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Diffusion in two-temperature thermal plasmas

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Combined diffusion coefficients, which allow species to be grouped into their parent gases, are derived in a thermal plasma in which the kinetic temperature of the electrons is different from that of the heavy species. As in previous calculations of combined diffusion coefficients for a one-temperature plasma, chemical equilibrium is assumed, and a plasma in a mixture of two homonuclear nonreacting gases is treated. Expressions for ambipolar diffusion in a two-temperature plasma are derived. Coupling between the electrons and the heavy species is retained in the calculations. It is confirmed that the values of the diffusion coefficients are consistent with mass conservation, in contrast to previous calculations that were based on a theory in which the electrons and heavy species were decoupled. Illustrative results are presented for a thermal plasma in different mixtures of argon and hydrogen at 1 bar, for temperatures up to 25 000 K and different ratios of electron to heavy species temperature.

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I. INTRODUCTION

Thermal plasmas [1] are widely used in material processing, for example, for deposition, cutting, welding, or surface modification. Their applications are diverse, encompassing the alteration of optical, mechanical (hardness, corrosion, wear, thermal barrier), and electronic properties of the materials. The reproducibility of plasma processes is improving because of, on one hand, the increasing understanding of plasma properties and, on the other hand, the development of plasma flow modeling.

Plasma flow modeling requires the solution of conservation equations of mass, momentum, and energy, and species, taking into account boundary conditions and the plasma geometry. To solve these conservation equations requires the knowledge of transport coefficients. Because these coefficients are difficult to measure, especially at high temperature (above 6000 K), much effort has been put into their calculation. They are usually calculated under the assumption of local thermodynamic equilibrium (LTE) [2–5], using the Chapman-Enskog method for the approximate solution of the Boltzmann equation [6]. The distribution function of species is assumed to be a Maxwellian, perturbed by a first-order perturbation function that introduces forces (concentration, pressure, and temperature gradients) associated with transport phenomena.

The treatment of diffusion in modeling is often complex since, when considering a plasma with N species, $N(N-1)/2$ linearly independent ordinary diffusion coefficients D_{ij} and $N-1$ linearly independent thermal diffusion coefficients D_i^T have to be calculated, and $N-1$ species conservation equations have to be solved at each position in the plasma. To overcome this complication, Murphy simplified the treatment of diffusion by defining combined diffusion coefficients. These were derived for binary mixtures of homonuclear gases that do not react with each other [7], under the assumption of chemical equilibrium. This approach enables the description of diffusion in terms of gases instead of species. The combined diffusion coefficients depend on ordinary and thermal diffusion coefficients and convey an overall description of the diffusion in a plasma. As a consequence, the $N-1$ species conservation equations can be replaced by a single gas conservation equation.

Diffusion is an important phenomenon in thermal plasmas in gas mixtures, and the combined diffusion coefficient formulation has been used to model diffusion in many different types of thermal plasmas in LTE. For example, Murphy [8,9] has modeled demixing in free-burning arcs in mixtures of argon with nitrogen, helium, oxygen, and hydrogen. As well as causing major departures from fully mixed compositions, demixing can lead to significant changes in other properties; for example, the anode heat flux can be enhanced by as much as 50% due to the influence of demixing in argon-hydrogen arcs. Fudolig and co-workers modeled an arc reactor in a mixture of argon and nitrogen [10], and the heat transfer to metal beads in an argon-hydrogen arc [11]. Chen, Sugasawa, and Kikukawa [12] modeled a radio-frequency plasma torch with argon and hydrogen as the working gases. Zhang *et al.* [13] investigated the effect of polytetrafluoroethylene ablation on the operation of a sulfur hexafluoride circuit breaker.

Many authors have presented evidence of departures from LTE (see, for example, Refs. [14–16]) in thermal plasmas, in particular, close to the electrodes of free-burning arcs, for which the kinetic temperature of electrons T_e is different from that of heavy species T_h. The modeling of plasmas in which $T_e \neq T_h$ requires the determination of two-temperature (2T) transport coefficients. A particularly relevant example is the discrepancies found in a recent study [17] between the composition determined by spectroscopic measurements and by modeling of a free-burning arc in a mixture of argon and hydrogen. The model used combined diffusion coefficients calculated assuming $T_e = T_h$. Close to the cathode, the measurements revealed a much greater level of demixing than the calculations, while at a greater distance from the cathode, good agreement was found. It was hypothesized that the discrepancies found near the cathode were due to deviations from LTE.

Devoto [18,19] introduced a simplified theory of transport properties, later modified by Bonnefoi [20], which assumes a complete decoupling between electrons and heavy species, and which was used to derive 2T transport coefficients. Recently, Rat *et al.* [21,22] showed that this simplified theory leads to unphysical results when calculating the combined diffusion coefficients of Murphy [7] at equilibrium. In particular, Rat *et al.* showed that mass conservation is not satisfied if the simplified transport properties theory is used. To correct this problem, they developed a 2T theory of transport properties that retains coupling between electrons and heavy species. Two-temperature diffusion coefficients, thermal and electrical conductivity, and viscosity were derived. The results of the application of the theory to a pure argon plasma [23] have been presented. They showed the dependence of transport coefficients on the degree of deviation from equilibrium, and demonstrated that retaining the coupling between the electrons and heavy species gives electrical and thermal conductivities that are significantly different from those obtained using the simplified theory.

This approach has been extended [24,25] to a mixture of argon and hydrogen, which is widely used, for example, in plasma spraying deposition processes. The 2T reaction thermal conductivity was defined such that it is independent of the method of 2T plasma composition calculation [26]. Once again, significant discrepancies have been observed between the results of this approach and those of the simplified theory.

The purpose of this paper is to derive combined diffusion coefficients in a thermal plasma in which the kinetic temperature of the electrons, T_e, is different from that of heavy species, T_h. The degree of deviation from equilibrium is described by the parameter $\theta = T_e/T_h$. As in previous calculations of combined diffusion coefficients, we assume chemical equilibrium and consider a plasma in a mixture of two homonuclear nonreacting gases.

In Sec. II, ambipolar diffusion coefficients are derived from the nonequilibrium diffusion fluxes of species introduced by Rat *et al.* [21]. In addition, 2T combined diffusion coefficients are derived in the presence of gradients in the concentration, pressure, heavy species temperature, and the nonequilibrium parameter θ. In Sec. III, the method is applied to an argon-hydrogen plasma. The dependence on temperature of the combined ordinary and thermal diffusion coefficients is investigated for different molar percentages of argon and for different values of θ. Particular attention is paid to the conservation of mass. Conclusions are given in Sec. IV.

II. NON-EQUILIBRIUM DIFFUSION

A. Ambipolar diffusion coefficients

Because of their small mass, electrons diffuse more rapidly than heavy species in the presence of a concentration, pressure or temperature gradient, resulting in the creation of a charge separation between electrons and ions. The diffusion velocities of species are influenced by the resulting ambipolar electric field $\vec{E}_a$, leading to an alteration of the standard diffusion coefficients. It has been shown [21] that the diffusion velocity of the ith species (the index 1 is attributed to electrons) relative to the mass-average velocity in a nonequilibrium thermal plasma is written, without taking into account the ambipolar electric field, as follows:

$$\overline{\vec{V}_i} = \frac{n}{n_i \rho k T_i}\sum_{j=1}^{N} m_j (D_{ij}\vec{d}_j + D_{ij}^{\theta} g_j \vec{\nabla}\ln\theta) - \frac{D_i^T}{n_i m_i}\vec{\nabla}\ln T_h - \frac{D_i^{\theta *}}{n_i m_i}\vec{\nabla}\ln\theta, \tag{2.1}$$

where

$$\vec{d}_1 = p\left[\frac{\rho_1}{\rho p}\sum_{i=1}^{N} n_i \vec{F}_i - \frac{n_1\vec{F}_1}{p} + \left(\frac{x_1\theta}{D} - \frac{\rho_1}{\rho}\right)\vec{\nabla}\ln p + \frac{\theta}{D^2}\vec{\nabla}x_1\right], \tag{2.2}$$

$$\vec{d}_j = p\left[\frac{\rho_i}{\rho p}\sum_{i=1}^{N} n_i \vec{F}_i - \frac{n_j\vec{F}_j}{p} + \left(\frac{x_j}{D} - \frac{\rho_j}{\rho}\right)\vec{\nabla}\ln p + \frac{\vec{\nabla}x_j}{D} - \frac{x_j(\theta-1)}{D^2}\vec{\nabla}x_1\right], \tag{2.3}$$

and p, ρ, and n are, respectively, the total pressure, total density, and total density number in the mixture; n_i, x_i, ρ_i, T_i, and m_i are, respectively, the number density, molar fraction, density, kinetic temperature, and mass of the ith species, and k is Boltzmann's constant. $\vec{F}_i$ is an external force acting on the ith species. The coefficients D_{ij}, D_i^T, D_{ij}^{θ}, and $D_i^{\theta *}$ are, respectively, ordinary diffusion coefficients, thermal diffusion coefficients, ordinary diffusion coefficients due to gradients in the nonequilibrium parameter, and thermal diffusion coefficients due to gradients in the nonequilibrium parameter. The factor D is defined as $D = 1 + x_1(\theta - 1)$, and $g_1 = x_1 p(1-x_1)/D^2$ for electrons and $g_1 = -x_i x_1 p/D^2$ for heavy species.

We consider an electrostatic force

$$\vec{F}_i = eZ_i\vec{E}_a \tag{2.4}$$

acting on the ith species, where e, Z_i, and $\overline{E_a}$ are, respectively, the elementary charge, the charge number of the ith species, and the ambipolar electric field. Substituting Eq. (2.4) into Eqs. (2.2) and (2.3) using the following neutrality condition,

$$\sum_{i=1}^{N} e n_i Z_i = 0, \tag{2.5}$$

it can be shown that

$$\vec{d}_j = -(e n_j Z_j/p)\vec{E}_a + \vec{d}\,'_j, \tag{2.6}$$

where

$$\vec{d}\,'_1 = p\left[\left(\frac{x_1\theta}{D} - \frac{\rho_1}{\rho}\right)\vec{\nabla}\ln p + \frac{\theta}{D^2}\vec{\nabla}x_1\right], \tag{2.7}$$

$$\overline{d'_j}=p\left[\left(\frac{x_j}{D}-\frac{\rho_j}{\rho}\right)\vec{\nabla}\ln p+\frac{\vec{\nabla}x_j}{D}-\frac{x_j(\theta-1)}{D^2}\vec{\nabla}x_1\right]\quad (j\geqslant 2). \tag{2.8}$$

When a stationary state is reached, the sum of current density vectors vanishes:

$$\sum_{i=1}^{N} e n_i Z_i \overline{\vec{V}_i}=\vec{0}. \tag{2.9}$$

Inserting Eqs. (2.1) and (2.6) into Eq. (2.9), the ambipolar electric field $\vec{E}_a$ is written as follows:

$$\begin{aligned}-\frac{en}{\rho k}\vec{E}_a=\frac{1}{\beta}\Bigg(&\frac{np}{\rho k}\sum_{i=1}^{N}\frac{Z_i}{T_i}\sum_{j=1}^{N} m_j D_{ij}\vec{d}'_j\\&+\frac{np}{\rho k}\sum_{i=1}^{N}\frac{Z_i}{T_i}\sum_{j=1}^{N} m_j D_{ij}^{\theta} g_j \vec{\nabla}\ln\theta\\&-\sum_{i=1}^{N}\frac{Z_i D_i^T}{m_i}\vec{\nabla}\ln T_h-\sum_{i=1}^{N}\frac{Z_i D_i^{\theta *}}{m_i}\vec{\nabla}\ln\theta\Bigg),\end{aligned} \tag{2.10}$$

where

$$\beta=-\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{Z_i}{T_i}Z_j n_j m_j D_{ij} \tag{2.11}$$

with $T_1=T_e$, and $T_i=T_h$ if $i\geqslant 2$.

Using Eq. (2.6), Eq. (2.1) is written as

$$\begin{aligned}\overline{\vec{V}_i}=&\frac{n}{n_i\rho k T_i}\sum_{j=1}^{N} m_j\left[D_{ij}\left(-\frac{e n_j Z_j}{p}\vec{E}_a+\vec{d}'_j\right)+D_{ij}^{\theta} g_j\vec{\nabla}\ln\theta\right]\\&-\frac{D_i^T}{n_i m_i}\vec{\nabla}\ln T_h-\frac{D_i^{\theta *}}{n_i m_i}\vec{\nabla}\ln\theta.\end{aligned} \tag{2.12}$$

Substituting Eq. (2.10) into Eq. (2.12) to take into account the ambipolar electric field, we obtain

$$\begin{aligned}\overline{\vec{V}_i}=&\frac{np}{n_i\rho k T_i}\sum_{j=1}^{N} m_j\left(D_{ij}^{a}\vec{d}'_j+\frac{D_{ij}^{\theta a} g_j}{p}\vec{\nabla}\ln\theta\right)\\&-\frac{D_i^{Ta}}{n_i m_i}\vec{\nabla}\ln T_h-\frac{D_i^{\theta a *}}{n_i m_i}\vec{\nabla}\ln\theta,\end{aligned} \tag{2.13}$$

with

$$D_{ij}^{a}=D_{ij}+\frac{\alpha_i}{\beta}\sum_{\ell=1}^{N}\frac{Z_\ell}{T_\ell}D_{\ell j}, \tag{2.14}$$

$$D_i^{Ta}=D_i^T+\frac{\alpha_i m_i}{\beta T_i}\sum_{\ell=1}^{N}\frac{Z_\ell D_\ell^T}{m_\ell}, \tag{2.15}$$

$$D_{ij}^{\theta a}=D_{ij}^{\theta}+\frac{\alpha_i}{\beta}\sum_{\ell=1}^{N}\frac{Z_\ell}{T_\ell}D_{\ell j}^{\theta}, \tag{2.16}$$

$$D_i^{\theta a *}=D_i^{\theta *}+\frac{\alpha_i m_i}{\beta T_i}\sum_{\ell=1}^{N}\frac{Z_\ell D_\ell^{\theta *}}{m_\ell}, \tag{2.17}$$

$$\alpha_i=\sum_{j=1}^{N} n_j m_j Z_j D_{ij}, \tag{2.18}$$

and with $T_1=T_e$, and $T_i=T_h$ if $i\geqslant 2$.

The diffusion coefficients D_{ij}^{a} and D_i^{Ta} are, respectively, the ordinary and thermal diffusion coefficients in 2T thermal plasmas. When $T_e=T_h$, they reduce to the respective coefficients of Murphy [7], which are defined at equilibrium. The diffusion coefficients $D_{ij}^{\theta a}$ and $D_i^{\theta a *}$ due to gradients in the nonequilibrium parameter do not, of course, have equivalents at equilibrium.

B. Two-temperature combined diffusion coefficients

We consider a nonequilibrium thermal plasma consisting of electrons with a kinetic temperature T_e that may be different from that of the heavy species T_h. We assume that the plasma is in chemical equilibrium. Following Murphy's notation [7], two partially ionized gases *A* and *B* are assumed to be homonuclear and to not react with each other. The index 1 is attributed to electrons, the indices $i=2,\dots,p$ correspond to species in gas *A*, and the indices $i=p+1,\dots,N$ correspond to species in gas *B*. *N* represents the total number of species.

The number flux of species *i*, relative to the mass-average velocity and taking into account ambipolar effects, is written, according to Eq. (2.13), as

$$\begin{aligned}\overline{\vec{g}_i}=&\frac{np}{\rho k T_i}\sum_{j=1}^{N} m_j\left(D_{ij}^{a}\vec{d}'_j+\frac{D_{ij}^{\theta a} g_j}{p}\vec{\nabla}\ln\theta\right)\\&-\frac{D_i^{Ta}}{m_i}\vec{\nabla}\ln T_h-\frac{D_i^{\theta a *}}{m_i}\vec{\nabla}\ln\theta.\end{aligned} \tag{2.19}$$

The number fluxes of gases *A* and *B*, relative to the mass-average velocity, are, respectively,

$$\overline{\vec{g}_A}=\sum_{i=2}^{p} s_i\overline{\vec{g}_i}, \tag{2.20}$$

$$\overline{\vec{g}_B}=\sum_{i=p+1}^{N} s_i\overline{\vec{g}_i}, \tag{2.21}$$

where the s_i are stoichiometric coefficients defined by [7]

$$s_i = b_i \sum_{k=2}^{p} x_k \Big/ \sum_{k=2}^{p} b_k x_k, \quad 2 \leqslant i \leqslant p, \tag{2.22}$$

$$s_i = b_i \sum_{k=p+1}^{N} x_k \Big/ \sum_{k=p+1}^{N} b_k x_k, \quad p+1 \leqslant i \leqslant N. \tag{2.23}$$

Introducing Eq. (2.19) into Eq. (2.20), it can be shown that

$$\overline{\vec{g}_A} = \sum_{i=2}^{\rho} s_i \left[\frac{np}{\rho k T_i} \sum_{j=1}^{N} m_j \left(D_{ij}^{a} \vec{d}_j' + \frac{D_{ij}^{\theta a} g_j}{p} \vec{\nabla} \ln \theta \right) - \frac{D_i^{Ta}}{m_i} \vec{\nabla} \ln T_h - \frac{D_i^{\theta a *}}{m_i} \vec{\nabla} \ln \theta \right]. \tag{2.24}$$

Hence, using Eqs. (2.7) and (2.8),

$$\begin{aligned} \overline{\vec{g}_A} = {} & \sum_{i=2}^{p} s_i \frac{np}{\rho k T_h} \sum_{j=2}^{N} \left\{ \frac{m_j D_{ij}^{a}}{D} + \frac{(\theta-1) A_i}{D^2} - \frac{m_1 D_{i1}^{a} \theta}{D^2} \right\} \vec{\nabla} x_j \\ & - \sum_{i=2}^{p} s_i \left(\frac{D_i^{Ta}}{m_i} \vec{\nabla} \ln T_h + \frac{D_i^{\theta a}}{m_i} \vec{\nabla} \ln \theta \right) \\ & + \sum_{i=2}^{p} s_i \frac{np}{\rho k T_h} \left\{ m_1 D_{i1}^{a} \left(\frac{x_1 \theta}{D} - \frac{\rho_1}{\rho} \right) \right. \\ & \left. + \sum_{j=2}^{N} m_j D_{ij}^{a} \left(\frac{x_j}{D} - \frac{\rho_j}{\rho} \right) \right\} \vec{\nabla} \ln p \\ & + \sum_{i=2}^{p} s_i \frac{n}{\rho k T_h} \sum_{j=2}^{N} \{ m_j D_{ij}^{\theta a} - m_1 D_{i1}^{\theta a} \} g_j \vec{\nabla} \ln \theta. \end{aligned} \tag{2.25}$$

The following relationships were used in deriving Eq. (2.25):

$$\vec{\nabla} x_1 = - \sum_{j=2}^{N} \vec{\nabla} x_j, \tag{2.26}$$

$$g_1 = - \sum_{j=2}^{N} g_j, \tag{2.27}$$

and

$$A_i = \sum_{j=2}^{N} m_j D_{ij}^{a} x_j. \tag{2.28}$$

Since we have assumed the plasma to be in chemical equilibrium, the plasma composition depends on the relative concentrations of gases A and B, the total pressure, the heavy species temperature T_h, and the nonequilibrium parameter θ. We can therefore write

$$\vec{\nabla} x_j = \left(\frac{\partial x_j}{\partial \overline{\overline{x_B}}} \right) \vec{\nabla} \overline{x_B} + \left(\frac{\partial x_j}{\partial p} \right) \vec{\nabla} p + \left(\frac{\partial x_j}{\partial T_h} \right) \vec{\nabla} T_h + \left(\frac{\partial x_j}{\partial \theta} \right) \vec{\nabla} \theta, \tag{2.29}$$

where $\overline{x_A}$, $\overline{x_B}$, $\overline{m_A}$, $\overline{m_B}$, respectively, the mole fractions of gas A and B and the average masses of the heavy species of gases A and B, are given by

$$\overline{x_A} = \sum_{i=2}^{p} (1 + Z_i) x_i, \tag{2.30}$$

$$\overline{x_B} = \sum_{i=p+1}^{N} (1 + Z_i) x_i = 1 - \overline{x_A}, \tag{2.31}$$

$$\overline{m_A} = \sum_{i=2}^{p} m_i x_i \Big/ \sum_{i=2}^{p} x_i, \tag{2.32}$$

$$\overline{m_B} = \sum_{i=p+1}^{N} m_i x_i \Big/ \sum_{i=p+1}^{N} x_i. \tag{2.33}$$

Inserting Eq. (2.29) into Eq. (2.25), it can be shown that

$$\begin{aligned} \overline{\vec{g}_A} = {} & \frac{n^2}{\rho} \overline{m_B} \left\{ \left[\frac{1}{\overline{\overline{m_B}}} \sum_{i=2}^{p} s_i \sum_{j=2}^{N} \left(m_j D_{ij}^{a} + \frac{(\theta-1) A_i}{D} - \frac{m_1 D_{i1}^{a} \theta}{D} \right) \left(\frac{\partial x_j}{\partial \overline{\overline{x_B}}} \right) \right] \vec{\nabla} \overline{x_B} \right. \\ & \left. + \left[\frac{1}{\overline{\overline{m_B}}} \sum_{i=2}^{p} s_i \left[m_1 D_{i1}^{a} \left(x_1 \theta \frac{\rho_1 D}{\rho} \right) + \sum_{j=2}^{N} \left\{ m_j D_{ij}^{a} \left(x_j - \frac{\rho_j D}{\rho} \right) + \left(m_j D_{ij}^{a} + \frac{(\theta-1) A_i}{D} - \frac{m_1 D_{i1}^{a} \theta}{D} \right) p \left(\frac{\partial x_i}{\partial p} \right) \right\} \right] \right] \vec{\nabla} \ln p \right\} \\ & - \frac{1}{\overline{\overline{m_A}}} \left[\overline{m_A} \sum_{i=2}^{p} s_i \left\{ \frac{D_i^{Ta}}{m_i} - \frac{n^2}{\rho} \sum_{j=2}^{q} \left(m_j D_{ij}^{a} + \frac{(\theta-1) A_i}{D} - \frac{m_1 D_{i1}^{a} \theta}{D} \right) T_h \left(\frac{\partial x_j}{\partial T_h} \right) \right\} \right] \vec{\nabla} \ln T_h \\ & + \frac{n^2}{\rho} \overline{m_A} \left[\frac{1}{\overline{\overline{m_A}}} \sum_{i=2}^{p} \frac{s_i}{n k T_h} \sum_{j=2}^{N} \{ (m_j D_{ij}^{\theta a} - m_1 D_{i1}^{\theta a}) g_j \} + \left(m_j D_{ij}^{a} + \frac{(\theta-1) A_i}{D} - \frac{m_1 D_{i1}^{a} \theta}{D} \right) \theta \left(\frac{\partial x_j}{\partial \theta} \right) \right] \vec{\nabla} \ln \theta \\ & - \frac{1}{\overline{\overline{m_A}}} \left[\overline{m_A} \sum_{i=2}^{p} s_i \frac{D_i^{\theta a *}}{m_i} \right] \vec{\nabla} \ln \theta. \end{aligned} \tag{2.34}$$

Hence, the diffusion number flux of gas A may be written as

$$\overline{\vec{g}_A}=\frac{n^2}{\rho}\overline{m_B}(\overline{D^x_{AB}}\vec{\nabla}\overline{x_B}+\overline{D^p_{AB}}\vec{\nabla}\ln p)-\frac{\overline{D^T_{AB}}}{\overline{m_A}}\vec{\nabla}\ln T_h$$
$$+\left(\frac{n^2}{\rho}\overline{m_B}\,\overline{D^\theta_{AB}}-\frac{\overline{D^{\theta *}_{AB}}}{\overline{m_A}}\right)\vec{\nabla}\ln\theta, \tag{2.35}$$

where

$$\overline{D^x_{AB}}=\frac{1}{\overline{m_B}}\sum_{i=2}^{p}s_i\sum_{j=2}^{N}\left(m_jD^a_{ij}+\frac{(\theta-1)A_i}{D}-\frac{m_1D^a_{i1}\theta}{D}\right)\left(\frac{\partial x_j}{\partial\overline{x_B}}\right), \tag{2.36}$$

$$\overline{D^p_{AB}}=\frac{1}{\overline{m_B}}\sum_{i=2}^{p}s_i\left\{m_1D^a_{i1}\left(x_1\theta-\frac{\rho_1D}{\rho}\right)+\sum_{j=2}^{N}\left[m_jD^a_{ij}\left(x_j\right.\right.\right.$$
$$\left.\left.\left.-\frac{\rho_jD}{\rho}\right)+\left(m_jD^a_{ij}+\frac{(\theta-1)A_i}{D}-\frac{m_1D^a_{i1}\theta}{D}\right)p\left(\frac{\partial x_j}{\partial p}\right)\right]\right\}, \tag{2.37}$$

$$\overline{D^T_{AB}}=\overline{m_A}\sum_{i=2}^{p}s_i\left[\frac{D^{Ta}_i}{m_i}\frac{n^2}{\rho}\sum_{j=2}^{N}\left(m_jD^a_{ij}+\frac{(\theta-1)A_i}{D}\right.\right.$$
$$\left.\left.-\frac{m_1D^a_{i1}\theta}{D}\right)T_h\left(\frac{\partial x_j}{\partial T_h}\right)\right], \tag{2.38}$$

$$\overline{D^\theta_{AB}}=\frac{1}{\overline{m_B}}\sum_{i=2}^{p}\frac{s_i}{nkT_h}\sum_{j=2}^{N}\left[(m_jD^{\theta a}_{ij}-m_1D^{\theta a}_{i1})g_j\right.$$
$$\left.+\left(m_jD^a_{ij}+\frac{(\theta-1)A_i}{D}-\frac{m_1D^a_{i1}\theta}{D}\right)\theta\left(\frac{\partial x_j}{\partial\theta}\right)\right], \tag{2.39}$$

and

$$\overline{D^{\theta *}_{AB}}=\overline{m_A}\sum_{i=2}^{p}s_i\frac{D^{\theta a *}_i}{m_i}. \tag{2.40}$$

The coefficients $\overline{D^x_{AB}}$, $\overline{D^p_{AB}}$, and $\overline{D^T_{AB}}$ are, respectively, the 2T combined diffusion coefficients due to gradients in concentration, pressure, and heavy species temperature. The coefficients $\overline{D^\theta_{AB}}$ and $\overline{D^{\theta *}_{AB}}$ are 2T combined diffusion coefficients due to the gradient in the nonequilibrium parameter. Defining the diffusion flux of the ionized gas B,

$$\overline{\vec{g}_B}=\frac{n^2}{\rho}\overline{m_A}(\overline{D^x_{BA}}\vec{\nabla}\overline{x_A}+\overline{D^p_{BA}}\vec{\nabla}\ln p)-\frac{\overline{D^T_{BA}}}{\overline{m_B}}\vec{\nabla}\ln T_h$$
$$+\left(\frac{n^2}{\rho}\overline{m_A}\;\overline{D^\theta_{BA}}-\frac{\overline{D^{\theta *}_{BA}}}{\overline{m_B}}\right)\vec{\nabla}\ln\theta, \tag{2.41}$$

it can also be shown that

$$\overline{D^x_{BA}}=-\frac{1}{\overline{m_A}}\sum_{i=p+1}^{N}s_i\sum_{j=2}^{N}\left(m_jD^a_{ij}+\frac{(\theta-1)A_i}{D}\right.$$
$$\left.-\frac{m_1D^a_{i1}\theta}{D}\right)\left(\frac{\partial x_j}{\partial\overline{x_B}}\right), \tag{2.42}$$

$$\overline{D^p_{BA}}=\frac{1}{\overline{m_A}}\sum_{i=p+1}^{N}s_i\left\{m_1D^a_{i1}\left(x_1\theta-\frac{\rho_1D}{\rho}\right)\right.$$
$$+\sum_{j=2}^{N}\left[m_jD^a_{ij}\left(x_j-\frac{\rho_jD}{\rho}\right)\right.$$
$$\left.\left.+\left(m_jD^a_{ij}+\frac{(\theta-1)A_i}{D}-\frac{m_1D^a_{i1}\theta}{D}\right)p\left(\frac{\partial x_j}{\partial p}\right)\right]\right\}, \tag{2.43}$$

$$\overline{D^T_{BA}}=\overline{m_B}\sum_{i=p+1}^{N}s_i\left[\frac{D^{Ta}_i}{m_i}-\frac{n^2}{\rho}\sum_{j=2}^{N}\left(m_jD^a_{ij}+\frac{(\theta-1)A_i}{D}\right.\right.$$
$$\left.\left.-\frac{m_1D^a_{i1}\theta}{D}\right)T_h\left(\frac{\partial x_j}{\partial T_h}\right)\right], \tag{2.44}$$

$$\overline{D^\theta_{BA}}=\frac{1}{\overline{m_A}}\sum_{i=p+1}^{N}\frac{s_i}{nkT_h}\sum_{j=2}^{N}\left[(m_jD^{\theta a}_{ij}-m_1D^{\theta a}_{i1})g_i\right.$$
$$\left.+\left(m_jD^a_{ij}+\frac{(\theta-1)A_i}{D}-\frac{m_1D^a_{i1}\theta}{D}\right)\theta\left(\frac{\partial x_j}{\partial\theta}\right)\right], \tag{2.45}$$

$$\overline{D^{\theta *}_{BA}}=\overline{m_B}\sum_{i=p+1}^{N}s_i\frac{D^{\theta a *}_i}{m_i}. \tag{2.46}$$

In order for the sum of mass fluxes relative to the average mass flux to vanish, the 2T combined diffusion coefficients have to obey the following symmetric relationships:

$$\overline{D^x_{AB}}=\overline{D^x_{BA}}, \tag{2.47}$$

$$\overline{D^p_{AB}}=-\overline{D^p_{BA}}, \tag{2.48}$$

$$\overline{D^T_{AB}}=-\overline{D^T_{BA}}, \tag{2.49}$$

$$\overline{D^\theta_{AB}}=-\overline{D^\theta_{BA}}, \tag{2.50}$$

$$\overline{D^{\theta *}_{AB}}=-\overline{D^{\theta *}_{BA}}. \tag{2.51}$$

We may separate the components of the combined thermal diffusion coefficient corresponding to thermal diffusion and ordinary diffusion as follows:

$$\overline{D^T_{AB}}=\overline{D^T_A}+\overline{D^{T1}_{AB}}, \tag{2.52}$$

where

$$\overline{D^T_A}=\overline{m_A}\sum_{i=2}^{p}\frac{D^{Ta}_i}{m_i} \tag{2.53}$$

and

$$\overline{D^{T1}_{AB}} = -\overline{m_A}\frac{n^2}{\rho}\sum_{i=2}^{p} s_i\left[\sum_{j=2}^{N}\left(m_j D^a_{ij} + \frac{(\theta-1)A_i}{D} - \frac{m_1 D^a_{i1}\theta}{D}\right) T_h\left(\frac{\partial x_j}{\partial T_h}\right)\right]. \tag{2.54}$$

III. APPLICATION TO AN ARGON-HYDROGEN THERMAL PLASMA

In this section, we investigate the behaviors of the combined ordinary and thermal diffusion coefficients in an argon-hydrogen mixture for different compositions and for different values of the nonequilibrium parameter $\theta = T_e/T_h$. Particular attention is paid to mass conservation. For the purposes of this paper, we assume that θ is fixed, and consequently, diffusion coefficients due to gradients in θ are not evaluated. The individual ordinary and thermal diffusion coefficients are calculated to the third order of approximation. The values of the combined diffusion coefficients are altered only negligibly when the second order of approximation is used.

Methods to calculate the composition of non-LTE thermal plasmas may be divided into two main classes. In the first class, a stationary kinetic calculation (neglecting diffusion and convection) is used, based on the work of Richley and Tuma [27]. In this case, many reaction paths are considered, in contrast to the second class, which are multitemperature methods based on mass action laws (Potapov [28], van de Sanden *et al.* [29], Chen and Han [30], and André [31]). The two classes of methods lead to very different results [26]. Here, for the purposes of illustration, we give results for plasma compositions calculated using a stationary kinetic calculation. The method of calculation, the required data, and the resulting compositions are described in detail elsewhere [25]. Briefly, the method consists of determining the kinetic coefficients of the forward and reverse reactions involving the species that are considered. In order to calculate the number density of species, linear systems of equations with constraints on pressure, charge conservation, and the argon-hydrogen molar ratio are solved. An atmospheric pressure plasma has been considered with eight species: electrons, Ar, Ar^+, Ar^{2+}, H_2, H, H_2^+, and H^+.

A. Mass conservation

It was shown in an earlier paper [22] that the 2T combined diffusion coefficients derived using the simplified theory of transport properties, i.e., neglecting coupling between the electrons and the heavy particles [18–20], did not satisfy Eq. (2.49) even at equilibrium ($T_e = T_h$), except when the degree of ionization was very low. When the ionization degree exceeded 8%, Eq. (2.49) was not satisfied, and hence mass conservation was violated.

We have checked that Eqs. (2.47) and (2.49) are satisfied using the 2T combined diffusion coefficients derived in Sec. II B, and hence that mass conservation is satisfied. In particular, we confirmed that for an argon-hydrogen plasma at atmospheric pressure that $\overline{D^x_{\text{Ar-H}_2}} = \overline{D^x_{\text{H}_2\text{-Ar}}}$ and $\overline{D^T_{\text{Ar-H}_2}} = -\overline{D^T_{\text{H}_2\text{-Ar}}}$ for all temperatures up to at least 25 000 K, for all argon-hydrogen molar ratios, and for all values of θ up to at least 3.0.

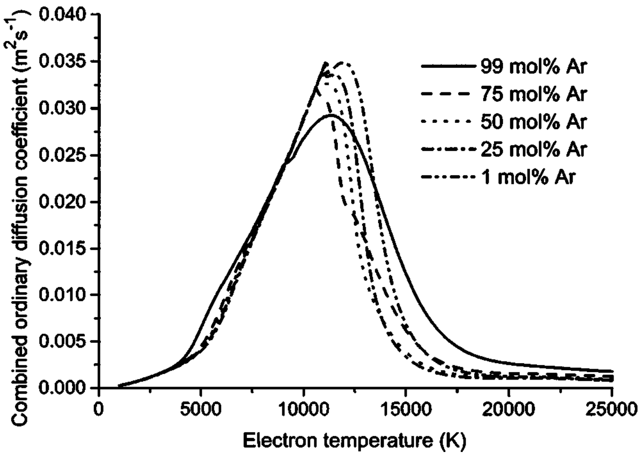

FIG. 1. Dependence on electron temperature of the combined ordinary diffusion coefficient for different molar percentages of argon in an argon-hydrogen mixture at 1 bar for $\theta = T_e/T_h = 1.6$.

B. Results

1. Two-temperature combined ordinary diffusion coefficients

Figure 1 shows the electron temperature dependence of the combined ordinary diffusion coefficient $\overline{D^x_{\text{Ar-H}_2}}$ for different molar percentages of argon in an Ar-H_2 mixture for $\theta = 1.6$. At temperatures close to the dissociation temperature of hydrogen, and the ionization temperature of argon and hydrogen, the coefficient depends on the percentage of argon in the mixture. This is because the degree of dissociation and ionization depends on this percentage, and as Eq. (2.36) shows, $\overline{D^x_{\text{Ar-H}_2}}$ depends on the concentration of the individual species.

The combined ordinary diffusion coefficient increases with the electron temperature until the degree of ionization is high; it then starts to increase as a result of the high collision cross sections for interactions between charged species.

A change of slope occurs at 12 500 K for the case of 75% argon by mole. This is due to the rapid increase in the number density of Ar^+ ions between 11 000 and 12 500 K for this composition, so that the number density of Ar^+ ions is greater than that of H^+ ions at 12 500 K. This is in contrast to the case of 50% argon by mole (at 12 500 K, $n_{\text{Ar}^+} = 5.68 \times 10^{22}\ \text{m}^{-3}$ and $n_{\text{H}^+} = 3.66 \times 10^{22}\ \text{m}^{-3}$ for 75% argon by mole, compared to $n_{\text{Ar}^+} = 1.42 \times 10^{22}\ \text{m}^{-3}$ and $n_{\text{H}^+} = 6.80 \times 10^{22}\ \text{m}^{-3}$ for 50% argon by mole). The collision integral $\overline{Q}^{(1,1)}_{\text{H}^+,\text{H}}$ is larger than $\overline{Q}^{(1,1)}_{\text{Ar}^+,\text{H}}$ between 11 000 and 12 500 K ($\overline{Q}^{(1,1)}_{\text{H}^+,\text{H}}/\overline{Q}^{(1,1)}_{\text{Ar}^+,H} \approx 5$ at 12 500 K), so an increase in n_{Ar^+} relative to n_{H^+} causes the diffusion coefficient to decrease less rapidly.

A discontinuity occurs at about 11 000 K for the cases in which there is at least 50% hydrogen by mole present. This is

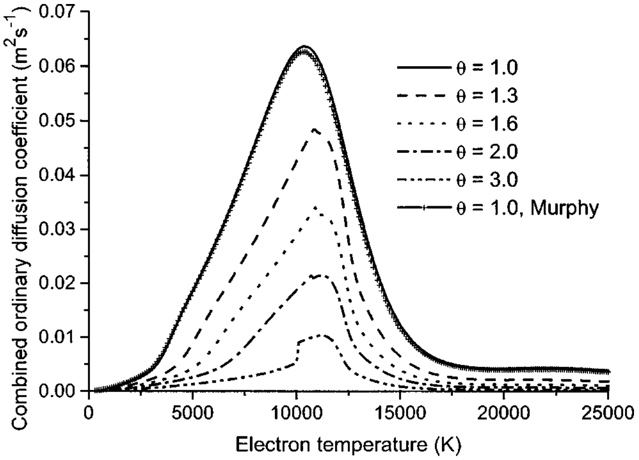

FIG. 2. Dependence on electron temperature of the combined ordinary diffusion coefficient for different values of $\theta = T_e/T_h$ in an argon-hydrogen mixture (50% by mole) at 1 bar.

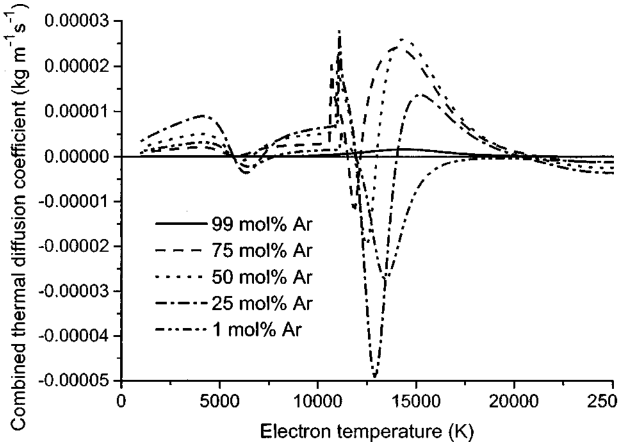

FIG. 3. Dependence on electron temperature of the combined thermal diffusion coefficient for different molar percentages of argon in an argon-hydrogen mixture at 1 bar for $\theta = T_e/T_h = 1.6$.

due to the onset of an ionization avalanche, which is discussed in detail in Ref. [25]. Briefly, the ionization of argon and hydrogen atoms is limited by charge transfer reactions ($Ar^+ + H_2 \rightarrow Ar + H_2^+$ and $H^+ + H_2 \rightarrow H_2^+ + H$) and dissociative recombination reactions of hydrogen molecules ($H_2^+ + e \rightarrow 2H$) until the number density of H_2 reaches a critically low value ($\approx 5 \times 10^{20}$ m^{-3}), whereupon an ionization avalanche occurs.

Figure 2 depicts the dependence on electron temperature of the combined ordinary diffusion coefficients in a mixture of equal molar percentages of argon and hydrogen for different values of θ. It can be seen that the diffusion coefficients decrease as θ increases for any given value of T_e. The results of Murphy [2] for the same percentages of argon and hydrogen for $\theta = 1$ are also shown. The agreement between our results and those of Murphy is excellent.

A discontinuity caused by the onset of an ionization avalanche is again seen at 11 000 K. The shape of the discontinuity is different for $\theta = 3.0$ and $\theta \leqslant 2.0$, depending on the dominant hydrogen species. The dominant species is H_2 for $\theta = 3.0$ and H for $\theta \leqslant 2.0$, for temperatures below that at which the discontinuity occurs, because of the shift of dissociation toward higher electron temperature as θ increases [25]. The collision integral $\overline{Q}^{(1,1)}_{\mathrm{Ar,H_2}}$ is larger than $\overline{Q}^{(1,1)}_{\mathrm{Ar,H}}$, so the diffusion coefficient is relatively low for temperatures below that at which the discontinuity occurs for $\theta = 3.0$. For $\theta = 1.0$, the diffusion coefficient is already decreasing at 11 000 K, and there is no discontinuity.

2. Two-temperature combined thermal diffusion coefficients

The dependence on electron temperature of the combined thermal diffusion coefficient $\overline{D^T_{\mathrm{Ar\text{-}H_2}}}$ is shown in Fig. 3 for different molar percentages of argon in the Ar-H_2 mixture for $\theta = 1.6$. The combined thermal diffusion coefficient depends strongly on the molar percentage of argon through $\partial x_j/\partial T$, as shown by Eq. (2.38).

Figure 4 shows the dependence on electron temperature of the combined thermal diffusion coefficient for different values of θ in a mixture of equal molar percentages of argon and hydrogen. It can be seen that the diffusion coefficients decrease as θ increases for $T_e > 12\,500$ K. The first group of peaks, at low temperature, is associated with the dissociation of H_2. They occur at $T_h \approx 3800$ K; when plotted against T_e, the curves are shifted according to the value of θ. The second group of peaks, at about $T_e \approx 14\,500$ K, is associated with the ionization of atoms. For $\theta = 3.0$, dissociation is not complete, and the dissociation peak does not reach its maximum, before the onset of ionization. The results of Murphy [2] for the same percentages of argon and hydrogen for $\theta = 1$ are also shown. The agreement is not as good as that found for the combined ordinary diffusion coefficient. In particular, for $T_e \approx 5000$ K, there is a significant difference between our results and those of Murphy. We have carefully investigated this discrepancy, and found that it is due to small differences in the individual ordinary diffusion coefficients D^a_{ij} that are used to calculate $\overline{D^{T1}_{\mathrm{Ar\text{-}H_2}}}$. The differences become significant because $\overline{D^{T1}_{\mathrm{Ar\text{-}H_2}}}$ is the sum of relatively large positive and negative terms, since the D^a_{ij} are multiplied by $\partial x_j/\partial T_h$ be-

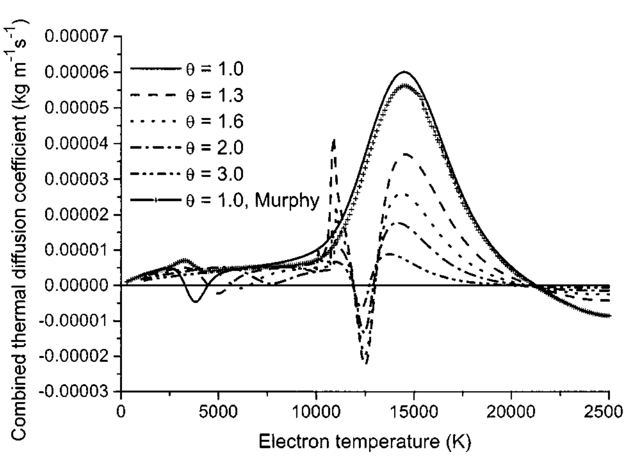

FIG. 4. Dependence on electron temperature of the combined thermal diffusion coefficient for different values of $\theta = T_e/T_h$ in an argon-hydrogen mixture (50% by mole) at 1 bar.

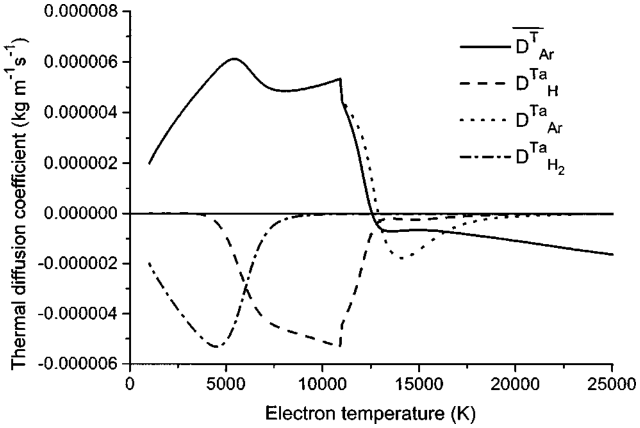

FIG. 5. Dependence on electron temperature of the component of the combined thermal diffusion coefficient corresponding to thermal diffusion coefficient $\overline{D_{\mathrm{Ar}}^{T}}$ and the ambipolar thermal diffusion coefficients $D_{\mathrm{Ar}}^{T^a}$, $D_{\mathrm{H}_2}^{T^a}$, and $D_{\mathrm{H}}^{T_a}$ in an argon-hydrogen mixture (50% by mole) at 1 bar for $\theta = T_e/T_h = 1.6$.

fore being summed [see Eq. (2.54)]. In contrast, the terms making up $\overline{D_{\mathrm{Ar\text{-}H_2}}^{x}}$ are all positive, so the small differences in the D_{ij}^{a} have little effect on the combined ordinary diffusion coefficient.

Figure 5 shows the dependence on electron temperature of the combined diffusion coefficient $\overline{D_{\mathrm{Ar}}^{T}}$ and the ambipolar thermal diffusion coefficients D_{Ar}^{Ta}, $D_{\mathrm{H}_2}^{Ta}$, D_{H}^{Ta} for $\theta = 3.0$ and a mixture of equal molar percentages of argon and hydrogen. We expect similar behavior to that pointed out by Murphy [7] for an equilibrium mixture; i.e., $\overline{D_{\mathrm{Ar}}^{T}}$ should reflect the values of D^{Ta} of the dominant species present. Below $T_e \approx 4000$ K, where Ar and H$_2$ dominate, it can be confirmed that $\overline{D_{\mathrm{Ar}}^{T}} \approx D_{\mathrm{Ar}}^{Ta} \approx -D_{\mathrm{H}_2}^{Ta}$. Moreover, between $T_e \approx 5000$ and 8000 K, where Ar and H are the main species, $\overline{D_{\mathrm{Ar}}^{T}} \approx D_{\mathrm{Ar}}^{Ta} \approx -D_{\mathrm{H}}^{Ta}$. However, when significant ionization occurs, such simple relationships between diffusion coefficients cannot be found.

IV. CONCLUSIONS

Diffusion is an important phenomenon in thermal plasmas, for example, in demixing in free-burning arcs [8]. Combined diffusion coefficients, which allow diffusion to be treated in terms of gases rather than species, have been defined for LTE conditions [7]. However, close to the electrodes of free-burning arcs, where deviations from equilibrium occur, non-LTE combined diffusion coefficients are required [17].

In this paper, we have derived two-temperature combined diffusion coefficients from the nonequilibrium diffusion fluxes recently introduced by Rat *et al.* [21]. Combined diffusion coefficients due to gradients in concentration, temperature, pressure, and the nonequilibrium parameter $\theta = T_e/T_h$ have been defined in a thermal plasma consisting of two homonuclear nonreacting gases, where the kinetic temperature of electrons T_e is different from that of the heavy species T_h. Illustrative results have been presented for a plasma in a mixture of argon and hydrogen. The plasma composition was obtained from a nonequilibrium stationary kinetic calculation [25].

We found that, in general, the combined diffusion coefficients decrease with $\theta = T_e/T_h$ for a given value of T_e. Two different behaviors can be distinguished, separated by an ionization avalanche at electron temperatures of around 11 000 K. Below 11 000 K, the combined diffusion coefficients are governed by the heavy species temperature, and features related to the dissociation of hydrogen molecules are shifted to higher electron temperatures as θ increases. Above 11 000 K, the combined diffusion coefficients depend on the electron temperature, since ionization dominates. If the plasma composition had been calculated using multitemperature methods based on mass action laws, different values of the combined diffusion coefficients would be obtained, but similar trends would be observed, apart from the absence of the ionization avalanche, which is only found in the stationary kinetic calculation of composition.

It has been shown previously [22] that the simplified theory of transport properties, in which coupling between electrons and heavy particles is neglected [18–20], leads to values of combined diffusion coefficients for which mass conservation is not satisfied. The combined diffusion coefficients derived in the current paper are derived using the nonequilibrium expressions for diffusion fluxes defined in Ref. [21], in whose calculation the coupling between electrons and heavy particles is taken into account. We have confirmed that these combined diffusion coefficients satisfy the relations $\overline{D_{AB}^{x}} = \overline{D_{BA}^{x}}$ and $\overline{D_{AB}^{T}} = -\overline{D_{BA}^{T}}$, indicating that mass conservation is satisfied.

The two-temperature combined diffusion coefficients have many potential applications. There are regions out of LTE in all thermal plasmas, and some, such as microwave plasmas, have $T_e \gg T_h$ everywhere. We are planning to use the two-temperature diffusion coefficients derived here to model demixing in an argon-hydrogen arc. By comparing the results of this modeling with the predictions of the equilibrium model and the spectroscopic measurements of Murphy and Hiraoka [17], it may be possible to obtain an indirect experimental validation of the approach of Rat *et al.* [21].

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