Chemical Physics 153 (1991) 351–370
North-Holland

Generalized Einstein relations for ions in molecular gases

A.D. Koutselos [1] and E.A. Mason
Brown University, Providence, RI 02912, USA

Received 30 November 1990

Generalized Einstein relations (GER) connecting ion diffusion coefficients with the mobility are extended to include internal degrees of freedom and inelastic collisions. The Boltzmann equation is solved by means of a four-temperature theory that includes as parameters the gas temperature, two translational ion temperatures, and one internal ion temperature. The results reduce in the limit of elastic collisions to those obtained by Waldman and Mason from a three-temperature theory. In addition, an analytic procedure is developed for the calculation of the unobservable ion temperatures and correction terms that appear in the GER. The analytic procedure is checked by comparison with numerical results and experimental data for the elastic-collision limit. The general results are tested numerically with an inelastic two-state model and with a semiempirical analysis of experimental results on K^+ in H_2 and N_2. More details on ion–molecule inelastic collisions are needed for further progress.

1. Introduction and background

The transport of trace amounts of ions and electrons in neutral gases under the influence of an electrostatic field has been studied for many years [1–3]. The existence of a relation between mobility and diffusion has long been expected on physical grounds, and it is now well understood how to produce such a relation on the basis of solutions of the Boltzmann equation [3,4]. At low fields the relation is the exact Nernst–Townsend–Einstein relation [3],

$$qD/K=kT, \tag{1}$$

where D and K are the diffusion and mobility coefficients, q is the ionic charge, k is Boltzmann's constant, and T is the temperature. However, at high fields both D and T become different in directions perpendicular and parallel to the field, correction terms appear in eq. (1), and the relations between mobility and diffusion, now usually called generalized Einstein relations (GER), become only approximate. These GER are nevertheless quite useful because ion mobilities are easier to measure than are ion diffusion coefficients.

There is no essential difficulty in obtaining *formal* relations between diffusion and mobility from the Boltzmann equation, even if inelastic collisions occur, but two main problems must still be solved in order to obtain useful final results:

(i) find expressions for the correction terms which can be evaluated from measured mobilities or from simple models of ion-neutral interactions;

(ii) find expressions whereby the ion temperatures can be calculated from measured mobilities or from simple models.

The second problem is especially important because the diffusion coefficients are directly proportional to the ion temperatures, and the latter have proved essentially impossible to measure independently, with two notable exceptions involving Ba^+ ions [5]. Both problems can be summarized by saying that the correction terms and the ion temperatures are not directly measurable.

---

[1] Present address: Department of Chemistry, University of Athens, Athens, Greece.

0301-0104/91/$ 03.50 © 1991 – Elsevier Science Publishers B.V. (North-Holland)

Reasonably satisfactory results have been obtained for the case where only elastic collisions occur, but only fragmentary results are available for the case where inelastic collisions occur. The purpose of this paper is to obtain GER that can be used when inelastic ion-neutral collisions occur.

We first briefly summarize the current status of GER for the elastic-collision case, since the structure of the present more general results is quite similar. The present results must also reduce to the elastic-collision results as a limiting case.

If all ion-neutral collisions are elastic, then suitable moment solutions of the Boltzmann equation yield relations of the form [4],

$$qD_{\perp}/K = kT_{\perp}[1 + \Delta_{\perp}K'/(2+K')] , \tag{2}$$

$$qD_{\parallel}/K = kT_{\parallel}(1 + K' + \Delta_{\parallel}K') , \tag{3}$$

where the subscripts $\perp$ and $\parallel$ refer to directions perpendicular and parallel to the electric field, respectively, and

$$K' \equiv \mathrm{d}\ln K/\mathrm{d}\ln(E/N) , \tag{4}$$

in which E is the electric field strength and N is the neutral gas number density. The quantities K and K' can be taken from experiment. A small term involving a second derivative K'' has been dropped from eq. (3). The correction terms $\Delta_{\perp,\parallel}$ and the temperatures $T_{\perp,\parallel}$ can be found by numerical solution of some coupled moment equations. Since this is a laborious procedure requiring knowledge of the ion-neutral interaction potential, simple parameterized formulas for these quantities have been developed [3,4], as follows.

The correction terms $\Delta_{\perp,\parallel}$ depend primarily on the ion-neutral mass ratio and only weakly on the ion-neutral interaction, and so can be given accurately enough for most purposes by a small numerical table [3,4].

The temperatures are more difficult to parameterize, but can be put in the following form:

$$kT_{\perp} = kT + \zeta_{\perp}Mv_{\mathrm{d}}^{2}(1 + \beta_{\perp}K') , \tag{5}$$

$$kT_{\parallel} = kT + \zeta_{\parallel}Mv_{\mathrm{d}}^{2}(1 + \beta_{\parallel}K') , \tag{6}$$

where $v_{\mathrm{d}} = KE$ is the drift velocity (an experimental quantity), and M is the mass of a neutral gas molecule. The dimensionless coefficients $\zeta_{\perp,\parallel}$ can be found in a low order of solution of the moment equations, but the dimensionless parameters $\beta_{\perp,\parallel}$ are treated in a strictly empirical manner. The coefficients $\zeta_{\perp,\parallel}$ are given by

$$\zeta_{\perp} = \frac{(m+M)\tilde{A}}{4m+3M\tilde{A}} , \quad \zeta_{\parallel} = 1 - 2\zeta_{\perp} , \tag{7}$$

where m is the mass of an ion and $\tilde{A}$ is a dimensionless ratio of two collision integrals (temperature-dependent cross sections). It depends only on the ion-neutral interaction, but not very sensitively because it is a ratio. Tabulations of $\tilde{A}$ for several kinds of interactions are available [3,4]. The factor $(1+\beta_{\parallel}K')$ was introduced empirically by Skullerud [6] because the analytical formula for $T_{\parallel}$ gave poor results when tested against accurate numerical calculations for specific ion-neutral models. These model calculations indicated that $\beta_{\perp} \approx 0$ and that $\beta_{\parallel}$ depends primarily on the ion-neutral mass ratio and only weakly on the ion-neutral interaction, so that it too can be given in the form of a small numerical table [3,4,6].

Refinements of the foregoing results have been given for the special cases of resonant charge transfer [3,7] and of electron diffusion in monatomic gases [8], but the details need not concern us here.

The introduction of inelastic collisions modifies the foregoing elastic-collision results in the following five main ways:

First, the appearance of the GER, namely eqs. (2) and (3), is not changed by the introduction of inelastic collisions, but the correction terms $\Delta_{\perp,\parallel}$ and the temperatures $T_{\perp,\parallel}$ must be handled somewhat differently. They are still to be found by numerical solution of a set of coupled moment equations, but the coefficients of these equations (i.e., matrix elements) contain inelastic cross sections that affect the solutions of the equations.

Second, the most serious result of the presence of inelastic cross sections is that a parameterization for the

$\Delta_{\perp,\parallel}$ is no longer generally possible – these correction terms now depend on the inelastic cross sections and the ion temperatures as well as on the mass ratio, and cannot be summarized by a convenient numerical table. However, we are able to make some physically reasonable approximations that greatly reduce the complexity of the calculations. In particular, only two simultaneous moment equations need to be solved to find the $\Delta_{\perp,\parallel}$.

Third, the moment equations for the temperatures can be solved to yield results that have nearly the same appearance as the elastic-collision result of eqs. (5) and (6), but with more complicated expressions for the coefficients. In place of eqs. (5) and (6) we obtain

$$kT_{\perp}[1+\tfrac{1}{2}(M/m)\tilde{G}]=kT+\zeta_{\perp}Mv_{\mathrm{d}}^{2}(1+\beta_{\perp}K')\,, \tag{8}$$

$$kT_{\parallel}[1+\tfrac{1}{2}(M/m)\tilde{G}]=kT+\zeta_{\parallel}Mv_{\mathrm{d}}^{2}(1+\beta_{\parallel}K')\,, \tag{9}$$

where $\tilde{G}$ is a dimensionless ratio of a collision integral for inelastic energy loss to a collision integral for momentum transfer.

Fourth, the coefficients $\zeta_{\perp,\parallel}$ are modified to

$$\zeta_{\perp}=\frac{(m+M)(\tilde{A}-\tilde{G})}{4m+M(3\tilde{A}-\tilde{G})}\,,\quad \zeta_{\parallel}=1-2\zeta_{\perp}-\tfrac{1}{2}\tilde{G}\,. \tag{10}$$

For elastic collisions, $\tilde{G}=0$ and the previous results for $T_{\perp,\parallel}$ and $\zeta_{\perp,\parallel}$ are recovered. Unfortunately, $\tilde{G}$ depends on the ion temperatures and so eqs. (8)–(10) must be solved iteratively.

Fifth, a significant new result, applying to both elastic and inelastic collisions, is the derivation of explicit expressions for the correction terms $\beta_{\perp,\parallel}$, which were originally introduced empirically. We still find $\beta_{\perp}\approx 0$, but $\beta_{\parallel}$ is now given by

$$\beta_{\parallel}=\left(\frac{1-\kappa}{1+\frac{1}{2}\kappa K'}\right)\frac{1+[1-\kappa-\frac{3}{4}\tilde{G}(kT/Mv_{\mathrm{d}}^{2})]K'}{1+(1+\frac{1}{2}\kappa)K'}\,, \tag{11}$$

where

$$\kappa\equiv\frac{M}{m+M}(1-\tfrac{1}{2}\tilde{G})\,. \tag{12}$$

This gives fair agreement with the empirical values of $\beta_{\parallel}$ recommended for the elastic-collision case ($\tilde{G}=0$), and is more widely applicable.

In short, the introduction of inelastic collisions does not change the formal appearance of the GER very much, but the determination of the ion temperatures and of the correction terms is, not unexpectedly, more complicated. In particular, a simple parameterization in terms of mass ratio is no longer possible, so some numerical iteration is unavoidable in practical applications.

Tests of the present GER by comparison with model calculations and with experimental measurements generally show good agreement. However, the problem of electron transport remains difficult, as it is even in the elastic-collision case [8].

Finally, we should mention some precursors of the present GER, particularly the use of momentum-transfer theory by Robson [9,10] to discuss the correction terms $\Delta_{\perp,\parallel}$. Momentum-transfer theory is a form of low-order moment theory that emphasizes physical interpretation [3]. Robson obtained $\Delta_{\perp}=0$ and an approximation for $\Delta_{\parallel}$, which he used to discuss the phenomenon of negative differential conductivity, in which $(\mathrm{d}v_{\mathrm{d}}/\mathrm{d}E)_{\parallel}<0$ for a range of E [10,11]. This phenomenon has been observed for electrons in some polyatomic gases. It requires the term $\Delta_{\parallel}$ to play a major role rather than act as just a small correction, in order to avoid predicting a negative value of $D_{\parallel}$. Unfortunately, momentum-transfer theory in its present form does not offer an independent way of determining $T_{\perp}$ and $T_{\parallel}$. Use of a full moment theory by Viehland et al. [12] to calculate ion temperatures was only partially successful, since the calculation scheme they used did not produce the important correction represented by $\beta_{\parallel}$ in a low order of approximation.

2. General theory

The mobility is conventionally defined in terms of the drift velocity as $K \equiv v_d/E$, rather than as a differential mobility, $\mathrm{d}v_d/\mathrm{d}E$. Attempts to find GER by straightforward moment solutions of the Boltzmann equation in terms of K have not been particularly successful, and in retrospect the reason seems to be that the diffusion coefficients are physically most directly related to $\mathrm{d}v_d/\mathrm{d}E$ rather than to v_d/E [3]. The main reason for the success of Waldman and Mason [4] in obtaining accurate GER is probably their introduction of the differential mobility as a tensorial quantity, and their use of the Boltzmann equation to solve directly for the differential mobility rather than the conventional mobility. We follow the same general procedure here, but we now use a four-temperature theory [12] rather than the previous three-temperature theory, which applies only for elastic collisions. The four temperatures are the gas temperature, T, two ion translational temperatures, $T_{\perp}$ and $T_{\parallel}$, and one ion internal temperature, T_i, which is the new parameter. We give only the main points of the calculation here, since the details are very similar to those for the three-temperature theory, which are described at some length in section 6.4 of ref. [3] and in ref. [4].

2.1. Four-temperature theory

The procedure is first to form a set of moment equations from the Boltzmann equation, and then consider two kinds of perturbations from a spatially homogeneous reference case. The first perturbation to the moments is that caused by a small gradient of ion density, with the electric field vector $\boldsymbol{E}$ held fixed. We keep only perturbations that are linear in the density gradient, since we are not concerned with deviations from Fick's law of diffusion. The second perturbation is that caused by adding small increments, δE_x, δE_y, δE_z, to the field $\boldsymbol{E}$, which is taken to point originally in the z-direction. Here we must keep quadratic terms in order to obtain the correction terms $\Delta_{\perp,\parallel}$, because the linear terms in δE just rotate $\boldsymbol{E}$ through a small angle while increasing its magnitude by δE_z.

These perturbation expansions are substituted back into the general moment equations, which are then separated into three sets, one for the moments of the spatially homogeneous reference system, one for the density-perturbed moments, and one for the field-perturbed moments. The diffusion coefficients are related to the density-perturbed moments, the components of the differential mobility are related to the field-perturbed moments, and the ion temperatures are related to the spatially homogeneous moments.

So far the procedure is only formal, and two further major steps must be taken before any GER emerge. The first step is to solve the three infinite sets of moment equations for the lower moments that determine $D_{\perp,\parallel}$, $T_{\perp,\parallel}$, and the differential mobilities. This is done by truncation. The simplest first-approximation truncation produces only the known lowest-order GER, and it is necessary to go to a second approximation. This produces solutions in terms of the matrix elements that are the coefficients of the moment equations. The second step is to examine the matrix elements in order to find any relations among them, and to make some reasonable approximations to simplify the solutions. It is from this second step that useful GER finally emerge.

2.2. Basis functions and perturbation expansions

Some of the more pertinent details of the above broad outline are as follows. The orthogonal basis functions used to form the moment equations are those used in an expansion for the distribution function for the ion velocities and internal energies, which for the four-temperature theory is,

$$f(v,\epsilon)=f^{(0)}(v,\epsilon)\sum_{pqrs}a_{pqrs}\psi_{pqrs}(v,\epsilon)\,, \tag{13}$$

where $f(v,\epsilon)$ is the distribution function, $f^{(0)}(v,\epsilon)$ is its zero-order approximation, the a_{pqrs} are expansion coefficients, and the functions $\psi_{pqrs}(v,\epsilon)$ are those used as a basis set for the moment equations. The ψ_{pqrs} are orthogonal with respect to $f^{(0)}$ as a weight function. The functions used are,

$$f^{(0)}=Z^{-1}\exp(-w_x^2-w_y^2-w_z^2-x^{\alpha})\,, \tag{14}$$

$$\psi_{pqrs}=H_p(w_x)\,H_q(w_y)\,H_r(w_z)\,R_s(x^{\alpha})\,, \tag{15}$$

where Z is a normalization factor, and

$$w_x^2\equiv mv_x^2/2kT_{\perp}\,,\quad w_y^2=mv_y^2/2kT_{\perp}\,, \tag{16}$$

$$w_z^2\equiv m(v_z-v_{\mathrm{d}})^2/2kT_{\parallel}\,, \tag{17}$$

$$x^{\alpha}\equiv\epsilon^{\alpha}/kT_{\mathrm{i}}\,, \tag{18}$$

in which ϵ^{α} are the internal energy states of the ion, H_p, H_q, H_r are Hermite polynomials, and R_s are the Wang Chang–Uhlenbeck polynomials for the internal energy [12]. We do not write down the corresponding set of equations for $\langle\psi_{pqrs}\rangle$, the moments of $\psi_{pqrs}(v,\epsilon)$ over $f(v,\epsilon)$, because they are the same as those of the standard four-temperature theory [12].

The first move towards GER is taken via the two perturbation expansions of the moments,

$$\langle\psi_{pqrs}\rangle=\langle\psi_{pqrs}\rangle_0-\langle\psi_{pqrs}\rangle_D^x\frac{\partial\ln n}{\partial x}-\dots\,, \tag{19}$$

and

$$\langle\psi_{pqrs}\rangle=\langle\psi_{pqrs}\rangle_0+\langle\psi_{pqrs}\rangle_E^x\,\delta E_x+\dots+\langle\psi_{pqrs}\rangle_E^{xx}(\delta E_x)^2+\dots+\langle\psi_{pqrs}\rangle_E^{xy}\,\delta E_x\,\delta E_y+\dots\,, \tag{20}$$

where n is the number density of the ions and the $\langle\psi_{pqrs}\rangle_0$ are the moments for the spatially homogeneous case. These expansions are substituted back into the moment equations, which can then be separated into three sets of moment equations, one set for each of the moments $\langle\psi_{pqrs}\rangle_0$, $\langle\psi_{pqrs}\rangle_D$, and $\langle\psi_{pqrs}\rangle_E$. The problem is now reduced to solving these sets of moment equations to find the general relations between diffusion and mobility, which are given by

$$D_{\perp}/K=\langle\psi_{1000}\rangle_D^x/\langle\psi_{1000}\rangle_E^x\,, \tag{21}$$

$$D_{\parallel}/[K(1+K')]=\langle\psi_{0010}\rangle_D^z/\langle\psi_{0010}\rangle_E^z\,. \tag{22}$$

Of course, the development of useful GER then further depends on the simplification of the right-hand sides of these equations.

2.3. Solution of the moment equations

In a first approximation, the solution of the moment equations gives simply $kT_{\perp}/q$ and $kT_{\parallel}/q$ for the right-hand sides of eqs. (21) and (22). A second approximation is considerably more complicated, but a formal solution using Cramer's rule yields

$$\frac{qD_{\perp}}{K}=kT_{\perp}\left[1+\frac{1}{2}\langle\psi_{2010}\rangle_0\frac{B_x^{21}}{B_x^{11}}\right], \tag{23}$$

$$\frac{qD_{\parallel}}{K}=kT_{\parallel}\left[1+\frac{1}{2}\langle\psi_{0030}\rangle_0\frac{B_z^{21}}{B_z^{11}}+\frac{1}{2}\langle\psi_{2010}\rangle_0\frac{B_z^{31}}{B_z^{11}}+\frac{1}{2}\langle\psi_{0011}\rangle_0\frac{B_z^{41}}{B_z^{11}}\right], \tag{24}$$

where the B^{ij} are the ijth cofactors of matrices of coefficients, defined as

$$B_x \equiv \begin{pmatrix} b(1000,1000) & b(1000,1010) \\ b(1010,1000)-2\mathscr{E} & b(1010,1010) \end{pmatrix}, \tag{25}$$

$$B_z \equiv \begin{bmatrix} b(0010,0010) & b(0010,0020) & 2b(0010,2000) & b(0010,0001) \\ \{b(0020,0010)-4\mathscr{E}\} & b(0020,0020) & 2b(0020,2000) & b(0020,0001) \\ b(2000,0010) & b(2000,0020) & \{b(2000,2000)+b(2000,0200)\} & b(2000,0001) \\ b(0001,0010) & b(0001,0020) & 2b(0001,2000) & b(0001,0001) \end{bmatrix}, \tag{26}$$

where

$$\mathscr{E} \equiv (m/2kT_\parallel)^{1/2}(qE/mN)\,. \tag{27}$$

The matrix elements are

$$b(pqrs,p'q'r's') \equiv \sum_\alpha \int dv f^{(0)} \psi_{p'q'r's'} J \psi_{pqrs}\,, \tag{28}$$

where J is the Boltzmann collision operator [3,12]. For a given ion–molecule system of known masses and cross sections, the matrix elements can be calculated in terms of v_d and the four temperatures that characterize $f^{(0)}$, and thereby eqs. (23) and (24) can be evaluated to find $D_{\perp,\parallel}$ in terms of $T_{\perp,\parallel}$, $\langle \psi_{2010} \rangle_0$, and $\langle \psi_{0030} \rangle_0$. But the purpose of the GER is to avoid the brute-force calculations implied by such formal results.

In other words, the foregoing results are correct but not yet useful, and further reductions of the cofactor ratios must be made. We have not succeeded in doing this reduction in the same general way that proved feasible for the case of elastic collisions and the three-temperature theory, in which the cofactor ratios in eqs. (23) and (24) were expressed in terms of higher-order differential mobilities. This was the major simplification that led to useful GER. The difficulty now is the term involving $\langle \psi_{0011} \rangle_0$ in eq. (24) for $D_\parallel$, which corresponds to the flux of ion internal energy ($s=1$) in the field direction ($r=1$). We therefore adopt an approximation in which we neglect the influence of the flux of ion internal energy on the diffusion. This allows us to drop the term $\langle \psi_{0011} \rangle_0$ in eq. (24), and also to drop the fourth row and fourth column in B_z, which contains the matrix elements involving $s=1$ or $s'=1$.

This is a crucial step that deserves some discussion before continuing. Physically, the importance of inelastic collisions comes from the fact that they affect the translational energy and momentum of the ions, thereby altering the translational motion of the ions and affecting their mobility and diffusion. But the internal degrees of freedom of the ions and of the neutral molecules behave quite differently in this regard. Because the neutrals are in large excess, the ions encounter only neutrals of thermal energy, whose internal degrees of freedom only absorb ion energy on the average. The internal degrees of freedom of the ions, however, after a few initial collisions reach a steady state corresponding to the ion internal temperature T_i [12]; thereafter they do not gain or lose energy, on the average. That is, if an ion loses internal energy in one collision, it must soon gain it back on the average in a subsequent collision in order to maintain a steady state. In other words, the internal degrees of freedom of the neutrals act as an infinite sink for ion translational energy, whereas those of the ions act as neither a sink nor a source, except in a fluctuating way, and thus have little effect on the translational motion and hence on the mobility and diffusion, at least to a first approximation. It therefore seems reasonable to ignore the effect of the ion internal energy on the ion transport. In any case, this is an exact result for atomic ions and electrons in molecular gases.

On making this approximation, we can reduce the ratios of cofactors in eqs. (23) and (24) in the same way as in the elastic-collision case [4], and thereby obtain (including now the small second-derivative term K'' for completeness),

$$\frac{qD_\perp}{K} = kT_\perp\left[1+\Delta_\perp\left(\frac{K'}{2+K'}\right)\right], \tag{29}$$

$$\frac{qD_\parallel}{K} = kT_\parallel\left[1+K'+\Delta_\parallel K'+\left(\Delta_\parallel-\frac{1}{2}\frac{T_\perp}{T_\parallel}\Delta_\perp\right)\frac{K''}{1+K'}\right], \tag{30}$$

where

$$K'' \equiv \mathrm{d}^2(\ln K)/\mathrm{d}[\ln(E/N)]^2, \tag{31}$$

$$\Delta_\perp \equiv \langle\psi_{2010}\rangle_0/4\hat{v}_\mathrm{d}, \tag{32}$$

$$\Delta_\parallel \equiv \frac{\langle\psi_{0030}\rangle_0}{16\hat{v}_\mathrm{d}} + \frac{\langle\psi_{2010}\rangle_0}{8\hat{v}_\mathrm{d}}\frac{T_\perp}{T_\parallel}, \tag{33}$$

$$\hat{v}_\mathrm{d} \equiv (mv_\mathrm{d}^2/2kT_\parallel)^{1/2}. \tag{34}$$

Although these equations have the same external appearance as those for the elastic-collision case, the inelastic collisions can greatly affect $T_{\perp,\parallel}$ and $\Delta_{\perp,\parallel}$ because the internal degrees of freedom of the neutral molecules can act as an energy sink. We must therefore develop procedures for the determination of the essentially unobservable $T_{\perp,\parallel}$ and $\Delta_{\perp,\parallel}$, as described next.

2.4. Determination of $T_{\perp,\parallel}$ and $\Delta_{\perp\parallel}$

We now set up the general procedure for calculating the temperatures and correction terms, which we obtain from the unperturbed moment equations in the second approximation. As in the elastic-collision case, we reduce the infinite set of moment equations to a closed set of nine equations in nine unknowns (two T's, two Δ's, and five "elementary" matrix elements). This reduction is carried out in several steps. First the infinite set of moment equations is truncated by setting all but the most important matrix elements equal to zero; this step constitutes the second approximation. Then the remaining matrix elements in the four moment equations for the T's and Δ's are expressed in terms of five elementary matrix elements. The expressions are not exact, but are obtained under the approximation that certain ratios of collision integrals are universal – that is, that a ratio of collision integrals such as $[p,q]^{(l)}/[p,q]^{(1)}$ depends only on the index l and not on the indices p and q. (The collision integrals are defined in appendix A.) Finally, five more moment equations are chosen in order to determine the five elementary matrix elements. These nine moment equations are all coupled together in a highly nonlinear manner, because the matrix elements and the moments depend nonlinearly on $T_\perp$ and $T_\parallel$, which themselves are unknowns in the equations.

Without approximation of any matrix elements, the second-approximation moment equations that determine the T's and Δ's are,

$$b(0010,0000) = 2\mathscr{E}, \tag{35}$$

$$b(2000,0000)+b(2000,0030)\langle\psi_{0030}\rangle_0+[b(2000,2010)+b(2000,0210)]\langle\psi_{2010}\rangle_0 = 0, \tag{36}$$

$$b(0020,0000)+b(0020,0030)\langle\psi_{0030}\rangle_0+2b(0020,2010)\langle\psi_{2010}\rangle_0 = 0, \tag{37}$$

$$b(0030,0000)+b(0030,0030)\langle\psi_{0030}\rangle_0+2b(0030,2010)\langle\psi_{2010}\rangle_0 = 0, \tag{38}$$

$$b(2010,0000)+b(2010,0030)\langle\psi_{0030}\rangle_0+[b(2010,2010)+b(2010,0210)]\langle\psi_{2010}\rangle_0 = 0. \tag{39}$$

The first of these equations determines the matrix element $b(0010,0000)$, the second and third equations are used to find $T_\perp$ and $T_\parallel$, and the fourth and fifth equations to find $\Delta_\perp$ and $\Delta_\parallel$ via the moments $\langle\psi_{0030}\rangle_0$ and $\langle\psi_{2010}\rangle_0$. These equations have the same formal appearance as those of the three-temperature theory [4], except for the additional indices s and s', which are zero in this order of approximation.

The next step is to express the matrix elements of eqs. (36)–(39) in terms of $b(0010, 0000)$ and the following five other elementary matrix elements:

$$b(1) \equiv b(0010, 0010), \quad b(2) \equiv b(1000, 1000), \quad b(3) \equiv b(0010, 0020),$$
$$b(4) \equiv b(0010, 2000), \quad b(5) \equiv b(1000, 1010) . \tag{40}$$

The relations giving the other matrix elements in terms of these elements are given in appendix B. These relations depend on the following assumptions concerning ratios of collision integrals:

$$[p, q]^{(2)} / [p, q]^{(1)} \approx [0, 0]^{(2)} / [0, 0]^{(1)} \equiv \tilde{A}, \tag{41}$$
$$[p, q]^{(3)} / [p, q]^{(1)} \approx [0, 0]^{(3)} / [0, 0]^{(1)} \equiv \tilde{F}, \tag{42}$$
$$[p, q]' / [p, q]^{(1)} \approx [0, 0]' / [0, 0]^{(1)} \equiv \tilde{G}, \tag{43}$$
$$[p, q]'' / [p, q]^{(1)} \approx [0, 0]'' / [0, 0]^{(1)} \equiv \tilde{H}, \tag{44}$$

where the collision integrals are defined in appendix A.

To finish the closure we need five additional equations to determine the five unknown elementary matrix elements, $b(1)$–$b(5)$; the sixth elementary matrix element is given directly by eq. (35). They are obtained in the same way as in the three-temperature theory, but now include some extra terms that arise from the inelastic collisions, and are as follows:

$$d_{\parallel}^{-1} b(2) + \hat{v}_d b(2) = 2 d_{\perp}^{-1} b(4) + \mathscr{E}, \tag{45}$$

$$\begin{aligned} & b(1) [1 + (1 - \tfrac{1}{2}e + \tfrac{1}{4}e\tilde{G}) K' + \tfrac{1}{4}e(\tilde{A} - 2) K'' (1 + K')^{-1}] \hat{v}_d \\ & \quad + b(5) [(2f_{\perp} + e\tilde{G}) K' - \tfrac{1}{2}e(\tilde{A} - \tilde{G}) K'' (1 + K')^{-1}] (2d_{\perp})^{-1} (T_{\perp}/T_{\parallel}) \\ & \quad + b(3) [(2f_{\parallel} + e\tilde{G}) K' + (2f_{\parallel} + e\tilde{A}) K'' (1 + K')^{-1}] (2d_{\parallel})^{-1} \\ & \quad = \hat{v}_d (q/mNK) [1 + \tfrac{1}{2}e(1 - \tfrac{1}{2}\tilde{G}) K' - \tfrac{1}{4}e(\tilde{A} - 2) K'' (1 + K')^{-1}] , \end{aligned} \tag{46}$$

$$\begin{aligned} & b(3) [\tilde{A} - \tilde{G} - (2 - 2e + \tfrac{3}{2}e\tilde{A} - \tfrac{1}{2}e\tilde{G})(1 - \tfrac{1}{2}\tilde{G}) K' - 2(\tilde{A} - \tilde{G}) K'] (2e\hat{v}_d) \\ & \quad + b(4) [b(1)/b(2)] [2 - 2e + e\tilde{A} + (2 - 2e + \tfrac{1}{2}e\tilde{A} + \tfrac{1}{2}e\tilde{G}) K'] (4\hat{v}_d)(T_{\parallel}/T_{\perp}) \\ & \quad + b(1) [(1 - e + \tfrac{1}{2}e\tilde{G})(2 - 2e + \tfrac{3}{2}e\tilde{A} - \tfrac{1}{2}e\tilde{G}) K'] = 0 , \end{aligned} \tag{47}$$

$$\begin{aligned} & b(3) \{2(1 - e) + e\tilde{G} - \tfrac{1}{4}e[(4 - 4e + 3e\tilde{A} - e\tilde{G})(1 - \tfrac{1}{2}\tilde{G}) - 2(\tilde{A} - \tilde{G})] K'' (1 + K')^{-2}\} (4\hat{v}_d) \\ & \quad - b(4) [b(1)/b(2)] [2(1 - e) + e\tilde{G} + \tfrac{1}{2}e(\tilde{A} - \tilde{G}) K'' (1 + K')^{-2}] (4\hat{v}_d)(T_{\parallel}/T_{\perp}) \\ & \quad + b(1) [(1 - e + \tfrac{1}{2}e\tilde{G})(2 - 2e + \tfrac{3}{2}e\tilde{A} - \tfrac{1}{2}e\tilde{G}) K'' (1 + K')^{-2}] = 0 , \end{aligned} \tag{48}$$

$$\hat{v}_d b(2) + [1 - (T_{\perp}/T_{\parallel})] b(5) = \hat{v}_d (q/mNK) , \tag{49}$$

where

$$d_{\perp,\parallel} \equiv M T_{\perp,\parallel} / (mT + M T_{\perp,\parallel}) , \tag{50}$$
$$e \equiv M/(m + M) , \tag{51}$$
$$f_{\perp,\parallel} \equiv d_{\perp,\parallel} - e . \tag{52}$$

On setting $\tilde{G} = 0$, the five eqs. (45)–(49) have the same formal appearance as eqs. (72), (74), (76), (77), and (80) of ref. [4], except for the fourth indices (s, $s' = 0$). The first equation of the five is exact, but the others involve the approximation of universal values of collision-integral ratios, as given in eqs. (41)–(44).

To solve the set of nine equations consisting of eqs. (36)–(39) and (45)–(49) for the nine unknowns $T_\perp$, $T_\parallel$, $\langle \psi_{0030} \rangle_0$, $\langle \psi_{2010} \rangle_0$, and the five $b(i)$ of eq. (40), it is first necessary to know the four ratios $\tilde{A}$, $\tilde{F}$, $\tilde{G}$ and $\tilde{H}$. The ratios $\tilde{A}$ and $\tilde{G}$ appear explicitly in eqs. (46)–(49), and $\tilde{F}$ and $\tilde{H}$ appear when the matrix elements of eqs. (36)–(39) are reduced to the elementary matrix elements. The ratios $\tilde{A}$ and $\tilde{F}$ are analogous to the same ratios in the three-temperature theory, but $\tilde{G}$ and $\tilde{H}$ are new and are zero when only elastic collisions occur. The proper evaluation of these four ratios requires knowledge of the various elastic and inelastic cross sections. In the elastic-collision case, however, $\tilde{A}$ and $\tilde{F}$ are only weakly dependent on temperature and field strength, and can be estimated with sufficient accuracy from simple models of ion-neutral interactions [4,7]. This is not necessarily the case when inelastic collisions occur, because energy thresholds for various inelastic processes may make all four ratios depend significantly on the field strength. In any case, the set of nine equations is highly nonlinear because both the elementary matrix elements and the moments $\langle \psi_{0030} \rangle_0$ and $\langle \psi_{2010} \rangle_0$ depend nonlinearly on $T_\perp$ and $T_\parallel$. Their solution by numerical iteration on a computer is thus a laborious procedure [4], even though it involves much less work than a converged moment solution of the Boltzman equation, and a practical simplification is much to be desired. Such a simplification was achieved in the elastic-collision case by a parameterization based heavily on numerical experimentation [4,6,7], but this is not generally possible when inelastic collisions occur, as was mentioned in the introduction. We therefore now turn to the development of a simplified analytic procedure for approximating the solutions to the general set of nine coupled nonlinear equations in nine unknowns.

3. Analytic approximations

We begin by solving eqs. (36) and (37) for $T_\perp$ and $T_\parallel$ in first approximation, which means neglecting the terms involving $\langle \psi_{0030} \rangle_0$ and $\langle \psi_{2010} \rangle_0$; after expressing the matrix elements in terms of the elementary matrix elements according to the relations in appendix B, and performing some algebra, we obtain

$$kT_\perp [1+\tfrac{1}{2}(M/m)\tilde{G}] = kT[1+\zeta_\perp(\lambda-1)] + \zeta_\perp M v_\mathrm{d}^2/B(2)\,, \tag{53}$$

$$kT_\parallel [1+\tfrac{1}{2}(M/m)\tilde{G}] = kT[1+(1-\zeta_\parallel)(\lambda^{-1}-1)] + \zeta_\parallel M v_\mathrm{d}^2/\lambda B(2)\,, \tag{54}$$

where $\zeta_\perp$ and $\zeta_\parallel$ are given by eq. (10), and

$$\lambda \equiv b(1)/b(2)\,, \tag{55}$$

$$B(2) \equiv (mNK/q)b(2)\,, \tag{56}$$

which are dimensionless. These expressions already contain the dominant behavior of $T_{\perp,\parallel}$, and higher approximations do not contribute much. Moreover, even further simplifications are possible after estimates of λ and $B(2)$ are made by solving eqs. (45)–(49) for the elementary matrix elements.

From experiment we find that it is almost always safe to set $K'' \approx 0$, which simplifies eqs. (46) and (48). From eqs. (47) and (48) we then find that $b(3) \approx b(4) \approx 0$ if K' is small, and from eqs. (45) and (49) we find that $b(5) \approx 0$ and $B(2) \approx 1$. Substitution of these results back into eq. (46) yields a first approximation for $b(1)$ or λ,

$$\lambda \approx \frac{1+\frac{1}{2}e(1-\frac{1}{2}\tilde{G})K'}{1+[1-\frac{1}{2}e(1-\frac{1}{2}\tilde{G})]K'} = 1+O(K')\,. \tag{57}$$

The fact that λ is approximately unity leads to an immediate simplification in the expressions (53) and (54) for $T_{\perp,\parallel}$: since the terms in kT do not contribute much at high fields, and $K' \approx 0$ at low fields, it is safe to take $\lambda = 1$ in these terms in all orders of approximation.

A second approximation requires a more careful simultaneous solution of eqs. (45)–(49) for the elementary matrix elements, although we still keep $K'' = 0$. The values of $T_{\perp,\parallel}$ that occur in these equations are represented by their first approximations, which are eqs. (53) and (54) with $B(2)=1$ and $\lambda=1$. The results are fairly complicated, but some numerical experimentation with models indicates that it is still sufficient to take $B(2)\approx 1$, which leads to a second approximation for λ of the form,

$$1/\lambda \approx 1+\beta_{\parallel} K' , \tag{58}$$

where $\beta_{\parallel}$ is given by eq. (11).

We thus finally obtain eqs. (8) and (9) for $T_{\perp}$ and $T_{\parallel}$, with $\zeta_{\perp,\parallel}$ given by eq. (10), and with $\beta_{\perp}\approx 0$ and $\beta_{\parallel}$ given by eq. (11).

Once $T_{\perp}$ and $T_{\parallel}$ are known, the correction terms $\Delta_{\perp,\parallel}$ are obtained by solving eqs. (38) and (39) for the moments $\langle\psi_{0030}\rangle_0$ and $\langle\psi_{2010}\rangle_0$. We first express the matrix elements in terms of the elementary matrix elements via the relations of appendix B, and then use the approximations obtained above for the elementary matrix elements, namely $B(2)\approx 1$, $b(3)\approx b(4)\approx b(5)\approx 0$, and $\lambda^{-1}\approx 1+\beta_{\parallel}K'$. The result is

$$\begin{aligned}
&\lambda[1+e(\tilde{A}-2)+e^2(1-\tilde{A}+\tfrac{1}{3}\tilde{F})]\langle\psi_{0030}\rangle_0+(T_{\perp}/T_{\parallel})[\lambda e^2(1-\tilde{F}+\tilde{H})-e(1-e)(\tilde{A}-\tilde{G})]\langle\psi_{2010}\rangle_0\\
&\quad =4e\,\hat{v}_{\mathrm{d}}[2-\tilde{A}-e(1-\tilde{A}+\tfrac{1}{3}\tilde{F})(d_{\parallel}^{-1}+2\hat{v}_{\mathrm{d}}^2)-e\,d_{\perp}^{-1}(T_{\perp}/T_{\parallel})(1-\tilde{F}+\tilde{H})]\\
&\quad +4\lambda e\,\hat{v}_{\mathrm{d}}[2-\tilde{A}-2e\,d_{\parallel}^{-1}(1-\tilde{A}+\tfrac{1}{3}\tilde{F})]\,,
\end{aligned} \tag{59}$$

$$\begin{aligned}
&e\lambda(T_{\parallel}/T_{\perp})[e(1+\tilde{A}-\tilde{G}-\tilde{F}+\tilde{H})-\tilde{A}+\tilde{G}]\langle\psi_{0030}\rangle_0\\
&\quad +[2\lambda(1-e)^2+4+e(7\tilde{A}-\tilde{G}-8)+e^2(3-7\tilde{A}+\tilde{G}+3\tilde{F}-\tilde{H})]\langle\psi_{2010}\rangle_0\\
&\quad =4e\,\hat{v}_{\mathrm{d}}[4+(T_{\parallel}/T_{\perp})(\tilde{A}-\tilde{G}-2e\,d_{\perp}^{-1})-e(T_{\parallel}/T_{\perp})(1+\tilde{A}-\tilde{G}-\tilde{F}+\tilde{H})(d_{\parallel}^{-1}+2\hat{v}_{\mathrm{d}}^2)]\\
&\quad -4\lambda e\,\hat{v}_{\mathrm{d}}(T_{\parallel}/T_{\perp})[2e\,d_{\parallel}^{-1}(1+\tilde{A}-\tilde{G}-\tilde{F}+\tilde{H})-\tilde{A}+\tilde{G}]\\
&\quad -8e\,\hat{v}_{\mathrm{d}}[\tfrac{1}{3}e(3\tilde{A}-\tilde{G})-2+\tfrac{1}{2}ed_{\perp}^{-1}(3-7\tilde{A}+\tilde{G}+3\tilde{F}-\tilde{H})]\,.
\end{aligned} \tag{60}$$

Despite the apparent complexity of the coefficients, these are just two simultaneous linear equations for the two moments.

There is one caution to be observed in the use of eqs. (59) and (60) – the right-hand sides go to incorrect limits when $m/M\rightarrow 0$ (i.e., electrons), because the elementary matrix elements that were taken as zero then become important. This defect is easily remedied because the matrix elements can be easily calculated correctly in the limit $m/M\rightarrow 0$, and a correction term can be added on as follows:

$$b_{\mathrm{corr}}(i)=b(i)-\frac{2b(1)(1-\kappa)K'}{[1+(1-\kappa/2)K']\hat{v}_{\mathrm{d}}}\,, \tag{61}$$

for $i=(2010, 0000)$ and $(0030, 0000)$, where κ is defined in eq. (12). For consistency we have kept this correction term for all mass ratios, even though it is important only for $m/M\rightarrow 0$.

We have now reduced the set of nine coupled equations to four simple equations: eqs. (8) and (9) for $T_{\perp,\parallel}$, and the pair of eqs. (59) and (60) for $\langle\psi_{0030}\rangle_0$ and $\langle\psi_{2101}\rangle_0$, which immediately yield the correction terms $\Delta_{\perp,\parallel}$ via eqs. (32) and (33). Despite appearances, the equations for $T_{\perp}$ and $T_{\parallel}$ are nonlinear and coupled, because the quantities $\tilde{A}$ and $\tilde{G}$ that occur in $\zeta_{\perp,\parallel}$ and $\beta_{\parallel}$ depend on $T_{\perp}$ and $T_{\parallel}$. However, a simple iteration scheme converges rapidly when the elastic and inelastic cross sections are known. At a given E/N, initial guesses are made for $\tilde{A}$ and $\tilde{G}$, and initial values of $T_{\perp}$ and $T_{\parallel}$ are then calculated from eqs. (8) and (9). The values of T, v_{d}, K', and $K''\approx 0$ are assumed to be known from experiment. New values of $\tilde{A}$ and $\tilde{G}$ are calculated from these values of $T_{\perp,\parallel}$ and the cross sections, according to the relations in appendix A, and the process is repeated until converged values of $T_{\perp,\parallel}$, $\tilde{A}$ and $\tilde{G}$ are obtained. Starting values of $\tilde{A}$ and $\tilde{G}$ for a given value of E/N can be guessed from results already obtained at lower values of E/N; in the absence of such information, the values $\tilde{A}\approx 0.85$ and $\tilde{G}\approx 0$ are reasonable starting values.

Once $T_{\perp,\parallel}$ are found, the values of $\tilde{F}$ and $\tilde{H}$ are calculated from the relations in appendix A, and then eqs.

(59) and (60) are solved for $\langle \psi_{0030} \rangle_0$ and $\langle \psi_{2010} \rangle_0$, without iteration. The values of $D_{\perp,\parallel}$ then follow immediately by substitution into eqs. (29)–(34), again without iteration.

The slowest step is the calculation of $\tilde{A}$, $\tilde{G}$, $\tilde{F}$, and $\tilde{H}$, which requires numerical integrations of the cross sections over effective velocity distributions characterized by $T_\perp$ and $T_\parallel$ (appendix A).

If the cross sections are not known, one is faced with the difficult inversion problem of extracting them from the experimental data on K and $D_{\perp,\parallel}$ as a function of E/N.

We turn now to testing the foregoing analytic approximations against experimental and computer-simulation data.

4. Elastic-collision limits

A first test of the present results is provided by the case of elastic collisions. The general formulas for $T_{\perp,\parallel}$ and $D_{\perp,\parallel}$ of course reduce to those of Waldman and Mason [4] on setting $\tilde{G}=\tilde{H}=0$, so we are really testing the analytic approximations for $\beta_\parallel$ and $\Delta_{\perp,\parallel}$ as given by eqs. (11), (59), and (60). These quantities were previously treated by numerical parameterization based on calculations for model ion-neutral potentials [4,7].

We compare first with accurate calculations for hard spheres and inverse-power potentials, and then with experimental data for alkali ions and electrons in monatomic gases.

4.1. Hard spheres and inverse-power potentials

Accurate calculations of drift velocities, ion temperatures, and diffusion coefficients have been made by Skullerud [6] for r^{-n} repulsive ion-neutral potentials in the cold-gas limit ($T=0$), essentially by numerical solution of the Boltzmann equation. Approximate calculations using the GER of the full three-temperature theory (i.e., using the nine coupled nonlinear equations) have been reported by Waldman and Mason [4] for hard spheres ($n=\infty$).

The present GER analytic approximations are compared with these results in table 1 ($T_{\perp,\parallel}$) and table 2 ($D_{\perp,\parallel}$). The analytic approximations require no iteration in these cases because $\tilde{A}$ and $\tilde{F}$ are constants and $\tilde{G}=\tilde{H}=0$; the results therefore depend only on the mass ratio, m/M. The values of $\tilde{A}$ and $\tilde{F}$ used are those given by Waldman and Mason [4].

The tables show that the analytic approximations agree with the accurate calculations of Skullerud, generally within a few percent, and also with the GER results from the full set of coupled equations. Thus the approximations do well on this test.

4.2. Alkali ions in noble gases

The most suitable data available for comparison consist of experimental measurements of $D_\parallel$ as a function of E/N at 300 K [3,13], corresponding computer solutions of the Boltzmann equation for $D_\perp$ [4], and calculations with the full Waldman–Mason GER (nine coupled equations) [4], all for the nine systems, K^+, Rb^+, Cs^+ in Ar, Kr, Xe. No ion temperatures have been measured for these systems. Since the results for all nine systems are rather similar, we select for comparison only a sample covering the range of mass ratios: K^+ in Xe ($m/M=0.30$), Rb^+ in Kr ($m/M=1.0$), and Cs^+ in Ar ($m/M=3.3$). We compare diffusion coefficients calculated from the analytic approximations with the above data, using as input the measured ion mobilities [3,13], the values of $\tilde{A}$ recommended by Waldman and Mason [4], and the constant value of $\tilde{F}=1.2$. We have as usual taken $K''=0$.

It is helpful in comparing ion diffusion coefficients to remove their approximately quadratic dependence on E/N by defining reduced diffusion coefficients,

Table 1
Ion temperatures as a function of mass ratio for r^{-n} potentials in the cold-gas limit ($T=0$). Percentage errors are shown in parentheses for the approximate theories

n	m/M	$kT_\perp/Mv_d^2$			$kT_\parallel/Mv_d^2$		
		accurate [a]	present	WM [b]	accurate [a]	present	WM [b]
∞	0	0.3535	1/3(−6)	1/3(−6)	0.3535	1/3(−6)	1/3(−6)
	0.1	0.326	0.306(−6)	0.316(−3)	0.382	0.359(−6)	0.359(−6)
	0.5	0.261	0.250(−4)	0.254(−3)	0.380	0.375(−1)	0.350(−8)
	1	0.223	0.222(0)	0.219(−2)	0.345	0.365(+6)	0.334(−3)
	4	0.186	0.185(−1)	0.181(−3)	0.321	0.340(+6)	0.326(+2)
	∞	1/6	1/6(0)	1/6(0)	1/3	1/3(0)	1/3(0)
12	0	0.3441	1/3(−3)		0.3441	1/3(−3)	
	0.1	0.32	0.315(−3)		0.37	0.350(−5)	
	0.5	0.275	0.274(0)		0.370	0.370(+6)	
	1	0.247	0.251(+2)		0.352	0.371(+5)	
	4	0.215	0.219(+2)		0.347	0.363(+5)	
	∞	0.2016	0.202(0)		0.3581	0.358(0)	
8	0	0.3401	1/3(−2)		0.3401	1/3(−2)	
	0.1	0.32	0.318(−1)		0.36	0.349(−3)	
	0.5	0.282	0.283(0)		0.369	0.372(+1)	
	1	0.258	0.263(+1)		0.361	0.379(+5)	
	4	0.231	0.233(+1)		0.363	0.379(+5)	
	∞	0.2169	0.217(0)		0.3774	0.378(0)	

[a] From ref. [6]. [b] From ref. [4].

$$\tilde{D}_{\perp,\parallel} \equiv qD_{\perp,\parallel}/K(0)kT_{\mathrm{eff}}(0)\ , \qquad (62)$$

$$kT_{\mathrm{eff}}(0) \equiv kT + \tfrac{1}{3}M[K(0)E]^2\ , \qquad (63)$$

where $K(0)$ is the zero-field mobility at gas temperature T.

The comparisons appear in figs. 1–3. The analytic approximations are, with one exception, in good agreement with the results from the nine coupled equations, and with the experimental and computer-generated values. The exception is $\tilde{D}_\parallel$ for K^+ in Xe, for which the analytic approximation appears to be in better agreement with experiment.

Finally, we should note that ion temperatures have been successfully measured only for the systems Ba^+ in He and in Ar; both results were in good agreement with the parameterization of Waldman and Mason as given by eqs. (5)–(7) [5]. The analytic approximation for $T_{\perp,\parallel}$ differs from this parameterization only in the value of $\beta_\parallel$, and in the case of Ba^+ in He the mass ratio is so large ($m/M=34$) that the two results are the same. In fact, the analytic approximation for $\beta_\parallel$ given by eq. (11) automatically goes to the same limits as the parameterization, namely $\beta_\parallel=0$ for $m/M=0$, and $\beta_\parallel=1$ for $m/M\to\infty$. thus neither very light nor very heavy ions serve as a useful test of the analytic approximation for $T_\parallel$ relative to the Waldman–Mason parameterization.

The case of Ba^+ in Ar is more favorable for a test because $m/M=3.44$ and K' is appreciable (maximum value about 0.3). The analytic approximation for $T_\parallel$ differs from the parameterized value by at most about 6% at the largest value of K'; this is within the mutual uncertainties of the measured values of $T_\parallel$ and the calculated values of $T_\parallel$ (whose uncertainties are due to uncertainties in the measured mobilities).

Thus the analytic approximations for $T_\perp$ and $T_\parallel$ agree with experiment for the two measured systems.

Table 2
Ion diffusion coefficients as a function of mass ratio for r^{-n} potentials in the cold-gas limit ($T=0$). Percentage errors are shown in parentheses for the approximate theories

n	m/M	$qD_\perp/Mv_d^2K$			$qD_\parallel/Mv_d^2K$		
		accurate [a]	present	WM [b]	accurate [a]	present	MW [b]
∞	0	0.4045	0.358(−12)	0.358(−12)	0.1986	0.194(−2)	0.194(−2)
	0.1	0.343	0.321(−6)	0.328(−4)	0.195	0.183(−6)	0.179(−8)
	0.5	0.249	0.244(−2)	0.244(−2)	0.158	0.155(−2)	0.141(−11)
	1	0.212	0.213(+1)	0.207(−2)	0.146	0.153(+5)	0.137(−6)
	4	0.182	0.183(+1)	0.177(−3)	0.153	0.162(+6)	0.153(0)
	∞	1/6	0.170(+2)	1/6(0)	1/6	0.171(+2)	1/6(0)
12	0	0.3689	0.346(−6)		0.2253	0.217(−4)	
	0.1	0.34	0.319(−6)		0.22	0.209(−5)	
	0.5	0.274	0.265(−3)		0.193	0.196(+1)	
	1	0.2365	0.242(+2)		0.189	0.198(+5)	
	4	0.212	0.217(+2)		0.200	0.211(+5)	
	∞	0.2016	0.204(+1)		0.2149	0.218(+2)	
8	0	0.3549	0.347(−2)		0.2347	0.237(+1)	
	0.1	0.32	0.319(0)		0.23	0.229(0)	
	0.5	0.270	0.273(+2)		0.222	0.225(+1)	
	1	0.248	0.254(+3)		0.220	0.231(+5)	
	4	0.228	0.231(+1)		0.235	0.246(+5)	
	∞	0.2169	0.219(+1)		0.2516	0.254(+1)	

[a] From ref. [6]. [b] From ref. [4].

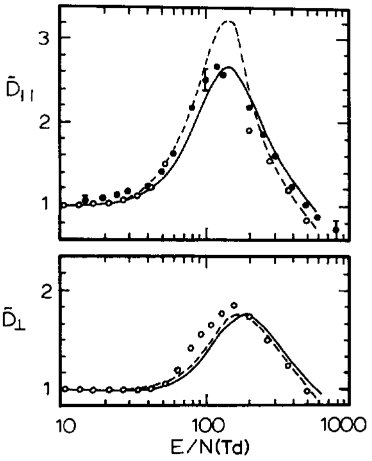

Fig. 1. Reduced diffusion coefficients for K^+ in Xe at 300 K as a function of E/N (1 Td$\equiv 10^{-17}$ V cm^2). The solid curves represent the present GER, and the dashed curves those from the full Waldman–Mason calculation. The filled circles represent smoothed experimental data [3,13] with representative error bars, and the open circles are computer-generated values [4].

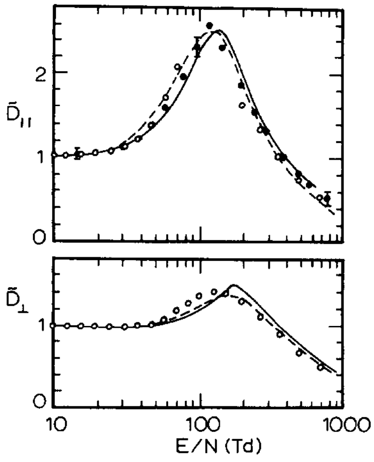

Fig. 2. Same as fig. 1, for Rb^+ in Kr.

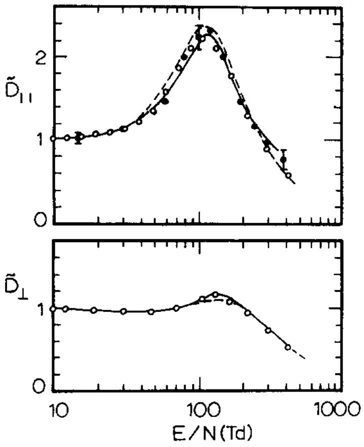

Fig. 3. Same as fig. 1, for Cs^+ in Ar.

4.3. Electrons in monatomic gases

In the light-ion limit, the coupled equations of Waldman and Mason can be solved analytically. The present results become identical to these solutions if a small correction term is added, as mentioned in section 3. However, even the elastic-collision case has serious limitations, as discussed by Uribe and Mason [8] in connection with electrons in monatomic gases. They proposed some useful improvements in the GER for electrons, but did not find a completely satisfactory method for calculating $T_{\perp,\parallel}$. We believe that progress on the problem of electron diffusion in molecular gases must await a more satisfactory treatment for monatomic gases. In any case, the present analytic approximations reduce to the expected elastic-collision limits for electrons, insofar as these are known.

In summary, the analytic approximations clearly meet the minimum test of satisfactorily reproducing the elastic-collision limits for all known cases.

5. Inelastic-collision comparisons

Comparisons of the present GER with experimental measurements are difficult because of the lack of information on inelastic cross sections, as embodied in the quantities $\tilde{A}$, $\tilde{F}$, $\tilde{G}$ and $\tilde{H}$. The best test therefore comes from the use of a simple two-state inelastic-collision model for which accurate calculations are available. From this comparison we learn enough to attempt a semiempirical treatment of $\tilde{A}$, $\tilde{F}$, $\tilde{G}$ and $\tilde{H}$, which we apply to an analysis of the experimental data for K^+ in H_2 and in N_2. We do not make any comparisons involving electron diffusion because of the difficulties, already mentioned, of GER even for electrons in monatomic gases. The sort of results that can be expected for electrons are sufficiently illustrated by an earlier analysis of $D_\parallel$ for electrons in methane, using eq. (3) with Boltzmann-equation estimates of $T_\parallel$ and $\Delta_\parallel$ [11], and we have nothing substantial to add at this time. (This system shows the phenomenon of negative differential conductivity.)

In the following comparisons we take $K'' = 0$ in the GER.

5.1. Two-state model

The model consists of structureless hard-sphere ions in a hard-sphere neutral gas having two internal states. Inelastic collisions occur only above a threshold energy, ϵ_{th}, and an inelastic collision causes the relative translational energy of the ion-neutral pair to be reduced by exactly ϵ_{th}. The elastic and inelastic cross sections are given by

$$\sigma_{\text{el}} = \sigma_0 = \text{constant}\,, \tag{64}$$

$$\begin{aligned} \sigma_{\text{in}} &= 0, \quad \epsilon < \epsilon_{\text{th}}\,, \\ &= \sigma_0, \quad \epsilon \geqslant \epsilon_{\text{th}}\,, \end{aligned} \tag{65}$$

where $\epsilon = \frac{1}{2}\mu v^2$ and v is the relative speed. At very low energies essentially all collisions are elastic, and at very high energies essentially half the collisions are inelastic. The total cross section, $\sigma_{\text{el}} + \sigma_{\text{in}}$, varies from σ_0 at low energies to $2\sigma_0$ at high energies.

Accurate calculations are available for this model for the case $m = M$ and $T = 0$, both from Monte Carlo simulations and from a three-temperature solution of the Boltzmann equation [12].

For this model the inelastic-collision parameters are calculated to be

$$\tilde{G} = 3(\tilde{A} - \tfrac{2}{3})\,, \tag{66}$$

$$\tilde{F} = 1, \quad \tilde{H} = 0\,. \tag{67}$$

Elastic hard-sphere collisions give $\tilde{A} = \frac{2}{3}$ and hence $\tilde{G} = 0$, but for this inelastic model the value of $\tilde{A}$ depends on the ion energy. More specifically, it depends on the ratio of the ion energy to the threshold energy, so that the relevant dimensionless variable is

$$a\lambda / v_{\text{th}}^2 = qE / 4N\sigma_0 \epsilon_{\text{th}}\,, \tag{68}$$

which can also be considered as a reduced electric field strength. Here $a \equiv qE/m$ is the ion acceleration and $\lambda \equiv 1/N\sigma_0$ is a mean free path. As a function of this variable $\tilde{A}$ begins to rise from its limiting value of $\frac{2}{3}$ at about $a\lambda / v_{\text{th}}^2 = 0.1$, reaches a broad maximum of about 0.74 at $a\lambda / v_{\text{th}}^2 \approx 0.9$, and then slowly falls back towards 2/3, being about 0.69 at $a\lambda / v_{\text{th}}^2 = 10$. The value of $\tilde{A}$ must be found by iteration because it depends on $T_{\perp,\parallel}$ (see appendix A), but $T_{\perp,\parallel}$ depends on $\tilde{A}$ according to eqs. (8)–(10). Fortunately, convergence is rapid.

The results are shown in reduced form in fig. 4 ($T_{\perp,\parallel}$) and fig. 5 ($D_{\perp,\parallel}$). In all cases there is a non-monotonic transition from the low-field value, where all collisions are elastic, to the high-field value, where half the collisions are inelastic. The high-field values happen to be equal to half the low-field values because the cross section changes from σ_0 to $2\sigma_0$. The input data were taken to be the accurate values of the drift velocity. The good

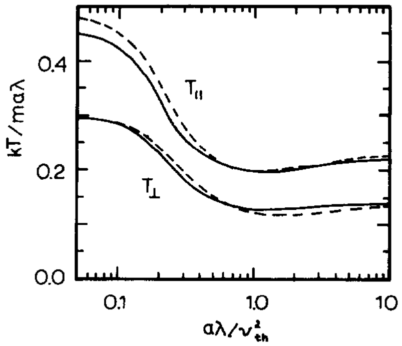

Fig. 4. Reduced ion temperatures as a function of reduced field strength for the two-state inelastic-collision model discussed in the text. The solid curves are the accurate results [12] and the dashed curves are the present analytical approximations of eqs. (8)–(12).

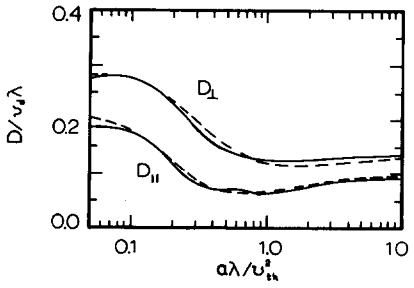

Fig. 5. Reduced ion diffusion coefficients for the two-state inelastic-collision model. Legend as in fig. 4.

agreement between the accurate results and the present calculations tests both the general form of the GER and the present analytic approximations for $T_{\perp,\parallel}$ and $\Delta_{\perp,\parallel}$.

5.2. K^+ in H_2 and N_2

For real systems our ignorance of inelastic cross sections forces us to adopt a semiempirical procedure. All we can hope to learn at this point is whether or not the present GER are capable of giving a reasonable account of experimental measurements, although we expect that advances in classical-trajectory calculations of inelastic cross sections will alleviate this situation in the near future [14].

A little numerical experimentation shows that the results are relatively insensitive to $\tilde{F}$ and $\tilde{H}$, and that $\tilde{A}$ and $\tilde{G}$ are the critical quantities. We therefore use the results of the two-state model to set $\tilde{F}=1$ and $\tilde{H}=0$, and to give a relation between $\tilde{G}$ and $\tilde{A}$,

$$\tilde{G}\approx 3(\tilde{A}-\tilde{A}_{\mathrm{el}})\,, \tag{69}$$

where $\tilde{A}_{\mathrm{el}}$ is the value of $\tilde{A}$ for elastic collisions. We thus obtain a one-parameter GER, in which $\tilde{A}$ (or $\tilde{G}$) for a particular system is considered to be a function of E/N, and can be adjusted to fit the measurements of $D_\parallel$ (say) as a function of E/N. As a check, the values of $D_\perp$ as a function of E/N can then be predicted.

We select the systems K^+ in H_2 and K^+ in N_2 for consideration because experimental values of both $D_\parallel$ and $D_\perp$ are available, as well as mobilities [3,13]. We choose a constant value of $\tilde{A}_{\mathrm{el}}=0.85$, which is typical of alkali ions in noble gases [4,6]. The results are shown in fig. 6 (K^+ in H_2) and fig. 7 (K^+ in N_2), in terms of the reduced $\tilde{D}_{\perp,\parallel}$ defined in eq. (61). The fit for $\tilde{D}_\parallel$ is of course very good because of the empirical adjustment of $\tilde{A}$, but the fit for $\tilde{D}_\perp$ is then not adjustable and serves as a test of the theory. In other words, we are using the GER to predict $D_\perp$ from measurements of K and $D_\parallel$, rather than the usual (preferred) procedure of predicting both $D_\perp$ and $D_\parallel$ from measurements of K. The agreement between calculated and measured $\tilde{D}_\perp$ is not perfect, but is well within the estimated experimental uncertainty of 15–20%. More importantly, the main features of $\tilde{D}_\perp$ as a function of E/N are correctly predicted – a minimum followed by a larger maximum for K^+ in H_2, and a single

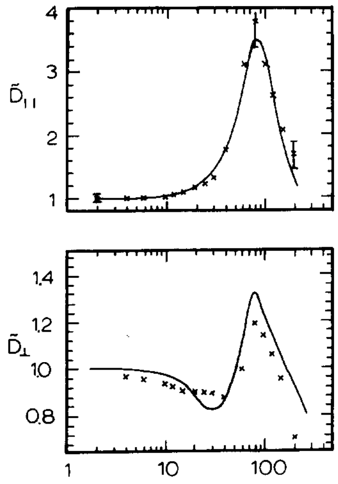

Fig. 6. Reduced diffusion coefficients as a function of field strength for K^+ in H_2. The crosses represent experimental measurements. The curve for $\tilde{D}_\parallel$ is a one-parameter fit, but that for $\tilde{D}_\perp$ involves no adjustable parameters.

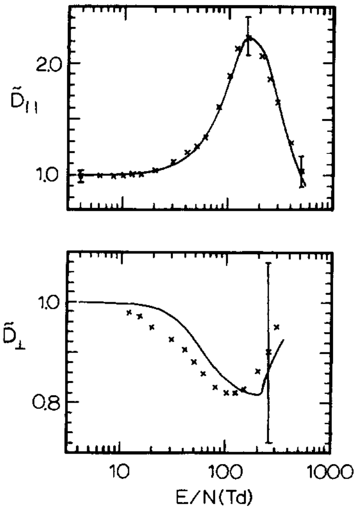

Fig. 7. Same as fig. 6, for K^+ in N_2.

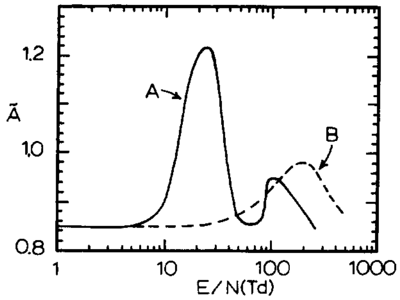

Fig. 8. Adjusted parameters $\tilde{A}$ as a function of E/N used for the curves in figs. 6 and 7. Curve A, K^+ in H_2; curve B, K^+ in N_2.

broad minimum for K^+ in N_2. Notice that the shapes of $\tilde{D}_\perp$ versus E/N for these molecular systems are quite different from those for alkali ions in noble gases, as illustrated in figs. 1–3.

The values of $\tilde{A}$ as a function of E/N that are required to fit the values of $\tilde{D}_\parallel$ are shown in fig. 8. These values, relative to the constant baseline of $\tilde{A}_{el} = 0.85$, can be considered as the values of $\tilde{G}/3$ according to eq. (68). The use of a value of $\tilde{A}_{el}$ that depended on E/N would mainly just make the baseline of fig. 8 a function of E/N, without substantially altering the results shown in figs. 6 and 7. Experimental uncertainties in K and $D_\parallel$, as well as uncertainty about the values chosen for $\tilde{F}$ and $\tilde{H}$, must lead to an uncertainty of at least 10% in $\tilde{A}$. The numerical magnitudes of $\tilde{A}$ are very reasonable, being not greatly different from values for alkali ions in noble gases [4]. However, lack of information about inelastic collisions for these systems prevents us from offering any comments on the detailed shapes of the curves.

The foregoing results show that the GER for ions in molecular gases at least have a reasonable mathematical structure, and even some predictive power in the face of ignorance about inelastic collisions ($D_\perp$ from K and $D_\parallel$).

6. Conclusions

Our main result is a set of GER for systems involving inelastic collisions, which has a firm basis in kinetic theory and includes as a special case the GER derived by Waldman and Mason for elastic collisions. In addition, a simple analytic procedure has been developed for the calculation of the unobservable quantities that appear in the GER, to avoid the need to solve a set of nine coupled nonlinear equations. Comparisons with limiting cases involving only elastic collisions serve to validate the analytic procedure.

Data required as input for the GER are mobilities and some ratios of collision integrals. Only limited testing is possible for systems involving inelastic collisions, owing to lack of knowledge of the required collision-integral ratios. Agreement with accurate calculations for an inelastic two-state model, and with semiempirical treatments of K^+ in H_2 and in N_2 in which $D_\perp$ is predicted from K and $D_\parallel$, appears to be satisfactory. Further progress awaits more information on details of inelastic collisions.

Acknowledgement

The authors are indebted to Dr. M. Waldman, who initiated work on this problem. The work was supported in part by NSF Grant 88-19370.

Appendix A. Collision integrals

Collision integrals $[p, q]^n$ are averages of cross sections Q over anisotropic velocity distributions,

$$[p, q]^n = 2\pi^{-1/2} Z_i^{-1} Z_N^{-1} \sum_{\alpha\alpha'\beta\beta'} \exp(\epsilon^\alpha/kT_i - \epsilon^\beta/kT) \int_0^\infty d\gamma_r\, \gamma_r^{p+1} \exp(-\gamma_r^2) \int_{-\infty}^\infty d\gamma_z\, \gamma_z^q \exp(-\gamma_z^2) g Q^n , \tag{A.1}$$

where Z_i and Z_N are the internal partition functions for the ions and the neutral gas, respectively,

$$Z_i \equiv \sum_\alpha \exp(-\epsilon^\alpha/kT_i) , \tag{A.2}$$

$$Z_N \equiv \sum_\beta \exp(-\epsilon^\beta/kT) . \tag{A.3}$$

Primes on the internal state indices α and β indicate post-collision quantities. The relative pre-collision speed is g, and the γ's are dimensionless components of the relative collision energy,

$$\tfrac{1}{2}\mu g^2 = \gamma_r^2 kT_\perp + (\gamma_z + v_\mathrm{d})^2 kT_\parallel , \tag{A.4}$$

with $\gamma_r^2 = \gamma_x^2 + \gamma_y^2$. That is, the γ's correspond to the w's of eqs. (14)–(17), but in center-of-mass coordinates.

The three types of cross sections that occur are

$$Q^{(l)}_{\alpha\alpha'\beta\beta'}(g) = 2\pi \int_0^\pi d\theta \sin\theta\, \sigma(\alpha\beta, \alpha'\beta', g, \theta)\{1 - [(g'/g)\cos\theta]^l\} , \tag{A.5}$$

$$Q'_{\alpha\alpha'\beta\beta'}(g) = 2\pi \int_0^\pi d\theta \sin\theta\, \sigma[1 - (g'/g)^2] , \tag{A.6}$$

$$Q''_{\alpha\alpha'\beta\beta'}(g) = 2\pi \int_0^\pi d\theta \sin\theta\, \sigma[1 - (g'/g)^2][(g'/g)\cos\theta] . \tag{A.7}$$

These give rise to the three types of collision integrals $[p, q]^{(l)}$, $[p, q]'$, and $[p, q]''$ of eqs. (41)–(44). The quantity $\sigma(\alpha\beta, \alpha'\beta', g, \theta)$ is the differential cross section for the scattering of an ion and a neutral molecule in states α and β through an angle θ into states α' and β'.

Appendix B. Matrix elements

Here we give the expressions for the eighteen matrix elements needed in the second-order approximation, in terms of $\tilde{A}$, $\tilde{F}$, $\tilde{G}$ and $\tilde{H}$, and the six elementary matrix elements $b(i)$ of eq. (40). We use the following dimensionless quantities from eqs. (34), (50)–(52):

$$\hat{v}_\mathrm{d} \equiv (mv_\mathrm{d}^2/2kT_\parallel)^{1/2} ,$$

$$d_{\perp,\parallel} \equiv MT_{\perp,\parallel}/(mT + MT_{\perp,\parallel}) ,$$

$$e \equiv M/(m+M), \quad f_{\perp,\parallel} \equiv d_{\perp,\parallel} - e .$$

These matrix elements reduce to those given by Waldman and Mason for elastic collisions on setting $\tilde{G} = \tilde{H} = 0$.

$$b(2000, 0000) = -e(\tilde{A} - \tilde{G})(T_\parallel/T_\perp)[2\hat{v}_\mathrm{d}\mathscr{E} + d_\parallel^{-1} b(1)] + [4f_\perp + e(\tilde{A} + \tilde{G})] d_\perp^{-1} b(2) , \tag{B.1}$$

$$b(2000,0010)=-e(\tilde{A}-\tilde{G})(T_\parallel/T_\perp)[\mathscr{E}+\hat{v}_\mathrm{d}b(1)+2d_\parallel^{-1}b(3)]+[4f_\perp+e(\tilde{A}+\tilde{G})]d_\perp^{-1}b(5)\,, \tag{B.2}$$

$$b(2000,0020)=-e(\tilde{A}-\tilde{G})(T_\parallel/T_\perp)[\tfrac{1}{2}b(1)+\hat{v}_\mathrm{d}b(3)]\,, \tag{B.3}$$

$$b(2000,0030)=-\tfrac{1}{2}e(\tilde{A}-\tilde{G})(T_\parallel/T_\perp)b(3)\,, \tag{B.4}$$

$$b(2000,2000)+b(2000,0200)=[2(1-e)+\tfrac{1}{2}e(\tilde{A}+\tilde{G})]b(2)-2e\,\hat{v}_\mathrm{d}(\tilde{A}-\tilde{G})(T_\parallel/T_\perp)b(4)\,, \tag{B.5}$$

$$b(2000,2010)+b(2000,0210)=-e(\tilde{A}-\tilde{G})(T_\parallel/T_\perp)b(4)+[2(1-e)+\tfrac{1}{2}e(\tilde{A}+\tilde{G})]b(5)\,, \tag{B.6}$$

$$b(0020,0000)=4e\,\hat{v}_\mathrm{d}(\tilde{A}-2)\mathscr{E}+(4f_\parallel+2e\tilde{A})d_\parallel^{-1}b(1)-2e(\tilde{A}-\tilde{G})(T_\perp/T_\parallel)d_\perp^{-1}b(2)\,, \tag{B.7}$$

$$b(0020,0010)=2[2(1-e)+e\tilde{A}]\mathscr{E}+2e\,\hat{v}_\mathrm{d}(\tilde{A}-2)b(1)+4(2f_\parallel+e\tilde{A})d_\parallel^{-1}b(3)-2e(\tilde{A}-\tilde{G})(T_\perp/T_\parallel)d_\perp^{-1}b(5), \tag{B.8}$$

$$b(0020,0020)=[2(1-e)+e\tilde{A}]b(1)+2e\,\hat{v}_\mathrm{d}(\tilde{A}-2)b(3)\,, \tag{B.9}$$

$$b(0020,0030)=[2(1-e)+e\tilde{A}]b(3)\,, \tag{B.10}$$

$$b(0020,2000)=-\tfrac{1}{2}e(\tilde{A}-\tilde{G})(T_\perp/T_\parallel)b(2)+2e\,\hat{v}_\mathrm{d}(\tilde{A}-2)b(4)\,, \tag{B.11}$$

$$b(0020,2010)=[2(1-e)+e\tilde{A}]b(4)-\tfrac{1}{2}e(\tilde{A}-\tilde{G})(T_\perp/T_\parallel)b(5)\,, \tag{B.12}$$

$$\begin{aligned}b(2010,0000)={}&2e\mathscr{E}\{-4-(\tilde{A}-\tilde{G})(T_\parallel/T_\perp)+e[2d_\perp^{-1}+(1+\tilde{A}-\tilde{G}-\tilde{F}+\tilde{H})(T_\parallel/T_\perp)(d_\parallel^{-1}+2\hat{v}_\mathrm{d}^2)]\}\\&+2e\,\hat{v}_\mathrm{d}(T_\parallel/T_\perp)[2ed_\parallel^{-1}(1+\tilde{A}-\tilde{G}-\tilde{F}+\tilde{H})-\tilde{A}+\tilde{G}]b(1)\\&+4e\,\hat{v}_\mathrm{d}[e(\tilde{A}-\tfrac{1}{3}\tilde{G})-2+\tfrac{1}{2}e\,d_\perp^{-1}(3-7\tilde{A}+\tilde{G}+3\tilde{F}-\tilde{H})]b(2)\\&+4e\,d_\parallel^{-1}(T_\parallel/T_\perp)[e\,d_\parallel^{-1}(1+\tilde{A}-\tilde{G}-\tilde{F}+\tilde{H})-\tilde{A}+\tilde{G}]b(3)+8(1-e\,d_\perp^{-1})^2b(4)\\&+4[2+e\,d_\parallel^{-1}(3\tilde{A}-\tilde{G}-2)+\tfrac{1}{2}e\,d_\perp^{-1}(\tilde{A}+\tilde{G}-4)+\tfrac{1}{2}e^2d_\perp^{-1}d_\parallel^{-1}(3-7\tilde{A}+\tilde{G}+3\tilde{F}-\tilde{H})]b(5),\end{aligned} \tag{B.13}$$

$$\begin{aligned}b(2010,0030)={}&\tfrac{1}{2}e(T_\parallel/T_\perp)[e(1+\tilde{A}-\tilde{G}-\tilde{F}+\tilde{H})-\tilde{A}+\tilde{G}]b(1)\\&+e\,\hat{v}_\mathrm{d}(T_\parallel/T_\perp)[2e(1+\tilde{A}-\tilde{G}-\tilde{F}+\tilde{H})-\tilde{A}+\tilde{G}]b(3)\,,\end{aligned} \tag{B.14}$$

$$\begin{aligned}b(2010,2010)+b(2010,0210)={}&(1-e)^2b(1)+[2+\tfrac{1}{2}e(7\tilde{A}-\tilde{G}-8)+\tfrac{1}{2}e^2(3-7\tilde{A}+\tilde{G}+3\tilde{F}-\tilde{H})]b(2)\\&+2e\,\hat{v}_\mathrm{d}(T_\parallel/T_\perp)[2e(1+\tilde{A}-\tilde{G}-\tilde{F}+\tilde{H})-\tilde{A}+\tilde{G}]b(4)+e\,\hat{v}_\mathrm{d}[6\tilde{A}-2\tilde{G}-4+e(3-7\tilde{A}+\tilde{G}+3\tilde{F}-\tilde{H})]b(5),\end{aligned} \tag{B.15}$$

$$\begin{aligned}b(0030,0000)={}&12e\mathscr{E}[\tilde{A}-2+e(1-\tilde{A}+\tfrac{1}{3}\tilde{F})(d_\parallel^{-1}+2\hat{v}_\mathrm{d}^2)+e\,d_\perp^{-1}(T_\perp/T_\parallel)(1-\tilde{F}+\tilde{H})]\\&+12e\,\hat{v}_\mathrm{d}[\tilde{A}-2+2e\,d_\parallel^{-1}(1-\tilde{A}+\tfrac{1}{3}\tilde{F})]b(1)+12e^2\hat{v}_\mathrm{d}(\tilde{A}-\tilde{G})(T_\perp/T_\parallel)d_\perp^{-1}b(2)\\&+24[1+e\,d_\parallel^{-1}(\tilde{A}-2)+(e\,d_\parallel^{-1})^2(1-\tilde{A}+\tfrac{1}{3}\tilde{F})]b(3)+24(T_\perp/T_\parallel)(e\,d_\perp^{-1})^2(1-\tilde{F}+\tilde{H})b(4)\\&+12e(\tilde{A}-\tilde{G})(T_\perp/T_\parallel)d_\perp^{-1}(e\,d_\parallel^{-1}-1)b(5)\,,\end{aligned} \tag{B.16}$$

$$b(0030,0030)=3[1+e(\tilde{A}-2)+e^2(1-\tilde{A}+\tfrac{1}{3}\tilde{F})]b(1)+6e\,\hat{v}_\mathrm{d}[\tilde{A}-2+2e(1-\tilde{A}+\tfrac{1}{3}\tilde{F})]b(3)\,, \tag{B.17}$$

$$\begin{aligned}b(0030,2010)={}&\tfrac{3}{2}e^2(T_\perp/T_\parallel)(1-\tilde{F}+\tilde{H})b(1)-\tfrac{3}{2}e(1-e)(T_\perp/T_\parallel)(\tilde{A}-\tilde{G})b(2)\\&+6e\,\hat{v}_\mathrm{d}[\tilde{A}-2+2e(1-\tilde{A}+\tfrac{1}{3}\tilde{F})]b(4)+3e^2\hat{v}_\mathrm{d}(T_\perp/T_\parallel)(\tilde{A}-\tilde{G})b(5)\,.\end{aligned} \tag{B.18}$$

References

[1] L.G.H. Huxley and R.W. Crompton, The Diffusion and Drift of Electrons in Gases (Wiley, New York, 1974).

[2] W. Lindinger, T.D. Märk and F. Howorka, Swarms of Ions and Electrons in Gases (Springer, Berlin, 1984).

[3] E.A. Mason and E.W. McDaniel, Transport Properties of Ions in Gases (Wiley, New York, 1988).
[4] M. Waldman and E.A. Mason, Chem. Phys. 58 (1981) 121.
[5] R.A. Dressler, J.P.M. Beijers, H. Meyer, S.M. Penn, V.M. Bierbaum and S.R. Leone, J. Chem. Phys. 89 (1988) 4707; S.M. Penn, K.P.M. Beijers, R.A. Dressler, V.M. Bierbaum and S.R. Leone, J. Chem. Phys. 93 (1990) 5188.
[6] H.R. Skullerud, J. Phys. B 9 (1976) 535.
[7] M. Waldman, E.A. Mason and L.A. Viehland, Chem. Phys. 66 (1982) 339.
[8] F.J. Uribe and E.A. Mason, Chem. Phys. 133 (1989) 335.
[9] R.E. Robson, J. Phys. B 9 (1976) L337.
[10] R.E. Robson, Aust. J. Phys. 37 (1984) 35.
[11] S.L. Lin, R.E. Robson and E.A. Mason, J. Chem. Phys. 71 (1979) 3483.
[12] L.A. Viehland, S.L. Lin and E.A. Mason, Chem. Phys. 54 (1981) 341.
[13] H.W. Ellis, M.G. Thackston, E.W. McDaniel and E.A. Mason, At. Data Nucl. Data Tables 31 (1984) 113, plus earlier papers in this series of data compilations.
[14] L.A. Viehland and A.S. Dickinson, to be published.