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Larry A. Viehland and E. A. Mason

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On the relation between gaseous ion mobility and diffusion coefficients at arbitrary electric field strengths*

Larry A. Viehland and E. A. Mason

Brown University, Providence, Rhode Island 02912
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A generalized Einstein relation for gaseous ions is shown to be accurate even at high electric field strengths, provided care is taken in the evaluation of the ion temperature. Comparison with experiment is made for K$^+$ ions in He, Ne, and Ar. The validity of this relation means that gaseous ion diffusion coefficients can be calculated from the more easily measured mobilities.

Although there now exists a rigorous kinetic-theory treatment of gaseous ion mobility in electrostatic fields of arbitrary strength, without restriction upon the ion–neutral mass ratio or interaction potential,[1] the more general problem of ion motion in the presence of both an electric field and an ion density gradient remains unsolved. This is true even when the density gradient ∇n is small enough that the ion flux density J is described by the linear relation[2]

$$\mathbf{J} = n K \mathbf{E} - \mathbf{D} \cdot \nabla n , \tag{1}$$

where n is the ion number density, E the electrostatic field strength, K the (scalar) ion mobility, and **D** the (tensorial) ion diffusion coefficient having diagonal components D_L and D_T describing diffusion parallel and perpendicular to the electric field. Despite the lack of a general theory describing such motion, we shall show in this paper that a known approximate relationship between K and **D** can be used to calculate accurate values of **D** from known values of K even at quite high field strengths, provided that sufficient care is taken with two theoretical quantities appearing in the relationship.

Since both K and **D** measure the ease with which ions can move through a neutral gas, it is not surprising that they should be related. It is well known[2] that the Einstein relation applies in the limit of vanishingly small electric fields,

$$eD_L/K = eD_T/K = kT , \tag{2}$$

where e is the ionic charge, k is Boltzmann's constant, and T is the gas temperature. At higher field strengths, however, the anisotropic nature of **D** and the radically different dependences of K and **D** on field strength completely invalidate Eq. (2).

Nonequilibrium thermodynamics has been used[3] to show that **D** and K are related even at nonzero field strengths by a generalized Einstein relation,

$$\frac{eD_L}{K} = kT_L \left(1 + \frac{d \ln K}{d \ln(E/N)} \right) , \tag{3a}$$

$$eD_T/K = kT_T , \tag{3b}$$

where N is the number density of neutral gas molecules. Note that the temperatures T_L and T_T cannot be determined from thermodynamic arguments and that Eqs. (3) should be expected to be only approximate, since the domain of nonequilibrium thermodynamics is restricted to situations where deviations from local equilibrium are not large. However, Eqs. (3) have also been ob-

tained by a variety of other arguments—from a collision model with constant mean free time between ion–neutral collisions,[4] by heuristic considerations based on the Langevin equation,[5] from simple momentum-transfer theory,[6] and from more elaborate kinetic-theory treatments.[1,7] Thus, there is reason to suspect that Eqs. (3) might be useful even under highly nonequilibrium (high field) conditions, despite the fact that no rigorous derivation has yet been presented for arbitrary field strengths. We show below that such is the case if care is taken in the determination of T_L and T_T.

Approximate expressions for T_L and T_T have previously been derived[1,7] for the case of a pure neutral gas in which only elastic ion–neutral collisions occur,

$$kT_L = kT + \left(\frac{5m - (2m - M)A^*}{5m + 3MA^*} \right) M[v_d]_1^2 , \tag{4a}$$

$$kT_T = kT + \left(\frac{(m + M)A^*}{5m + 3MA^*} \right) M[v_d]_1^2 , \tag{4b}$$

where m is the ion mass, M is the neutral molecule mass, A^* is a dimensionless ratio of collision integrals that depends on the ion–neutral interaction potential and the effective ion temperature,[1] and $[v_d]_1$ is the theoretical first approximation to the experimental drift velocity $v_d \equiv KE$. Expressions for mixtures have also been obtained,[1,6,7] but will not be discussed here. It is the value of A^* and especially the distinction between $[v_d]_1$ and v_d that are crucial for the accuracy of Eqs. (3)–(4) at high fields.

Experimental measurements of D_L as a function of E/N were recently reported[8] for K$^+$ ions in a number of pure neutral gases, and compared with results calculated from Eqs. (3)–(4) using literature data on the mobilities. Unfortunately, two rather severe (in retrospect) approximations were made in this comparison: it was assumed that $[v_d]_1 = v_d$ and $A^* = 0.8713$. These approximations are exact for the Maxwell model of constant mean free time,[4] but this model gives a reasonable description of ion–neutral interactions only at low fields and low temperatures, where the long-range polarization tail of the potential is dominant. These approximations are quite severe at high field strengths, and more reasonable assumptions must be made in order to provide a fair test of Eqs. (3)–(4).

As test cases for Eqs. (3)–(4) we use K$^+$ in He, Ne, and Ar, for which we can be sure that inelastic collisions are unimportant. Since errors arising from
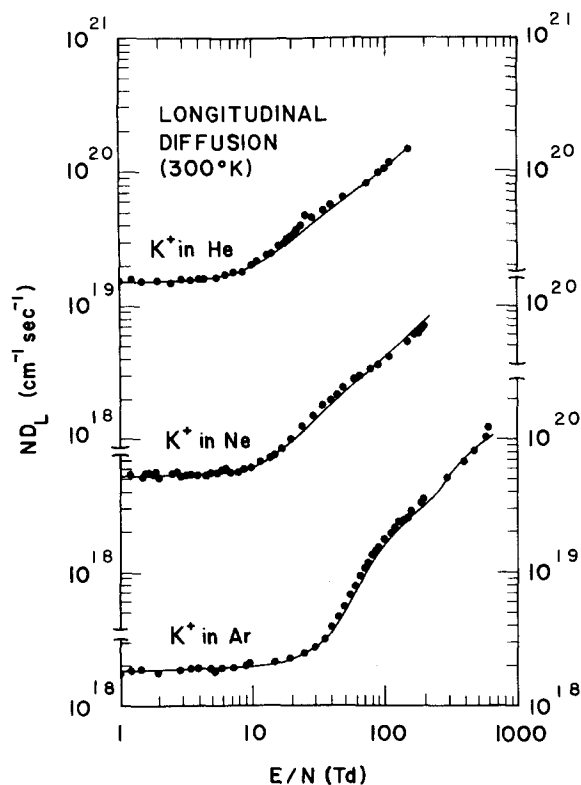
FIG. 1. Comparison of experimental (circles) and calculated (curves) values of ND_L as a function of E/N in units of the townsend (Td), where $1\ \text{Td} = 10^{-17}\ \text{V-cm}^2$.

the choice of A^* are of minor importance, it suffices to take $A^* = 1.2$ for K^+ in He, Ne, and Ar, which is the high-field value corresponding to the short-range repulsion found for these systems by ion-beam scattering measurements.[9] The errors arising from setting $[v_d]_1$ equal to v_d are more serious; we write

$$v_d = [v_d]_1 (1 - \gamma) , \tag{5}$$

where γ depends on the ion–neutral mass ratio and interaction potential, the field strength, and the temperature. Accurate evaluation of γ requires laborious higher-order kinetic-theory approximations, and the behavior of γ has as yet been only incompletely mapped out. However, enough is known[1] that the following reasonable approximations can be made. At low fields, γ

TABLE I. Values of γ_∞ as a function of mass ratio, as taken from Fig. 3 of Ref. 1.

$M/(m+M)$	γ_∞
0	−0.12
0.1	−0.10
0.2	−0.095
0.3	−0.083
0.4	−0.071
0.5	−0.055
0.6	−0.040
0.7	−0.023
0.8	−0.007
0.9	+0.011
1.0	+0.028

TABLE II. Values of v_d^0 (at standard gas number density of $2.69 \times 10^{19}\ \text{cm}^{-3}$) and γ_∞ for use in Eq. (6).

System	$v_d^0 (\text{cm/sec})$	γ_∞
K^+–He	1.07×10^5	−0.10
K^+–Ne	0.63×10^5	−0.08
K^+–Ar	1.11×10^5	−0.06

may be taken as zero with little loss of accuracy; at high fields, γ depends primarily upon the ion–neutral mass ratio and may be obtained with moderate accuracy from Table I; at intermediate fields a simple linear interpolation may be used. For purposes of interpolation we take the boundary between low-field and intermediate-field regions to be where the logarithmic derivative of the mobility is zero, and denote the corresponding value of the drift velocity as v_d^0; we take the boundary between the intermediate-field and high-field regions to be where $v_d = 2v_d^0$. Accordingly, we take γ to be given by

$$
\left.
\begin{aligned}
\gamma &= 0 & v_d &\le v_d^0 \\
\gamma &= \gamma_\infty (v_d - v_d^0)/v_d & v_d^0 &\le v_d \le 2v_d^0 \\
\gamma &= \gamma_\infty & v_d &\ge 2v_d^0
\end{aligned}
\right\} . \tag{6}
$$

Values of v_d^0 obtained from measured mobilities[10,11] of K^+ in He, Ne, and Ar are given in Table II, together with the corresponding values of γ_∞ from Table I.

Values of ND_L as a function of E/N for K^+ in He, Ne, and Ar as calculated from experimental mobilities[10,11] according to Eqs. (3)–(6) are compared in Fig. 1 with measured diffusion coefficients.[8,10] In view of the experimental uncertainties involved and the simplicity of the approximations used here, the agreement is excellent.

Some numerical calculations on ion diffusion and mobility in the limit of infinite field strength are available for rigid-sphere ion-neutral interactions.[12] Equations (3)–(4) appear to give satisfactory agreement with the numerical results for D_T but not for D_L. This may be a reflection of the fact that the logarithmic deviative in Eq. (3a) is quite large for rigid spheres at high fields, requiring the retention of higher-order derivative terms. Whatever the reason for the discrepancy, it is worth noting that the agreement is much better than that reported previously,[1] where $[v_d]_1$ was equated to v_d.

We conclude that Eqs. (3)–(4) relate K and D with reasonable accuracy for real systems at least up to values of E/N as high as have been experimentally attained, provided that inelastic collisions can be neglected and that care is taken with A^* and $[v_d]_1$. The importance of this relation is that K is much more easily measured than is D. This conclusion is further tested experimentally in the following paper.[13] An implication of this conclusion is that little additional information about the ion–neutral potential can be obtained from D beyond that already available in K, unless the value of A^* is greatly modified by additional processes such as inelastic collisions or charge transfer.

ACKNOWLEDGMENTS

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