

Longitudinal diffusion of K⁺ ions in He, Ne, Ar, H₂, NO, O₂, CO₂, N₂, and CO

D. R. James, E. Graham, G. R. Akridge, I. R. Gatland, and E. W. McDaniel

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Longitudinal diffusion of K^+ ions in He, Ne, Ar, H_2 , NO, O_2 , CO_2 , N_2 , and CO^*

D. R. James, E. Graham[†], G. R. Akridge, I. R. Gatland, and E. W. McDaniel

School of Physics, Georgia Institute of Technology, Atlanta, Georgia 30332

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Longitudinal diffusion coefficients, measured with a drift tube mass spectrometer, are reported for potassium ions in helium, neon, hydrogen, nitric oxide, oxygen, and carbon dioxide for E/N in the range 1–700 Td (E is the electric field strength, N the neutral gas number density, and 1 Td = 10^{-17} V·cm²). These results, together with those previously reported for potassium ions in argon, nitrogen, and carbon monoxide, are compared with the theories of Wannier and of Mason, Whealton, and Viehland, which relate mobilities and diffusion coefficients.

The mobilities and longitudinal diffusion coefficients for potassium ions in helium, neon, hydrogen, nitric oxide, oxygen, and carbon dioxide have been measured using a drift tube mass spectrometer which has been fully described elsewhere.¹ The observed time of arrival spectra were compared with a theoretical model based on the drift-diffusion equation,² the data reduction techniques being the same as those discussed in the papers on the mobility and diffusion of potassium ions in nitrogen, carbon monoxide,³ and argon.⁴

The mobility measurements for the six gases (He, Ne, H_2 , NO, O_2 , and CO_2) have been reported in a previous paper.⁵ The present paper will report on the measured diffusion coefficients for these six gases and give comparisons with the unmodified Wannier theory,⁶ the Wannier theory as modified by McDaniel and Moseley,⁷ and the theory of Mason, Whealton, and Viehland,^{8,9} for all nine gases, including N_2 , CO, and Ar.

The fundamental relation between mobility and diffusion is the Einstein relation¹⁰

$$ND/K_0 = N_0 k T^* / q, \quad (1)$$

where N is the neutral gas number density, D is the diffusion coefficient, K_0 is the ionic mobility reduced to STP, $N_0 = 269 \times 10^{17}$ cm⁻³ is the gas number density at STP, k is Boltzmann's constant, T^* is the ion temperature, and q is the ion charge. This equation may always be invoked provided thermal equilibrium is reached and the temperature is properly determined. In a drift tube operating at low E/N , where E is the applied electric field, the motion of the ions is dominated by the thermal contact with the gas so that, to a good approximation, $T^* = T$, the neutral gas temperature. Also, the drift velocity v_d , which is related to the mobility by

$$v_d = K_0 N_0 (E/N), \quad (2)$$

is found to vary linearly with E/N , which agrees with the theoretical requirement that K_0 be equal to its value in the zero field limit, $K_0(0)$. Hence, ND is almost independent of E/N . This is experimentally verified for $E/N \lesssim 10$ Td (1 Td = 10^{-17} V·cm² = 0.1 V·Å²).

However, the external field not only gives the ions a uniform drift but also contributes to their random motion as collisions with the neutral gas dissipate the energy received from the electric field. Wannier⁶ has shown that, for a constant mean free time scattering

model (such as a pure polarization force), the ratio of the drift energy E_D to the field induced random energy is the same as the ratio of the ion mass m to the neutral molecule mass M . Thus, in this model, the total random motion energy of the ion is

$$E_R = E_0 + (M/m)E_D, \quad (3)$$

where $E_0 = \frac{3}{2}kT$ is the contribution from the neutral gas thermal motion. In his original analysis of ionic transport properties, Wannier determined v_d from a scattering model giving a fixed value of K_0 , namely $K_0(0)$, so that

$$E_D = \frac{1}{2}m[K_0(0)N_0E/N]^2. \quad (4)$$

McDaniel and Moseley⁷ suggested using the drift velocity directly, i. e.,

$$E_D = \frac{1}{2}mv_d^2, \quad (5)$$

with v_d given by its value as measured at the particular E/N . This modified theory yields an ion temperature given by

$$\frac{3}{2}kT^* = \frac{3}{2}kT + \frac{1}{2}Mv_d^2. \quad (6)$$

Thus, as E/N is increased, the second term on the right of Eq. (6) will become nonnegligible and, eventually, dominant. While Eq. (3) gives a good estimate of the ion's random energy, it cannot be used in Eq. (1) directly since the direction of the electric field introduces anisotropy in the ion velocity distribution. The degree of anisotropy depends on the angular behavior of the differential cross section for ion-neutral collisions and was investigated by Wannier for both polarization and isotropic scattering. The random energies may be written

$$E_L = \frac{1}{3}[E_R + 2(\delta - 1)E_D] \quad (7)$$

for the longitudinal direction and

$$E_T = \frac{1}{3}[E_R - (\delta - 1)E_D] \quad (8)$$

for the two transverse directions. Here

$$\delta = \frac{m/M + 1}{m/M + \rho}, \quad (9)$$

with $\rho = 0.524$ for a polarization force and $\rho = 0.5$ for isotropic scattering. The longitudinal (D_L) and transverse (D_T) diffusion coefficients are then given by the Einstein equation (1) with $\frac{3}{2}kT^*$ replaced by E_L and E_T ,

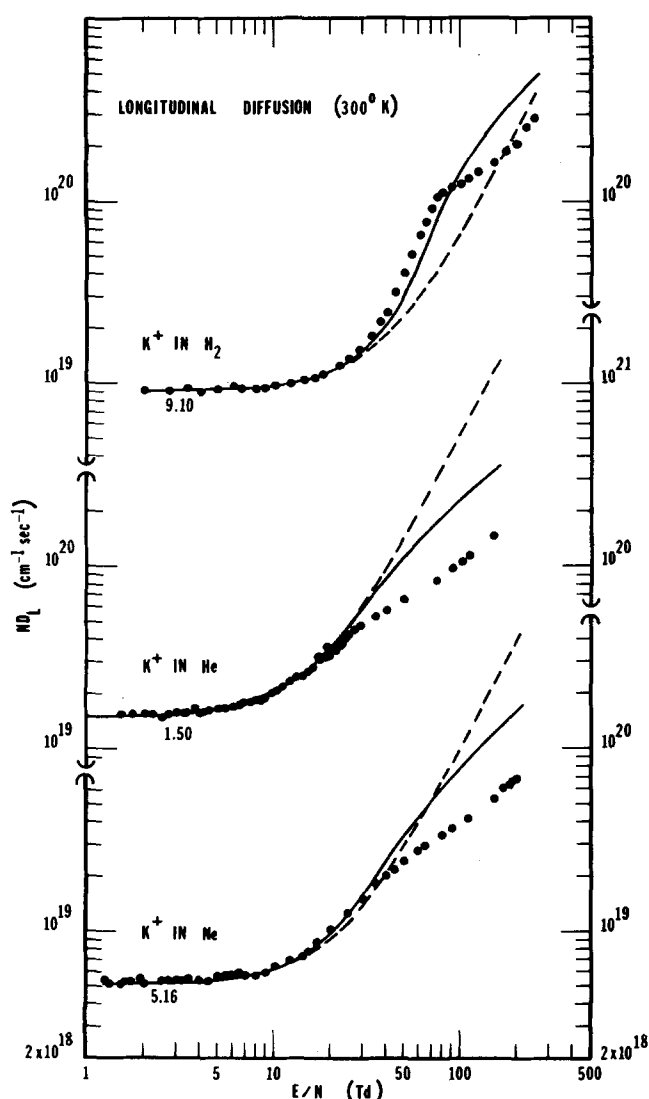


FIG. 1. Longitudinal diffusion coefficients for potassium ions in hydrogen, helium, and neon. Experimental data (points), unmodified Wannier theory (dashed lines), and modified Wannier theory (solid lines) assuming a polarization force model. The numbers below the curves at low E/N indicate the value derived from the Einstein equation at 300°K.

respectively. Thus,

$$\frac{1}{2}qND_L/K_0N_0 = E_L, \quad (10)$$

and

$$\frac{1}{2}qND_T/K_0N_0 = E_T. \quad (11)$$

For the unmodified Wannier model, K_0 should be replaced by $K_0(0)$ in Eqs. (10) and (11).

This method of presentation follows the approach of Viehland, Mason, and Whealton.⁹ Alternatively, explicit equations for ND_L and ND_T , as derived from the Wannier model, have been given in the paper by Thomson *et al.*³ for the unmodified theory [Eqs. (8) and (9) there] and the modified theory [Eqs. (10) and (11) there]. The latter pair of equations agree with Eqs. (10) and (11) of this paper for $\rho = 0.524$, i. e., the polarization force model.

The experimental values of the longitudinal diffusion coefficient were all obtained at a neutral gas temperature of 300°K and at a variety of pressures in the range 0.025–1.0 torr. For a given value of E/N , the quantity ND_L is independent of pressure, so the results are presented in terms of ND_L as a function of E/N . The lowest values of E/N were all less than about 10 Td except for K^+ in O_2 (35 Td) and K^+ in NO (30 Td). The highest values varied from 150 Td (K^+ in He) to 700 Td (K^+ in CO_2 and K^+ in NO). The experimental errors are about 5% for $E/N \lesssim 100$ Td but thereafter increase and may be about 20% at the highest E/N values.

A comparison of the unmodified (dashed line) and modified (solid line) Wannier models for a polarization force is shown in Figs. 1, 2, and 3, together with the experimental results. (The size of the data points corresponds to a 5% error.) It appears that the modified theory gives reasonable agreement to higher values of E/N than does the unmodified theory, but both fail at very high E/N . Tabulations of the experimental data, including mobility values, are available from the authors on request.

A more extensive theoretical analysis has been car-

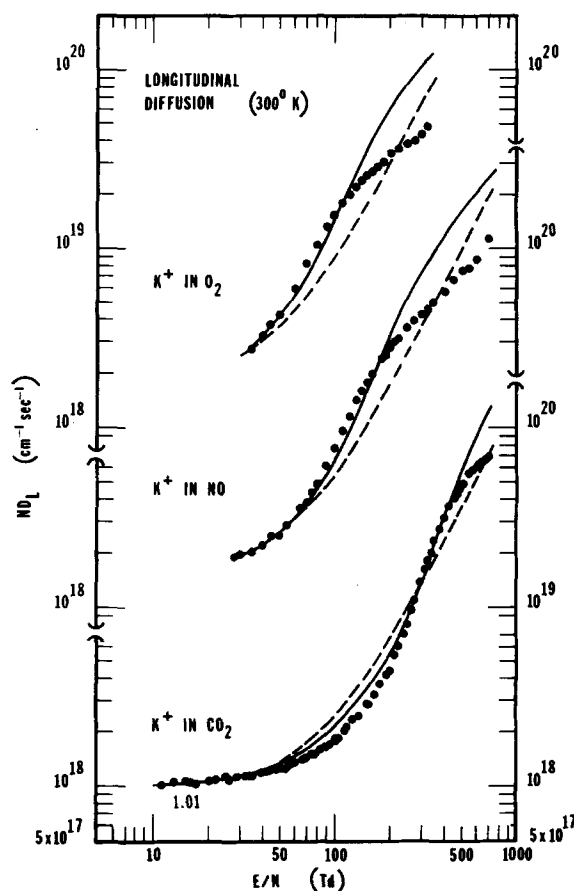


FIG. 2. Longitudinal diffusion coefficients for potassium ions in oxygen, nitric oxide, and carbon dioxide. Experimental data (points), unmodified Wannier theory (dashed lines), and modified Wannier theory (solid lines) assuming a polarization force model. The numbers below the curves at low E/N indicate the value derived from the Einstein equation at 300°K.

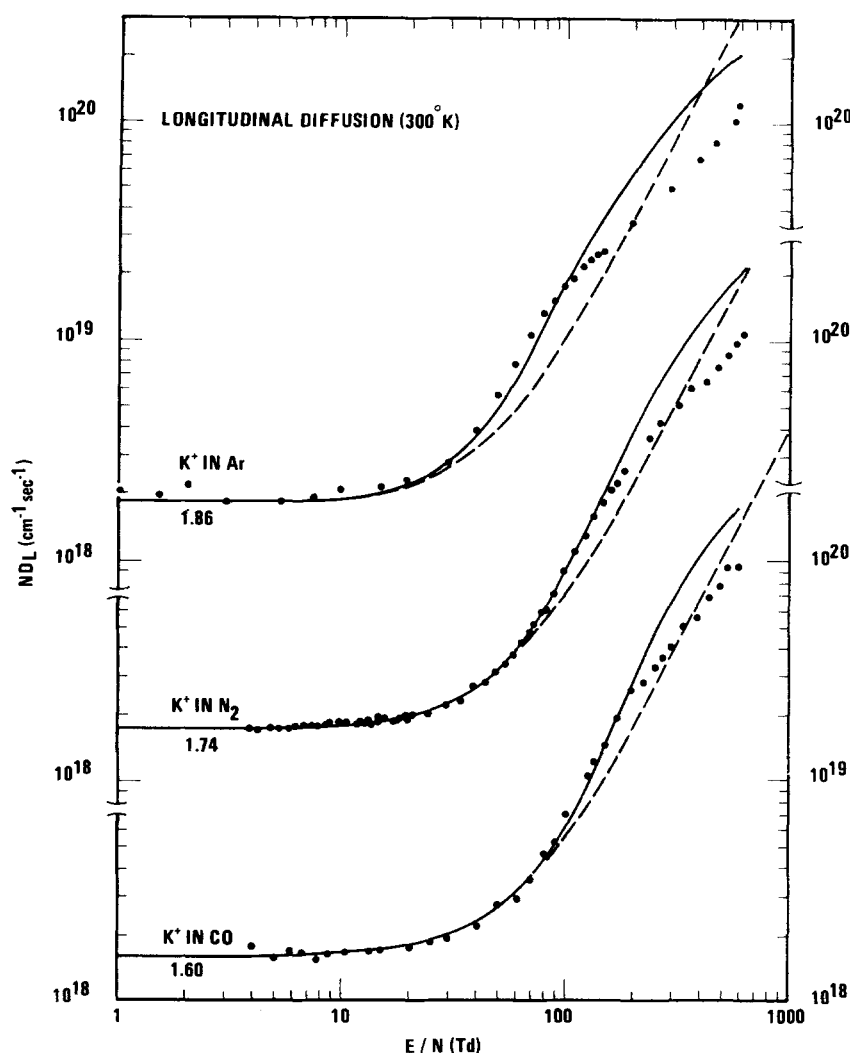


FIG. 3. Longitudinal diffusion coefficients for potassium ions in argon, nitrogen, and carbon monoxide. Experimental data (points), unmodified Wannier theory (dashed lines), and modified Wannier theory (solid lines) assuming a polarization force model. The numbers below the curves at low E/N indicate the value derived from the Einstein equation at 300°K.

ried out by Mason, Whealton, and Viehland^{8,9} to remove the model dependence of the Wannier theory. This results in corrections of higher order in $(E/N)^2$ with appropriate coefficients. These coefficients may be determined experimentally by relating them to a Taylor series expansion of the mobility and, in particular, the first order correction is given in terms of

$$\kappa = \frac{d \ln K_0}{d \ln(E/N)} \quad (12)$$

For present purposes E_R , E_L , and E_T are all calculated as above, but Eqs. (10) and (11) require modification. For the longitudinal diffusion, the lowest order correction yields

$$\frac{1}{2} q N D_L / K_0 N_0 = E_L (1 + \kappa). \quad (13)$$

[A factor $(1 + 3\kappa/2)$ used in two previous papers was incorrect.]^{4,11} For the transverse diffusion coefficient, the lowest order correction is of order $(E/N)^2$; i.e., there is no term involving κ .

A comparison of the modified Wannier theory [Eq. (10): solid line] and the Viehland, Mason, Whealton theory [Eq. (13): dashed line] for the longitudinal diffusion coefficient is shown in Figs. 4, 5, and 6, again

with the experimental data. As before, a polarization force is assumed so that $\rho = 0.524$. The factor $(1 + \kappa)$ improves the fit in the intermediate E/N range but still fails at high E/N . The correction is in the right direction but is too small. Indeed, since κ has been introduced to replace the lowest order $(E/N)^2$ term in a series expansion, it is to be expected that higher order terms must be included when the correction is over 50%. On the other hand, this would not affect the point at which the two theoretical curves cross, since there $\kappa = 0$. In all cases, this occurs at an E/N value which is too high (K^+ in He is excluded from these considerations since no crossing is apparent). This implies that terms dependent on the second derivative $d^2 \ln K_0 / d \ln(E/N)^2$ must be included to explain the high E/N results and, since the second derivative is negative in the region of interest, these terms must be multiplied by a positive constant to explain the relatively low experimental values for the longitudinal diffusion coefficient. Of course, the magnitude of the required correction makes it questionable whether arguments based on a series expansion are even appropriate.

The theoretical curves are not sensitive to the scattering model used. Changing ρ to its isotropic scatter-

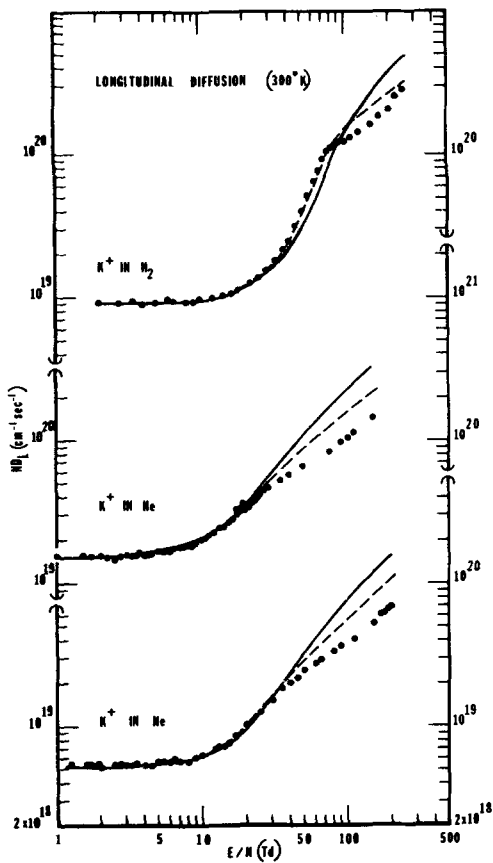


FIG. 4. Experimental data (points) for the longitudinal diffusion coefficients of potassium ions in hydrogen, helium, and neon compared with the modified Wannier theory (solid line) and the Mason, Whealton, Viehland theory (dashed line) for a polarization force.

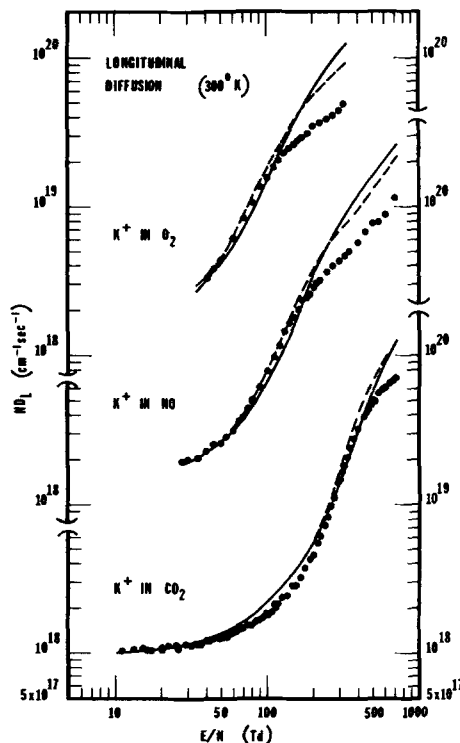


FIG. 5. Experimental data (points) for the longitudinal diffusion coefficients of potassium ions in oxygen, nitric oxide, and carbon dioxide compared with the modified Wannier theory (solid line) and the Mason, Whealton, Viehland theory (dashed line) for a polarization force.

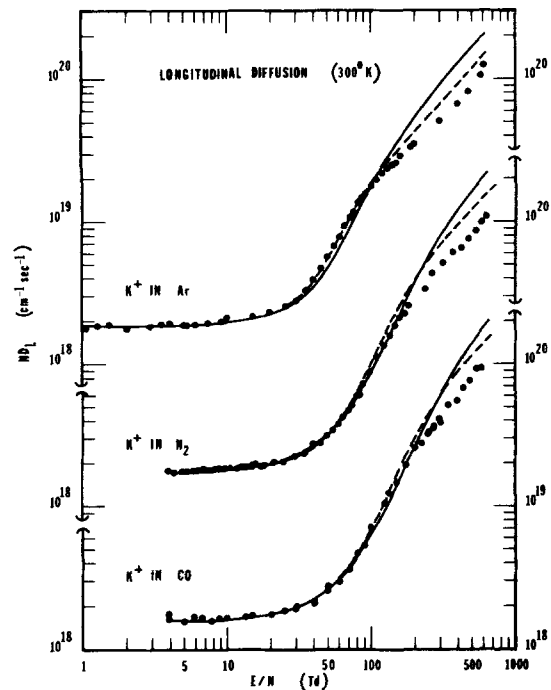


FIG. 6. Experimental data (points) for the longitudinal diffusion coefficients of potassium ions in argon, nitrogen, and carbon monoxide compared with the modified Wannier theory (solid line) and the Mason, Whealton, Viehland theory (dashed line) for a polarization force.

ing value of 0.5 makes very slight changes in the results and leaves the conclusions unaltered. Attempts to improve the fit require large values of ρ and, in some cases, $\rho > 1$ so that $D_T > D_L$. It is difficult to understand ion molecule scattering with this behavior, but direct measurements of the transverse diffusion coefficients would be significant in this respect.

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†Present address: Physics Department, University of Pittsburgh, Pittsburgh, PA.

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