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Measurement of Transport Properties of Ions in Gases; Results for K^+ Ions in N_2 [†,‡]

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A solution is developed to the transport equation describing the drift, diffusion, and reaction of an ion swarm moving under the influence of a uniform electric field E in a gas of uniform number density N. An easily applied analytical expression is obtained for a particular type of source input of the ions under the assumption that the only reaction occurring is one which results in the depletion of the ion species under consideration. Data obtained with a drift-tube mass spectrometer on K^+ ions in N_2 at low E/N, where the parameters in the solution can be determined from other considerations, are presented to show that the solution does closely describe the drifting ion swarm. The solution is then applied to K^+ data obtained at higher E/N to determine the mobility, the longitudinal diffusion coefficient and the transverse diffusion coefficient for K^+ in N_2, up to an E/N of 350×10^{-17} V cm^2. The zero-field reduced mobility of K^+ in N_2 is determined to be 2.55 cm^2/V sec, in excellent agreement with the non-mass analyzed data of other experiments and with the Langevin polarization limit prediction of 2.60 cm^2/V sec. Both diffusion coefficients are found to be in agreement with the value predicted from the Einstein relation at low E/N, and to increase as E/N is increased.

I. INTRODUCTION

It has been stated for many years that drift-tube experiments can provide information about the drift velocities, diffusion coefficients, and ion-molecule reaction rates of ions in gases. However, the vast majority of such experiments to date have yielded only drift-velocity results. Except for measurements reported by this laboratory,[1] there apparently exist no determinations of the coefficient for diffusion parallel to the applied electric field (the longitudinal diffusion coefficient) and only a few measurements[2-4] of the coefficient for diffusion perpendicular to the applied electric field (the transverse coefficient). Approximately 16 measurements of reaction rates have been reported[5] from drift-tube experiments but most of these have fairly large uncertainties. The purpose of this paper is to present an analysis which allows the extraction of both the longitudinal and transverse diffusion coefficients from the measured flux of an ion swarm after it has drifted a known distance through a gas of uniform pressure under the influence of a uniform electric field. In addition, this analysis will allow the accurate determination of the rate coefficient for a reaction which results only in the depletion of the ion species under consideration. Although portions of this analysis have been discussed in previous publications,[1,2,6] the present paper is the first to give a unified presentation and to include in detail the use of the analysis to determine diffusion coefficients. In addition, new data for potassium ions in nitrogen are utilized to verify that the analysis does closely describe the experiment.

The ratio of the drift velocity to the electric field intensity, v_d/E, is defined[7] as the mobility, K. The mobility is inversely proportional to the gas number density N. To simplify comparisons 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. For fixed temperature T, the parameter E/N determines the drift velocity and average energy as well as other transport properties of the ions; therefore data are presented here 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". Thus at sufficiently low E/N, the drift velocity is directly proportional to E/N.

The suggestion has been made[8] that the units of E/N be denoted by the "Townsend" or "Td", where $1\ \text{Td} = 10^{-17}\ \text{V cm}^2$. Although this designation has not been universally adopted, it is a convenient one and will be used in this paper.

II. THE TRANSPORT EQUATION AND ITS SOLUTION

Consider an ion population created at one end of a cylindrically symmetric drift space filled with gas of uniform pressure p, in which there exists an externally applied uniform electric field $\vec{E}$ along the axis. Assume that the number density of the ion swarm, $n(\vec{r},t)$, is low enough that the space charge field is negligible. For this situation, Wannier[9] has shown that the ionic current density is given by

$$\vec{j}(\vec{r},t)=\vec{v}_d n(\vec{r},t)-\overleftrightarrow{D}\cdot\vec{\nabla}_r n(\vec{r},t)\,, \tag{1}$$

where $\overleftrightarrow{D}$ is a 3×3 diagonal tensor, the first two components of which are equal. If we do not allow for the possibility of any gain in numbers of the species under consideration during the movement down the drift tube, but do consider the loss of these ions through ion-molecule reactions with the frequency α, then the ion swarm is subject to a continuity equation of the form

$$\frac{\partial n}{\partial t}+\vec{\nabla}\cdot\vec{j}+\alpha n=0\,. \tag{2}$$

If we denote the first two equal components of $\overleftrightarrow{D}$ (the transverse components) by D_T and the third component (the longitudinal component) by D_L, and add a source term, $\beta(\vec{r},t)$, to represent the source of ions at the initial end of the drift space and, possibly, an input due to ion-molecule reactions as the swarm drifts, the equation for consideration becomes, in rectangular coordinates,

$$\frac{\partial n(x,y,z,t)}{\partial t}=D_T\left(\frac{\partial^2 n}{\partial x^2}+\frac{\partial^2 n}{\partial y^2}\right)+D_L\frac{\partial^2 n}{\partial z^2}-v_d\frac{\partial n}{\partial z}-\alpha n+\beta(x,y,z,t)\,. \tag{3}$$

In the apparatus for which this analysis was developed, the ions enter the drift space through a circular aperture lying in a plane normal to the drift-tube axis and centered on the axis. If the coordinate system is taken to have its origin at the center of this aperture and the electric field along z is in such a direction as to cause the ions to drift in the positive z direction, then the solution to Eq. (3) in unbounded space[10] is

$$n(x,y,z,t)=\int_{-\infty}^{t}dt'\int_{-\infty}^{\infty}dx'\int_{-\infty}^{\infty}dy'\int_{-\infty}^{\infty}dz'\,\frac{\beta(x',y',z',t')}{[4\pi(t-t')]^{3/2}D_T D_L^{1/2}}$$

$$\times\exp\left(-\alpha(t-t')-\frac{(x-x')^2+(y-y')^2}{4D_T(t-t')}-\frac{[z-z'-v_d(t-t')]^2}{4D_L(t-t')}\right) \tag{4}$$

That (4) is indeed a solution to (3) can easily be verified by direct substitution.

Suppose the input β is given by

$$\beta(r',z',t')=(b/\pi r_0^2)\,S(r_0-r')\delta(z')\delta(t')\,, \tag{5}$$

where $S(\varphi)=0$ if $\varphi<0$, $S(\varphi)=1$ otherwise. This function describes an axially thin disk source of b ions with uniform surface density and radius r_0, being created instantaneously at $t'=0$ in the plane $z'=0$. Let $b/\pi r_0^2=s$, the planar source density. Then (in cylindrical coordinates)

$$n(r,z,t)=\frac{s\,e^{-\alpha t}\exp[-(z-v_d t)^2/4D_L t]}{(4\pi t)^{3/2}D_T D_L^{1/2}}\int_0^{r_0} r'dr'\int_0^{2\pi} d\theta'\exp\left(-\frac{r^2+r'^2-2rr'\cos\theta'}{4D_T t}\right)\,. \tag{6}$$

The remaining two integrals can be performed[11] to yield

$$n(r,z,t)=[s/(4\pi D_L t)^{1/2}]\exp[-\alpha t-(z-v_d t)^2/4D_L t]$$

$$\times\left[1-\sum_{m=0}^{\infty}\sum_{i=0}^{m}\frac{1}{m!\,i!}\left(\frac{r^2}{4D_T t}\right)^m\left(\frac{r_0^2}{4D_T t}\right)^i\exp\left(-\frac{r_0^2+r^2}{4D_T t}\right)\right]. \tag{7}$$

Equation (7) is an expression for the ion number density at any given time at any point in space for an ion swarm which (1) was instantaneously created with uniform density across an axially thin disk, (2) drifts in unbounded space under the influence of a constant electric field, and (3) possibly undergoes a depleting reaction with the gas molecules.

Since the apparatus to be considered here samples the ion swarm on the axis, the result of interest is the axial ionic number density

$$n(0,z,t)=[s\,e^{-\alpha t}/(4\pi D_L t)^{\frac{1}{2}}][1-\exp(-r_0^2/4D_T t)]\exp[-(z-v_d t)^2/4D_L t]\,, \tag{8}$$

where s is the initial ion surface density of the delta-function input of ions and r_0 is the radius of the ion entrance aperture.

The quantity measured experimentally[2] is the flux Φ of ions leaving the drift tube through an exit aperture of area A at a fixed distance z from the source plane:

$$\Phi(0,z,t)=Aj(0,z,t)\,, \tag{9}$$

where $j(0,z,t)$ is the z component of the ionic current density in the drift tube, on the axis, at the end of the drift distance z.

The ionic current density is related to the ionic number density by Eq. (1), so that

$$j(0,z,t)=-D_L(\partial n/\partial z)+v_d n\,, \tag{10}$$

where $n(0,z,t)$ is given by (8). Differentiation and substitution into (9) gives

$$\Phi(0,z,t)=[As\,e^{-\alpha t}/4(\pi D_L t)^{\frac{1}{2}}](v_d+z/t)[1-\exp(-r_0^2/4D_T t)]\exp[-(z-v_d t)^2/4D_L t]\,. \tag{11}$$

In summary, Eq. (11) gives the flux of ions reaching the sampling location on the axis of the drift tube as a function of the time t and the drift distance z. All of the ions of the species under consideration are assumed to be introduced from the ion source in periodic delta-function bursts, and none are produced by reactions in the drift space. However, loss of the ions in reactions producing other species is allowed, the rate of loss being described by the frequency α.

III. POTASSIUM-ION RESULTS

The measurements were made by a time-of-flight technique using a drift-tube mass spectrometer of ultra-high-vacuum construction (see Refs. 6 and 12). A thermionic emitter is combined with an electric shutter in the ion entrance aperture to admit to the drift tube, repetitively, bursts of potassium ions that conform accurately to the description of Eq. (5). The ion swarm migrates down the drift tube under the influence of a weak uniform electric field. The distance of drift is variable from 1 to 44 cm. During this migration the swarm spreads due to diffusion, and may undergo ion-molecule reactions with the neutral gas. The ion population is sampled on the axis at the end of the drift tube by a small exit aperture, and a particular species is mass selected by an rf quadrupole spectrometer. Ions are individually detected. The time of arrival of each ion at the detector is recorded by a 256-channel time analyzer. By repetitive pulsing of the ion source, a histogram of arrival times can be built up. From such time profiles the drift velocities, diffusion coefficients, and ion-molecule reaction rates can be obtained.

Alkali ions are ideal for illustrating the diffusion-induced changes in the time profiles because they do not react with the gas molecules. A typical set of superimposed arrival-time spectra of K^+ ions in N_2 for seven different source positions is shown in Fig. 1. For this illustration, the same counting time has been used for each spectrum. The points represent data from the time analyzer; the smooth curves are obtained from the analysis described here. Although in principle determination of v_d, D_L, D_T, and α by comparison of the experimental data with Eq. (11) involves a multiparameter fit, in practice the effects of each of these parameters on the spectra can be separated, and each one determined essentially independently. The drift velocity may be obtained to an excellent approximation from the known distance traveled by a swarm divided by the mean time of the resulting spectrum. Differencing of two or more spectra will almost completely eliminate end effects. The widths of the spectra are determined by the longitudinal diffusion coefficient (but may also be affected by ion-molecule reactions when they are present). The change in the relative total number of ions making up each of the spectra at the various drift distances is governed by the transverse diffusion coefficient (but may also be affected by reactions if they are present).

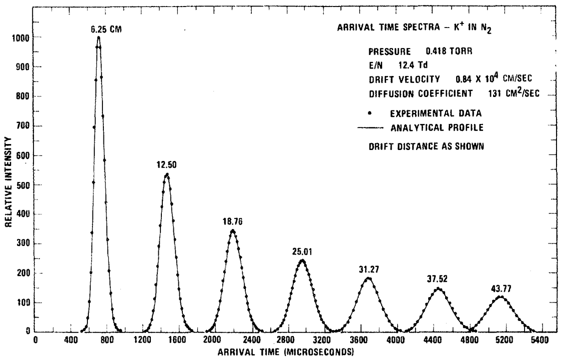

FIG. 1. Comparison of experimental arrival-time spectra and analytically calculated profiles for K^+ ions in N_2 for seven drift distances.

The data shown in Fig. 1 verify these statements. At low E/N, where the mobility is constant, the longitudinal and transverse diffusion coefficients are equal and can be calculated from the Einstein relation

$$D_L = D_T = K(\kappa T/e) \tag{12}$$

if the mobility is known. For potassium ions the reaction frequency is zero. Hence from the experimental values of $\bar{t}$ the values of v_d, K, D_L, and D_T can be calculated and the flux given by Eq. (11) evaluated. (Actually, the planar source density s is not known, nor is the efficiency of the ion-sampling apparatus, but these factors are held constant for all of the seven profiles illustrated. Since only relative intensities are being considered here, exact knowledge of such multiplicative factors is not required.) The solid curves in Fig. 1 represent Eq. (11) evaluated in this way, normalized to match the height of the peak calculated for only the shortest drift distance to the corresponding experimental data. (The remaining profiles for the other values of the drift distance are not independently normalized.) The agreement is clearly quite good. Variation of v_d in (11) from the value predicted by $\bar{t}$ shifts the analytical profiles along the abscissa, as would be expected. Variation of D_L changes the widths of the profiles, but does not change the total number of counts represented by a profile, i.e.,

$$I(z) = \int_0^\infty \Phi(0, z, t)\, dt \tag{13}$$

remains a constant. Variation of D_T changes $I(z)$, but does not change the basic shape of the profiles. If the reaction frequency, α, is different from zero it will also change $I(z)$.

Figure 2 shows $I(z)$ (on the ordinate, labeled "Count Rate") at several pressures. [Note, from (12), that since $K \propto 1/N$, $D_T \propto 1/N$ also.] The curves are $I(z)$ calculated from Eq. (13) using the Einstein relation to evaluate D_L and D_T from v_d. The points shown are comparable experimental evaluations of $I(z)$. Since D_L does not significantly affect $I(z)$, this represents further verification that the analysis presented does adequately describe transverse diffusion.

Figure 3 shows the mobility of K^+ in N_2 as determined by this experiment, and compares the present results with the results of other experiments.[13–15] Since the three other experiments were performed on systems which did not allow for mass analysis, these results represent the first positive confirmation that the earlier experiments had indeed observed K^+ ions, and that no clustering of the ions with the N_2 molecules occur-

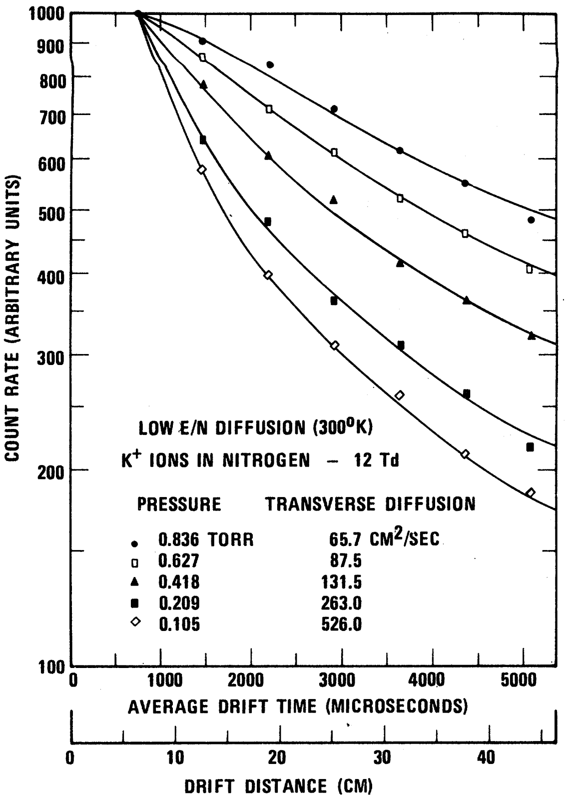

FIG. 2. Comparison of the experimental decrease in count rate as the drift distance is increased with the predictions of Eq. (13) at low *E/N*.

red. The zero-field reduced mobility of K^+ in N_2 was determined to be 2.55 ± 0.10 cm^2/V sec.

The fact that D_L and D_T can be calculated at low E/N from the drift velocities using Eq. (12) has been used to verify that Eq. (11) closely describes the experimental flux. However, at higher E/N, (12) is not expected to be valid, nor are the two diffusion coefficients expected to be equal.

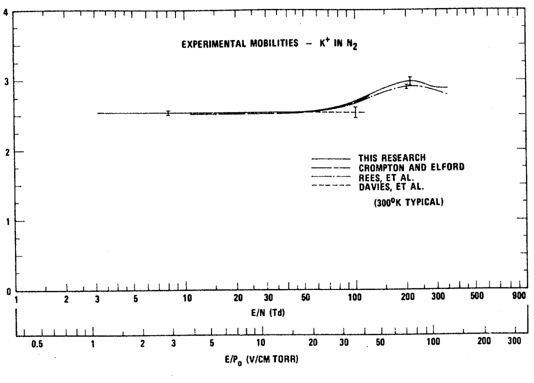

FIG. 3. Mobility results for K^+ ions in nitrogen.

The analysis can now be applied to determine D_L and D_T at high E/N.

Figure 4 shows the longitudinal diffusion coefficient for K^+ in N_2. The results are presented as ND_L versus E/N, since $D_L \propto 1/N$. The values shown were obtained by adjusting D_L in the expression for the flux, Eq. (11), until a best fit in the least-squares sense is obtained. This procedure is insensitive to the value of D_T assumed in (11), as mentioned here, and as shown more fully in Ref. 11. As can be seen, D_L increases rapidly as E/N increases above 50 Td. Values of D_L for N^+ and $N_2{}^+$ in N_2, which have been published in Ref. 1, are presented for comparison.

Figure 5 presents the transverse diffusion coefficient for K^+ in N_2. The values were obtained by adjusting D_T in the expression for $I(z)$, Eq. (13), until a best fit of the analytical expression to the data was obtained. Figure 5 also gives a comparison with the recent, non – mass-analyzed

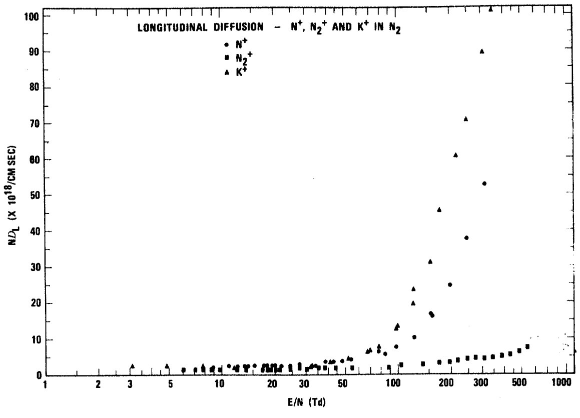

FIG. 4. Longitudinal diffusion coefficients for K^+ ions in nitrogen. Values for N^+ and $N_2{}^+$ are included for comparison.

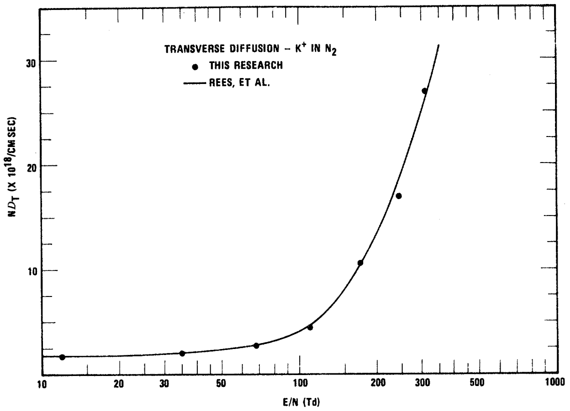

FIG. 5. Comparison of the transverse diffusion coefficients for K^+ ions in N_2 with the results of Rees *et al.* (see Ref. 14).

results of Rees *et al.*[3] The agreement is quite good. Note that the scale on the ordinate in Fig. 5 is much expanded over the scale of Fig. 4. D_T increases much less rapidly than D_L, and $D_T \leq D_L$ for a given ion over the entire range of this experiment in all cases examined.

IV. REACTIONS

When a depleting reaction is occurring, analysis of the experimental results is complicated by the fact that both transverse diffusion and a depletion reaction have similar effects on the measured profiles – both result in an attenuation of the counting rate as the drift distance (and hence drift time) is increased. However, separation of the effects of D_T and α is possible. The paper immediately following this one[12] discusses in detail the evaluation of two such reaction rates involving nitrogen ions in nitrogen.

V. CONCLUSIONS

A reasonably simple analysis has been presented which will allow evaluation of both the longitudinal and transverse diffusion coefficients as well as the mobility from time-of-flight data on ion swarms which drift under conditions meeting the described boundary conditions and which are of sufficiently low density for space-charge fields to be negligible. In addition, as will be shown in the following paper,[12] this analysis allows the evaluation of the rate of a reaction which depletes the observed species. Data on K^+ ions in N_2 have verified the correctness of the analysis at low E/N, where D_L and D_T can be calculated, and the analysis has been applied to the evaluation of D_L and D_T at higher E/N.

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