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Combined diffusion coefficients for a mixture of three ionized gases

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Abstract

The combined diffusion coefficient method has been demonstrated to greatly simplify the treatment of diffusion in the modelling of thermal plasmas in gas mixtures without loss of accuracy. In this paper, an extension of this method to allow treatment of diffusion of a three-gas mixture has been achieved, provided that the gases are homonuclear and do not react with each other, and satisfy local chemical equilibrium. Formulas for the combined diffusion coefficients are presented, and combined diffusion coefficients for different mixtures of helium, argon and carbon at temperatures up to 30 000 K and at atmosphere pressure are calculated as an example.

Keywords: thermal plasma, mass transport, diffusion, transport coefficients

(Some figures may appear in colour only in the online journal)

1. Introduction

Accurate treatment of the diffusion of different gases with respect to each other is essential for reliable modelling of thermal plasmas, since practically all industrial arc and plasma processes involve more than one gas. For example, helium or hydrogen is often added to argon in gas–tungsten arc welding; argon–oxygen and argon–carbon-dioxide mixtures are widely used in gas–metal arc welding, helium, hydrogen and/or nitrogen are usually added to argon to increase the enthalpy of the plasma jet in plasma spraying, and plasma cutting is often performed in air. Even in those cases in which a pure plasma gas is used, vaporization or ablation of electrodes and other surfaces occurs, and the surrounding atmosphere mixes with the plasma gas.

It is generally impractical to treat the diffusion by considering each species separately, since there are typically a large number of species which have to be considered in plasmas. In a gas mixture containing r species, a total of $(r - 1)$ species conservation equations have to be solved, and $r(r - 1)/2$ ordinary and $(r - 1)$ thermal diffusion coefficients must be calculated at each point in the plasma. Murphy [1, 2] introduced the combined diffusion coefficient

method, which greatly simplifies the treatment of diffusion for many gas mixtures without sacrificing accuracy, through combining the individual species into their parent gas, and dealing with the diffusion of the gases rather than of the species. Four combined diffusion coefficients: the combined ordinary diffusion coefficient, combined pressure diffusion coefficient, combined electric field diffusion coefficient and combined temperature diffusion coefficient, are derived to describe, respectively, diffusion due to mole fraction gradients, gradients in the total pressure, externally applied electric fields and temperature gradients. The method is mathematically equivalent to the full multicomponent diffusion coefficient treatment for mixtures of homonuclear gases that do not react with each other, under the assumption of local chemical equilibrium (LCE). In cases in which reactions occur, or in which one or more of the gases is heteronuclear, the method can still be applied, but with some loss of accuracy.

The combined diffusion coefficient method has been successfully applied to a wide range of plasma processes involving the diffusive mixing and demixing of gases and vapours, such as demixing in welding arcs [3, 4], plasma torches [5], arc plasma reactors [6, 7], and inductively coupled rf plasmas in gas mixtures [8, 9], mixing of metal vapour in

welding arcs [10, 11], mixing of air into plasmas [12, 13], mixing of polymer vapours into the arc in circuit breakers [14, 15], and expansion of metal vapour ablated by a laser into the surrounding air [16].

In these previous studies, the combined diffusion coefficients were employed for the diffusion of only two gases. While many plasma processes use mixtures of two gases, it is often necessary to consider three gases. For instance, in plasma metallurgy, mineral processing and waste destruction, very complicated mixtures of gases are generally present. Furthermore, in many applications, metal vapour from electrodes, workpieces or surrounding materials have to be considered in the gas mixture. Specific examples of three-gas systems of particular interest include: mixing of metal vapour into an argon–oxygen gas–metal arc welding arc, mixing of metal vapour into an argon–helium gas–tungsten arc welding arc, mixing of carbon vapour with argon and helium plasma gases in carbon arcs used for production of carbon nanostructures, mixing of two different types of metal vapour formed from an alloy electrode into an argon welding arc, and mixing of ambient air into an argon–helium welding arc or plasma jet.

In this paper, we present an extension of the combined diffusion coefficient method that allows calculation of diffusion of mixtures of three gases. In section 2, the definition and the calculation of the combined diffusion coefficients are discussed. An illustrative calculation of the combined diffusion coefficients for a mixture of helium, argon and carbon at atmosphere pressure is presented in section 3, and conclusions are given in section 4.

2. Combined diffusion coefficients of three gases

Consider a mixture of three homonuclear non-reacting gases A, B and C with arbitrary degree of ionization. The requirements that the gases are homonuclear and do not react with each other allow all species to be unambiguously assigned to one of the three gases; electrons are assigned according to the gas from which they are derived. Let the three gases consist of r species, and denote the electrons as species 1, and the heavy species of gas A, B and C by 2 to p , $p+1$ to q and $q+1$ to r , respectively. We assume the plasma is in local chemical equilibrium (LCE), so that the local composition depends only on the local temperature, pressure and mole fractions of gases A, B and C.

For generality, the effect of ambipolar diffusion arising due to the tendency of electrons to diffuse more rapidly than ions is taken into account. The mass flux of species i is given by [1]

$$\mathbf{J}_i = \frac{n^2 m_i}{\rho} \sum_{j=1}^r m_j \left\{ D_{ij}^a \left[\nabla x_j + \left(x_j - \frac{\rho_j}{\rho} \right) \nabla \ln P \right] - D_{ij} \frac{e x_j Z_j}{k_B T} \mathbf{E} \right\} - D_i^{\text{Ta}} \nabla \ln T, \quad (1)$$

where T is the temperature, \mathbf{E} is the external electrical field, n , ρ and P are respectively the number density, mass density and pressure, ρ_j , n_j , m_j , Z_j and x_j are respectively the

mass density, number density, mass, charge number and mole fraction of the j th species; e is the elementary charge and k_B is Boltzmann constant. The ambipolar ordinary and thermal diffusion coefficients are respectively given by

$$D_{ij}^a = D_{ij} + \frac{\alpha_i}{\beta} \sum_{l=1}^r Z_l D_{lj} \quad (2)$$

$$D_i^{\text{Ta}} = D_i^{\text{T}} + \frac{\alpha_i m_i}{\beta} \sum_{l=1}^r \frac{Z_l D_l^{\text{T}}}{m_l}, \quad (3)$$

where D_{ij} and D_i^{T} are respectively the ordinary and thermal diffusion coefficients, and

$$\alpha_i = \sum_{j=1}^r n_j m_j Z_j D_{ij} \quad (4)$$

$$\beta = - \sum_{i,j=1}^r Z_i Z_j n_j m_j D_{ij}. \quad (5)$$

Note that, when there is no ionization, ambipolar effects do not occur, and we write $D_{ij}^a = D_{ij}$ and $D_i^{\text{Ta}} = D_i^{\text{T}}$.

The mass flux of gas A is defined as the sum of the mass fluxes of all the species that make up gas A:

$$\bar{\mathbf{J}}_A = k_{1A} \mathbf{J}_1 + \sum_{i=2}^p k_{iA} \mathbf{J}_i. \quad (6)$$

Analogously, the mass fluxes of gases B and C are given by

$$\bar{\mathbf{J}}_B = k_{1B} \mathbf{J}_1 + \sum_{i=p+1}^q k_{iB} \mathbf{J}_i \quad (7)$$

$$\bar{\mathbf{J}}_C = k_{1C} \mathbf{J}_1 + \sum_{i=q+1}^r k_{iC} \mathbf{J}_i, \quad (8)$$

where

$$k_{1A} = \sum_{k=2}^p Z_k x_k / x_1,$$

$$k_{1B} = \sum_{k=p+1}^q Z_k x_k / x_1,$$

$$k_{1C} = \sum_{k=q+1}^r Z_k x_k / x_1,$$

$$k_{iA} = k_{iB} = k_{iC} = 1, \quad i \neq 1 \quad (9)$$

are stoichiometric coefficients used to assign the electrons to the three gases according to their parent species [17]. Note that $k_{1A} + k_{1B} + k_{1C} = 1$, because of the condition of charge neutrality in a plasma system.

We wish to obtain an expression for $\bar{\mathbf{J}}_A$ of the form

$$\bar{\mathbf{J}}_A = \frac{n^2}{\rho} \frac{\bar{m}_A}{\bar{m}_B \bar{m}_C} \left[\left(\overline{D}_{AB}^x \nabla \bar{x}_B + \overline{D}_{AC}^x \nabla \bar{x}_C \right) + \overline{D}_A^{\text{P}} \nabla \ln P + \overline{D}_A^{\text{E}} \mathbf{E} \right] - \overline{D}_A^{\text{T}} \nabla \ln T. \quad (10)$$

The corresponding expressions for the mass fluxes of gases B and C are

$$\begin{aligned} \overline{J}_B = \frac{n^2}{\rho} \overline{m}_A \overline{m}_B \overline{m}_C \left[\left(\overline{D}_{BA}^x \nabla \overline{x}_A + \overline{D}_{BC}^x \nabla \overline{x}_C \right) + \overline{D}_B^p \nabla \ln P \right. \\ \left. + \overline{D}_B^E \mathbf{E} \right] - \overline{D}_B^T \nabla \ln T \end{aligned} \quad (11)$$

$$\begin{aligned} \overline{J}_C = \frac{n^2}{\rho} \overline{m}_A \overline{m}_B \overline{m}_C \left[\left(\overline{D}_{CA}^x \nabla \overline{x}_A + \overline{D}_{CB}^x \nabla \overline{x}_B \right) + \overline{D}_C^p \nabla \ln P \right. \\ \left. + \overline{D}_C^E \mathbf{E} \right] - \overline{D}_C^T \nabla \ln T, \end{aligned} \quad (12)$$

where the \overline{D}_{AB}^x , \overline{D}_A^p , etc are combined diffusion coefficients, \overline{m}_A , \overline{m}_B and \overline{m}_C are the average masses of the heavy species of the respective gases

$$\begin{aligned} \overline{m}_A &= \sum_{k=2}^p m_k x_k / \sum_{k=2}^p x_k \\ \overline{m}_B &= \sum_{k=p+1}^q m_k x_k / \sum_{k=p+1}^q x_k \\ \overline{m}_C &= \sum_{k=q+1}^r m_k x_k / \sum_{k=q+1}^r x_k \end{aligned} \quad (13)$$

and \overline{x}_A , \overline{x}_B and \overline{x}_C are respectively the sums of the mole fractions of the species of the gases A, B and C

$$\begin{aligned} \overline{x}_A &= \sum_{k=2}^p (1 + Z_k) x_k \\ \overline{x}_B &= \sum_{k=p+1}^q (1 + Z_k) x_k \\ \overline{x}_C &= \sum_{k=q+1}^r (1 + Z_k) x_k, \end{aligned} \quad (14)$$

where Z_k is used to apportion the electrons among the three gases.

By substituting equation (1) into the equation (6), and comparing the resulting equation with equation (10), we obtain expressions for the combined ordinary diffusion coefficients \overline{D}_{AB}^x and \overline{D}_{AC}^x , combined pressure diffusion coefficient \overline{D}_A^p , combined electric field diffusion coefficient \overline{D}_A^E and combined temperature diffusion coefficient \overline{D}_A^T of gas A:

$$\overline{D}_{AB}^x = \frac{1}{\overline{m}_A \overline{m}_B \overline{m}_C} \sum_{i=1}^p m_i k_{iA} \sum_{j=1}^r m_j D_{ij}^a \left(\frac{\partial x_j}{\partial \overline{x}_B} \right) \quad (15)$$

$$\overline{D}_{AC}^x = \frac{1}{\overline{m}_A \overline{m}_B \overline{m}_C} \sum_{i=1}^p m_i k_{iA} \sum_{j=1}^r m_j D_{ij}^a \left(\frac{\partial x_j}{\partial \overline{x}_C} \right) \quad (16)$$

$$\overline{D}_A^p = \frac{1}{\overline{m}_A \overline{m}_B \overline{m}_C} \sum_{i=1}^p m_i k_{iA} \sum_{j=1}^r m_j D_{ij}^a \left(x_j - \frac{\rho_j}{\rho} + P \frac{\partial x_j}{\partial P} \right) \quad (17)$$

$$\overline{D}_A^E = -\frac{1}{\overline{m}_A \overline{m}_B \overline{m}_C} \sum_{i=1}^p m_i k_{iA} \sum_{j=1}^r \frac{e m_j D_{ij} x_j Z_j}{k_B T} \quad (18)$$

$$\overline{D}_A^T = \sum_{i=1}^p k_{iA} \left(D_i^{Ta} - \frac{n^2}{\rho} m_i \sum_{j=1}^r m_j D_{ij}^a T \frac{\partial x_j}{\partial T} \right), \quad (19)$$

where we have used the relation

$$\begin{aligned} \nabla x_j = (\partial x_j / \partial \overline{x}_B) \nabla \overline{x}_B + (\partial x_j / \partial \overline{x}_C) \nabla \overline{x}_C + (\partial x_j / \partial P) \nabla P \\ + (\partial x_j / \partial T) \nabla T, \end{aligned} \quad (20)$$

which is valid since LCE has been assumed.

It is noted that $\partial x_j / \partial P$ has to be calculated with \overline{x}_B , \overline{x}_C and T held constant, and similarly \overline{x}_B , \overline{x}_C and P must be kept constant when $\partial x_j / \partial T$ is calculated. For a given gas mixture, however, \overline{x}_B and \overline{x}_C are functions of temperature and pressure, due to the occurrence of dissociation and ionization reactions. In standard computer programs for the calculation of plasma composition, the relative mole fractions of the gases are set at a given temperature and pressure, typically 298 K and 1 atm. Maintaining these mole fractions constant does not ensure that \overline{x}_B and \overline{x}_C stay constant with changes in temperature and pressure. To solve this problem, the following correction equations are adopted (analogously to the two-gas case considered previously [17])

$$\begin{aligned} \frac{\partial x_j}{\partial T} \Big|_{\overline{x}_B, \overline{x}_C, P} = \frac{\partial x_j}{\partial T} \Big|_{\overline{x}_B 298 \text{ K}, \overline{x}_C 298 \text{ K}, P} - \frac{\partial x_j}{\partial \overline{x}_B} \Big|_{\overline{x}_C 298 \text{ K}, T, P} \\ \times \frac{\partial \overline{x}_B}{\partial T} \Big|_{\overline{x}_B 298 \text{ K}, \overline{x}_C 298 \text{ K}, P} - \frac{\partial x_j}{\partial \overline{x}_C} \Big|_{\overline{x}_B 298 \text{ K}, T, P} \times \frac{\partial \overline{x}_C}{\partial T} \Big|_{\overline{x}_B 298 \text{ K}, \overline{x}_C 298 \text{ K}, P} \end{aligned} \quad (21)$$

$$\begin{aligned} \frac{\partial x_j}{\partial P} \Big|_{\overline{x}_B, \overline{x}_C, T} = \frac{\partial x_j}{\partial P} \Big|_{\overline{x}_B 1 \text{ atm}, \overline{x}_C 1 \text{ atm}, T} - \frac{\partial x_j}{\partial \overline{x}_B} \Big|_{\overline{x}_C 1 \text{ atm}, T, P} \\ \times \frac{\partial \overline{x}_B}{\partial P} \Big|_{\overline{x}_B 1 \text{ atm}, \overline{x}_C 1 \text{ atm}, T} - \frac{\partial x_j}{\partial \overline{x}_C} \Big|_{\overline{x}_B 1 \text{ atm}, T, P} \times \frac{\partial \overline{x}_C}{\partial P} \Big|_{\overline{x}_B 1 \text{ atm}, \overline{x}_C 1 \text{ atm}, T}, \end{aligned} \quad (22)$$

where $\overline{x}_B 298 \text{ K}$ and $\overline{x}_C 298 \text{ K}$ are respectively the values of \overline{x}_B and \overline{x}_C at 298 K, and $\overline{x}_B 1 \text{ atm}$ and $\overline{x}_C 1 \text{ atm}$ are respectively the values of \overline{x}_B and \overline{x}_C at 1 atm.

The combined diffusion coefficients of gases B and C can be calculated using the same approach:

$$\overline{D}_{BA}^x = \frac{1}{\overline{m}_A \overline{m}_B \overline{m}_C} \sum_{i=p+1}^q m_i k_{iB} \sum_{j=1}^r m_j D_{ij}^a \left(-\frac{\partial x_j}{\partial \overline{x}_B} \right) \quad (23)$$

$$\overline{D}_{BC}^x = \frac{1}{\overline{m}_A \overline{m}_B \overline{m}_C} \sum_{i=p+1}^q m_i k_{iB} \sum_{j=1}^r m_j D_{ij}^a \left(\frac{\partial x_j}{\partial \overline{x}_C} - \frac{\partial x_j}{\partial \overline{x}_B} \right) \quad (24)$$

$$\overline{D}_B^p = \frac{1}{\overline{m}_A \overline{m}_B \overline{m}_C} \sum_{i=p+1}^q m_i k_{iB} \sum_{j=1}^r m_j D_{ij}^a \left(x_j - \frac{\rho_j}{\rho} + P \frac{\partial x_j}{\partial P} \right) \quad (25)$$

$$\overline{D}_B^E = -\frac{1}{\overline{m}_A \overline{m}_B \overline{m}_C} \sum_{i=p+1}^q m_i k_{iB} \sum_{j=1}^r \frac{e m_j D_{ij} x_j Z_j}{k_B T} \quad (26)$$

$$\overline{D_B^T} = \sum_{i=p+1}^q k_{iB} \left(D_i^{Ta} - \frac{n^2}{\rho} m_i \sum_{j=1}^r m_j D_{ij}^a T \frac{\partial x_j}{\partial T} \right) \quad (27)$$

$$\overline{D_{CA}^x} = \frac{1}{\overline{m_A} \overline{m_B} \overline{m_C}} \sum_{i=q+1}^r m_i k_{iC} \sum_{j=1}^r m_j D_{ij}^a \left(-\frac{\partial x_j}{\partial x_C} \right) \quad (28)$$

$$\overline{D_{CB}^x} = \frac{1}{\overline{m_A} \overline{m_B} \overline{m_C}} \sum_{i=q+1}^r m_i k_{iC} \sum_{j=1}^r m_j D_{ij}^a \left(\frac{\partial x_j}{\partial x_B} - \frac{\partial x_j}{\partial x_C} \right) \quad (29)$$

$$\overline{D_C^P} = \frac{1}{\overline{m_A} \overline{m_B} \overline{m_C}} \sum_{i=q+1}^r m_i k_{iC} \sum_{j=1}^r m_j D_{ij}^a \left(x_j - \frac{\rho_j}{\rho} + P \frac{\partial x_j}{\partial P} \right) \quad (30)$$

$$\overline{D_C^E} = -\frac{1}{\overline{m_A} \overline{m_B} \overline{m_C}} \sum_{i=q+1}^r m_i k_{iC} \sum_{j=1}^r \frac{e m_j D_{ij} x_j Z_j}{k_B T} \quad (31)$$

$$\overline{D_C^T} = \sum_{i=q+1}^r k_{iC} \left(D_i^{Ta} - \frac{n^2}{\rho} m_i \sum_{j=1}^r m_j D_{ij}^a T \frac{\partial x_j}{\partial T} \right). \quad (32)$$

To satisfy the law of mass conservation, the mass fluxes of gases A, B and C have to satisfy the relation $\overline{J_A} + \overline{J_B} + \overline{J_C} = 0$, which requires the following conditions to be satisfied:

$$\overline{D_{AB}^x} + \overline{D_{CB}^x} = \overline{D_{BA}^x} + \overline{D_{CA}^x} = \overline{D_{AC}^x} + \overline{D_{BC}^x} \quad (33)$$

$$\overline{D_A^T} + \overline{D_B^T} + \overline{D_C^T} = 0 \quad (34)$$

$$\overline{D_A^P} + \overline{D_B^P} + \overline{D_C^P} = 0 \quad (35)$$

$$\overline{D_A^E} + \overline{D_B^E} + \overline{D_C^E} = 0. \quad (36)$$

These conditions will be checked in section 3. Note that the unit of the combined ordinary diffusion coefficients is $\text{m}^2 \text{kg}^{-1} \text{s}^{-1}$, rather than the usual $\text{m}^2 \text{s}^{-1}$. It is convenient in some circumstances to use another definition of the coefficients, presented in the appendix, in which the unit is $\text{m}^2 \text{s}^{-1}$. While this is the conventional unit for ordinary diffusion coefficients, the second definition has the disadvantage that the relations between the different diffusion coefficients are more complicated than those given in equations (33) to (36).

3. A sample calculation

In this section, a calculation of the combined diffusion coefficients in mixtures of helium, argon and carbon at atmosphere pressure is presented. Such mixtures will occur, for example, in arcs between graphite electrodes using argon and helium plasma gases, which are used for the production of carbon nanostructures.

For the sake of clarity, helium, argon and carbon are respectively denoted as gas A, B and C.

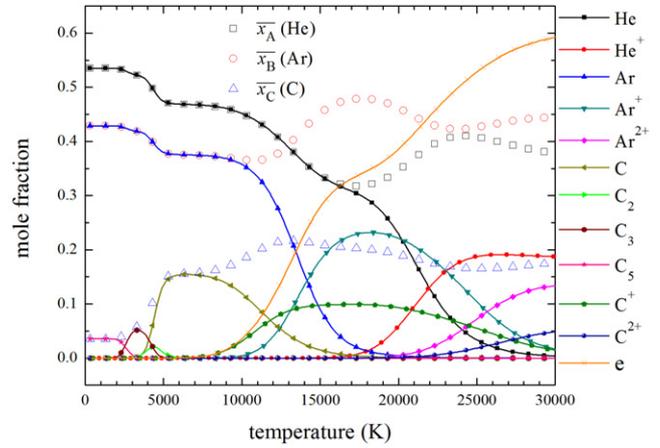


Figure 1. Equilibrium concentrations of a mixture of 10% helium, 80% argon and 10% carbon by mass at atmospheric pressure. Only those species that have mole fraction more than 0.01 are shown. The sums of the mole fractions of the helium, argon and carbon species are also shown.

The equilibrium composition of the gas mixture is a prerequisite for the calculation of combined diffusion coefficients. This is obtained using the method of minimization of Gibbs free energy, which has been described in [18]. The species considered here are He, He⁺, He²⁺, Ar, Ar⁺, Ar²⁺, Ar³⁺, Ar⁴⁺, Ar⁵⁺, C, C₂, C₃, C₄, C₅, C⁺, C²⁺, C³⁺, C₂⁻ and the electron. The results for the mixture of 10% helium, 80% argon and 10% carbon by mass as a function of temperature at atmosphere pressure are shown in figure 1. Species that have mole fraction less than 0.01 over the full temperature range are not shown. All species are considered in the diffusion calculations.

In reality, solid carbon will be present at temperatures below about 4000 K under chemical equilibrium conditions, and this will reduce the mole fraction of the gas-phase carbon species in this temperature range. Wang *et al* [19] showed that the presence of solid carbon has a significant influence on the transport properties of carbon–water–vapour mixtures below 4000 K. We have not considered solid carbon for two reasons. First, in most situations of practical interest (for example, modelling of an arc with carbon electrodes), it is appropriate to consider only the gaseous species, since the temperature of the solid carbon is not in equilibrium with that of the plasma. Second, for the purposes of an illustrative example, including solid phases will lead to undesirable complication. In any case, the combined diffusion coefficients are relatively small at low temperatures, so the absolute size of the changes will be relatively small.

The individual diffusion coefficients D_{ij} and D_i^T required to calculate the ambipolar diffusion coefficients D_{ij}^a and D_i^{Ta} were obtained using the Chapman–Enskog method [20–22]. The expressions for D_{ij}^a and D_i^{Ta} are given in equations (2) and (3). $\partial x_j / \partial P$ and $\partial x_j / \partial T$ were calculated using the correction expressions (21) and (22). The calculation of the combined diffusion coefficients were performed using the equations (15)–(19) and (23)–(32).

The temperature dependence of the combined diffusion coefficients was calculated for the gas mixture considered

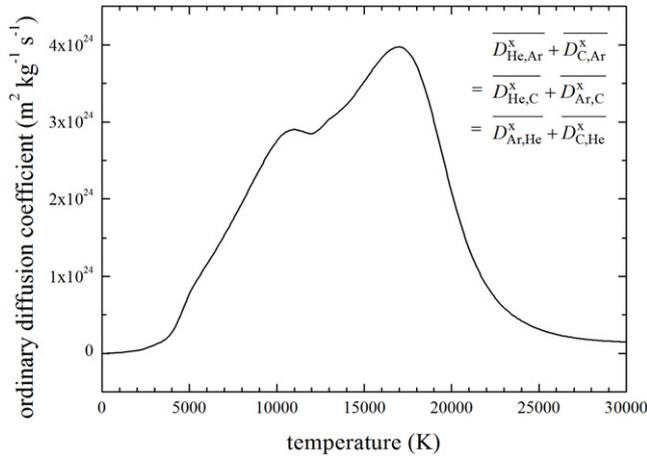


Figure 2. Sums of the specified pairs of combined ordinary diffusion coefficients presented in equation (33) in a mixture of 10% helium, 80% argon and 10% carbon by mass at atmospheric pressure.

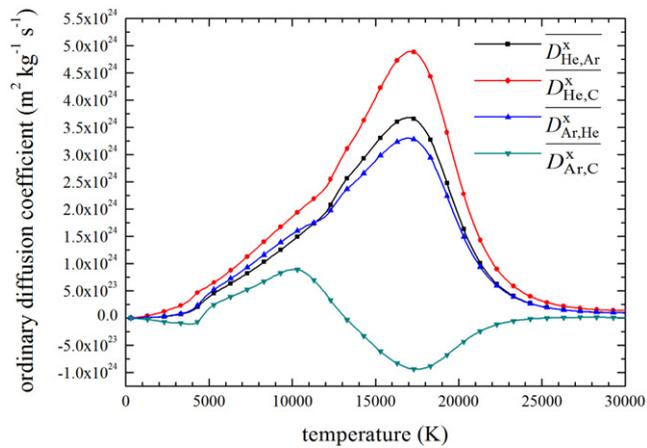


Figure 3. Linearly independent combined ordinary diffusion coefficients as a function of temperature for a mixture of 10% helium, 80% argon and 10% carbon by mass at atmospheric pressure.

in figure 1. It is demonstrated in figure 2 that the sums $\overline{D_{He,Ar}^x} + \overline{D_{C,Ar}^x}$, $\overline{D_{Ar,He}^x} + \overline{D_{C,He}^x}$ and $\overline{D_{He,C}^x} + \overline{D_{Ar,C}^x}$ exactly satisfy the condition (33). This is a good test of the correctness of the calculated values, since the calculation does not rely on the condition. Consequently, only four of the combined ordinary diffusion coefficients are linearly independent, and $\overline{D_{He,Ar}^x}$, $\overline{D_{He,C}^x}$, $\overline{D_{Ar,He}^x}$ and $\overline{D_{Ar,C}^x}$ are chosen to be shown in figure 3. It can be seen that $\overline{D_{He,Ar}^x}$, $\overline{D_{He,C}^x}$ and $\overline{D_{Ar,He}^x}$ increase with temperature up to around 17 000 K, by which temperature significant ionization has occurred; at higher temperatures, they decrease rapidly, because of 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 larger collision cross sections and hence lower diffusion rates. At first, $\overline{D_{Ar,C}^x}$ increases with temperature and reaches a maximum at 10 000 K, at which temperature the first ionization of argon starts. As temperature increases, $\overline{D_{Ar,C}^x}$ then decreases, becoming negative and reaching a minimum at about the same temperature area at which the other combined diffusion coefficients reach their peak values. Of the four linearly

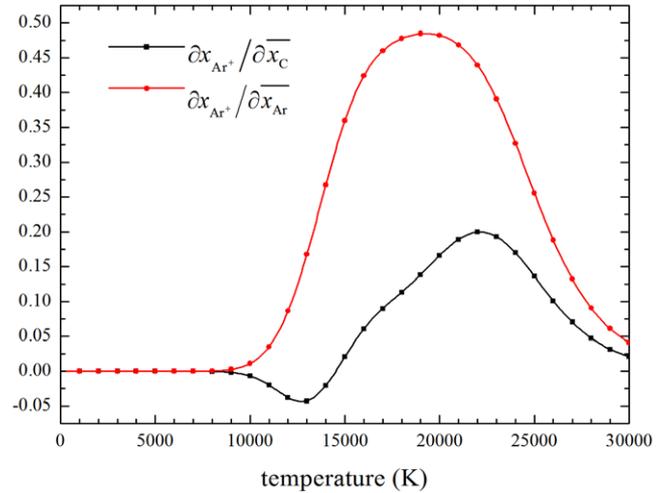


Figure 4. Values of $\partial x_{Ar^+}/\partial \overline{x_{Ar}}$ and $\partial x_{Ar^+}/\partial \overline{x_C}$ as a function of temperature in a mixture of 10% helium, 80% argon and 10% carbon by mass at atmospheric pressure.

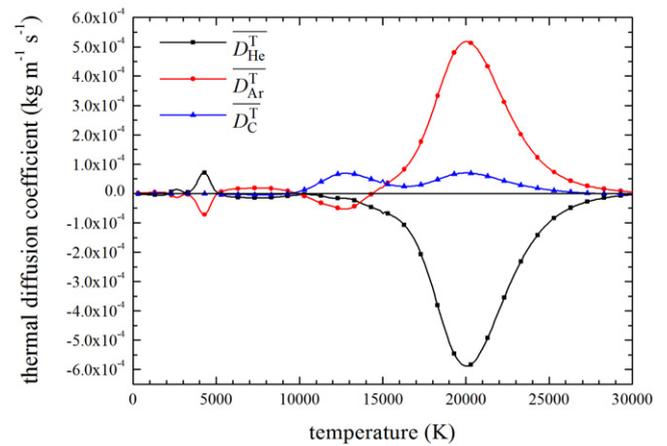


Figure 5. Combined temperature diffusion coefficients as a function of temperature in a mixture of 10% helium, 80% argon and 10% carbon by mass at atmospheric pressure.

independent combined ordinary diffusion coefficients shown in figure 3, $\overline{D_{Ar,C}^x}$, given by equation (24), is the only one dependent on the difference between pairs of partial derivative terms. The terms $\partial x_{Ar^+}/\partial \overline{x_{Ar}}$ and $\partial x_{Ar^+}/\partial \overline{x_C}$ are shown in figure 4. For temperatures above 10 000 K, Ar^+ is present with increasingly high number density (see figure 1), and we have $\partial x_{Ar^+}/\partial \overline{x_{Ar}} > \partial x_{Ar^+}/\partial \overline{x_C}$, leading to a decreasing and then negative value of $\overline{D_{Ar,C}^x}$; the minimum value occurs at approximately the same temperature as the peak number density of Ar^+ .

Figure 5 shows the combined temperature diffusion coefficients. Comparing figures 1 and 5, it can be seen that the temperatures at which dissociation of C_5 and C_3 , and ionization of Ar and He, occur correspond to the temperatures of the maximum and minimum values of the combined temperature diffusion coefficients. It is thus clear that the combined temperature diffusion coefficients are very sensitive to the occurrence of dissociation and ionization reactions. This is because the terms $\partial x_j/\partial T$ in the expressions of combined temperature diffusion coefficients (19), (27) and (32) are large

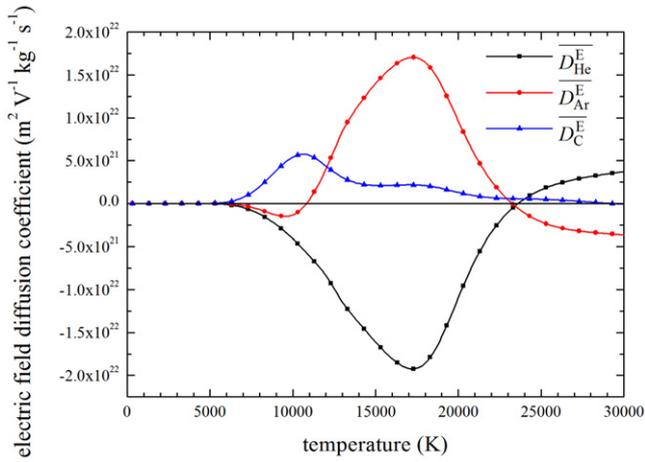


Figure 6. Combined electric field diffusion coefficients as a function of temperature in a mixture of 10% helium, 80% argon and 10% carbon by mass at atmospheric pressure.

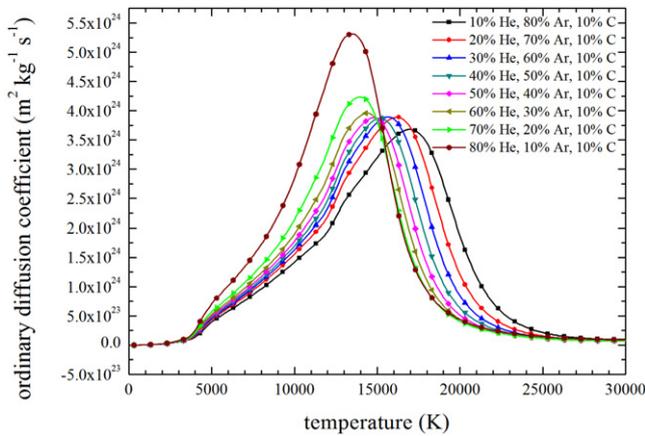


Figure 7. Temperature dependence of combined ordinary diffusion coefficient $\overline{D_{He,Ar}^x}$ for eight different mixtures of helium, argon and carbon at atmospheric pressure. The percentages are by mass.

at the temperatures at which the dissociation and ionization reactions occur. They play a dominant role, since the terms containing D_i^{Ta} are usually negligible.

The combined electric field diffusion coefficients are a linear combination of the multicomponent ordinary diffusion coefficients for each pair of species of which at least one of the pair is charged. They are therefore zero or close to zero until significant ionization occurs, as shown in figure 6.

The temperature dependence of the combined ordinary diffusion coefficients $\overline{D_{He,Ar}^x}$ and $\overline{D_{Ar,He}^x}$ for different mixtures of helium, argon and carbon are illustrated in figures 7 and 8, respectively. As the mass fraction of helium increases (with that of carbon held constant), the peaks of $\overline{D_{He,Ar}^x}$ and $\overline{D_{Ar,He}^x}$ both shift to lower temperatures, since the ionization of argon occurs at lower temperatures as its mass fraction decreases. The coefficient $\overline{D_{He,Ar}^x}$ exhibits a strong dependence on the relative concentrations of helium, argon and carbon at all temperatures, whereas the similar dependence only happens at high temperature for $\overline{D_{Ar,He}^x}$; at low temperature $\overline{D_{Ar,He}^x}$ is almost independent of the relative concentrations of helium, argon and carbon. It was noted in section 2 that each

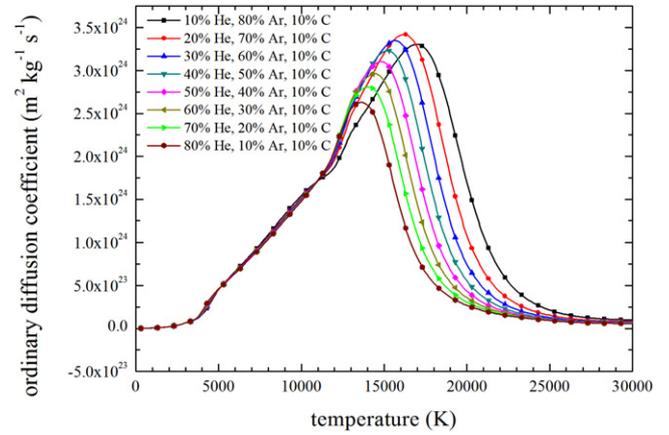


Figure 8. Temperature dependence of combined ordinary diffusion coefficient $\overline{D_{Ar,He}^x}$ for eight different mixtures of helium, argon and carbon at atmospheric pressure. The percentages are by mass.

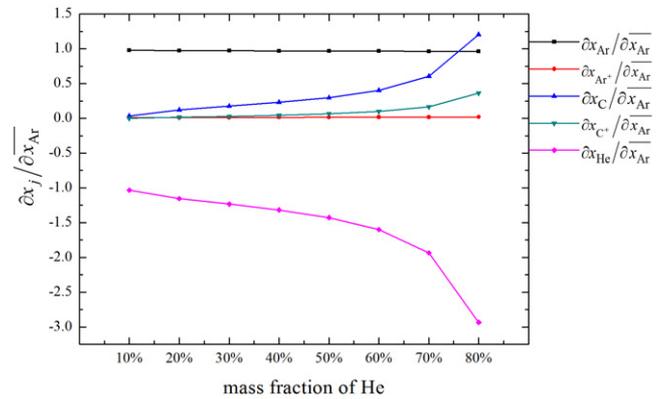


Figure 9. Weight factor $\partial x_j / \partial \overline{x_{Ar}}$ as a function of mass fraction of helium, in a mixture containing argon and 10% carbon by mass, at 10000 K and atmospheric pressure.

combined ordinary diffusion coefficient is a weighted average of the ambipolar ordinary diffusion coefficients of the pairs of relevant species. Equations (15) and (23) suggest that the different behaviours of $\overline{D_{He,Ar}^x}$ and $\overline{D_{Ar,He}^x}$ can be explained in terms of the sum of $m_j D_{ij}^a (\partial x_j / \partial \overline{x_B})$ over all species.

The weight factors $\partial x_j / \partial \overline{x_{Ar}}$ for the species j that are dominant at 10000 K are shown in figure 9 as a function of the mass fraction of helium, with the mass fraction of carbon held constant at 10%. We see that $\partial x_C / \partial \overline{x_{Ar}}$, $\partial x_{C^+} / \partial \overline{x_{Ar}}$ and $|\partial x_{He} / \partial \overline{x_{Ar}}|$ increase with the mass fraction of helium, while the other weight factors remain constant. For the conditions of figure 9, $D_{He,j}^a$ and $D_{Ar,j}^a$ are shown in figures 10 and 11, respectively. Since $D_{Ar,Ar}^a$ is very small (less than $1.8 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ at all temperatures), it makes a negligible contribution to $\overline{D_{Ar,He}^x}$, and is not shown in these figures. It can be seen that the ambipolar ordinary diffusion coefficients $D_{He,C}^a$, D_{He,C^+}^a and $D_{He,He}^a$ decrease as the mass fraction of helium increases; however, they decrease more slowly than the corresponding weight factors increase. Furthermore, both $\partial x_{He} / \partial \overline{x_{Ar}}$ and $D_{He,He}^a$ have negative values. Together, these trends ensure that $\overline{D_{He,Ar}^x}$ increases with the mass fraction of helium at low temperatures, as shown in figure 7. In contrast, $\overline{D_{Ar,He}^x}$ is independent of the relative concentration of helium,

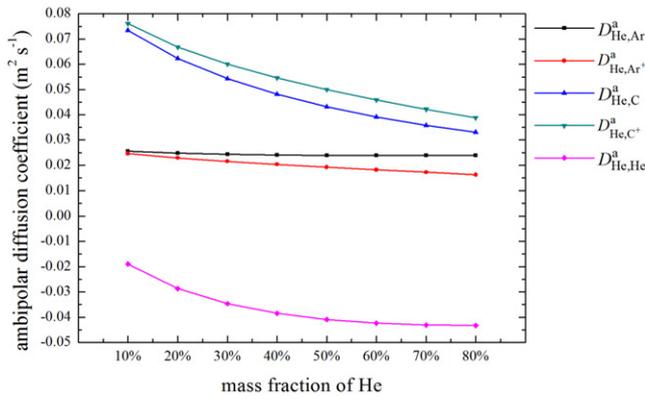


Figure 10. Ambipolar ordinary diffusion coefficients $D_{\text{He},j}^a$ for the dominant species j at 10 000 K, as a function of helium mass fraction, in a mixture containing argon and 10% carbon by mass, at atmospheric pressure.

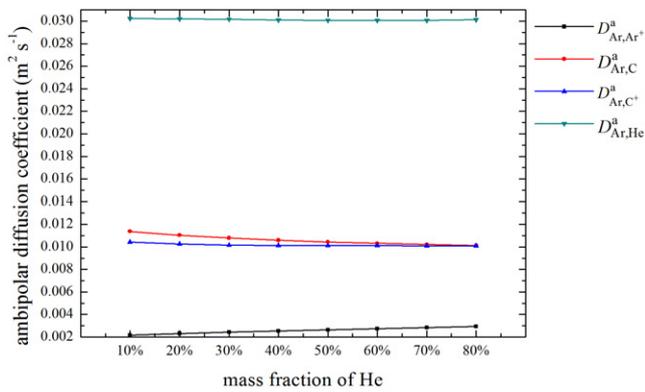


Figure 11. Ambipolar ordinary diffusion coefficients $D_{\text{Ar},j}^a$ for the dominant species j at 10 000 K, as a function of helium mass fraction, in a mixture containing argon and 10% carbon by mass, at atmospheric pressure.

argon and carbon, since the increase arising from $\partial x_C / \partial \bar{x}_{\text{Ar}}$ and $\partial x_{C^+} / \partial \bar{x}_{\text{Ar}}$ is almost exactly offset by the decrease arising from the negative value and gradient of $\partial x_{\text{He}} / \partial \bar{x}_{\text{Ar}}$, and further all of the $D_{\text{Ar},j}^a$ shown in figure 11 are approximately constant.

4. Conclusions

We have presented a method of calculating combined diffusion coefficients for a mixture of three homonuclear non-reacting gases with arbitrary degree of ionization. Ambipolar effects are taken into account in the calculation. Formulas for the combined diffusion coefficients have been given, and a sample calculation for a mixture of helium, argon and carbon at atmosphere pressure has been presented. We have also discussed the dependence of the combined diffusion coefficients on the temperature and composition.

The example presented is relevant to carbon nanostructure production in an argon and helium plasma; as noted in the introduction, there are many applications of thermal plasmas in which mixtures of three gases or vapours are present.

Compared to the method for two gases introduced by Murphy, six additional combined diffusion coefficients, comprising three combined ordinary diffusion coefficients,

one combined temperature diffusion coefficient, one combined pressure diffusion coefficient and one electric field diffusion coefficient, are required to describe the diffusion process in a mixture of three gases. This is still very much simpler than the full treatment using multicomponent ordinary and thermal diffusion coefficients, which requires $r(r-1)/2$ ordinary and $(r-1)$ thermal diffusion coefficients; in our sample calculation, $r = 19$. When the combined diffusion coefficient method is used in the thermal plasma modelling, the mixture of three gases can be treated by solving only two-gas conservation equations, instead of $(r-1)$ species conservation equations. Since the method is equivalent to the full treatment in the case of an LCE plasma consisting of homonuclear gases that do not react with other, it clearly allows a major simplification in development of models without any loss of accuracy.

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Appendix

Here we present an alternative definition of the combined diffusion coefficient, for which the combined ordinary diffusion coefficients have the unit $\text{m}^2 \text{s}^{-1}$.

The expressions of the mass fluxes of gases A, B and C can be written as

$$\bar{J}_A = \frac{n^2}{\rho} \bar{m}_A \left[\left(\bar{m}_B \bar{D}_{AB}^x \nabla \bar{x}_B + \bar{m}_C \bar{D}_{AC}^x \nabla \bar{x}_C \right) + \bar{D}_A^p \nabla \ln P + \bar{D}_A^E \mathbf{E} \right] - \bar{D}_A^T \nabla \ln T \quad (\text{A.1})$$

$$\bar{J}_B = \frac{n^2}{\rho} \bar{m}_B \left[\left(\bar{m}_A \bar{D}_{BA}^x \nabla \bar{x}_A + \bar{m}_C \bar{D}_{BC}^x \nabla \bar{x}_C \right) + \bar{D}_B^p \nabla \ln P + \bar{D}_B^E \mathbf{E} \right] - \bar{D}_B^T \nabla \ln T \quad (\text{A.2})$$

$$\bar{J}_C = \frac{n^2}{\rho} \bar{m}_C \left[\left(\bar{m}_A \bar{D}_{CA}^x \nabla \bar{x}_A + \bar{m}_B \bar{D}_{CB}^x \nabla \bar{x}_B \right) + \bar{D}_C^p \nabla \ln P + \bar{D}_C^E \mathbf{E} \right] - \bar{D}_C^T \nabla \ln T. \quad (\text{A.3})$$

These are analogous to the form of equation (1) for a mixture of three species. We then proceed as in section 2 to obtain

$$\bar{D}_{AB}^x = \frac{1}{\bar{m}_A \bar{m}_B} \sum_{i=1}^p m_i k_{iA} \sum_{j=1}^r m_j D_{ij}^a \left(\frac{\partial x_j}{\partial \bar{x}_B} \right) \quad (\text{A.4})$$

$$\bar{D}_{AC}^x = \frac{1}{\bar{m}_A \bar{m}_C} \sum_{i=1}^p m_i k_{iA} \sum_{j=1}^r m_j D_{ij}^a \left(\frac{\partial x_j}{\partial \bar{x}_C} \right) \quad (\text{A.5})$$

$$\bar{D}_A^p = \frac{1}{\bar{m}_A} \sum_{i=1}^p m_i k_{iA} \sum_{j=1}^r m_j D_{ij}^a \left(x_j - \frac{\rho_j}{\rho} + P \frac{\partial x_j}{\partial P} \right) \quad (\text{A.6})$$

$$\overline{D_A^E} = -\frac{1}{\overline{m_A}} \sum_{i=1}^p m_i k_{iA} \sum_{j=1}^r \frac{em_j D_{ij} x_j Z_j}{k_B T} \quad (\text{A.7})$$

$$\overline{D_A^T} = \sum_{i=1}^p k_{iA} \left(D_i^{Ta} - \frac{n^2}{\rho} m_i \sum_{j=1}^r m_j D_{ij}^a T \frac{\partial x_j}{\partial T} \right). \quad (\text{A.8})$$

Similar expressions for $\overline{D_{BA}^x}$, $\overline{D_{BC}^x}$, $\overline{D_{CA}^x}$, $\overline{D_{CB}^x}$, $\overline{D_B^P}$, $\overline{D_C^P}$, $\overline{D_B^E}$, $\overline{D_C^E}$, $\overline{D_B^T}$ and $\overline{D_C^T}$ can be calculated. Except for the combined temperature diffusion coefficients, they obey different conditions from those given in equations (33) to (36):

$$\begin{aligned} \overline{m_A} \overline{m_B} \overline{D_{AB}^x} + \overline{m_B} \overline{m_C} \overline{D_{CB}^x} &= \overline{m_A} \overline{m_B} \overline{D_{BA}^x} + \overline{m_A} \overline{m_C} \overline{D_{CA}^x} \\ &= \overline{m_A} \overline{m_C} \overline{D_{AC}^x} + \overline{m_B} \overline{m_C} \overline{D_{BC}^x} \end{aligned} \quad (\text{A.9})$$

$$\overline{m_A} \overline{D_A^P} + \overline{m_B} \overline{D_B^P} + \overline{m_C} \overline{D_C^P} = 0 \quad (\text{A.10})$$

$$\overline{m_A} \overline{D_A^E} + \overline{m_B} \overline{D_B^E} + \overline{m_C} \overline{D_C^E} = 0. \quad (\text{A.11})$$

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