

MOBILITY AND DIFFUSION

II.* DEPENDENCE ON EXPERIMENTAL VARIABLES AND INTERACTION POTENTIAL FOR ALKALI IONS IN RARE GASES

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Abstract

Formulae derived in Part I are used here to calculate mobility and diffusion coefficients for K^+ ions in helium and in neon gases. The formulae are evaluated by inverting truncated matrices, and the effect of using successively larger matrices is investigated numerically. It is found that close agreement with the measurement of ion mobilities can be obtained over a significant range of values of E/n_0 and this determines the potential parameters of an assumed 12-6-4 potential within narrow limits. Diffusion coefficients are calculated from the potential so obtained. The sensitivity of the mobility to variations in potential parameters is discussed and some observations of interest for future experiments are made.

I. INTRODUCTION

In Part I (Kumar and Robson 1973, present issue pp. 157-86) expressions for the mobility and diffusion of ions in a neutral gas were obtained from a polynomial expansion method of solving the Boltzmann equation. The results were given in terms of the inverse of certain infinite dimensional matrices (Part I equations (I, 117) and (I, 136)). A procedure for evaluating these expressions by inverting truncated matrices was also discussed in Section IV of Part I, and it was foreshadowed that very large matrices would be required at high values of the field strength parameter E/n_0 .

In the present paper we pursue this investigation further by means of some concrete examples. For the sake of definiteness we confine ourselves to the case of potassium ions in helium and neon gases. These are the cases for which the assumption that collisions are entirely elastic is well justified, and the formulae referred to above are directly applicable. These are also among the few cases for which accurate and reliable experimental data on mobility are available. An earlier theoretical investigation by Mason and Schamp (1958) has suggested a realistic (12-6-4) model potential which provides a good basis for our more detailed study.

In Section II we discuss the numerical evaluation of the elements of the matrices which have to be inverted. In this an important step is the calculation of the interaction integrals (Section II(b)). It will be seen that for a realistic potential there are practical difficulties in calculating these integrals and hence the matrix elements for

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high values of the indices. Thus, since the size of the matrices are limited, the calculations can only extend up to the low and intermediate values of E/n_0 . The precise range that can be covered also depends upon the temperature and masses of the particles and has to be found separately for each particular case. Nevertheless, calculations can be made for a useful range of E/n_0 in which accurate comparison with experimental data is possible.

In Section III we study the effect on the mobility of varying different parameters of the Mason-Schamp (12-6-4) potential. It is shown that the comparison with experiment serves to determine the potential parameters within narrow limits. Using the parameters found from mobility experiments we have also calculated the longitudinal and transverse diffusion coefficients (Section III(e)). As in the electron case, experimental measurement of these quantities will provide an additional check on the values of potential parameters.

It may be noted that the qualitative features of the transport coefficients are now well understood. In particular Wannier (1970) has shown how the "bump" in the mobility versus field strength curve can be understood as a balancing of the contributions from the attractive and repulsive parts of the potential which occurs for certain particle energies. In a qualitative way this is related to the "dip" in the cross section versus energy curve (Wannier 1970, Figs. 1 and 2). Similar qualitative arguments can be applied to the diffusion coefficients also, especially since they have been related to mobility by a thermodynamic argument (Robson 1972). In the present work we do not seek an alternative qualitative understanding of this sort, but aim at a further stage of development where the main concern is with precision in calculations and comparison with experiment. Our results confirm this qualitative description and we find it convenient to describe some of them in terms of this picture.

II. NUMERICAL PROCEDURE

(a) Definition of Dimensionless Quantities

In numerical computation, it is desirable to work with dimensionless quantities. Following the usual practice (e.g. Hirschfelder *et al.* 1954; Mason and Schamp 1958) we use the parameters r_m and ε , which respectively characterize the range and depth of the attractive part of the ion-atom interaction, to define the dimensionless quantities. Thus the dimensionless field parameter is

$$\mathcal{E}^* \equiv \frac{\gamma}{\pi r_m^2} \mathcal{E} = \left(\frac{m_0}{m + m_0} \right)^{\frac{1}{2}} \frac{eE}{n_0 \pi r_m^2 k T_0}, \quad (1)$$

where the parameters γ and \mathcal{E} were introduced in Part I:

$$\gamma^2 \equiv m m_0 / (m + m_0) k T_0, \quad (2)$$

$$\mathcal{E} \equiv (m/k T_0)^{\frac{1}{2}} e E / n_0 m. \quad (3)$$

The energies are made dimensionless by using ε as a scaling parameter. Thus we have the dimensionless temperature

$$T^* = k T_0 / \varepsilon. \quad (4)$$

The dimensionless partial cross sections σ_l^* are expressed as functions of the dimensionless energy of relative motion. Thus, with

$$x = \frac{1}{2}\gamma^2 g^2 \quad (5)$$

and

$$\{\frac{1}{2}mm_0/(m+m_0)\}g^2/\varepsilon = xT^* \quad (6)$$

we have

$$\begin{aligned} \sigma_l^* &\equiv \sigma_l^*(xT^*) \equiv \sigma_l(g)/\pi r_m^2 \\ &= (2/r_m^2) \int P_l(\cos \chi) b \, db, \end{aligned} \quad (7)$$

where b is the impact parameter (see Appendix II of Kumar 1967).

The dimensionless interaction integrals are now defined as

$$\begin{aligned} V_{vv'}^{*l} &\equiv (\gamma/\pi r_m^2) V_{vv'}^l \\ &= N_{vv'}^l \int_0^\infty \exp(-x) x^{l+1} S_{l+\frac{1}{2}}^v(x) S_{l+\frac{1}{2}}^{v'}(x) \{\sigma_0^*(xT) - \sigma_l^*(xT^*)\} dx, \end{aligned} \quad (8)$$

with

$$N_{vv'}^l = \{v'! v! 2/\Gamma(v+l+\frac{3}{2})\Gamma(v'+l+\frac{3}{2})\}^{\frac{1}{2}}. \quad (9)$$

These quantities will be used below to express the mobility and diffusion coefficients also in terms of dimensionless matrices.

(b) Computation of Interaction Integrals

The scattering angle χ can be evaluated in terms of the impact parameter b and relative velocity g through well-known classical or quantum mechanical formulae (Smith and Munn 1964). A purely classical calculation was performed in the present work; quantum effects become apparent at only very low energies (see e.g. Catlow *et al.* 1970). The most efficient method for numerical evaluation of the classical integral for χ is by means of an adaptive quadrature formula (Hillstrom 1970). This technique is particularly suitable for dealing with the problem of orbiting, since the nodes of the integration are automatically distributed most densely in the region where the integrand is badly behaved, and it avoids the need for special precautions that are required in usual procedures (see e.g. Smith and Munn 1964; O'Hara and Smith 1970), and furthermore there is complete control over accuracy.

The quantities

$$\Delta\sigma_l^* \equiv \sigma_0^* - \sigma_l^* = (2/r_m^2) \int \{1 - P_l(\cos \chi)\} b \, db \quad (10)$$

can be calculated numerically using Gauss-Legendre quadrature in the same way as for the more familiar cross sections,

$$Q_l^* = (2/r_m^2) \int (1 - \cos^l \chi) b \, db$$

(Smith and Munn 1964). These integrals are difficult to evaluate to a high degree of

accuracy when l is large, since the integrand becomes highly oscillatory for such l values.

The quantities $\Delta\sigma_l^*$ are then used in equation (8) for computing the interaction integrals $V_{vv'}^{*l}$. Gauss-Laguerre quadrature generated by the weight function

$$w(x) = \exp(-x)x^{l+\frac{1}{2}}, \quad 0 \leq x \leq \infty,$$

(e.g. Stroud and Secrest 1966) was used for this purpose. Again because of the oscillatory character of the integrand, errors are greatest for large values of the indices. This is particularly important when the difference $|v-v'|$ is large, since in that case many subtractions are involved. However, these distant off-diagonal elements are generally much smaller than the diagonal elements (they vanish for the inverse fourth power potential; see Part I, Section IV), and are important in the calculation of mobility and diffusion only at high fields. The high l interaction integrals have a similar significance. Using the method outlined above, it was estimated that for low l (< 3) values, the errors for diagonal and the farthest off-diagonal ($|v-v'| = 10$) elements of $V_{vv'}^{*l}$ were no more than a few parts in 10000 and 1% respectively; for high l these errors were estimated to be a few parts in 1000 and a few per cent respectively. With the interaction integrals known to this accuracy the transport coefficients are estimated to be obtainable to an accuracy within 0.1%, up to intermediate values of the field strength parameter E/n_0 .

(c) Computation of Transport Coefficients

If we define the dimensionless collision matrix

$$\begin{aligned} J_{v_1 v_2}^{*l_1} &\equiv (\gamma/\pi r_m^2) J_{v_1 v_2}^{l_1} \\ &= \sum_{v=0}^{v_1} \sum_{v'=0}^{v_2} \sum_{l=0}^{l_1+v_1-v} X(l_1 v_1 v_2 | l v v') \left(\frac{m}{m+m_0} \right)^{2(v_1-v)+l_1-l} \\ &\quad \times \left(\frac{m_0}{m+m_0} \right)^{l+v+v'} V_{vv'}^{*l}, \end{aligned} \quad (11)$$

where the quantity $X(l_1 v_1 v_2 | l v v')$ is given by equation (I, 82), the expression for the reduced mobility (equations (I, 118) and (I, 117)) becomes

$$\mathcal{K} = \frac{e}{n_s \pi r_m^2} \left(\frac{m_0}{m(m+m_0)kT_0} \right)^{\frac{1}{2}} (M^*)_{01,01}^{-1}, \quad (12)$$

with

$$M_{v_1 l_1, v_2 l_2}^* \equiv (\gamma/\pi r_m^2) M_{v_1 l_1, v_2 l_2} = J_{v_1 v_2}^{*l_1} \delta_{l_2 l_1} + \mathcal{E}^* D_{v_1 l_1, v_2 l_2}. \quad (13)$$

The matrix \mathbf{D} is defined by equations (I, 97)–(I, 99) and the structure of \mathbf{M}^* is shown in Section III(c) of Part I.

In terms of dimensionless quantities, equations (I, 119) and (I, 136) for the effective temperature and diffusion tensor become respectively

$$T^{\text{eff}}/T_0 = 1 - \frac{1}{3}\sqrt{2} \mathcal{E}^* (M^*)_{10,01}^{-1} \quad (14)$$

and

$$\mathcal{D}_\mu = \frac{1}{n_0 \pi r_m^2} \left(\frac{m_0 k T_0}{m(m+m_0)} \right)^{\frac{1}{2}} \sum_{v'l'} [P^*(\mu)]_{01, v'l'}^{-1} k(\mu)^{v'l'}, \quad \mu = 0, \pm 1, \quad (15)$$

where $k(\mu)$ is defined by equation (I, 131) and

$$\begin{aligned} P^*(\mu)_{v_1 l_1, v_2 l_2} &\equiv (\gamma/\pi r_m^2) P(\mu)_{v_1 l_1, v_2 l_2} \\ &= J_{v_1 v_2}^{* l_1} \delta_{l_2 l_1} + i \mathcal{E}^* (10 l_2 \mu | l_1 \mu) (v_1 l_1 || K^{[1]} || v_2 l_2). \end{aligned} \quad (16)$$

Other notation has been introduced in Part I, Section III. The longitudinal and transverse diffusion coefficients are given by

$$\mathcal{D}_L = \mathcal{D}_0, \quad \mathcal{D}_T = \mathcal{D}_{\pm 1}. \quad (17)$$

Note that the results of calculation of the diffusion coefficients are conventionally given in terms of the ratio \mathcal{D}/K , which is the quantity measured in experiments (Huxley and Crompton 1962). In this ratio K is the mobility which is related to the reduced mobility \mathcal{K} of equation (12) by

$$K = (n_s/n_0) \mathcal{K} \quad (18)$$

Equations (12), (14), and (15) are evaluated by setting upper limits l_{\max} and v_{\max} to the Legendre and Sonine polynomial indices respectively. A physical interpretation of this type of truncation has been given previously (Part I, Section IV; Robson and Kumar 1971). The dimension of the matrices \mathbf{M}^* and \mathbf{P}^* corresponding to this truncation is $\{(l_{\max}+1)(v_{\max}+1)-1\}$. It can be seen from equation (11) that interaction integrals $V_{vv'}^{* l}$ with l and v indices up to $l_{\max}+v_{\max}$ and v_{\max} respectively are required in this approximation.

The parameter \mathcal{E}^* defined by equation (1) and occurring in equations (13), (14), and (16) is a measure of the ratio of the energy gained by an ion from the field during a mean free path to the thermal energy of gas atoms. Conventionally (e.g. McDaniel 1964), the field is "high" for $\mathcal{E}^* \gg 1$ and "low" for $\mathcal{E}^* \ll 1$. The intermediate region here is taken to be $\mathcal{E}^* \approx 1$.

We have already remarked in Part I upon the similarity between the present problem and the sound propagation calculations. On the basis of experience in the latter problem, it can be anticipated that very large matrices (i.e. large values of l_{\max} and v_{\max}) will be required for $\mathcal{E}^* \gg 1$. We illustrate the nature of the convergence of $(M^*)^{-1}$ with the order of truncation for a hard sphere interaction of radius r_m . This model was chosen initially because the partial cross sections have a simple form, namely

$$\sigma_l^* = \delta_{l0},$$

and the interaction integrals of equation (8) can be evaluated analytically.

The matrix element appropriate to mobility is $(M^*)_{01,01}^{-1}$. For K^+ ions in helium, Figure 1(a) shows successive approximations to this matrix element obtained by fixing $l_{\max} = 2$ and varying v_{\max} . It is evident that the value of v_{\max} required to achieve convergence to within a reasonable accuracy increases rapidly with \mathcal{E}^* . Thus,

for example, setting $\nu_{\max} \geq 4$ fixes $(M^*)_{01,01}^{-1}$ to within 1% at $\mathcal{E}^* = 1$, but for $\mathcal{E}^* = 1.75$ we require $\nu_{\max} \geq 10$ in order to achieve a similar degree of accuracy. For $\mathcal{E}^* \gg 2$ (high fields) Sonine polynomials of very large indices ($\nu_{\max} \gg 10$) are needed. On the other hand, convergence with respect to Legendre polynomial

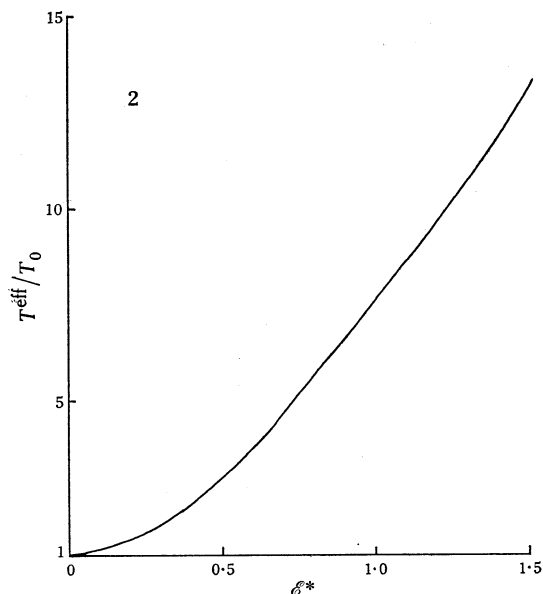
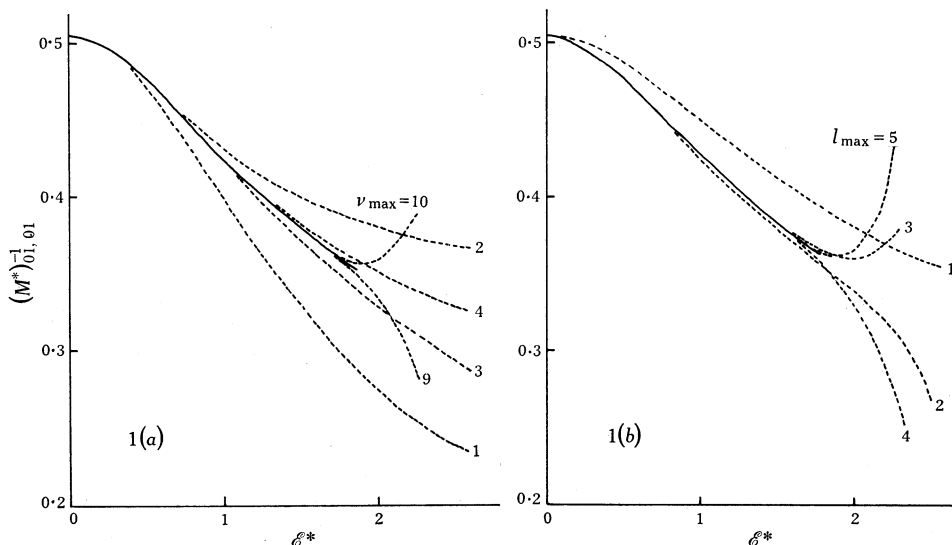


Fig. 1 (*above*).—Convergence with ν -truncation of the inverse matrix element $(M^*)_{01,01}^{-1}$ associated with the mobility (equation (12)) for K^+ ions in helium (hard sphere interaction). The dashed curves show the approximations provided by taking (*a*) a fixed order of Legendre polynomial truncation ($l_{\max} = 2$) with the indicated values of ν_{\max} and (*b*) a fixed order of Sonine polynomial truncation ($\nu_{\max} = 7$) with the indicated values of l_{\max} . The solid curves represent the values to which successive approximations converge.

Fig. 2 (*left*).—Temperature ratio T^{eff}/T_0 of equation (14) for potassium ions in helium with $l_{\max} = 3$ and $\nu_{\max} = 10$.

truncation for a fixed value of ν_{\max} (Fig. 1(*b*)) is relatively fast in the low and intermediate field regions ($\mathcal{E}^* \leq 2$). Setting $l_{\max} = 2$ furnishes a reasonable estimate of the matrix element in this range. However, for $\mathcal{E}^* \gg 2$, it is clear that very large values of l_{\max} are required. Note that the mobility, which is proportional to $(M^*)_{01,01}^{-1}$,

is a monotonically decreasing function of field strength for a hard sphere interaction (this would be expected from the arguments of Part I, Section IV, since in this case it can be shown from equation (8) that all off-diagonal elements of V_{vv}^l are negative).

In Figure 2 the ratio T^{eff}/T_0 of equation (14) has been plotted as a function of \mathcal{E}^* for $l_{\text{max}} = 3$ and $v_{\text{max}} = 10$. The nature of the convergence of these values with successive orders of truncation is similar to that for the matrix element $(M^*)_{01,01}^{-1}$, and errors are at worst a few per cent at higher values of \mathcal{E}^* . It is clear that the mean ion energy $\frac{1}{2}m\langle c^2 \rangle = \frac{3}{2}kT^{\text{eff}}$ increases rapidly with field strength. (Note that the curves in Figures 1 and 2 are independent of T_0 for this hard sphere interaction.)

Although the model of hard sphere interaction used above is rather unphysical, it is found that the pattern of convergence is much the same for more realistic models. Thus, to intermediate field strengths, mobility can be determined to quite a high degree of accuracy (estimated to be 0.1% in the following work) by comparing successive orders of truncation in the range $2 \leq l_{\text{max}} \leq 4$ and $5 \leq v_{\text{max}} \leq 10$. Similar remarks apply to calculation of diffusion coefficients, since the matrices \mathbf{M}^* and \mathbf{P}^* have a similar block structure.

The very high field region ($\mathcal{E}^* \gg 2$) seems inaccessible with the present method for the following reasons. Firstly, it is found that the computing time increases quite sharply with the increase in the size of matrices. Secondly, the matrices become increasingly ill-conditioned for inversion (Forsyth and Moler 1967) at high values of field and for large dimensions. The third and perhaps most serious limitation arises from the fact that the number of interaction integrals required to form the matrices \mathbf{M}^* and \mathbf{P}^* increases dramatically with the order of truncation, and it has already been remarked (see subsection (b) above) that for realistic potentials the V_{vv}^{*l} with large indices are difficult to calculate to high accuracy. For the extremely large indices that will be required for a high field calculation, computation of V_{vv}^{*l} may not always be practicable.

The nature of the last-mentioned difficulty may be better understood if we note that by virtue of the linear relation between V_{vv}^l and the more familiar collision integrals $\Omega^{(l,s)}$ (Kumar 1967, Appendix II) the range of indices of $\Omega^{(l,s)}$ required for a calculation to order $l_{\text{max}}, v_{\text{max}}$ is

$$1 \leq l \leq l_{\text{max}} + v_{\text{max}}, \quad 1 \leq s \leq 2v_{\text{max}} + l_{\text{max}}.$$

This means that for the largest matrices used in the present work ($l_{\text{max}} = 4$, $v_{\text{max}} = 10$) we have in effect used $\Omega^{(l,s)}$ with indices up to $l = 14$, $s = 24$. This is to be compared with the tables of $\Omega^{(l,s)}$ published in the literature (see e.g. Mason 1969, and references listed therein), which normally are within the ranges $1 \leq l \leq 5$, $1 \leq s \leq 7$.

III. COMPARISON OF THEORY AND EXPERIMENT

(a) Mason-Schamp Potential

Mason and Schamp (1958) suggested the form

$$\phi(r) = \varepsilon \{ A_N (r_m/r)^{2N} - B_N (r_m/r)^6 - C_N (r_m/r)^4 \} \quad (19)$$

for the ion-atom interaction potential. Here ε and r_m denote the depth and position

of the potential minimum, while

$$A_N = 2(\gamma + 1)/(N - 2), \quad (20)$$

$$B_N = 2\gamma, \quad (21)$$

$$C_N = \{N - 2\gamma(N - 3)\}/(N - 2). \quad (22)$$

The new parameter γ is not to be confused with the symbol appearing in Section I.

In the original work of Mason and Schamp (1958), N was fixed equal to 6, but we wish to retain some flexibility in manipulation of the strength of the repulsive core, since representation of the latter by an inverse power law is questionable and indeed other forms may be more appropriate (Dalgarno *et al.* 1958; Catlow *et al.* 1970). In contrast to the *ad hoc* character of the repulsive part of the potential (19), the physical origin of the attractive terms is well established. Thus, the inverse fourth power represents point-charge-induced-dipole attraction or the polarization force, while the inverse sixth power accounts for point-charge-induced-quadrupole attraction and London dispersion energy.

In the following work we indicate how the parameters of the potential can be determined by fitting mobility data from ion swarm experiments. Note that *ab initio* determination of the potential is possible in principle from quantum mechanics, but the associated difficulties are prohibitive in all but the simplest cases (Catlow *et al.* 1970) and no such potentials are available for use in the present work.

(b) Dependence of Mobility on Gas Temperature

Most previous theoretical work has been devoted to the analysis of the temperature dependence of mobility at zero fields. For this situation, Mason and Schamp (1958) have illustrated the effects of variation of the parameters of equation (19) while Dalgarno *et al.* (1958) and Catlow *et al.* (1970) have used somewhat different forms of potentials together with quantum-mechanical cross sections. Other calculations of the zero-field mobility have been performed by Langevin (1905) using the so-called Sutherland potential and by Hassé and Cook (1931) using an 8-4 potential.

TABLE 1
PARAMETER SETS USED TO CALCULATE THEORETICAL CURVES

Parameter Set	Ions in gas	γ	ε (eV)	r_m (Å)
A	K ⁺ ions in helium	0.27	0.0246	2.72
B	K ⁺ ions in neon	0.28	0.0430	2.82

We consider only briefly the variation of the mobility with temperature, since the more accurate determination of interaction potential is obtained from the study of field dependence. Figure 3 shows the curves of \mathcal{K} versus T_0 for K⁺ ions in helium at three values of E/n_0 , calculated using a 12-6-4 potential with the parameter values given in set A of Table 1. Following convention, E/n_0 has been expressed in units of townsend (1 townsend (Td) = 10^{-17} V cm²). It is evident that the effect of an increase in field is to shift the mobility maximum towards a lower temperature. This

effect may be interpreted through the arguments given by Wannier (1970) (see also Kihara 1953; Mason and Schamp 1958): thus an increase in the field produces a corresponding increase in the mean ion energy (see Fig. 5 below) with the result that the influence of the repulsive core becomes apparent at a lower temperature. Note that the zero-field mobility increases with T_0 below about 380 K; for these temperatures it can be anticipated that the initial slope of the mobility versus field curve will be positive (Part I, Section IV).

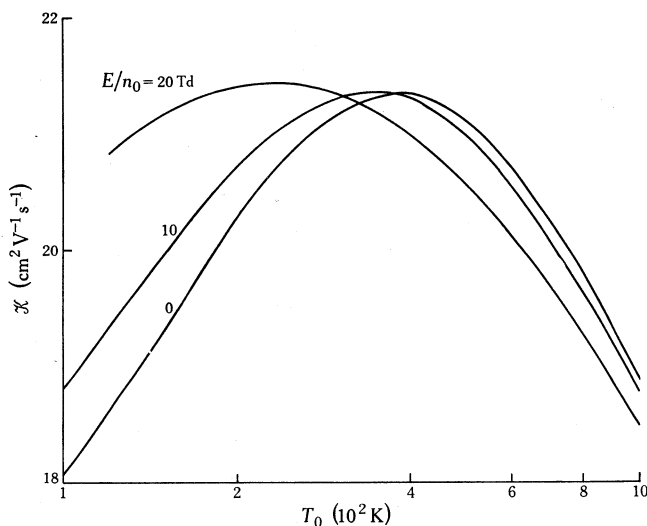


Fig. 3.—Reduced mobility \mathcal{K} of K^+ ions in helium as a function of gas temperature for three values of E/n_0 . The curves have been calculated assuming a 12-6-4 potential with the parameter set A in Table 1.

(c) *Dependence of Mobility on E/n_0 : Fitting Experimental Data*

Figures 4(a) and 4(b) show the calculated curves of \mathcal{K} versus E/n_0 using a 12-6-4 potential, with the parameters given in Table 1, for potassium ions in helium and neon respectively. Experimental measurements of mobility at room temperature (M. T. Elford, personal communication) are also included in the figures. The theoretical values were calculated to an accuracy of $\pm 0.1\%$ (or better) by increasing the size of the matrix in equation (12) until successive approximations converged to within the prescribed limits. As noted earlier, the convergence becomes slower with increasing field strength, and for this reason we have not covered the whole of the experimentally available range of E/n_0 . Nevertheless, even for this limited range of fields the control over the accuracy of the theoretical mobilities coupled with the high precision of the experimental data (the error is estimated to be less than 0.5% for K^+ ions in helium and 1% for K^+ ions in neon) fixes the potential parameters quite accurately.

A good initial estimate of the parameters can be obtained by considering extreme points on the experimental curve (e.g. points at zero field and on the “bump” respectively) and by taking into account the way in which each parameter separately influences the mobility (see subsection (d) below). The parameters can then be varied

until some criterion for goodness of fit (e.g. minimization of maximum difference between experimental and theoretical curves) is attained. The accuracy of the parameters is thus determined by the range over which they can be varied such that the theoretical curve always lies within the bounds of experimental error.

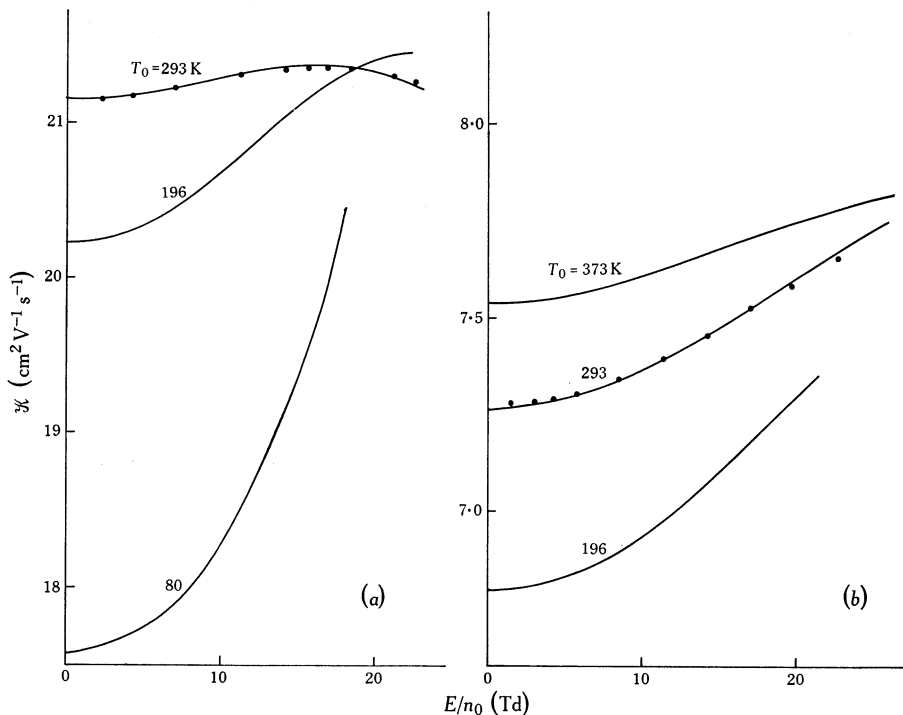


Fig. 4.—Calculated curves of the variation of the reduced mobility \mathcal{K} with E/n_0 at three different gas temperatures for (a) K^+ ions in helium, assuming a 12-6-4 potential with the parameter set A in Table 1, and (b) K^+ ions in neon, assuming a 12-6-4 potential with the parameter set B. The experimental points at 293 K are from M. T. Elford (personal communication).

The experimental mobility data at room temperature were sufficient to fix only the depth and position of the potential minimum. Since the mobility is sensitive to changes in the parameter γ only at low temperatures (see Fig. 6(b)) it was found necessary to determine it from the relation between ϵ , r_m , γ , and the polarizability p of the gas atom (Mason and Schamp 1958):

$$3\epsilon r_m^4(1-\gamma) = e^2 p. \quad (23)$$

Tables of polarizability given by Rothe and Bernstein (1959) were used. Final values obtained for the parameters of the 12-6-4 potential, together with their estimated accuracies, were:

	ϵ (eV)	r_m (Å)	γ	Exp. accuracy
K^+ ions in He	0.0246 ± 0.0002	2.72 ± 0.01	0.27 ± 0.01	0.5%
K^+ ions in Ne	0.0430 ± 0.0006	2.82 ± 0.02	0.28 ± 0.03	1%

If in the future accurate experimental mobilities become available at lower gas temperatures, it would be possible to fix γ independently of polarizability, and indeed equation (23) could then be used to predict p . It is hoped that the present work will serve to stimulate progress in this direction.

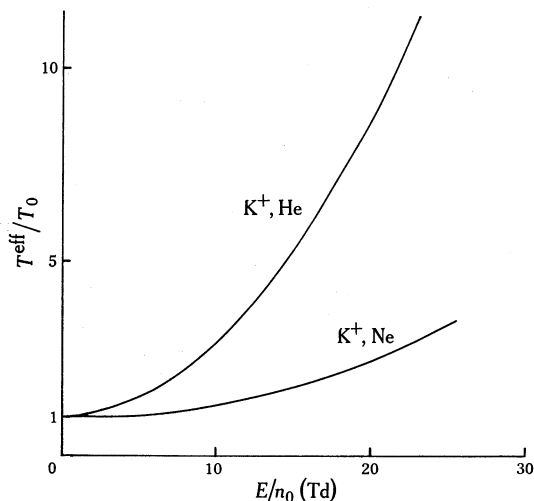


Fig. 5.—Variation with field of the mean energy of K^+ ions in helium and neon, as shown by curves for the temperature ratios at $T_0 = 293$ K calculated using the potential parameter sets A and B in Table 1.

It is interesting to note the way in which the mean ion energy $\frac{1}{2}m\langle c^2 \rangle (= \frac{3}{2}kT^{\text{eff}})$ increases with field. Figure 5 shows that the ratio T^{eff}/T_0 of the mean ion energy to the thermal energy of the gas atoms increases more strongly for K^+ ions in helium, so that the effects of the repulsive core (as evidenced by the appearance of a “bump” in the mobility curve) become apparent at a lower value of the field strength parameter than for K^+ ions in neon. Physically speaking, the steep rise in the energy of the ions in helium may be attributed to the large disparity between the masses of the ion and the neutral atom ($m/m_0 \approx 10$): because of this large mass ratio, energy is not efficiently exchanged in collisions and the ions have a greater capacity to store energy gained from the field. On the other hand, for K^+ ions in neon, the masses are more comparable ($m/m_0 \approx 2$) and therefore energy is exchanged more efficiently in collisions and the capacity of the ions to store energy is not as great (Wannier 1953).

(d) Effects of Varying Potential Parameters

We illustrate here, by way of direct numerical calculation, how the parameters of the potential (19) control the shape of the mobility versus field curve for K^+ ions in helium. Only variations in N , γ , and ϵ are shown explicitly since the parameter r_m enters solely as a scaling factor for both mobility and field axes.

Figure 6(a) shows that the effect of an increase (10% in this case) in the depth ϵ of the potential well is to increase the height of the mobility maximum above the zero-field value. Thus, a deepening of the potential broadens the range of energies over which the effects of attractive and repulsive parts of the potential tend to balance, and the transparency of the gas to the ions is significantly enhanced.

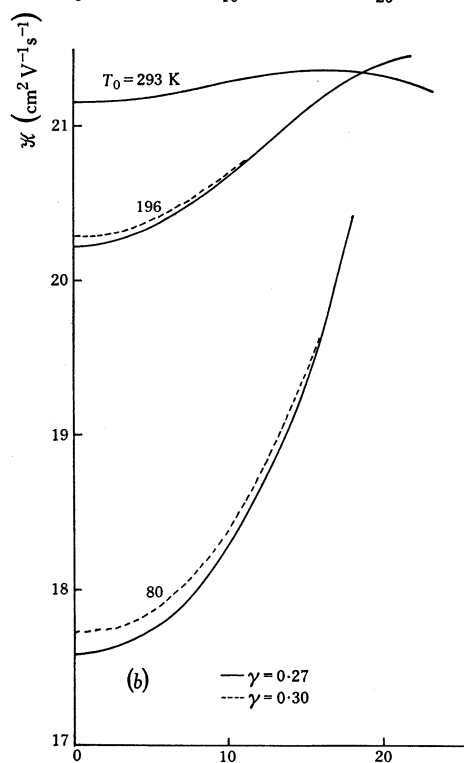
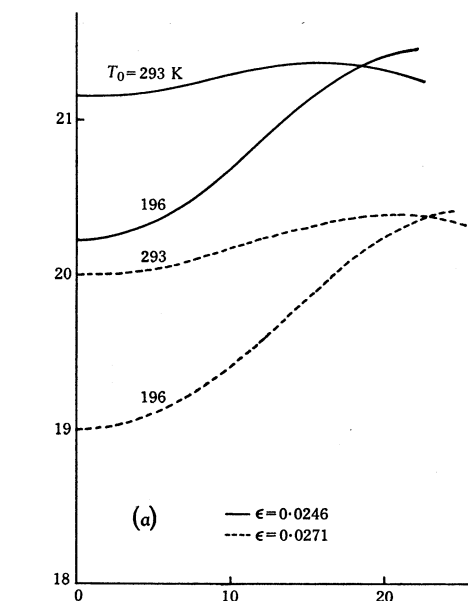
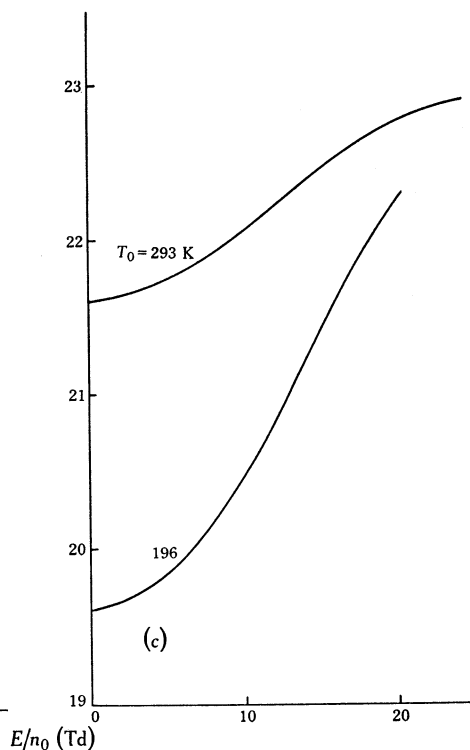


Fig. 6.—Reduced mobilities \mathcal{K} of K^+ ions in helium for:

(a) two values of the well-depth parameter ϵ for a 12-6-4 potential, with γ and r_m as in parameter set A of Table 1;

(b) two values of γ for a 12-6-4 potential, with ϵ and r_m as in parameter set A (the changes produced by variations in γ at 293 K are too small to be shown);

(c) an 8-6-4 potential and parameter set A. Note in (c) the substantial increase in the height of the mobility maximum due to softening of the repulsive core.



The effect of a small change in γ (the parameter which determines the strength of the inverse sixth power attraction) is shown in Figure 6(b). At high fields and temperatures, the repulsive core of the interaction dominates and the effect of the attractive terms is insignificant. As would be expected, it is the mobility at low fields and temperatures which is most sensitive to changes in γ .

Figure 6(c) shows how a softening of the repulsive core greatly increases the height of the mobility maximum. In terms of the arguments of Wannier (1970) this means that a softer core can balance the contributions from the attractive part of the potential more effectively and thus give a higher mobility at the maximum.

It was found that an inverse twelfth power repulsion was adequate for fitting experimental data for K^+ ions in helium and neon in the low and intermediate range of fields. However, in another case which is presently being examined (Li^+ ions in helium), it seems that a much softer repulsive core is required to obtain good agreement at even low fields.

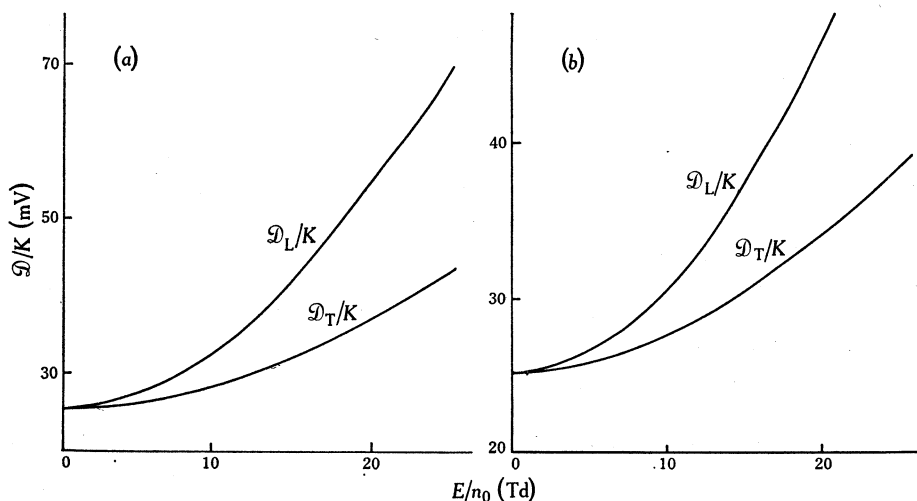


Fig. 7.—Longitudinal and transverse diffusion coefficients at $T_0 = 293$ K calculated from a 12-6-4 potential for (a) K^+ ions in helium, with the parameter set A in Table 1, and (b) K^+ ions in neon, with the parameter set B.

(e) Anisotropic Diffusion Coefficients

With the interaction potential determined from the mobility data one can calculate the transverse and longitudinal diffusion coefficients from equations (15) and (17). At present, no experimental data are available which can be compared with the calculated diffusion coefficients, but we present the results of such a calculation here as an example of what is now theoretically possible. Since mobility and diffusion coefficients have markedly different dependences upon the field strength, a simultaneous fitting of all experimental coefficients when it becomes possible would yield very precise information on the interaction potential.

Figures 7(a) and 7(b) show longitudinal and transverse diffusion coefficients (expressed as the ratio \mathcal{D}/K , where K is the mobility) for K^+ ions in helium and neon

respectively at room temperature. The curves at other temperatures have much the same qualitative features, namely that both \mathcal{D}_L and \mathcal{D}_T increase strongly with field and that $\mathcal{D}_L/\mathcal{D}_T$ is greater than unity and increases with field. A thermodynamic analysis of this problem has been given by Robson (1972), where it has been shown that \mathcal{D}_L and \mathcal{D}_T in the low field region are largely controlled by the random energies of the ions that are parallel and perpendicular to the field respectively.

We have also used equation (15) to calculate \mathcal{D}_L and \mathcal{D}_T for electrons in helium and have compared the results with those of Lowke and Parker (1969). In order to obtain a check on the correctness of equation (15), we set $l_{\max} = 1$ (corresponding to a two-term approximation) and varied v_{\max} to obtain convergence. The results agreed to within 1% of Lowke and Parker values over a significant range of field strengths. The importance of higher Legendre polynomials for electron diffusion coefficients was also investigated along the lines of an earlier work on mobilities (Robson and Kumar 1971). As in that case, it was found that the corrections to the two-term approximation would be very small. It will be noted that for ions it is necessary to take $l_{\max} \geq 2$ to adequately represent even the region of very low values of E/n_0 .

IV. CONCLUSIONS

When considering the transport of ions, the distribution function is substantially anisotropic so that a large number of terms are needed in the Legendre polynomial expansions. In the present formulae this means that high values of l must be retained. Our calculations of ion transport coefficients, and of the very small corrections to the two-term approximations in the electron case, show that the effect of anisotropy can be treated with reasonable success. This success is somewhat limited, however, because the whole range of the field strength parameter E/n_0 (or \mathcal{E}^*) cannot be covered, mainly due to the truncation in the Sonine polynomial indices v . It was argued in Part I that the approximation obtained from any size of (truncated) matrix will not be good over the whole range of this parameter. Numerical work in connection with the present paper shows that this limitation becomes quite severe in some cases and the region of high values of E/n_0 (or \mathcal{E}^*) remains inaccessible to such treatments because of the difficulties in calculating the corresponding interaction integrals (Section II). In some cases it is possible to cover only a very small range of E/n_0 .

In spite of the limitations, the present numerical work has shown that in the cases considered here it is possible to cover a useful range of the field strength parameter, and, using mobility data alone, the potential parameters appear to be determined to an accuracy† as good as that of the experimental measurements. Further improvement of the potential may be possible if diffusion coefficients are also measured for these values of the parameters.

Certain ion-molecule interactions have been calculated from first principles, and different theoretical treatments lead to cross sections differing in some respects, mainly at low energies. Since the present method is well suited for calculations at low values of E/n_0 , transport coefficients from these different cross sections may be

† This point requires investigation, which can be best carried out by fitting a greater variety of experimental data over a wider range of E/n_0 and T_0 , and using other forms of potentials.

calculated for a suitable range of E/n_0 . Sufficiently accurate experimental determination of these quantities may then be useful in deciding between the theories.

We have indicated here the scope of the present method by means of some specific examples. Our main concern has been to keep track of the accuracy of calculations at all stages, so that potentials are determined to within known limits. It is difficult to make comparison with other methods. Wannier (1953) has proposed a theory for high fields while Monte Carlo calculations by Skullerud (1972) cover the whole range of the field strength parameter, but it is not clear how well the potential can be determined from these theories.

V. REFERENCES

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