrometer at room temperatures. In addition, the variable drift distance of this apparatus has been used to vary the residence time of the ions in the gases to determine ion-molecule reaction rates. The zero-field reduced mobilities of H^+ and H_3^+ in H_2 were found to be 15.7± 0.6 and 11.1± 0.5 cm^2/V sec, respectively. Those for D^+ and D_3^+ in D_2 were found to be 11.2± 0.5 and 8.0± 0.3 cm^2/V sec, respectively. The zero-field reduced mobilities for Li^+, Na^+, and K^+ ions in H_2 were measured to be 12.3± 0.6, 12.2± 0.6, and 12.8± 0.6 cm^2/V sec. The zero-field reduced mobilities for these same alkali ions in D_2 were measured to be 9.6± 0.5, 8.9± 0.4, and 9.4± 0.5 cm^2/V sec, respectively. The mobilities of H^+, H_3^+, Li^+, Na^+, and K^+ in H_2 were found to be related to the mobilities of D^+, D_3^+, Li^+, Na^+, and K^+ in D_2, respectively, by the appropriate ratios of the square roots of the reduced masses in each case, as predicted by Langevin's theory. However, the mobilities within either set of ions in a given gas did not follow the $M_r^{-1/2}$ reduced mass dependence. The three-body reaction rate coefficients for the reactions $H^+ + 2H_2 \rightarrow H_3^+ + H_2$ and $D^+ + 2D_2 \rightarrow D_3^+ + D_2$ were found to be (3.2± 0.3) and (3.0± 0.4) × 10^{-29} cm^6/sec, respectively, and were observed to be independent of E/N in the thermal range ($E/N < 28 \times 10^{-17}$ V cm^2) and independent of the gas pressure from 0.1 to 0.6 Torr. A classical calculation shows that the assumption of Langevin-type spiraling collisions between the ions and gas molecules does not yield collision times long enough to account for the large three-body rate coefficients measured. Finally, a few measurements of the radial diffusion coefficient for H_3^+ ions in H_2 have been made, and they agree with those reported by Dutton *et al.*, within the scatter in the data, but not with those reported by Skullerud.

I. INTRODUCTION

In this article, the results of a study of the transport and reaction properties of low-energy ions in hydrogen and deuterium gases will be presented. A drift-tube mass-spectrometer apparatus was used to obtain the data. Recently, some results of this experiment were given by Albritton *et al.*,[1] namely, the mobilities of H^+ and H_3^+ ions in hydrogen gas. These measurements have been extended to include the mobilities of D^+ and D_3^+ ions in deuterium gas, the mobilities of the alkali ions Li^+, Na^+, and K^+ in H_2 and D_2 gases, and the reaction rate coefficients for the three-body ion-molecule reactions

$$H^+ + H_2 + H_2 \rightarrow H_3^+ + H_2, \tag{1}$$

$$\text{and } D^+ + D_2 + D_2 \rightarrow D_3^+ + D_2. \tag{2}$$

In addition, a few data have been gathered for the radial, or lateral, diffusion coefficient of H_3^+ ions in H_2 gas in order to attempt to resolve a large discrepancy between the published results of two other laboratories.

The three-body ion-molecule processes (1) and (2), together with the corresponding reaction in helium gas which has been studied by Beaty and Patterson,[2] are the simplest three-body ion-molecule reactions, which makes the measurements of substantial theoretical interest.

A brief historical sketch of hydrogen-ion swarm research has been given in Ref. 1.

The usual definitions will be employed in this article. The *mobility K* is defined as the ratio of the drift velocity v_d to the electric field strength E. The mobility is inversely proportional to the gas number density N. In order to facilitate comparisons of sets of data obtained at different gas number densities, the *reduced mobility* K_0 is defined by $K_0 = K(p/760)(273.16/T)$, where p and T are the gas pressure and temperature at which the measurement was made and the normalization is to a gas pressure of 760 Torr at 273.16°K. The data are presented as a function of E/N, a parameter which is related to the average energy acquired by the ions from the electric field.

II. APPARATUS

These measurements were made in a drift-tube mass-spectrometer apparatus of ultrahigh vacuum construction. The basic components are illustrated in Fig. 1. A movable electron-impact ion source is pulsed to produce bursts of hydrogen or deuterium ions of accurately known initial spatial extent and temporal duration. A thermionic emitter supplies the alkali ions. The ion swarm drifts through the gas in the drift tube under the influence of a uniform axial electric field. The drift distance is variable from 1 to 44 cm. A sample of the ion population passes out an exit aperture at the end of the drift tube and into a differentially pumped region where the ions

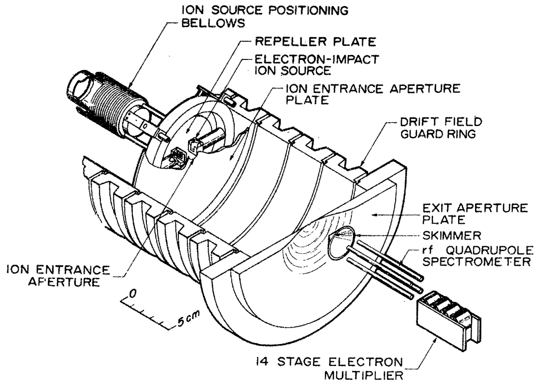


FIG. 1. Basic components of the drift-tube mass-spectrometer apparatus.

are mass-analyzed and individually detected. The times of arrival of the detected ions are measured and recorded by a 256-channel time analyzer.

The apparatus used in the present work was the same as that described in greater detail in Ref. 1, except for a few changes which will be listed here: (a) An ion source was used which was similar to that of Ref. 1, but which had a larger entrance aperture to the drift region (1.9 cm) and a thermionic alkali-ion emitter mounted behind the ion source. (b) A small focusing electric field was applied to guide the ions through the skimmer; no resulting dissociation of H_3^+ or D_3^+ was observed. (c) A larger rf quadrupole-mass spectrometer is presently used. (d) Improved baking of the internal components of the apparatus has lowered the equilibrium background pressure of the drift tube by a factor of 5, to less than 10^{-7} Torr, after the vacuum pumps are valved off.

Both D_2 and H_2 gases were admitted to the drift tube through a silver-palladium diffusion tube, and no impurity ions could be detected with the mass spectrometer. However, the deuterium-gas mass scans did show HD_2^+.

III. ANALYSIS

The apparatus was constructed to approximate an idealized mathematical model. If a cylindrical coordinate system is chosen with the electric field in the z direction, the equation

$$\partial n/\partial t = D_r[\partial^2 n/\partial r^2 + (\partial n/\partial r)/r] + D_L \partial^2 n/\partial z^2 - v_d(\partial n/\partial z) - \alpha n + \beta(r,z,t) \quad (3)$$

describes the time rate of change of the number density $n(r,z,t)$ of a single ion species in an infinite volume. It is assumed that there is no variation with the azimuthal angle. The last term is a source term which will be specified below. The reaction frequency α determines the rate of conversion of the ion species under consideration into another ion type, with no reconversion. Equation (3) does not cover the case where there is a *gain* of ions due to ion-molecule reactions. Such a gain would introduce terms involving the time-varying number densities of other ion species, and that complication is not necessary for the particular cases reported here. The term involving the drift velocity v_d simply imposes a constant translational velocity in the z direction on the centroid of the ion swarm. The first two terms on the right side of Eq. (3) describe the radial and longitudinal diffusion of the swarm, respectively, where D_r and D_L are the radial and longitudinal diffusion coefficients. At low field strengths, D_r and D_L are identical and are given by the Einstein relation[3]

$$D/K = \mathcal{K}T/e \,, \quad (4)$$

where $\mathcal{K}$ is Boltzmann's constant. At high field strengths, $D_L > D_r$, since collisions with the gas molecules do not completely randomize the energy gained by the ions from the field.

The ion source used with the present apparatus initially creates an axially thin, uniform disk of ions at $t=0$ and at $z=0$, and its output may be approximated by

$$\beta(r,z,t) = s_0 H(r_0 - r)\,\delta(t)\,\delta(z)\,, \quad (5)$$

where s_0 is the initial ion surface density, r_0 is the radius of the ion-source aperture, and $H(x)$ is the Heaviside step function $H(x<0)=0$, $H(x>0)=1$. Since the ions detected in this apparatus are those which exit the drift tube through a central aperture, the desired expression is the solution to Eq. (3) evaluated[4] at $r=0$:

$$n(0,z,t) = s_0 e^{-\alpha t}(4\pi D_L t)^{-\frac{1}{2}}(1 - e^{-r_0^2/4D_r t}) \times e^{-(z - v_d t)^2/4D_L t}. \quad (6)$$

It may be shown[4,5] that for all of the cases considered here the presence of the end boundary (the drift-tube exit plate) has the effect of an imaginary plane, i.e., the particle current density J_z is given by

$$J_z = -D_L(\partial n/\partial z) + v_d n \quad (7)$$

at the boundary. The measured flux of ions is the number per unit time which pass through the exit aperture, $\Phi = aJ_z$, where a is the area of the aperture. With the use of Eq. (6), the final result is

$$\Phi(0,z,t) = a s_0 e^{-\alpha t}(16\pi D_L t)^{-\frac{1}{2}}(v_d + z/t) \times (1 - e^{-r_0^2/4D_r t})e^{-(z - v_d t)^2/4D_L t}. \quad (8)$$

Equation (8) has been demonstrated[1,4] to predict accurately the shapes of arrival-time spectra for an ion species which is affected by ion-molecule reactions only to the extent of a disappearance of ions of that type.

The analysis from which the above equations were abstracted indicates that the coefficients appearing in Eq. (3) may be determined as follows. Drift velocities (and hence mobilities) of ions are determined by calculating the average arrival times $\bar{t}_i$ of the experimental arrival-time spectra corresponding to several drift distances z_i, and a least-squares fit of the $\bar{t}_i$-versus-z_i data yields v_d. Both end effects and diffusion errors are thus eliminated to first order. The reaction frequency α is determined by a comparison of the measured attenuation of the ion count rate $I(z)$ as the drift distance z is increased, to the attenuation predicted by

$$I(z) = \int_0^\infty \Phi(0, z, t) dt \; . \tag{9}$$

The parameter α[Eq. (8)] is varied until $I(z)$ as given by Eq. (9) agrees with the corresponding experimental data. This procedure requires known values of v_d, D_r, and D_L. The v_d values used are those which have been predetermined experimentally for the given conditions, and the diffusion coefficients are obtained from v_d through Eq. (4), at low E/N. Eqs. (8) and (9) may be evaluated at high E/N (in order to determine high-E/N values of α) only if high-E/N values for D_r and D_L are first measured. Since, for a three-body reaction, α is proportional to N^2, it may be possible to measure D_r and D_L at low pressures, where α is negligible. Since D_rN and D_LN are constants for a given ion-gas combination, at a given value of E/N, the diffusion coefficients may then be calculated for any pressure, e.g., pressures where α is not negligible. However, this procedure has not yet been used, and no rate coefficients at high E/N are reported here. The reaction frequency α is usually converted to a pressure-independent reaction-rate coefficient k, by the use of the equation $k = \alpha/N^2$ if α is observed to vary quadratically with N, i.e., if the reaction is a pure three-body process.

The variable drift distance of this apparatus permits measurements of D_r and D_L to be made independently. The radial diffusion coefficient D_r is determined from the attenuation of the integrated ion count rate as z is increased; this rate is insensitive to D_L. The longitudinal diffusion coefficient D_L may be determined from a fit of Eq. (8) to an arrival-time spectrum, and this fit is insensitive to D_r. At present, this procedure is possible only for ion species which are only weakly affected by ion-molecule reactions, at least over some part of the accessible pressure range; otherwise, a multiparameter fitting procedure would have to be used. (The shapes of the arrival-time spectra at high E/N values have been studied only to get a rough idea of the values of D_L and no results will be reported here.) A few data for D_r for H_3^+ ions will be given below.

IV. MOBILITY RESULTS

Figure 2 shows the mobility results for H^+ and H_3^+ ions in H_2 gas, and D^+ and D_3^+ ions in D_2 gas, obtained with gas pressures in the range 0.95–0.035 Torr. Below the E/N scale, an E/p_0 scale is shown, since most past results have been presented as functions of E/p_0, where p_0 is usually defined by $p_0 = p(273.16/T)$. The results for E/N values greater than about 100×10^{-17} V cm^2 were obtained only with low gas pressures in the range 0.050–0.035 Torr, and are subject to greater error than are the lower E/N data. A striking feature of Fig. 2 is that changes in the mobilities of the monatomic ions with E/N are roughly mirrored by opposite changes in the mobilities of the triatomic ions. The mobilities were found to be independent of E/N below $E/N = 15 \times 10^{-17}$ Vcm^2, and yield the following zero-field reduced mobilities: 15.7 (H^+), 11.1 (H_3^+), 11.2 (D^+), and 8.0 cm^2/V sec (D_3^+). These mobility values for these ions are free from errors which can be introduced by ion-molecule reactions. In the case of the protons or deuterons, the reaction (1) or (2) does not affect the shapes of the arrival-time spectra significantly if the spectral width is much less than the total drift time, as is the case here. Also, there is seen to be very little, if any, creation of protons or deuterons through ion-molecule reactions in the drift region. In the case of H_3^+ or D_3^+, the relative abundance of these ions leaving the ion source is so great that the observed ion-molecule reactions contribute only a very small fraction of the total number of H_3^+ or D_3^+ ions detected. H_5^+ and D_5^+ are observed in small quantities at higher pressures (above approximately 0.4 Torr), but are so closely coupled to the H_3^+ and D_3^+ species, respectively, that no meaningful results for the H_5^+ and D_5^+ species have been obtained.

The present data for H^+ and H_3^+ are slightly different from those given earlier in Ref. 1 because of a small adjustment in the pressure calibration and the use of lower ion currents. Otherwise, the comparisons of the H^+ and H_3^+ results of this experiment to past research are the same as have been discussed in Ref. 1. It was not mentioned there, however, that Rees[6] observed a fast ion in hydrogen with a zero-field reduced mobility of 15.8 cm^2/V sec, which agrees well with the present result of 15.7 cm^2/V sec for H^+.

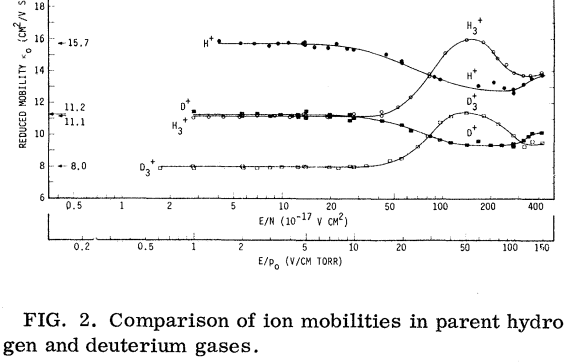


FIG. 2. Comparison of ion mobilities in parent hydrogen and deuterium gases.

A comparison of the present results for D^+ and D_3^+ in deuterium with past work is given in Fig. 3. Saporoschenko's[7] work utilized a mass spectrometer, while Rose's[8] did not. Values of the zero-field reduced mobility of (presumed) D_3^+ ions in deuterium have also been given by Boucique and Mortier[9] (7.9 cm²/Vsec), and Bennett and Thomas[10] (7.53 cm²/Vsec). Except for the very high-E/N range, the agreement in deuterium is considered quite good.

The mobility of K^+ ions in H_2 was measured for comparison with the high-accuracy measurements of Elford,[11] who obtained data over the pressure range 1–50 Torr in an apparatus employing electric shutters, but without positive mass analysis. Since the K^+ ions do not react with the gas molecules, there is little possible ambiguity in Elford's K^+ mobilities, and comparison with his mobilities serves as a check on systematic errors in our experiment. Clustering of alkali ions with gas molecules is presumably possible, but no such clusters were observed in the present work (300°K, below 1 Torr). The thermionic emitter which produced the K^+ ions also provided Li^+ and Na^+, and the mobilities of these three alkali ions were measured in both H_2 and D_2 gases. The results are given in Fig. 4. The zero-field reduced mobilities found for Li^+, Na^+, and K^+ in H_2 were 12.3, 12.2, and 12.8 cm²/Vsec, respectively, and may be compared with Tyndall's[12] values of 12.5, 12.8, and 12.7 cm²/Vsec, respectively. Elford[11] found a value of 12.75 ± 0.04 cm²/Vsec for K^+ in H_2. For Li^+, Na^+, and K^+ in D_2 the zero-field reduced mobility values 9.6, 8.9, and 9.4 cm²/Vsec were obtained in the present research.

V. REACTION RESULTS

The loss of protons to H_3^+ and deuterons to D_3^+ was evident from a detailed examination of the H_3^+ and D_3^+ arrival-time spectra, as illustrated in Fig. 5 for the deuterium case. In order to achieve good time separation of the two spectra in Fig. 5, a long drift distance was used (43.8 cm). For the purpose of obtaining a visual comparison of the spectra, the deuteron spectrum shown has been enhanced by roughly a factor of 25, relative to the D_3^+ spectrum, by increasing the ion source output. The points shown in Fig. 5 are the output of the multichannel time analyzer. Solid curves have been sketched through the points. The dashed curve represents an estimate of the total deuteron contribution to the D_3^+ arrival-time spectrum. There is no other channel for loss of the monatomic ions; over most of the pressure range studied, only the monatomic and triatomic ions are present. At higher pressures H_5^+ (or D_5^+) appears in small quantities but is obviously closely coupled to H_3^+ (or D_3^+).

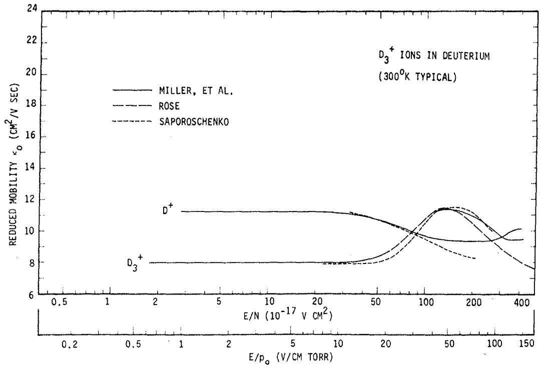


FIG. 3. Comparison of deuterium ion mobility results with past work. The solid curve (present work) is not drawn where it overlays Rose's data.

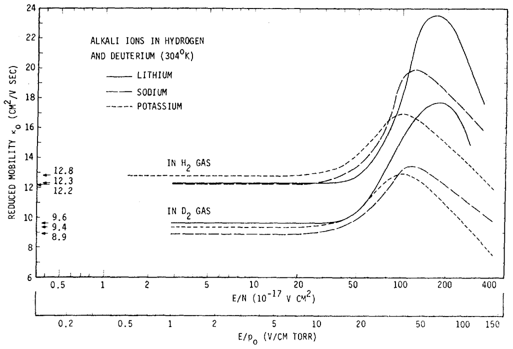


FIG. 4. Comparison of alkali-ion mobilities in hydrogen and deuterium.

Examples of the attenuation data obtained are given in Figs. 6(a) (low-pressure case) and 6(b) (high-pressure case). The smooth curves were calculated from Eq. (9) for various assumed values of the reaction rate k (where $k = \alpha/N^2$). The experimental data were normalized to the calculated curves at the shortest drift distance normally used, 6.25 cm. The curve for $k = 0.0 \times 10^{-29}$ cm⁶/sec represents the attenuation in the count rate with drift distance, which would be expected if diffusion were the only factor to consider. Calculated results for a *zero* reaction rate coefficient have been found to describe the attenuation of the count rate of the triatomic ions with increasing drift distance, since they are

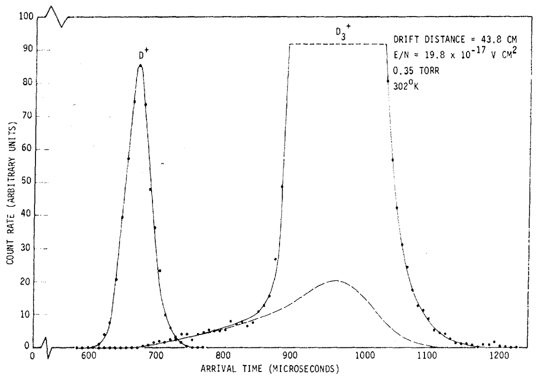
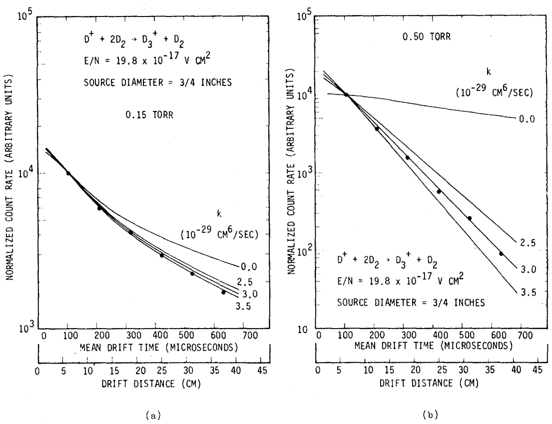


FIG. 5. Comparison of D^+ and D_3^+ arrival-time spectra. The dashed curve represents an estimate of the ion-molecule reaction contribution to the D_3^+ spectrum.



(a) (b)

FIG. 6. Typical normalized attenuation data for deuterons, showing the decrease in the ion count rate with increasing drift distance. (a) A low-pressure case. (b) A high-pressure case. The curve calculated for $k = 0.0 \times 10^{-29}$ cm^6/sec represents the attenuation which would be expected if radial diffusion were the only factor to consider. At high pressures, e.g., (b), the diffusion losses are so small that the attenuation is approximately given by $e^{-\alpha t}$.

affected by ion-molecule reactions only to a small degree. The count rate scale is given in arbitrary units, but the scale factors have been chosen to represent the approximate number of ions counted in 30-sec periods. The main feature of Figs. 6(a) and 6(b) to be noted is the following. At low pressures [6(a)], diffusion accounts for most of the attenuation in the count rate as the drift distance is increased, because α is small at low pressures. Hence there is some ambiguity in the determination of which of the calculated curves best matches the data. At high pressures [6(b)], however, diffusion accounts for only a small percent of the total attenuation in the count rate, and there is little uncertainty in the determination of k. In fact, for the high-pressure cases, $I(z) \approx I_0 \exp(-\alpha t)$, and α may be determined directly from the slope of the semilog plot of the data.

Figures 7 and 8 present some of the results of the reaction rate coefficient measurements. Each point represents the k value determined from a set of data as in Fig. 6(a) or 6(b). Data were gathered for three values of E/N: 11.3, 19.8, and 28.3×10^{-17} V cm^2 and for pressures in the range 0.1–0.65 Torr. Figure 7 shows the results obtained for the reaction (1) in hydrogen, at the intermediate value of E/N, 19.8×10^{-17} V cm^2. Preliminary data for the reaction (1), obtained with the apparatus as it was described in Ref. 1, were presented at the Fifth International Conference on the Physics of Electronic and Atomic Collisions.[13] Figure 8 shows the results for the reaction (2) in deuterium, also for $E/N = 19.8 \times 10^{-17}$ V cm^2. Points corresponding to the same pressure value in these figures have been displaced slightly to avoid overlapping. Within the scatter in the data, the reaction rate coefficients are seen to be independent of the gas pressure.

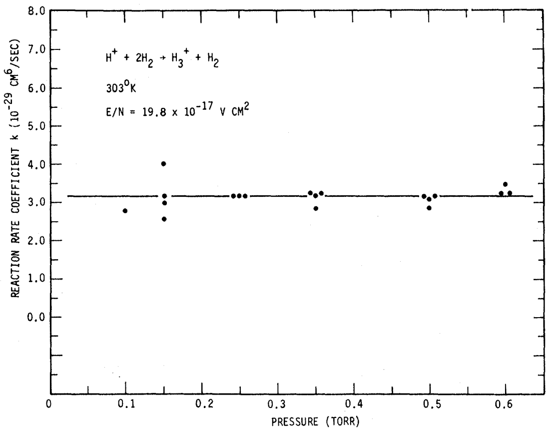


FIG. 7. Measurements of the reaction rate coefficient k for the conversion of protons into H_3^+, for $E/N = 19.8 \times 10^{-17}$ V cm^2.

The results were independent of E/N in the thermal range studied. The best estimates for the two rate coefficients are determined from the high-pressure results ($p \geq 0.35$ Torr); and the results obtained at the intermediate-E/N value have been favored, since the balance between the signal intensity and the drift time at this E/N value gave the best conditions for obtaining reliable data. For the reaction (1), the conversion of protons into H_3^+, the reaction rate coefficient 3.2×10^{-29} cm^6/sec was determined. For the reaction (2), the conversion of deuterons into D_3^+ ions, the reaction rate coefficient was measured to be 3.0×10^{-29} cm^6/sec.

VI. DIFFUSION

A few results have been obtained for the radial diffusion coefficient D_r for H_3^+ ions in H_2. Although measurements of D_r and D_L are in general subject to greater error than are the measure-

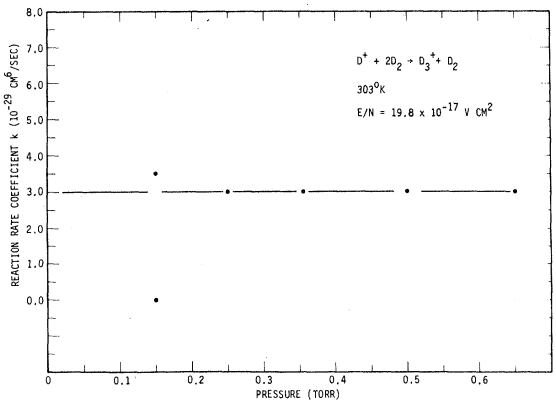


FIG. 8. Measurements of the reaction rate coefficient k for the conversion of deuterons into D_3^+, for $E/N = 19.8 \times 10^{-17}$ V cm^2.

ments of v_d, they can yield more information on the interactions of the ions with the gas molecules. The method used here is the same as described in Sec. V for the reaction rate coefficients, except that D_γ is varied instead of α to determine the best fit to the data. This procedure is possible whenever the effect of the reaction is negligible. For the case of H_3^+ ions, the number of ions created in the ion source far outweighs the number of H_3^+ ions created in the drift space. Values of D_γ were obtained over the pressure range 0.07–0.40 Torr for four values of E/N. The following average values for $D_\gamma p$, which should be independent of p, were found, at the values of E/N given in parentheses: 240 (16×10^{-17}), 255 (37×10^{-17}), 440 (65×10^{-17}), and 670 cm²Torr/sec (88×10^{-17} V cm²). The diffusion results are usually presented in the form D_γ/K, and the present results are compared in this form with those of two other experiments in Fig. 9. The experiments of both Skullerud[5] and Dutton *et al.*[14] were dc-type experiments, but differed in the method of operation. In both cases the apparatus could also be operated in a pulse mode to obtain the mobility K independently of the D_γ/K measurements. Skullerud found 11 ± 1 cm²/V sec and Dutton *et al.* found 10.8 ± 0.5 cm²/V sec for the zero-field reduced mobility of H_3^+ in H_2, which may be compared to the present 11.1 cm²/V sec.

VII. DISCUSSION OF RESULTS

The zero-field reduced mobility of each of the alkali ions in H_2 gas has been found here to be related to the mobility of the same ion in D_2 gas by the appropriate ratio of the square roots of the reduced masses, which may be predicted on the basis of Langevin's theory.[3] At high E/N, the same ratios are found approximately, but the scatter in the alkali-ion mobility data at high E/N is too large to detect small changes in the ratios of the mobilities. The present low-field mobilities of the alkali ions in H_2 gas do not follow a $M_\gamma^{-1/2}$ reduced mass dependence. The same situation is found in D_2 gas. Thus the product $K'=K_0M_\gamma^{1/2}$, which was defined by Dalgarno, McDowell, and Williams[15] and is expected to be mass-independent according to classical mobility theory, is, in fact, found to be systematically dependent on the ion mass. With the present values of the alkali ion mobilities, K' varies linearly with the ion mass for masses 7, 23, and 39 in H_2 or D_2 gas. Table I summarizes the above discussion. In the last column of Table I, values of the zero-field reduced mobility K_p calculated from Langevin's polarization limit are given. The values of K_p were calculated from the expression used by Dalgarno, McDowell, and Williams, $K_p=35.9/(\alpha_pM_\gamma)^{1/2}$ cm²/V sec, where α_p is the polarizability of the gas in a_0^3 and M_γ is the reduced mass of the ion and gas molecule in amu. The value of α_p used to calculate K_p was the same as that used by Mason and Vanderslice,[16] $5.33a_0^3$ (0.79×10^{-24} cm³), and was taken to be the same for both H_2 and D_2.

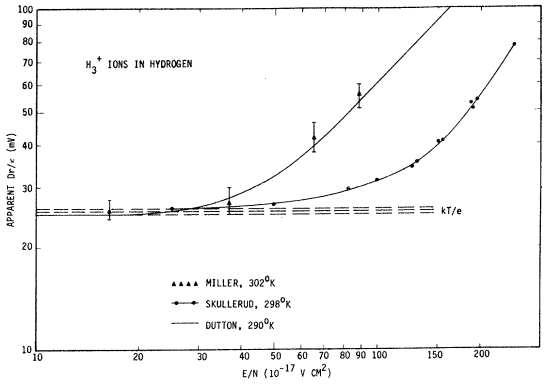


FIG. 9. Measurements of the ratio of the radial (lateral) diffusion coefficient to the mobility for H_3^+ ions in H_2. The vertical bars show the scatter in the present data.

The zero-field reduced mobilities of the ions H^+ and H_3^+ in H_2 were found to be related to the mobilities of D^+ and D_3^+, respectively, in the ratio 1.4, which is close to the $\sqrt{2}$ ratio expected on the basis of Langevin's theory. Within the estimated $1\frac{1}{2}\%$ relative accuracy of this experiment, Langevin's theory does seem to give the correct ratios of mobilities between these isotopic ion-gas molecule pairs. A slight discrepancy might have been expected because of the different H_2 and D_2 rotational and vibrational levels, or possibly because of any difference in H_2 and D_2 polarizabilities, but the experiment does not show any such discrepancy within the relative accuracy.

The ratio of the measured zero-field mobilities of H^+ and H_3^+ in H_2 is about 1.4. The mobilities of D^+ and D_3^+ in D_2 are also in the ratio 1.4. This ratio is surprisingly close to the reduced-mass factor 1.34 which would be expected on the basis of Langevin's theory; however, the interactions of the monatomic ion with the gas molecules are generally assumed to be quite different from the interactions of the triatomic ion with the gas molecules. For example, Mason and Vanderslice[16] find the short-range forces between H^+ and H_2 to be strongly *attractive* chemical valence forces which heavily influence the H^+ mobility at 300°K. For H_3^+ in H_2, they found *repulsive* short-range forces which were likewise calculated to be influential at 300°K; in addition, Varney[17] has suggested that a proton-transfer mechanism is important in the H_3^+–H_2 interactions.

Table II presents a summary for the gaseous ions similar to that which was given for the alkali ions.

The measured reaction rate coefficients for the reactions (1) and (2) are unexpectedly close numerically; there is a 6.5% difference, which is not much larger than the estimated 5% relative accuracy of the reaction rate coefficient measurements. Estimates based on classical mechanics indicate that the rate coefficients should differ by about 20%. The three-body reaction may be thought of as a two-step process on a microscopic level, and the three-body rate coefficient k may be expressed as

$$k=k_2\tau k_2' . \tag{10}$$

TABLE I. Alkali-ion zero-field reduced mobilities K_0, with the quantity $K' = K_0 M_r^{1/2}$ (which is mass-independent according to classical mobility theory), and Langevin's polarization limit to the mobility $K_p = 35.9/(\alpha_p M_r)^{1/2}$, as expressed by Dalgarno *et al.*[15] The mobility values are in cm^2/V sec, and α_p and M_r are in atomic units.

Ion	Gas	K_0	$M_r^{1/2}$	K'	K_p
Li^+	H_2	12.3	1.247	15.3	12.47
Na^+	H_2	12.2	1.357	16.6	11.46
K^+	H_2	12.8	1.397	17.8	11.28
Li^+	D_2	9.6	1.595	15.3	9.75
Na^+	D_2	8.9	1.846	16.4	8.42
K^+	D_2	9.4	1.905	17.9	8.16

Here k_2 is a two-body rate coefficient which determines the rate of formation of unstable intermediate-state $H^+ + H_2$ or $D^+ + D_2$ pairs, τ represents the average lifetime with respect to dissociation of the intermediate-state ions, and k_2' is a two-body rate coefficient which determines the rate of encounters between the intermediate-state ions and a third body, a gas molecule, which stabilizes the system. Equation (10) should hold provided the lifetime of the intermediate-state ion is short compared to the mean free time for collisions with the third body, i.e., if $\tau \ll 1/k_2'N$. (If $\tau \gg 1/k_2'N$, then the stabilization by the third body almost always occurs. In this case, although a third body is required to remove excess energy, the stabilization is so certain that the three-body rate coefficient k will not be found to be pressure-independent—in fact, the two-body rate coefficient k_2 should be used to represent the reaction. The pressure range over which a reaction rate coefficient is found to be pressure-independent must therefore be specified.)

TABLE II. Gaseous ion zero-field reduced mobilities K_0, with the quantity $K' = K_0 M_r^{1/2}$ (which is mass-independent according to classical mobility theory), and Langevin's polarization limit to the mobility $K_p = 35.9/(\alpha_p M_r)^{1/2}$, as expressed by Dalgarno *et al.*[15] The mobility values are in cm^2/V sec, and α_p and M_r are in atomic units.

Ion	Gas	K_0	$M_r^{1/2}$	K'	K_p
H^+	H_2	15.7	0.8165	12.8	19.04
H_3^+	H_2	11.1	1.096	12.2	14.19
D^+	D_2	11.2	1.155	12.9	13.46
D_3^+	D_2	8.0	1.549	12.4	10.04

The two-body rate coefficients k_2 and k_2' in Eq. (10) may be estimated by the method used by Eyring, Hirschfelder, and Taylor,[18] where the two-body rate coefficient is given by $2\pi(e^2\alpha_p/M_r)^{1/2}P$. This result is based on the spiraling collision model developed by Langevin.[3] The factor $2\pi(e^2\alpha_p/M_r)^{1/2}$ determines the frequency of encounters between ions and gas molecules, and P is a stabilization probability. P is usually taken to be unity if the reaction is energetically possible. This assumption is motivated by the inability to calculate P.

Classical estimates of τ were obtained here by calculating the average orbiting time for Langevin-type spiraling orbits of ions approaching gas molecules. An approximate potential function between H^+ and H_2 given by Mason and Vanderslice[16] was used. For a given value of the relative velocity v_0 between the monatomic ion and the gas molecule, only those encounters with impact parameters less than a certain critical value result in spiraling collisions. If the impact parameter has exactly the critical value, an orbit of constant radius r_c and infinite lifetime τ results. For each selected value of v_0, the orbiting times were calculated numerically and averaged over the allowed impact parameters. The orbit time was taken to be the time that the ion and molecule spent approaching and separating, inside the radius r_c. The times were then numerically averaged over the Maxwellian relative-velocity distributions at 303°K for the H_2 and D_2 cases. The final results for the average lifetimes τ were 0.113 $\mu\mu$sec for $H^+ + H_2$ and 0.189 $\mu\mu$sec for $D^+ + D_2$.

With k_2 and k_2' determined from $2\pi(e^2\alpha_p/M_r)^{1/2}$ for the appropriate M_r values, and τ as given above, the three-body rate coefficients $k = 0.055 \times 10^{-29}$ cm^6/sec [reaction (1), in H_2] and $k = 0.046 \times 10^{-29}$ cm^6/sec [reaction (2), in D_2] may be calculated. These rate coefficients are about a factor of 60 below the measured rate coefficients, 3.2×10^{-29} cm^6/sec (H_2) and 3.0×10^{-29} cm^6/sec (D_2), meaning that the classical orbiting times cannot account for the large measured rate coefficients. It must be assumed that quantum-mechanical exchange effects significantly lengthen the collision time between H^+ and H_2, or D^+ and D_2. The ratio of the calculated rate coefficients is 1.2, which may be compared with the ratio 1.07 of the measured rate coefficients for the reactions (1) and (2). If the measured values are used to calculate the lifetimes of $H^+ + H_2$ and $D^+ + D_2$ from Eq. (10), with values of k_2 and k_2' as above, then $\tau = 6.6$ $\mu\mu$sec and $\tau = 12.4$ $\mu\mu$sec are found for the hydrogen and deuterium cases, respectively.

If the variation of the classical orbiting times with v_0 is taken to be indicative of the variation of the three-body rate coefficients with v_0, then some predictions as to the temperature variation of the k values may be given. For the reaction (1) in H_2, above 300°K, k will decrease slowly with increasing temperature and should be about 2.3×10^{-29} cm^6/sec at 500°K. Below 300°K, k

will increase as the temperature is decreased and should be about 6×10^{-29} cm^6/sec at 77°K. For Eq. (2) in D_2, the changes should be about the same: $k = 6.5 \times 10^{-29}$ cm^6/sec (77°K) and $k = 2 \times 10^{-29}$ cm^6/sec (500°K).

VII. ANALYSIS OF UNCERTAINTIES

For the gaseous ion mobilities, the possible errors are the same as discussed in Ref. 1, except that the random error has been reduced from 2.5 to 1.7%, for a total error bound on the low-E/N data of ±4.1%. At high E/N, the low pressures used (0.050 and 0.035 Torr) require that a larger error bound of ±10% be assigned. For the alkali ions, there was greater scatter in the mobility data because the ions were extracted and pulsed with relatively high fields, and the ion-source output was not as constant as with the gaseous ions, particularly at very low pressures (high E/N). The low-E/N data are judged to be accurate to ±5%, but may be in error by as much as ±20% at high E/N (about 100×10^{-17} V cm^2).

For the measurements of the reaction rate coefficients, the possible systematic error is given by the error bounds on the mobilities, ±4.1%. The random uncertainty depends quadratically on the pressure, as can be understood from Fig. 6. The best estimates of the three-body reaction rate coefficients are derived from measurements for $p \geq 0.35$ Torr. From the scatter in the data in this pressure range and consideration of the possible systematic error, a ±11% error bound is placed on the rate coefficient for Eq. (1). Fewer data were obtained in the case of the reaction (2), primarily because of the high consumption rate of the expensive D_2 gas, and a larger uncertainty of ±14% must be assigned to the rate coefficient for the reaction (2).

The measurements of D_γ are subject to similar uncertainties as are the reaction rate coefficient measurements, since the method of measurement is the same. An error bound of ±11% is assigned to the values of $D_\gamma p$ given in the text, and a ±15% uncertainty should be associated with the values of D_γ/K shown in Fig. 9.

IX. CONCLUSIONS

The zero-field reduced mobilities of H^+ and $H_3{}^+$ in H_2 were found to be 15.7 ± 0.6 and 11.1 ± 0.5 cm^2/V sec, respectively. Those for D^+ and $D_3{}^+$ in D_2 were found to be 11.2 ± 0.5 and 8.0 ± 0.3 cm^2/V sec, respectively. Zero-field reduced mobilities for Li^+, Na^+, and K^+ in H_2 of 12.3 ± 0.6, 12.2 ± 0.6, and 12.8 ± 0.6 cm^2/V sec were obtained. Zero-field reduced mobilities for these same alkali ions in D_2 of 9.6 ± 0.5, 8.9 ± 0.4, and 9.4 ± 0.5 cm^2/V sec were obtained. The three-body reaction rate coefficients for the reactions $H^+ + 2H_2 \rightarrow H_3{}^+ + H_2$ and $D^+ + 2D_2 \rightarrow D_3{}^+ + D_2$ were found to be $(3.2 \pm 0.3) \times 10^{-29}$ cm^6/sec and $(3.0 \pm 0.4) \times 10^{-29}$ cm^6/sec, respectively, and were observed to be independent of E/N in the thermal range ($E/N < 28 \times 10^{-17}$ V cm^2) and independent of the gas pressure between 0.1 and 0.6 Torr. Finally, a few measurements of the radial diffusion coefficient for $H_3{}^+$ ions in H_2 have been made which agree with those reported by Dutton *et al.*, within the scatter in the data, but not with those reported by Skullerud.

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Calculation of Resonance Broadening*

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The line-shape function is expressed in terms of three boundary functions related to the two-particle Green's function. The transverse as well as the longitudinal interaction among atoms is considered, using the photon propagator approach. The broadening of one of the radiative states through the resonance interaction with the ground state is considered in detail. The contributions of multiple transfer of excitation and of two-body scattering are calculated separately. Several validity conditions are also obtained which clarify the approximations in the existing results. The velocity dependence of the width parameter is investigated in some detail; our results differ considerably from the existing results because we have included higher-order contributions. The extreme low-density region [where (collision width) ~ (natural width)] is also considered; the linewidth is found to be nonlinear in the number density. The additional contribution of the coupling between the radiative states is also calculated in a special case.

I. INTRODUCTION

In this paper we calculate the contributions to resonance broadening which arise from multiple transfer of excitation and from two-body scattering. In addition to width results, quantitative conditions are obtained which help in selecting the important terms in various situations of interest. These validity conditions also help in understanding the nature of approximations in the existing results.[1-3] A "photon propagator" approach is used to treat the interaction among atoms. This method simplifies the calculations, and permits a unified treatment of longitudinal and transverse interactions.

The line-shape function is expressed in terms of three boundary functions related to the two-particle Green's function. The particular case of a transition $\nu \to \mu$, in which only the level μ is broadened appreciably by resonance with perturbers in the ground state $\bar{\nu}$, is considered in detail. (This is the situation in the important experiments of Kuhn *et al.*[4]) In this case width and shift are given by a single parameter Σ_μ.

At high densities, multiple transfer is important and Σ_μ has a nonlinear dependence on the number density. (A result similar to that obtained by Reck *et al.*[2] arises when additional assumptions are made.) In the impact regime, only two-body scattering is important, but the lowest-order contribution to the T matrix is usually not sufficient. (In fact, the perturbation series may diverge.) We have obtained a solution of the integral equation for the T matrix which includes all orders of dipole-dipole interaction. The velocity dependence of Σ_μ is investigated in detail, and its effect on the line shape is discussed. The result obtained by Mizushima[3] is found to be inadequate in the experimental situation of interest.[4] (Mizushima considered only the lowest-order two-body contribution, using a classical path approach.)

At extremely low densities, when the collision width ~ the natural width, we find that Σ_μ again becomes nonlinear in the number density, because the transverse interaction is also important. This effect may be responsible for the "residual width" observed by Kuhn *et al.*[4]

The situation when $\bar{\nu}=\nu$ is also considered briefly. In this case the line shape is more complicated because of the coupling between the radiative states μ and ν. The additional contribution to the width and shift parameter is obtained under a specific set of assumptions.

In many of the results we have retained the frequency dependence of the width and shift parameter. This dependence can be important in the wings of the line, when $\Delta\omega^{-1} \gg$ average duration of a collision.

II. BASIC RELATIONS

Consider an isolated resonance transition $\nu \to \mu$ with unperturbed frequency $\omega_{\mu\nu}$, where μ and ν denote the two internal energy states of the atoms comprising the gas. The line shape is essentially given by the following function of frequency, ω.[5]

$$\chi_{\mu\nu}(\vec{k}, \omega, \beta) = \int_{-\infty}^{+\infty} d(t-\bar{t}) \times e^{i\omega(t-\bar{t})} \chi_{\mu\nu}(\vec{k}, t, \bar{t}, \beta) . \quad (1)$$