PHYSICAL REVIEW E VOLUME 48, NUMBER 5 NOVEMBER 1993

Diffusion in equilibrium mixtures of ionized gases

A. B. Murphy
Commonwealth Scientific and Industrial Research Organization, Division of Applied Physics,
P.O. Box 218, Lindfield, New South Wales 2070, Australia
(Received 29 September 1992)

Diffusion in a mixture of two nonreacting homonuclear gases with an arbitrary degree of ionization is considered. It is shown that, provided that an equilibrium composition of the gas mixture can be defined as a function of temperature, pressure, and relative concentrations of the two gases, diffusive mixing of the gases can be fully described by three combined diffusion coefficients. These coefficients describe diffusion due to concentration, temperature, and pressure gradients, respectively, and replace the $\frac{1}{2}(q^2+q-2)$ independent diffusion coefficients required in previous treatments to describe diffusion in a q-species gas mixture. Diffusion due to applied electric and gravitational fields is also considered. Formulas for the combined diffusion coefficients are presented, and combined diffusion coefficients in a mixture of argon and nitrogen at temperatures up to 30 000 K are calculated as an example.

PACS number(s): 51.10.+y, 52.25.Fi, 05.60.+w

I. INTRODUCTION

The Chapman-Enskog method [1–3] is widely used to calculate the transport properties of gases. Of these properties, viscosity, thermal conductivity, and electrical conductivity are each described by a single coefficient, irrespective of the number of species present in the gas. In contrast, in a gas containing q species, a total of $\frac{1}{2}q(q-1)$ independent ordinary diffusion coefficients D_{ij}, describing diffusion due to species concentration gradients, pressure gradients, and external forces, and a total of $q-1$ independent thermal diffusion coefficients D_i^T, describing diffusion due to temperature gradients, must be defined. Only in the special case of a two-species mixture are ordinary diffusion and thermal diffusion, respectively, described by one coefficient.

There is a wide range of problems, such as vaporization of a condensed particle in a hot gas and cooling of a plasma jet by an ambient gas, in which the diffusive mixing of two high-temperature gases is important. The occurrence of dissociation and ionization means that a large number of species are generally present in such gas mixtures. A species is defined here to be any type of molecule, atom, or ion, or the electron. At present, the treatment of such problems requires each species to be considered separately. A species conservation equation and a momentum conservation equation then have to be solved for each species [4]. Treatment of these problems would be greatly simplified if diffusion could be described in terms of the two gases rather than the many species present. In fact, many workers use this simplification, without properly calculating the required diffusion coefficients. For example, Chen *et al.* [5] assume the ordinary diffusion coefficient for the diffusion of copper vapor and argon to be equal to the binary diffusion coefficient for atomic copper and atomic argon (which is equivalent to the ordinary diffusion coefficient calculated assuming that only these two species are present), even at temperatures at which the mixture is fully ionized. In calculations of the properties of plasma jets discharging into air, ordinary diffusion coefficients have been calculated using a simple mixing rule [6], or neglected altogether relative to the large turbulent mixing rate [7]; both approaches can introduce inaccuracies.

In a previous paper [8], combined diffusion coefficients were derived to describe the diffusive mixing of two nonionized gases due to concentration and temperature gradients. Here I extend the calculations to the more general case of ionized gases, and I include the influence of pressure gradients and externally applied fields on diffusion. I consider a mixture of two nonreacting homonuclear gases, with an arbitrary degree of ionization, containing a total of q species. I show that the diffusion in the gas mixture due to concentration, pressure, and temperature gradients, and under the influence of applied electric and gravitational fields, may be described by four coefficients: (1) a combined ordinary diffusion coefficient; (2) a combined pressure diffusion coefficient; (3) a combined thermal diffusion coefficient, describing, respectively, diffusion of the two gases due to concentration, pressure, and temperature gradients; and (4) the electrical conductivity, describing diffusion of charged particles due to the applied electric field. The applied gravitational field is shown to have no effect. The three combined diffusion coefficients replace the $\frac{1}{2}q(q-1)$ ordinary diffusion coefficients and the $q-1$ thermal diffusion coefficients that are required to describe diffusive mixing of the gases in other treatments.

In order for the three combined diffusion coefficients to be calculated, an equilibrium composition of the gas mixture must be defined as a function of temperature, pressure, and mole fractions of the two gases. This is because the various species diffuse with different velocities; the imposition of an equilibrium condition means that we are in fact assuming that dissociation, ionization, and recombination reactions occur to maintain the equilibrium composition. This is always possible for homonuclear gases because the species required for the reactions will always be present at any position in the mixture. In mixtures of heteronuclear gases, the different diffusion velocities of the various species mean that this will not be true. The question of equilibrium composition is further discussed in Sec. II C.

In Sec. II A, I discuss the definition and the usual method of calculation of diffusion coefficients in a nonionized neutral gas. The effect of the presence of charged particles on these diffusion coefficients is treated in Sec. II B. The method of calculation of the combined diffusion coefficients is given in Sec. II C. An illustrative calculation of the combined diffusion coefficients for a mixture of nitrogen and argon at high temperatures is presented in Sec. III, and conclusions are given in Sec. IV.

II. CALCULATION OF DIFFUSION COEFFICIENTS

A. Present method

I consider a mixture of two homonuclear gases, denoted gas A and gas B, consisting of a total of q species. For generality, I allow the gases to be partially ionized. Zero and full ionization can be treated as special cases by neglecting charged or neutral species, respectively. The individual species present are denoted by the subscript i, where $i = 1$ denotes the electron, $i = 2, \ldots, p$ denote the species derived from gas A, and $i = p+1, \ldots, q$ the species derived from gas B. I assume that gases A and B do not react; there is thus no ambiguity regarding the gas to which species 2 to q are assigned.

There is considerable variation in the definition of the diffusion coefficients employed by different authors. For example, Hirschfelder, Curtiss, and Bird [1], Chapman and Cowling [2], and Devoto [9] define the ordinary diffusion coefficients D_{ij} and the thermal diffusion coefficient D_i^T using the equation for the number flux of the species i relative to the mass-average velocity:

$$\mathbf{g}_i \equiv n_i \mathbf{v}_i = \frac{n^2}{\rho} \sum_{j=1}^{q} m_j D_{ij} \mathbf{d}_j - \frac{D_i^T}{m_i} \nabla \ln T, \qquad (1)$$

where $\mathbf{v}_i$ is the diffusion flux of species i relative to the mass-average velocity, T is the temperature, and

$$\mathbf{d}_j = \nabla x_j + \left(x_j - \frac{\rho_j}{\rho} \right) \nabla \ln P - \frac{\rho_j}{P\rho} \left(\frac{\rho}{m_j} \mathbf{F}_j - \sum_{l=1}^{q} n_l \mathbf{F}_l \right) \qquad (2)$$

describes the diffusion forces due to gradients in concentration $x_j = n_j/n$ and pressure P, and due to external forces $\mathbf{F}_j$. n and ρ are, respectively, the number and mass densities of the gas mixture, and n_j, ρ_j, and m_j are, respectively, the number density, mass density, and mass of the jth species. Under this definition, we have $D_{ii} = 0$, but in general $D_{ij} \neq D_{ji}$ for $i \neq j$, except for the special case of $q = 2$.

Ferziger and Kaper [3] prefer the definition, adapted from that suggested by Curtiss [10],

$$\mathbf{g}_i = -n_i \left(\sum_{j=1}^{q} \tilde{D}_{ij} \mathbf{d}_j + \tilde{D}_i^T \nabla \ln T \right). \qquad (3)$$

The notation $\tilde{D}_{ij}$ and $\tilde{D}_i^T$ is used to differentiate the ordinary and thermal diffusion coefficients from those under the previous definition. In this case, the ordinary diffusion coefficients are symmetric, i.e., $\tilde{D}_{ij} = \tilde{D}_{ji}$, and are thus explicitly consistent with Onsager's reciprocity relations. Also, $\tilde{D}_{ij}$ and $\tilde{D}_i^T$ have the same dimension.

Despite these advantages, the definition of Eq. (1) appears to be used almost exclusively in the thermal plasma literature; see, for example, Refs. [5,6,11–13]. For this reason, I choose to use this equation, rather than Eq. (3), as the definition of the diffusion coefficients. For completeness, and to allow direct comparison between Ref. [8] and this paper, I present a summary of results calculated under the definition of Eq. (3) in Appendix A.

The diffusion coefficients D_{ij} and D_i^T may be calculated from series of linear equations, with terms incorporating the collision integrals describing interactions between the species present in the plasma. The appropriate equations are given by, for example, Hirschfelder, Curtiss, and Bird [1] and Devoto [9].

B. Ambipolar diffusion

The diffusion of charged particles is affected by both externally applied electric fields and the electric field that arises because of the tendency of electrons to diffuse more rapidly than ions. For generality, I consider the effect on transport of both types of electric field, as well as an externally applied gravitational field. The force on a particle of species i is then

$$\mathbf{F}_i = eZ_i(\mathbf{E}^e + \mathbf{E}^a) + m_i \mathbf{g}, \qquad (4)$$

where $\mathbf{E}^e$ is the externally applied electric field, $\mathbf{E}^a$ is the electric field caused by the separation of electrons and ions, $\mathbf{g}$ is the acceleration due to the gravitational field, and where $Z_i e$ is the charge on a particle of species i, e being the electronic charge. Substituting Eq. (4) into Eq. (2) gives, after applying the charge neutrality condition $\sum_{i=1}^{q} n_i Z_i = 0$,

$$\mathbf{d}_i = \nabla x_i + \left(x_i - \frac{\rho_i}{\rho} \right) \nabla \ln P - \frac{n_i Z_i e}{nkT} (\mathbf{E}^e + \mathbf{E}^a). \qquad (5)$$

Note that the terms in $\mathbf{g}$ cancel, so the gravitational field has no direct effect. Separation of gases of different molecular weights can, however, occur due to the pressure gradient term.

The electric field $\mathbf{E}^a$ slows the diffusion of the electrons and speeds the diffusion of the ions so that charge neutrality is maintained; a steady state is reached in which the current is due only to the applied electric field:

$$e\sum_{i=1}^{q} Z_i \mathbf{g}_i = \sigma \mathbf{E}^e, \tag{6}$$

where σ is the electrical conductivity. This is a generalization of the ambipolar condition, which is obtained by setting $\mathbf{E}^e = 0$. Substituting Eq. (5) into Eq. (6) and equating terms in $\mathbf{E}^e$ gives an expression for the electrical conductivity:

$$\sigma = \frac{e^2 n}{\rho k T} \sum_{j=2}^{q} \left(n_j m_j Z_j D_{1j} - Z_j \sum_{i=1}^{q} n_i m_i Z_i D_{ji} \right), \tag{7}$$

which is the same as that obtained by Devoto [9]. The remaining terms may be solved for $\mathbf{E}^a$; substituting the resulting expression into Eq. (5) gives

$$\begin{aligned}\mathbf{g}_i = \frac{n^2}{\rho} \sum_{j=1}^{q} \Bigg\{ & m_j \left(D_{ij} + \frac{\alpha_i}{\beta} \sum_{l=1}^{q} Z_l D_{lj} \right) \\ & \times \left[\nabla x_j + \left(x_j - \frac{\rho_j}{\rho} \right) \nabla \ln P \right] - \frac{n_j Z_j e D_{ij}}{nkT} \mathbf{E}^e \Bigg\} \\ & - \left(\frac{D_i^T}{m_i} + \frac{\alpha_i}{\beta} \sum_{l=1}^{q} \frac{Z_l D_l^T}{m_l} \right) \nabla \ln T, \end{aligned} \tag{8}$$

where

$$\alpha_i = \sum_{j=1}^{q} n_j m_j Z_j D_{ij}, \tag{9}$$

and

$$\beta = - \sum_{i,j=1}^{q} Z_i Z_j n_j m_j D_{ij}. \tag{10}$$

Equation (8) is the same expression as given by Devoto [9], apart from the addition of the term in $\mathbf{E}^e$. It shows that diffusion due to an applied electric field is not altered by the electric field $\mathbf{E}^a$, and thus can be represented by the expression for electrical conductivity given in Eq. (7). Diffusion due to concentration, pressure and temperature gradients is, however, affected: the ordinary diffusion coefficient D_{ij} and the thermal diffusion coefficient D_i^T must be replaced, respectively, by

$$D_{ij}^a = D_{ij} + \frac{\alpha_i}{\beta} \sum_{l=1}^{q} Z_l D_{lj} \tag{11}$$

and

$$D_i^{Ta} = D_i^T + \frac{\alpha_i m_i}{\beta} \sum_{l=1}^{q} \frac{Z_l D_l^T}{m_l}. \tag{12}$$

Note that when $n_1 = 0$, ambipolar effects do not occur, and we write $D_{ij}^a = D_{ij}$ and $D_i^{Ta} = D_i^T$.

C. Combined diffusion coefficients

We wish to combine the ambipolar diffusion coefficients D_{ij}^a and D_i^{Ta} defined in Eqs. (11) and (12) to give combined diffusion coefficients that describe the diffusion of the two gases relative to one another. A necessary assumption is that the concentrations of the individual species are defined as a function of temperature, pressure, and relative concentration of the two gases. This requires an equilibrium description of dissociation and ionization reactions; this is usually provided by the requirement that Gibbs free energy be minimized, or, equivalently, by the Guldberg-Waage equation for dissociation and the Saha equation for ionization.

It is emphasized that there is no requirement that the relative concentration of the two gases be uniform in the plasma; hence phenomena such as mixing of two gases, and demixing [4], may be treated. It is also not necessary that the equilibrium descriptions of the dissociation and ionization reactions correspond to those given by the Guldberg-Waage and Saha equations; any set of species concentrations as a function of temperature, pressure, and relative concentrations of the two gases may be used. It should be noted, however, that departures from Saha equilibrium are generally, in physically realistic situations, associated with the electron temperature being greater than the heavy-particle temperature. Such two-temperature plasmas cannot be treated using the standard Chapman-Enskog method; however, many adaptations of the Chapman-Enskog method to two-temperature plasmas have been suggested; see, for example, Refs. [14–17]. The use of one of these adaptations would allow the concept of combined diffusion coefficients to be applied to two-temperature plasmas.

The required combined diffusion coefficients are defined by an expression for the number flux of gas A, of equivalent form to that of Eq. (1) for a two-species gas:

$$\overline{\mathbf{g}_A} = \frac{n^2}{\rho} \overline{m_B} \left(\overline{D_{AB}^x} \nabla \overline{x_B} + \overline{D_{AB}^P} \nabla \ln P \right) - \frac{\overline{D_{AB}^T}}{\overline{m_A}} \nabla \ln T; \tag{13a}$$

the corresponding expression for the number flux of gas B is

$$\overline{\mathbf{g}_B} = \frac{n^2}{\rho} \overline{m_A} \left(\overline{D_{BA}^x} \nabla \overline{x_A} + \overline{D_{BA}^P} \nabla \ln P \right) - \frac{\overline{D_{BA}^T}}{\overline{m_B}} \nabla \ln T. \tag{13b}$$

The term $x_j - \rho_j/\rho$ in Eq. (2) has been included in $\overline{D_{AB}^P}$ and $\overline{D_{BA}^P}$, and the external force terms have been omitted for reasons discussed in Sec. II B. The bar notation indicates that a variable refers to a gas rather than to a species. In Eqs. (13a) and (13b),

$$\overline{m_A} = \sum_{k=2}^{p} (m_k x_k + m_1 Z_k x_k) \Bigg/ \sum_{k=2}^{p} x_k , \tag{14a}$$

$$\overline{m_B} = \sum_{k=p+1}^{q} (m_k x_k + m_1 Z_k x_k) \Bigg/ \sum_{k=p+1}^{q} x_k , \tag{14b}$$

$$\overline{x_A} = \sum_{k=2}^{p} (1 + Z_k) x_k, \tag{15a}$$

$$\overline{x_B} = \sum_{k=p+1}^{q} (1 + Z_k) x_k = 1 - \overline{x_A}, \tag{15b}$$

are, respectively, the average masses of the species of gases A and B, and the relative concentrations of gases A and B. The terms in Z_k include the electrons resulting from ionization of gas A, while excluding those resulting from ionization of gas B, in calculating $\overline{m_A}$ and $\overline{x_A}$, and vice versa in calculating $\overline{m_B}$ and $\overline{x_B}$.

We wish to find appropriate expressions for $\overline{D^x_{AB}}$, $\overline{D^P_{AB}}$, and $\overline{D^T_{AB}}$, which we will call the combined ordinary diffusion coefficient, the combined pressure diffusion coefficient, and the combined thermal diffusion coefficient, respectively. We start by defining $\overline{\mathbf{g}_A}$ and $\overline{\mathbf{g}_B}$ in terms of the total flux of atoms contained in the species of gas A and gas B, respectively:

$$\overline{\mathbf{g}_A} = \sum_{i=2}^{p} s_i \mathbf{g}_i, \tag{16a}$$

$$\overline{\mathbf{g}_B} = \sum_{i=p+1}^{q} s_i \mathbf{g}_i, \tag{16b}$$

where the s_i are stoichiometric coefficients, defined by

$$s_1 = 0, \tag{17a}$$

$$s_i = b_i \sum_{k=2}^{p} x_k \Bigg/ \sum_{k=2}^{p} b_k x_k\ , \qquad 2 \leq i \leq p, \tag{17b}$$

$$s_i = b_i \sum_{k=p+1}^{q} x_k \Bigg/ \sum_{k=p+1}^{q} b_k x_k\ , \ p+1 \leq i \leq q, \tag{17c}$$

where b_i is the number of atoms in a molecule of species i; thus $b_i = 2$ for a diatomic molecule or ion, and $b_i = 1$ for an atom or monatomic ion.

Substituting Eq. (1) into Eq. (16a), replacing D_{ij} and D^T_i by D^a_{ij} and D^{Ta}_{ij}, respectively, to account for ambipolar effects, and rearranging into the same form as Eq. (13a), gives

$$\overline{\mathbf{g}_A} = \frac{n^2}{\rho}\overline{m_B}\left\{\left[\frac{1}{\overline{m_B}}\sum_{i=2}^{p} s_i \sum_{j=1}^{q} m_j D^a_{ij}\frac{\partial x_j}{\partial \overline{x_B}}\right]\nabla \overline{x_B} + \left[\frac{1}{\overline{m_B}}\sum_{i=2}^{p} s_i \sum_{j=1}^{q} m_j D^a_{ij}\left(x_j - \frac{\rho_j}{\rho} + P\frac{\partial x_j}{\partial P}\right)\right]\nabla \ln P\right\}$$
$$-\frac{1}{\overline{m_A}}\left[\overline{m_A}\sum_{i=2}^{p} s_i\left(\frac{D^{Ta}_i}{m_i} - \frac{n^2}{\rho}\sum_{j=1}^{q} m_j D^a_{ij} T\frac{\partial x_j}{\partial T}\right)\right]\nabla \ln T, \tag{18}$$

where we have used

$$\nabla x_j = \left(\frac{\partial x_j}{\partial \overline{x_B}}\right)\nabla \overline{x_B} + \left(\frac{\partial x_j}{\partial P}\right)\nabla P + \left(\frac{\partial x_j}{\partial T}\right)\nabla T, \tag{19}$$

which is valid since we have assumed that an equilibrium composition can be defined as a function of temperature, pressure, and the relative concentrations of the two gases. Comparing Eq. (18) with Eq. (13a) gives

$$\overline{D^x_{AB}} = \frac{1}{\overline{m_B}}\sum_{i=2}^{p} s_i \sum_{j=1}^{q} m_j D^a_{ij}\frac{\partial x_j}{\partial \overline{x_B}}, \tag{20}$$

$$\overline{D^P_{AB}} = \frac{1}{\overline{m_B}}\sum_{i=2}^{p} s_i \sum_{j=1}^{q} m_j D^a_{ij}\left(x_j - \frac{\rho_j}{\rho} + P\frac{\partial x_j}{\partial P}\right), \tag{21}$$

and

$$\overline{D^T_{AB}} = \overline{m_A}\sum_{i=2}^{p} s_i\left(\frac{D^{Ta}_i}{m_i} - \frac{n^2}{\rho}\sum_{j=1}^{q} m_j D^a_{ij} T\frac{\partial x_j}{\partial T}\right). \tag{22}$$

Similarly, we can calculate expressions for $\overline{D^x_{BA}}$, $\overline{D^P_{BA}}$, and $\overline{D^T_{BA}}$, using Eqs. (1), (13b), and (16b):

$$\overline{D^x_{BA}} = -\frac{1}{\overline{m_A}}\sum_{i=p+1}^{q} s_i \sum_{j=1}^{q} m_j D^a_{ij}\frac{\partial x_j}{\partial \overline{x_B}}, \tag{23}$$

$$\overline{D^P_{BA}} = \frac{1}{\overline{m_A}}\sum_{i=p+1}^{q} s_i \sum_{j=1}^{q} m_j D^a_{ij}\left(x_j - \frac{\rho_j}{\rho} + P\frac{\partial x_j}{\partial P}\right), \tag{24}$$

$$\overline{D^T_{BA}} = \overline{m_B}\sum_{i=p+1}^{q} s_i\left(\frac{D^{Ta}_i}{m_i} - \frac{n^2}{\rho}\sum_{j=1}^{q} m_j D^a_{ij} T\frac{\partial x_j}{\partial T}\right). \tag{25}$$

Equations (20)–(25) satisfy the conditions $\overline{D^x_{AB}} = \overline{D^x_{BA}}$, $\overline{D^P_{AB}} = -\overline{D^P_{BA}}$, and $\overline{D^T_{AB}} = -\overline{D^T_{BA}}$, which are analogous to the requirements that $D_{ij} = D_{ji}$ and $D^T_i = -D^T_j$ in a two-species gas (Sec. II A), and which may be derived from Eq. (13a) and the relation $\overline{m_A}\overline{\mathbf{g}_A} = -\overline{m_B}\overline{\mathbf{g}_B}$, which follows from the definition of $\mathbf{v}_i$. The diffusive mixing of two gases due to concentration, pressure, and temperature gradients can thus be fully described by the three parameters $\overline{D^x_{AB}}$, $\overline{D^P_{AB}}$, and $\overline{D^T_{AB}}$, respectively.

It is useful in some contexts to consider the terms in Eqs. (21), (22), (24), and (25) separately. We may write

$$\overline{D^P_{AB}} = \overline{D^{P1}_{AB}} + \overline{D^{P2}_{AB}}, \tag{26}$$

with

$$\overline{D^{P1}_{AB}} = \frac{1}{\overline{m_B}}\sum_{i=2}^{p} s_i \sum_{j=1}^{q} m_j D^a_{ij}\left(x_j - \frac{\rho_j}{\rho}\right) \tag{27}$$

and

$$\overline{D_{AB}^{P2}} = \frac{1}{m_B} \sum_{i=2}^{p} s_i \sum_{j=1}^{q} m_j D_{ij}^{a} P \frac{\partial x_j}{\partial P}, \tag{28}$$

and similarly

$$\overline{D_{AB}^{T}} = \overline{D_{A}^{T}} + \overline{D_{AB}^{T1}}, \tag{29}$$

with

$$\overline{D_{A}^{T}} = \overline{m_A} \sum_{i=2}^{p} \frac{s_i D_i^{Ta}}{m_i} \tag{30}$$

and

$$\overline{D_{AB}^{T1}} = -\frac{n^2 \overline{m_A}}{\rho} \sum_{i=2}^{p} s_i \sum_{j=1}^{q} m_j D_{ij}^{a} T \frac{\partial x_j}{\partial T}. \tag{31}$$

Similar expressions apply for $\overline{D_{BA}^{P}}$ and $\overline{D_{BA}^{T}}$.

The terms $\overline{D_{AB}^{P2}}$ and $\overline{D_{AB}^{T1}}$ arise from the change in concentration, with pressure and temperature, respectively, of the species in the two gases. These terms, unlike the terms $\overline{D_{AB}^{P1}}$ and $\overline{D_{A}^{T}}$, have no equivalent in a two-species mixture.

I note that $\overline{D_{AB}^{x}}$ and $\overline{D_{AB}^{P1}}$ are linear combinations of the coefficients D_{ij}^{a}; similarly, $\overline{D_{A}^{T}}$ is a linear combination of the coefficients D_i^{Ta}. These relations are investigated in Sec. III.

III. AN ILLUSTRATIVE EXAMPLE

I now present a calculation of the combined diffusion coefficients in mixtures of argon and nitrogen. The results illustrate some important properties of these coefficients.

The equilibrium concentrations of the species present in the argon-nitrogen mixture were determined by the method of minimization of Gibbs free energy [18]. The required thermodynamic data for the species were found using the data in the JANAF tables [19], or calculated using the atomic energy levels listed by Moore [20]. Figure 1 shows the results for a mixture of 50% argon and 50% nitrogen by weight at a pressure of 101.3 kPa. Only those species that were present with a mole fraction of more than 0.01 are shown. Other species considered in the calculation were $N_2{}^+$, N^-, Ar^{3+}, and N^{3+}; the maximum mole fractions of these species for temperatures below 30 000 K were 5×10^{-5}, 1×10^{-5}, 1.6×10^{-3}, and 6×10^{-5}, respectively. All species except N^- were considered in the diffusion calculations.

The combined diffusion coefficients were calculated using Eqs. (20)–(22). The required ambipolar diffusion coefficients D_{ij}^{a} and D_i^{Ta} are given in Eqs. (11) and (12) in terms of the individual diffusion coefficients D_{ij} and D_i^T. The collision integrals required to calculate D_{ij} and D_i^T were obtained by the methods outlined in Appendix B.

Figure 2 shows the temperature dependence of the combined ordinary diffusion coefficient $\overline{D_{\mathrm{Ar,N_2}}^{x}}$ for the conditions of Fig. 1. The behavior of $\overline{D_{\mathrm{Ar,N_2}}^{x}}$ can be understood by referring to the ambipolar ordinary diffusion coefficients D_{ij}^{a} of the pairs of species present. Since $q = 11$ species are considered in the calculations, there is a total of $q^2 = 121$ such coefficients, of which $\frac{1}{2}q(q-1) = 55$ are independent. Some of these are also shown in Fig. 2. At low temperature, for which Ar and N_2 are the only species present, $\overline{D_{\mathrm{Ar,N_2}}^{x}} = D_{\mathrm{Ar,N_2}}^{a}$. At temperatures around 9000 K, for which Ar and N are the dominant species present, $\overline{D_{\mathrm{Ar,N_2}}^{x}} \approx D_{\mathrm{Ar,N}}^{a}$. We see that $\overline{D_{\mathrm{Ar,N_2}}^{x}}$ increases with temperature up to temperatures at which significant ionization occurs; at higher temperatures, it falls rapidly, owing to the lower values of D_{ij}^{a} for ionized species. These lower values are due to the strength of the Coulomb interaction, which leads to

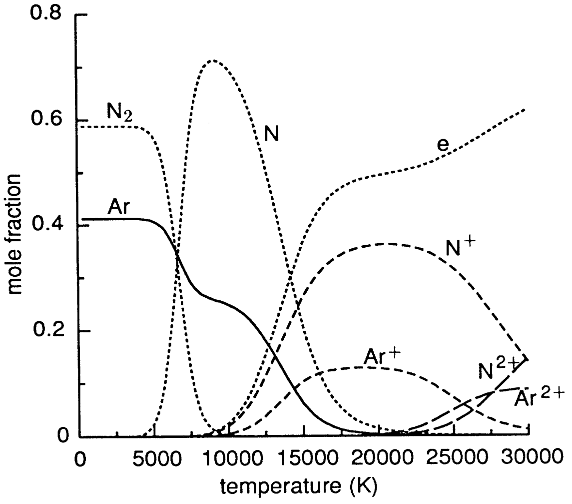

FIG. 1. Equilibrium concentration of a mixture of 50% argon and 50% nitrogen by weight at a pressure of 101.3 kPa. Species that have mole fractions less than 0.01 over the full temperature range are not shown.

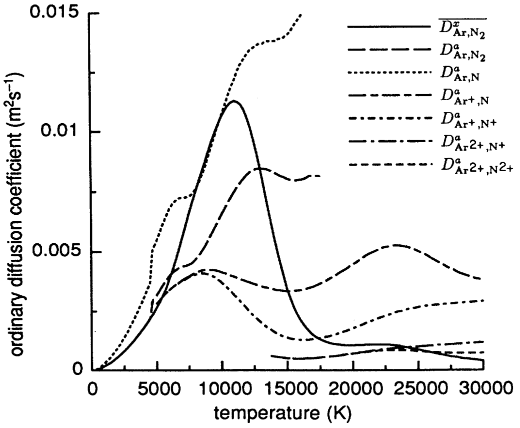

FIG. 2. Combined ordinary diffusion coefficient, and ordinary diffusion coefficients for some pairs of species, as a function of temperature, in a mixture of 50% argon and 50% nitrogen by weight.

larger collision cross sections and hence lower diffusion rates. At all temperatures, $\overline{D^x_{\mathrm{Ar,N_2}}}$ represents a weighted average of the ordinary diffusion coefficients of the pairs of species present.

It was mentioned in Sec. I that some authors have used binary diffusion coefficients as a substitute for $\overline{D^x_{AB}}$. It is interesting to establish the magnitude of the error introduced by this substitution. Figure 3 compares the binary diffusion coefficients $\mathcal{D}_{\mathrm{Ar,N_2}}$ and $\mathcal{D}_{\mathrm{Ar,N}}$ with $\overline{D^x_{\mathrm{Ar,N_2}}}$. It is clear that although $\mathcal{D}_{\mathrm{Ar,N_2}}$ and $\mathcal{D}_{\mathrm{Ar,N}}$ are good approximations to $\overline{D^x_{\mathrm{Ar,N_2}}}$ at temperatures below those at which significant ionization occurs, at higher temperatures the use of binary diffusion coefficients leads to very large errors.

It was noted in Sec. II C that the combined thermal diffusion coefficient component $\overline{D^T_A}$ is a linear combination of the ambipolar thermal diffusion coefficients D^{Ta}_i. The temperature dependence of the term $\overline{D^T_{\mathrm{Ar}}} = -\overline{D^T_{\mathrm{N_2}}}$ is compared in Fig. 4 with seven of the $q = 11$ coefficients D^{Ta}_i, of which $q - 1 = 10$ are independent. At temperatures below those at which significant dissociation of nitrogen occurs, $\overline{D^T_{\mathrm{Ar}}} = D^{Ta}_{\mathrm{Ar}} = -D^{Ta}_{\mathrm{N_2}}$; at higher temperatures, up to around 9000 K, $\overline{D^T_{\mathrm{Ar}}} = D^{Ta}_{\mathrm{Ar}} \approx -D^{Ta}_{\mathrm{N}}$. At still higher temperatures, $\overline{D^T_{\mathrm{Ar}}}$ decreases rapidly, because of the lower thermal diffusion coefficients of charged species. As with $\overline{D^x_{\mathrm{Ar,N_2}}}$ for ordinary diffusion coefficients, $\overline{D^T_{\mathrm{Ar}}}$ is a weighted average of the thermal diffusion coefficients of all species present.

The dependence of $\overline{D^x_{\mathrm{Ar,N_2}}}$ on the relative concentrations of argon and nitrogen is shown in Fig. 5. We see that, unlike D_{ij} in a two-species gas, $\overline{D^x_{AB}}$ in a mixture of two gases can vary according to the relative concentration of the gases. This is because the degree of dissociation and ionization of the two gases depends on the relative concentrations of the gases; thus, for example, $x_{\mathrm{Ar^+}}/\overline{x_{\mathrm{Ar}}}$ is a function of $\overline{x_{\mathrm{Ar}}}$. At temperatures below those at which dissociation and ionization take place, $\overline{D^x_{\mathrm{Ar,N_2}}}$ is independent of $\overline{x_{\mathrm{Ar}}}$.

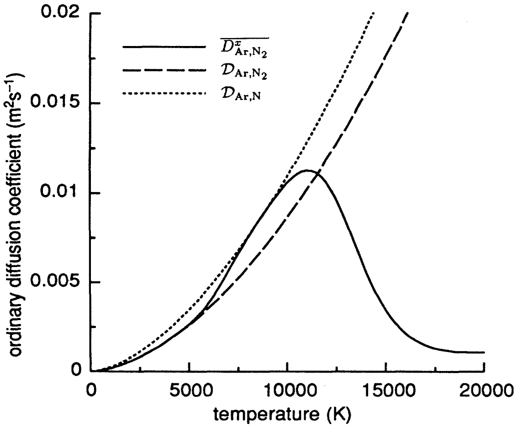

FIG. 3. Combined ordinary diffusion coefficient, and binary diffusion coefficients for Ar-N$_2$ and Ar-N, as a function of temperature, in a mixture of 50% argon and 50% nitrogen by weight.

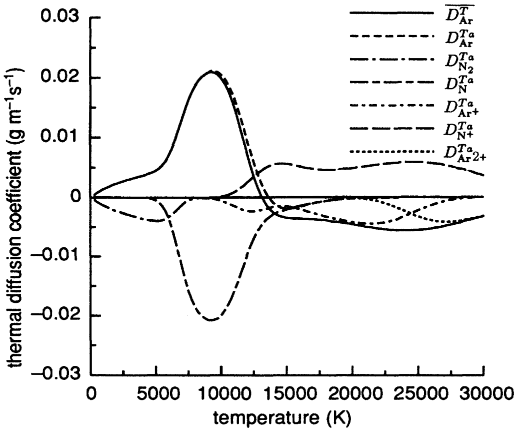

FIG. 4. The component $\overline{D^T_{\mathrm{Ar}}}$ of the combined thermal diffusion coefficient, and thermal diffusion coefficients of some species, as a function of temperature, in a mixture of 50% argon and 50% nitrogen by weight.

Figure 6 shows the dependence of $\overline{D^T_{\mathrm{Ar,N_2}}}$ and its two components, $\overline{D^T_{\mathrm{Ar}}}$ and $\overline{D^{T1}_{\mathrm{Ar,N_2}}}$, on $\overline{x_{\mathrm{Ar}}}$. We expect $\overline{D^T_{\mathrm{Ar}}}$ to have a strong dependence on $\overline{x_{\mathrm{Ar}}}$, since D^T_i, unlike D_{ij}, is a function of x_i in a two-species gas. This is illustrated in the figure by the low-temperature behavior of $\overline{D^T_{\mathrm{Ar}}}$: at temperatures at which Ar and N$_2$ are the only species present, $\overline{D^T_{\mathrm{Ar}}} = D^{Ta}_{\mathrm{Ar}}$, although relatively small, clearly depends strongly on $\overline{x_{\mathrm{Ar}}} = x_{\mathrm{Ar}}$. We also expect $\overline{D^{T1}_{\mathrm{Ar,N_2}}}$ to be a function of $\overline{x_{\mathrm{Ar}}}$, since $\partial x_i/\partial T$ is a function of $\overline{x_{\mathrm{Ar}}}$.

Figure 6 indicates that at temperatures below those at which dissociation of N$_2$ takes place, and also in the temperature range between the dissociation temperature of N$_2$ and the ionization temperatures of Ar and N, $\overline{D^T_{\mathrm{Ar}}}$ is the dominant component of $\overline{D^T_{\mathrm{Ar,N_2}}}$. At other temperatures, $\overline{D^{T1}_{\mathrm{Ar,N_2}}}$ is generally the more important.

Figure 7 shows the dependence of $\overline{D^P_{\mathrm{Ar,N_2}}}$ and its two

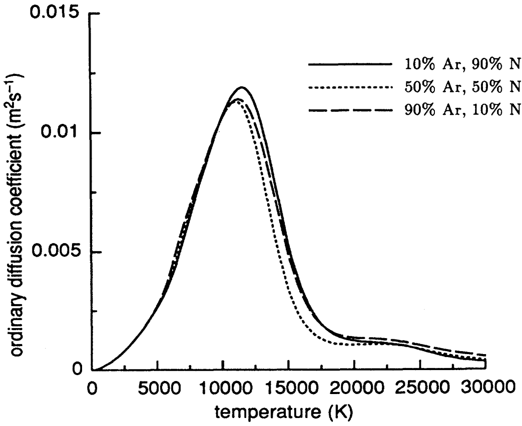

FIG. 5. Combined ordinary diffusion coefficient as a function of temperature for different mixtures of argon and nitrogen. Proportions are by weight.

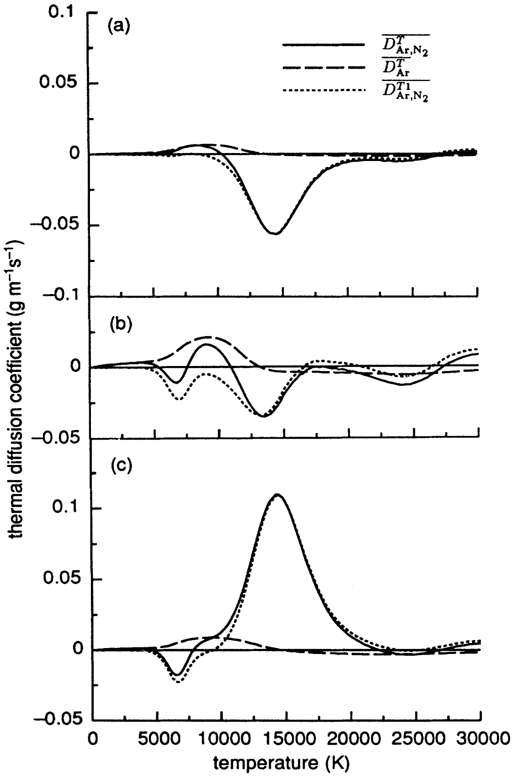

FIG. 6. Combined thermal diffusion coefficient, and its components, as a function of temperature for different mixtures of argon and nitrogen. (a) 10% argon, 90% nitrogen; (b) 50% argon, 50% nitrogen; (c) 90% argon, 10% nitrogen. Proportions are by weight.

components, $\overline{D^{P1}_{\mathrm{Ar,N_2}}}$ and $\overline{D^{P2}_{\mathrm{Ar,N_2}}}$, on $\overline{x_{\mathrm{Ar}}}$. We see that, similarly to $\overline{D^T_{\mathrm{Ar,N_2}}}$, $\overline{D^P_{\mathrm{Ar,N_2}}}$ and its two components strongly depend on the relative concentrations of the two gases. The dependence of $\overline{D^{P1}_{\mathrm{Ar,N_2}}}$ arises from the factor $x_j - \rho_j/\rho$ in the definition; see Eq. (27). The dependence of $\overline{D^{P2}_{\mathrm{Ar,N_2}}}$ is analogous to that of $\overline{D^{T1}_{\mathrm{Ar,N_2}}}$. For most temperatures and concentration ratios, $|\overline{D^{P1}_{\mathrm{Ar,N_2}}}| \gg |\overline{D^{P2}_{\mathrm{Ar,N_2}}}|$.

The magnitude of $\overline{D^P_{\mathrm{Ar,N_2}}}$ is generally within one order of magnitude of that of $\overline{D^x_{\mathrm{Ar,N_2}}}$; however, diffusion due to pressure gradients will in most cases be negligible compared to diffusion due to concentration gradients, because of the logarithmic dependence of $\mathbf{d}_j$ on P in Eq. (13a).

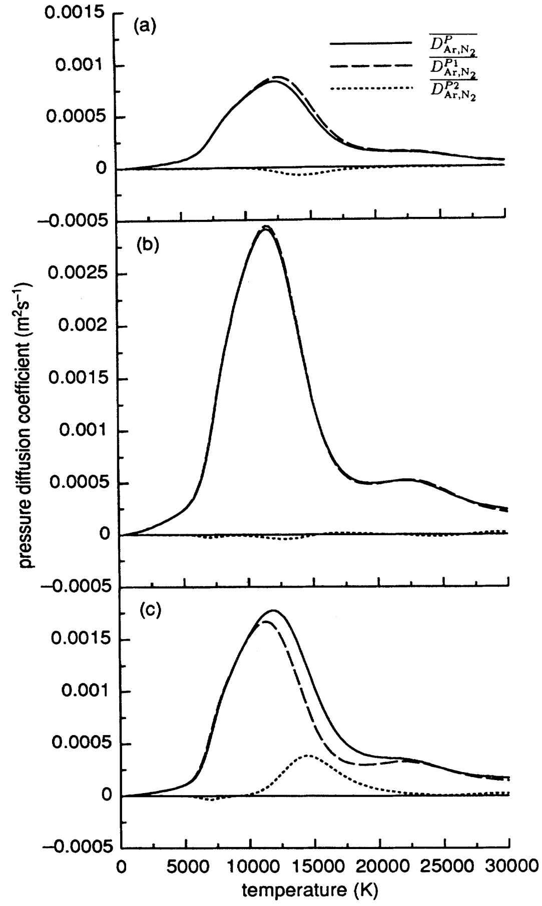

FIG. 7. Combined pressure diffusion coefficient, and its components, as a function of temperature for different mixtures of argon and nitrogen. (a) 10% argon, 90% nitrogen; (b) 50% argon, 50% nitrogen; (c) 90% argon, 10% nitrogen. Proportions are by weight.

IV. CONCLUSIONS

I have shown that the diffusive mixing of two nonreacting homonuclear gases can be fully described by three combined diffusion coefficients, provided that an equilibrium composition of the gas mixture can be defined as a function of temperature, pressure, and relative concentrations of the two gases.

The combined diffusion coefficients, termed the combined ordinary, thermal, and pressure diffusion coefficients, describe diffusion due to concentration, temperature, and pressure gradients, respectively. The combined ordinary diffusion coefficient is analogous to the ordinary diffusion coefficient in a two-species mixture. The combined thermal and pressure diffusion coefficients each have two components. The first components are, respectively, analogous to the thermal diffusion coefficient in a two-species mixture and the ordinary diffusion coefficient (which describes diffusion due to a pressure gradient as well as diffusion due to a concentration gradient) in a two-species mixture. The second components describe diffusion arising, respectively, from the temperature and pressure dependence of the concentrations of the species in the two gases.

The ambipolar effects that occur in ionized gases are included in the formulation employed. As in previous treatments, diffusion due to an applied electric field is described by the electrical conductivity, and an applied gravitational field has no influence on diffusion.

I have presented formulas for the combined diffusion coefficients and the electrical conductivity in terms of the ordinary diffusion coefficients of the pairs of species present and of the thermal diffusion coefficients of the species present. Combined diffusion coefficients in a mixture of argon and nitrogen at atmospheric pressure and at temperatures up to 30 000 K have been calculated as an example.

Previous treatments of diffusion in mixtures of ionized gases required $\frac{1}{2}q(q-1)$ independent ordinary diffusion coefficients and $q-1$ independent thermal diffusion coefficients to be considered. The complexity of such treatments has led some authors to make inappropriate approximations in an effort to simplify problems. The concept of combined diffusion coefficients that I have introduced will allow a wide range of problems encountered in modeling thermal plasmas and hot gases to be treated simply yet correctly.

ACKNOWLEDGEMENT

I wish to thank Professor E. A. Mason, of Brown University, for his helpful comments on a conference presentation of some of the material contained in this paper.

APPENDIX A: SYMMETRIC-DIFFUSION-COEFFICIENT FORMULATION

It was noted in Sec. II A that there is considerable variation among authors in the definition of diffusion coefficients. Here I present a summary of the main results of this paper in terms of the symmetric diffusion coefficients $\tilde{D}_{ij}$ and $\tilde{D}_i^T$, defined by Eq. (3).

The symmetric ambipolar diffusion coefficients $\tilde{D}_{ij}^a$ and $\tilde{D}_i^{Ta}$ may be calculated using the method outlined in Sec. II B, giving

$$\tilde{D}_{ij}^a = \tilde{D}_{ij} + \frac{\tilde{\alpha}_i}{\tilde{\beta}} \sum_{l=1}^{q} Z_l n_l \tilde{D}_{lj} \tag{A1}$$

and

$$\tilde{D}_i^{Ta} = \tilde{D}_i^T + \frac{\tilde{\alpha}_i}{\tilde{\beta}} \sum_{l=1}^{q} Z_l n_l \tilde{D}_l^T , \tag{A2}$$

where

$$\tilde{\alpha}_i = \sum_{j=1}^{q} Z_j n_j \tilde{D}_{ij} \tag{A3}$$

and

$$\tilde{\beta} = -\sum_{i,j=1}^{q} Z_i Z_j n_i n_j \tilde{D}_{ij} . \tag{A4}$$

When $n_1 = 0$, ambipolar effects do not occur, and we write $\tilde{D}_{ij}^a = \tilde{D}_{ij}$ and $\tilde{D}_i^{Ta} = \tilde{D}_i^T$.

To derive the combined symmetric diffusion coefficients $\overline{\tilde{D}_{AB}^x}$, $\overline{\tilde{D}_{AB}^P}$, and $\overline{\tilde{D}_{AB}^T}$, we begin with the analogous equation to Eq. (13a):

$$\overline{\mathbf{g}_A} = -\overline{n_A} \left(\overline{\tilde{D}_{AB}^x} \nabla \overline{x_B} + \overline{\tilde{D}_{AB}^P} \nabla \ln P + \overline{\tilde{D}_{AB}^T} \nabla \ln T \right) , \tag{A5}$$

where $\overline{n_A} = n\overline{x_A}$ is the number density of gas A. We then proceed as in Sec. II C to obtain

$$\overline{\tilde{D}_{AB}^x} = \frac{1}{\overline{n_A}} \sum_{i=2}^{p} s_i n_i \sum_{j=1}^{q} \tilde{D}_{ij}^a \frac{\partial x_j}{\partial \overline{x_B}} , \tag{A6}$$

$$\overline{\tilde{D}_{AB}^P} = \frac{1}{\overline{n_A}} \sum_{i=2}^{p} s_i n_i \sum_{j=1}^{q} \tilde{D}_{ij}^a \left(x_j - \frac{\rho_j}{\rho} + P \frac{\partial x_j}{\partial P} \right) , \tag{A7}$$

and

$$\overline{\tilde{D}_{AB}^T} = \frac{1}{\overline{n_A}} \sum_{i=2}^{p} s_i n_i \left(\tilde{D}_i^{Ta} + \sum_{j=1}^{q} \tilde{D}_{ij}^a T \frac{\partial x_j}{\partial T} \right) . \tag{A8}$$

Similar expressions for $\overline{\tilde{D}_{BA}^x}$, $\overline{\tilde{D}_{BA}^P}$, and $\overline{\tilde{D}_{BA}^T}$ may be calculated. They obey the relations $\overline{n_A m_A}\,\overline{\tilde{D}_{AB}^x} = \overline{n_B m_B}\,\overline{\tilde{D}_{BA}^x}$, $\overline{n_A m_A}\,\overline{\tilde{D}_{AB}^P} = -\overline{n_B m_B}\,\overline{\tilde{D}_{BA}^P}$, and $\overline{n_A m_A}\,\overline{\tilde{D}_{AB}^T} = -\overline{n_B m_B}\,\overline{\tilde{D}_{BA}^T}$, respectively.

APPENDIX B: CALCULATION OF COLLISION INTEGRALS

The diffusion coefficients D_{ij} and D_i^T, defined by Eq. (1), and their counterparts $\tilde{D}_{ij}$ and $\tilde{D}_i^T$ under the alternate definition of Eq. (3), were calculated using the Chapman-Enskog method [1–3,9]. The coefficients are calculated from sets of linear equations, the terms of which are functions of the number densities, masses, and collision integrals of the species present. The collision integrals $\bar{\Omega}_{ij}^{(l,s)}$ for interactions between species i and j are defined by

$$\bar{\Omega}_{ij}^{(l,s)} = \frac{4(l+1)}{\pi(s+1)![2l+1-(-1)^l]} \times \int_0^\infty e^{-\gamma^2} \gamma^{2s+3} Q_{ij}^{(l)}(g) d\gamma , \tag{B1}$$

where $\gamma^2 = \mu g^2/2kT$, μ being the reduced mass of the species i and j, g is their relative speed, and $Q_{ij}^{(l)}(g)$ are the gas-kinetic cross sections, given by

$$Q_{ij}^{(l)}(g) = 2\pi \int_0^\infty (1 - \cos^l \chi) b \, db . \tag{B2}$$

Here b is the impact parameter, and χ is the deflection angle, which is a function of b, g, and the intermolecular potential $V(r)$, where r is the separation between the interacting particles [1,3].

Diffusion coefficients were calculated to a second-order approximation; this required that $\tilde{\Omega}_{ij}^{(1,1)}$, $\tilde{\Omega}_{ij}^{(1,2)}$, $\tilde{\Omega}_{ij}^{(1,3)}$, and $\tilde{\Omega}_{ij}^{(2,2)}$ be calculated. (The order of the approximation is here defined to be the number of terms retained in the finite Sonine polynomial approximation used in the Chapman-Enskog method.)

The methods by which the collision integrals for the interactions of species derived from argon and nitrogen were obtained are now described. Considerable effort was expended to locate up-to-date and reliable data. The collision integrals were obtained in three ways: directly from tabulations, by numerical integration of experimental data for the momentum-transfer cross section $Q_{ij}^{(1)}(g)$ using Eq. (B1), and from published intermolecular potentials using Eqs. (B1) and (B2). In the latter case, the method of Barker, Fock, and Smith [21] was used to numerically evaluate the required integrals for all but exponential, polarization, and screened Coulomb potentials; collision integrals in these cases were obtained using the data of Monchick [22], Kihara, Taylor, and Hirschfelder [23], and Mason, Munn, and Smith [24], respectively.

Collision integrals for N-N interactions were taken from the tabulation of Levin, Partridge, and Stallcop [25]. All other collision integrals for neutral-neutral interactions were calculated from intermolecular potentials. Ar-Ar interactions were described using the Hartree-Fock-dispersion–total-cross-section-2 potential [26], N_2-N_2 and N_2-N interactions by exponential potentials [27], N_2-Ar interactions by an exponential-spline–Morse-spline–van der Waals potential [28], and N-Ar interactions by the Lennard-Jones (12,6) potential [28].

Collision integrals for N^+-N interactions were taken from the tabulation of Stallcop, Partridge, and Levin [29]. Collision integrals for the N^+-Ar interaction were calculated from the Morse potentials given by Weise and Mittmann [30]. The $\tilde{\Omega}_{ij}^{(1,s)}$ collision integrals for the Ar^+-Ar and Ar^+-N_2 interactions were calculated from the charge-exchange data given by Aubreton, Bonnefoi, and Mexmain [31] and Tosi, Dmitrijev, and Bassi [32], respectively. The $\tilde{\Omega}_{ij}^{(1,s)}$ collision integrals for the ${N_2}^+$-N_2 and N^+-N_2 interactions were calculated from the momentum-transfer cross-section data tabulated by Phelps [33]. The $l = s = 2$ collision integral for the Ar^+-Ar interaction was calculated using a combination of Morse and exponential potentials [31]; the $l = s = 2$ collision integral for the Ar^+-N_2, ${N_2}^+$-N_2, and N^+-N_2 interactions, and all collision integrals for the ${N_2}^+$-N, ${N_2}^+$-Ar, and Ar^+-N interactions were calculated using the polarization potential $V(r) = -\alpha(Ze)^2/32\pi^2\epsilon_0^2 r^4$, where α is the polarizability of the ion, Ze is the ionic charge, and ϵ_0 is the permittivity of free space. Values of α were taken from Ref. [34].

The $l = 1$ collision integrals for electron-neutral interactions were calculated from momentum-transfer cross-section data; it was assumed that $\tilde{\Omega}_{ij}^{(2,s)} = \tilde{\Omega}_{ij}^{(1,s)}$. The momentum-transfer cross-section measurements of Milloy *et al.* [35], supplemented by those of Frost and Phelps [36] for high-energy collisions, were used for e-Ar interactions. The measurements of Engelhardt, Phelps, and Risk [37] were used for e-N_2 interactions. The total cross-section measurements of Neynaber *et al.* [38] were used in place of momentum-transfer cross-section data for e-N interactions, since no measurements of the latter were available.

Collision integrals for interactions between charged species were calculated using the screened Coulomb potential [24], the screening distance being set equal to the Debye radius.

More detailed discussions of the general principles of the calculation of collision integrals in ionized gases have been presented by, for example, Capitelli [14] and Aubreton and Fauchais [39].

[1] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, 2nd ed. (Wiley, New York, 1964).

[2] S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases*, 3rd ed. (Cambridge University Press, Cambridge, England, 1970).

[3] J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases* (North-Holland, Amsterdam, 1972).

[4] W. Frie and H. Maecker, Z. Phys. **162**, 69 (1961).

[5] X. Chen, Y. P. Chyou, Y. C. Lee, and E. Pfender, Plasma Chem. Plasma Process. **5**, 119 (1985).

[6] Y. C. Lee and E. Pfender, Plasma Chem. Plasma Process. **7**, 1 (1987).

[7] A. H. Diliwari and J. Szekely, Plasma Chem. Plasma Process. **7**, 317 (1987).

[8] A. B. Murphy, J. Chem. Phys. **99**, 1340 (1993).

[9] R. S. Devoto, Phys. Fluids **9**, 1230 (1966).

[10] C. F. Curtiss, J. Chem. Phys. **49**, 2917 (1968).

[11] A. M. Rahal, B. Rahhaoui, and S. Vacquie, J. Phys. D **17**, 1807 (1984).

[12] J. Bacri, A.-M. Gomes, and M. Eymard, J. Phys. D **18**, 1339 (1985).

[13] J. D. Ramshaw, J. Non-Equilib. Thermodyn. **15**, 295 (1990).

[14] M. Capitelli, J. Phys. (Paris) Colloq. **38**, C3-227 (1977).

[15] C. Bonnefoi, J. Aubreton, and J.-M. Mexmain, Z. Naturforsch. Teil A **40**, 885 (1985).

[16] S. Paik and E. Pfender, Plasma Chem. Plasma Process. **10**, 291 (1990).

[17] R. Darrigo, High Temp. High Pressures **1**, 589 (1969).

[18] R. A. Svehla and B. J. McBride, NASA Technical Note NASA TN D-7056, 1973 (unpublished).

[19] M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, J. Phys. Chem. Ref. Data **14**, Suppl. 1 (1985).

[20] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) Circular No. 467 (U.S. GPO, Washington, DC, 1949), Vol. 1.

[21] J. A. Barker, W. Fock, and F. Smith, Phys. Fluids **7**, 897 (1964).

[22] L. Monchick, Phys. Fluids **2**, 695 (1959).

[23] T. Kihara, M. H. Taylor, and J. O. Hirschfelder, Phys. Fluids **3**, 715 (1960).

[24] E. A. Mason, R. J. Munn, and F. J. Smith, Phys. Fluids **10**, 1827 (1967).

[25] E. Levin, H. Partridge, and J. R. Stallcop, J. Thermophys. Heat Transf. **4**, 469 (1990).

[26] R. A. Aziz and M. J. Slaman, J. Chem. Phys. **92**, 1030 (1990).

[27] M. Capitelli and R. S. Devoto, Phys. Fluids **16**, 1835 (1973).

[28] B. Brunetti, G. Liuti, E. Luzatti, F. Pirani, and G. G. Volpi, J. Chem. Phys. **79**, 273 (1983).

[29] J. R. Stallcop, H. Partridge, and E. Levin, J. Chem. Phys. **95**, 6429 (1991).

[30] H. P. Weise and H.-U. Mittmann, Z. Naturforsch., Teil A **29**, 1143 (1974).

[31] J. Aubreton, C. Bonnefoi, and J. M. Mexmain, Rev. Phys. Appl. **21**, 365 (1986).

[32] P. Tosi, O. Dmitrijev, and D. Bassi, Chem. Phys. Lett. **200**, 483 (1992).

[33] A. V. Phelps, J. Phys. Chem. Ref. Data **20**, 557 (1991).

[34] T. M. Miller, in *CRC Handbook of Chemistry and Physics*, 72nd ed., edited by D. R. Lide (CRC Press, Boca Raton, FL, 1991), pp. 10-194–10-210.

[35] H. B. Milloy, R. W. Crompton, J. A. Rees, and A. G. Robertson, Aust. J. Phys. **30**, 61 (1977).

[36] L. S. Frost and A. V. Phelps, Phys. Rev. **136**, A1538 (1964).

[37] A. G. Engelhardt, A. V. Phelps, and C. G. Risk, Phys. Rev. **135**, A1566 (1964).

[38] R. H. Neynaber, L. L. Marino, E. W. Rothe, and S. M. Trujillo, Phys. Rev. **129**, 2069 (1963).

[39] J. Aubreton and P. Fauchais, Rev. Phys. Appl. **18**, 51 (1983).