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# Calculation and application of combined diffusion coefficients in thermal plasmas

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SUBJECT AREAS:

PLASMA PHYSICS  
STATISTICAL PHYSICS  
APPLIED MATHEMATICS

Received  
4 November 2013

Accepted  
13 February 2014

Published  
7 March 2014

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The combined diffusion coefficient method is widely used to treat the mixing and demixing of different plasma gases and vapours in thermal plasmas, such as welding arcs and plasma jets. It greatly simplifies the treatment of diffusion for many gas mixtures without sacrificing accuracy. Here, three subjects that are important in the implementation of the combined diffusion coefficient method are considered. First, it is shown that different expressions for the combined diffusion coefficients, arising from different definitions for the stoichiometric coefficients that assign the electrons to the two gases, are equivalent. Second, an approach is presented for calculating certain partial differential terms in the combined temperature and pressure diffusion coefficients that can cause difficulties. Finally, a method for applying the combined diffusion coefficients in computational models, which typically require diffusion to be expressed in terms of mass fraction gradients, is given.

The combined diffusion coefficient method<sup>1</sup> allows major simplifications in the modelling of thermal plasmas in gas mixtures, in most cases without loss of accuracy. Instead of solving conservation equations for the mass of each species (e.g.,  $N_2$ ,  $N_2^+$ ,  $N$ ,  $N^+$ ,  $N^{2+}$ ,  $N^{3+}$ ,  $Ar$ ,  $Ar^+$ ,  $Ar^{2+}$ ,  $Ar^{3+}$ ,  $e^-$  in an argon–nitrogen plasma), the species are combined into their parent gases, so only one conservation equation (e.g., for argon or nitrogen ‘gas’) has to be solved. The multicomponent diffusion coefficients for each pair of species (of which there are  $q(q - 1)/2$  ordinary and  $q - 1$  thermal diffusion coefficients for a plasma containing  $q$  species) are combined into just four combined diffusion coefficients, one each describing diffusion due to composition gradients, temperature gradients, pressure gradients and applied electric fields.

The method has been successfully applied to modelling a wide range of phenomena in thermal plasmas. These include demixing in welding arcs<sup>2,3</sup>, plasma torches<sup>4</sup>, arc plasma reactors<sup>5,6</sup>, and inductively-coupled rf plasmas in gas mixtures<sup>7–10</sup>, mixing of metal vapour in welding arcs<sup>11–13</sup>, mixing of air into plasmas<sup>14–23</sup>, mixing of polymer vapours into the arc in circuit breakers<sup>24–29</sup>, and expansion of metal vapour ablated by a laser into the surrounding air<sup>30</sup>.

Values of the combined diffusion coefficients have been presented for many gas mixtures, including argon–nitrogen<sup>31</sup>, argon–oxygen<sup>31</sup>, argon–air<sup>32</sup>, argon–helium<sup>33,34</sup>, argon–hydrogen<sup>35</sup>, nitrogen–hydrogen<sup>36</sup>, sulfur hexafluoride–tetrafluoroethene<sup>29</sup>, argon–metal vapours<sup>11,37,38</sup>, and air–metal vapours<sup>11,39,40</sup>. The methods have also been extended to two-temperature plasmas<sup>41–43</sup>.

Although determination of the combined diffusion coefficients is a relatively simple extension of the calculation of the multicomponent diffusion coefficients, three points of confusion have frequently been apparent in communications with researchers performing such calculations. The first concerns the method of assigning electrons to the two gases using stoichiometric coefficients, the second the treatment of the mole fraction gradient terms in the calculation of the combined pressure and temperature diffusion coefficients, and the third the method of application of the combined diffusion coefficients in computational models, which typically require the diffusion term to be written in terms of mass fraction gradients.

The purpose of this paper is to clarify these three points. To put this in context, an introduction to the combined diffusion coefficient approach is first presented.

In the most general treatment of thermal plasmas containing more than one chemical element, the mass conservation equations for each individual species (e.g.,  $Ar$ ,  $Ar^+$ ,  $Ar^{2+}$ ,  $N_2$ ,  $N_2^+$ ,  $N$ ,  $N^+$ ,  $N^{2+}$ ,  $e^-$ , etc., in an argon–nitrogen plasma):

$$\frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho \mathbf{v} Y_i) + \nabla \cdot \mathbf{J}_i = r_i, \quad (1)$$

have to be solved everywhere in the plasma. Here  $\rho$  is the mass density,  $\mathbf{v}$  is the mass-average velocity,  $Y_i$  is the mass fraction of species  $i$ , and  $r_i$  is the net rate of production of species  $i$  due to chemical reactions, vaporization,



etc. For a gas or plasma containing  $q$  species, the diffusion mass flux of species  $i$ ,  $J_i$ , is given by<sup>44,45</sup>

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

where  $\mathbf{v}_i$  is the diffusion velocity of species  $i$  (relative to the mass-average velocity),  $m_i$  and  $n_i$  are respectively the mass and the number density of the species  $i$ , and  $\mathbf{d}_j$  describes the driving forces for diffusion of species  $j$ . The ordinary diffusion coefficients  $D_{ij}$  and thermal diffusion coefficients  $D_i^T$  are in this case multicomponent diffusion coefficients<sup>44,45</sup>.

For thermal plasmas, in which values of  $E/n$  (electric field normalized to the gas number density) are very low (typically less than  $1 \text{ Td} = 1 \times 10^{-21} \text{ Vm}^2$ ) and the species velocity distributions can be closely approximated by a Maxwellian distribution, it is standard practice to use the Chapman–Enskog approximate solution to the Boltzmann equation to obtain the diffusion coefficients. Their calculation requires values of the mole fractions and the masses of all the species present and the collision cross-sections for binary interactions between each pair of species present<sup>45</sup>. Note that the much higher values of  $E/n$  present in swarms and many non-equilibrium discharges require different approaches<sup>46,47</sup>.

The driving force term  $\mathbf{d}_j$  is given by<sup>44,45</sup>

$$\mathbf{d}_j = \nabla x_j + \left( x_j - \frac{n_j m_j}{\rho} \right) \nabla \ln P - \frac{n_j m_j}{P \rho} \left( \frac{\rho}{m_j} \mathbf{F}_j - \sum_{l=1}^q n_l \mathbf{F}_l \right). \quad (3)$$

The three terms describe respectively diffusion due to gradients in the mole fraction  $x_j$ , the pressure  $P$ , and the external forces  $\mathbf{F}_j$  acting on species  $j$ . Here the only external force that is considered is that due to an applied electric field. It is interesting to note that gravity does not exert a driving force, since the third term cancels to zero.

Because diffusion velocities are defined with respect to the mass-average velocity, only  $N - 1$  need be calculated, and (1) has to be solved for only  $N - 1$  species. In plasmas, the diffusion coefficients have to be modified to take into account ambipolar diffusion<sup>1,45</sup>. This arises because electrons diffuse more rapidly than ions because of their lower mass, inducing an electric field that accelerates the ions and slows the electrons.

Clearly, solving the conservation equations (1) for each species, and calculating ordinary diffusion coefficient for each pair of species and thermal diffusion coefficients for each species, is computationally expensive. As a consequence, simplified methods are generally used; a range of methods of varying levels of simplicity and accuracy is available<sup>48,49</sup>. The combined diffusion coefficient approach has the advantage of being mathematically equivalent to the full multicomponent treatment if three conditions are satisfied: the gases are homonuclear, they do not react with each other, and the plasma is in local chemical equilibrium (LCE). Although different species will usually have different diffusion velocities, the imposition of LCE means that the local composition depends only on the local temperature, pressure and the relative concentrations of the two gases. For example, although nitrogen molecules and atoms diffuse at different rates, dissociation and recombination reactions will maintain the composition of nitrogen gas in accordance with LCE.

The diffusion mass flux of gas A is

$$\overline{J}_A = \frac{n^2}{\rho} \overline{m}_A \overline{m}_B \left( \overline{D}_{AB}^x \nabla \overline{x}_B + \overline{D}_{AB}^p \nabla \ln P + \overline{D}_{AB}^E \mathbf{E} \right) - \overline{D}_{AB}^T \nabla \ln T, \quad (4)$$

where  $\overline{m}_A$  and  $\overline{m}_B$  are the average masses of the heavy species of the respective gases

$$\overline{m}_A = \frac{\sum_{k=2}^p m_k x_k}{\sum_{k=2}^p x_k} \quad (5)$$

$$\overline{m}_B = \frac{\sum_{k=p+1}^q m_k x_k}{\sum_{k=p+1}^q x_k}$$

and  $\overline{x}_B$  is the sum of the mole fractions of the species of the gas B:

$$\overline{x}_A = \sum_{k=2}^p (1 + Z_k) x_k$$

$$\overline{x}_B = \sum_{k=p+1}^q (1 + Z_k) x_k = 1 - \overline{x}_A. \quad (6)$$

where  $Z_k$  is the charge number of species  $k$ , and is used to divide the electrons between the two gases.

The combined ordinary diffusion coefficient  $\overline{D}_{AB}^x$ , combined pressure diffusion coefficient  $\overline{D}_{AB}^p$ , combined electric field diffusion coefficient  $\overline{D}_{MG}^E$  and combined temperature diffusion coefficient  $\overline{D}_{MG}^T$  describe, respectively, diffusion due to mole fraction gradients, gradients of the total pressure, externally-applied electric fields and temperature gradients. They are calculated by writing  $\overline{J}_A$  and  $\overline{J}_B$  in terms of the total mass flux of the species of gas A and gas B respectively. Electrons arising from ionization of gas A species are assigned to gas A, and likewise for gas B, using the stoichiometric coefficients  $k_i$  and  $k'_i$ :

$$\overline{J}_A = \sum_{i=1}^p k_i J_i, \quad (7)$$

$$\overline{J}_B = k'_1 J_1 + \sum_{i=p+1}^q k'_i J_i = \sum_{i=1, i=p+1}^q k'_i J_i,$$

where

$$k_1 = \frac{\sum_{k=2}^p Z_k x_k}{x_1},$$

$$k'_1 = \frac{\sum_{k=p+1}^q Z_k x_k}{x_1}, \quad (8)$$

$$k_i, k'_i = 1, \quad i \neq 1.$$

The terms  $k_i$  and  $k'_i$  are used to apportion the electrons between gas A and gas B according to the degree of ionization of the respective gas. Using

$$\nabla x_j = \left( \frac{\partial x_j}{\partial \overline{x}_B} \right) \nabla \overline{x}_B + \left( \frac{\partial x_j}{\partial P} \right) \nabla P + \left( \frac{\partial x_j}{\partial T} \right) \nabla T, \quad (9)$$

which is valid since our assumption of LCE means that an equilibrium composition can be defined as a function of temperature, pressure, and the relative concentrations of the two gases, we obtain<sup>1,50</sup>:

$$\overline{D}_{AB}^x = \frac{1}{\overline{m}_A \overline{m}_B} \sum_{i=1}^p k_i m_i \sum_{j=1}^q m_j D_{ij}^a \frac{\partial x_i}{\partial \overline{x}_B}, \quad (10)$$

$$\overline{D}_{AB}^p = \frac{1}{\overline{m}_A \overline{m}_B} \sum_{i=1}^p k_i m_i \sum_{j=1}^q m_j D_{ij}^a \left( x_j - \frac{\rho_j}{\rho} + P \frac{\partial x_j}{\partial P} \right), \quad (11)$$

$$\overline{D}_{AB}^E = - \frac{e}{k_B T} \frac{1}{\overline{m}_A \overline{m}_B} \sum_{i=1}^p k_i m_i \sum_{j=1}^q m_j x_j Z_j D_{ij}, \quad (12)$$

and

$$\overline{D}_{AB}^T = \sum_{i=1}^p k_i \left( D_i^{Ta} - \frac{n^2}{\rho} m_i \sum_{j=1}^q m_j D_{ij}^a T \frac{\partial x_j}{\partial T} \right). \quad (13)$$

We can obtain analogous expressions for  $\overline{D}_{BA}^x$ ,  $\overline{D}_{BA}^p$ ,  $\overline{D}_{BA}^E$  and  $\overline{D}_{BA}^T$  that satisfy  $\overline{D}_{AB}^x = \overline{D}_{BA}^x$ ,  $\overline{D}_{AB}^p = -\overline{D}_{BA}^p$ ,  $\overline{D}_{AB}^E = -\overline{D}_{BA}^E$ , and  $\overline{D}_{AB}^T = -\overline{D}_{BA}^T$ .



## Results

**Stoichiometric coefficients.** In previous publications<sup>1,3,32,35,48,49</sup>, different expressions for the combined diffusion coefficients have been given. The derivation of the coefficients was performed using number fluxes rather than mass fluxes, leading to the following expressions:

$$\overline{D}_{AB}^x = \frac{1}{\overline{m}_B} \sum_{i=1}^p s_i \sum_{j=1}^q m_j D_{ij}^a \frac{\partial x_i}{\partial \overline{x}_B}, \quad (14)$$

$$\overline{D}_{AB}^P = \frac{1}{\overline{m}_B} \sum_{i=1}^p s_i \sum_{j=1}^q m_j D_{ij}^a \left( x_j - \frac{\rho_j}{\rho} + P \frac{\partial x_j}{\partial P} \right), \quad (15)$$

$$\overline{D}_{AB}^E = -\frac{e}{k_B T} \frac{1}{\overline{m}_B} \sum_{i=1}^p s_i \sum_{j=1}^q m_j x_j Z_j D_{ij}, \quad (16)$$

and

$$\overline{D}_{AB}^T = \overline{m}_A \sum_{i=1}^p s_i \left( \frac{D_i^{Ta}}{m_i} - \frac{n^2}{\rho} \sum_{j=1}^q m_j D_{ij}^a T \frac{\partial x_j}{\partial T} \right), \quad (17)$$

where the  $s_i$  are stoichiometric coefficients, defined by

$$\begin{aligned} s_1 &= \frac{m_1}{\overline{m}_A} \sum_{k=2}^p \frac{Z_k x_k}{x_1}, \\ s_i &= b_i \sum_{k=2}^p x_k / \sum_{k=2}^p b_k x_k, \quad 2 \leq i \leq p, \\ s_i &= b_i \sum_{k=p+1}^q x_k / \sum_{k=p+1}^q b_k x_k, \quad p+1 \leq i \leq q \end{aligned} \quad (18)$$

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.

In the initial publications,  $s_1 = 0$  was used<sup>1,48</sup>. This is equivalent to neglecting the mass flux of the electrons  $\mathbf{J}_1 = m_1 n_1 \mathbf{v}_1$ , which is reasonable when calculating  $\overline{D}_{AB}^x$ ,  $\overline{D}_{AB}^P$  and  $\overline{D}_{AB}^T$ , since the electron mass is much smaller than the heavy species mass, and the electron diffusion velocity is of the same order of that of the heavy species due to ambipolar effects. However, ambipolar effects do not play a role in electric field diffusion, meaning that  $v_1 \gg v_i (i \neq 1)$ , so  $\mathbf{J}_1$  cannot be neglected in calculating  $\overline{D}_{AB}^E$ .

The expressions for the combined diffusion coefficients given in equations (14) to (17) are in fact equivalent to the current expressions (10) to (13). We show here that the expressions given in equations (10) and (14) for  $\overline{D}_{AB}^x$  are equal; the expressions for the other coefficients can be shown to be equal in a similar manner.

Substituting equation (18) into equation (14) gives

$$\overline{D}_{AB}^x = \frac{m_1}{\overline{m}_A \overline{m}_B} \sum_{i=2}^p \frac{Z_i x_i}{x_1} \sum_{j=1}^q m_j D_{ij}^a \frac{\partial x_i}{\partial \overline{x}_B} + \frac{1}{\overline{m}_B} \sum_{i=2}^p b_i \frac{\sum_{k=2}^p x_k}{\sum_{k=2}^p b_k x_k} \sum_{j=1}^q m_j D_{ij}^a \frac{\partial x_i}{\partial \overline{x}_B} \quad (19)$$

Since  $b_i/b_j = m_i/m_j$  for species derived from the same gas, this can be written

$$\overline{D}_{AB}^x = \frac{m_1}{\overline{m}_A \overline{m}_B} \sum_{i=2}^p \frac{Z_i x_i}{x_1} \sum_{j=1}^q m_j D_{ij}^a \frac{\partial x_i}{\partial \overline{x}_B} + \frac{1}{\overline{m}_B} \sum_{k=2}^p \frac{x_k}{m_k x_k} \sum_{i=2}^p m_i \sum_{j=1}^q m_j D_{ij}^a \frac{\partial x_i}{\partial \overline{x}_B} \quad (20)$$

which can be shown to be equivalent to (10) using equations (5) and (8).

**Calculation of partial differentials in the expressions for combined diffusion coefficients.** Equation (9) is more formally written as

$$\nabla x_j = (\partial x_j / \partial \overline{x}_B) \Big|_{P,T} \nabla \overline{x}_B + (\partial x_j / \partial P) \Big|_{\overline{x}_B,T} \nabla P + (\partial x_j / \partial T) \Big|_{\overline{x}_B,P} \nabla T, \quad (21)$$

denoting that, for example,  $(\partial x_j / \partial T)$ , has to be calculated with  $\overline{x}_B$  and  $P$  held constant. Hence, equation (13) is written

$$\overline{D}_{AB}^T = \sum_{i=1}^p k_i \left( D_i^{Ta} - \frac{n^2}{\rho} m_i \sum_{j=1}^q m_j D_{ij}^a T \frac{\partial x_j}{\partial T} \Big|_{\overline{x}_B,P} \right), \quad (22)$$

and similarly for equation (11).

For a given gas mixture, however,  $\overline{x}_B$  is a function 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  $\overline{x}_B$  stays constant with changes in temperature and pressure.

This problem can be solved by obtaining expressions for  $(\partial x_j / \partial T) \Big|_{\overline{x}_B,P}$  and  $(\partial x_j / \partial P) \Big|_{\overline{x}_B,T}$  in terms of the value of  $\overline{x}_B$  at a particular temperature and pressure. These can be derived using the identity

$$\frac{\partial f}{\partial t} \Big|_s = \frac{\partial f}{\partial x} \Big|_y \frac{\partial x}{\partial t} \Big|_s + \frac{\partial f}{\partial y} \Big|_x \frac{\partial y}{\partial t} \Big|_s \quad (23)$$

where  $f = f(x, y)$ , with  $x = x(s, t)$  and  $y = y(s, t)$ .

If  $x = t$ , so  $y = y(s, x)$ , this gives

$$\frac{\partial f}{\partial x} \Big|_s = \frac{\partial f}{\partial x} \Big|_y + \frac{\partial f}{\partial y} \Big|_x \frac{\partial y}{\partial x} \Big|_s \quad (24)$$

Substituting  $x_j$  for  $f$ ,  $T$  for  $x$ ,  $\overline{x}_B$  for  $y$ , and  $\overline{x}_{298\text{K}}$  for  $s$ , we obtain

$$(\partial x_j / \partial T) \Big|_{\overline{x}_B,P} = (\partial x_j / \partial T) \Big|_{\overline{x}_{298\text{K}},P} - (\partial x_j / \partial \overline{x}_B) \Big|_{P,T} \times (\partial \overline{x}_B / \partial T) \Big|_{\overline{x}_{298\text{K}},P} \quad (25)$$

where  $\overline{x}_{298\text{K}}$  is the value of  $\overline{x}_B$  at 298 K.

Similarly, we obtain

$$(\partial x_j / \partial P) \Big|_{\overline{x}_B,T} = (\partial x_j / \partial P) \Big|_{\overline{x}_{1\text{atm}},T} - (\partial x_j / \partial \overline{x}_B) \Big|_{P,T} \times (\partial \overline{x}_B / \partial P) \Big|_{\overline{x}_{1\text{atm}},T} \quad (26)$$

where  $\overline{x}_{1\text{atm}}$  is the value of  $\overline{x}_B$  at 1 atm.

The values of  $(\partial x_j / \partial T)$  in equation (13) and  $(\partial x_j / \partial P)$  in equation (11) are then calculated using equations (25) and (26), respectively.

Figure 1 shows a comparison the combined temperature diffusion coefficient calculated with and without the 'correction term', i.e., with and without the second term on the right-hand side of equation (25). The collision integrals and methods used were those given in<sup>31</sup>, as updated in<sup>36</sup>. It is clear that the 'correction term' is very significant. The corresponding term in equation (26), used in calculating the combined pressure diffusion coefficient, is in contrast, negligible, because  $\overline{x}_B$  depends only weakly on pressure.

**Application of combined diffusion coefficients in computational models.** The combined diffusion coefficient approach allows us to calculate  $\overline{J}_A$ , the diffusion mass flux of gas A. The conservation equation for gas A, replacing the conservation equations (1) for each species  $i$ , can be written.

$$\frac{\partial \rho \overline{Y}_A}{\partial t} + \nabla \cdot (\rho \mathbf{v} \overline{Y}_A) = -\nabla \cdot \overline{J}_A + S_A \quad (27)$$



where  $\bar{Y}_A$  is the sum of mass fractions of the species making up gas A and  $S_A$  is the net rate of production for gas A (for example by vaporization of a surface).

For use in standard computational algorithms,  $\bar{J}_A$  has to be written in terms of  $\bar{Y}_A$ . We can modify Eq. (4) to read

$$\bar{J}_A = -\rho \frac{\bar{m}_A \bar{m}_B}{\bar{M}^2} \left( \bar{D}_{AB}^x \nabla \bar{x}_A - \bar{D}_{AB}^p \nabla \ln P - \bar{D}_{AB}^E \mathbf{E} \right) - \bar{D}_{AB}^T \nabla \ln T \quad (28)$$

noting that  $\nabla \bar{x}_A = -\nabla \bar{x}_B$  and  $n^2/\rho = \rho/\bar{M}^2$ , where  $\bar{M}$  is the average mass of all species in the gas mixture

$$M = \sum_{k=1}^q m_k x_k. \quad (29)$$

Since  $\bar{Y}_A = (\bar{M}_A/\bar{M})\bar{x}_A$ , where  $\bar{M}_A$  is the average mass of all species of gas A:

$$\bar{M}_A = \frac{\sum_{k=2}^p (m_k x_k + m_1 Z_k x_k)}{\sum_{k=2}^p (1 + Z_k) x_k}, \quad (30)$$

we have

$$\nabla \bar{x}_A = \frac{\bar{M}}{\bar{M}_A} \nabla \bar{Y}_A + \bar{Y}_A \nabla \left( \frac{\bar{M}}{\bar{M}_A} \right) \quad (31)$$

Therefore,

$$\begin{aligned} \bar{J}_A = & -\rho \frac{\bar{m}_A \bar{m}_B}{\bar{M}_A \bar{M}} \bar{D}_{AB}^x \nabla \bar{Y}_A - \rho \frac{\bar{m}_A \bar{m}_B}{\bar{M}^2} \bar{D}_{AB}^x \bar{Y}_A \nabla \left( \frac{\bar{M}}{\bar{M}_A} \right) \\ & + \rho \frac{\bar{m}_A \bar{m}_B}{\bar{M}^2} \bar{D}_{AB}^p \ln P + \rho \frac{\bar{m}_A \bar{m}_B}{\bar{M}^2} \bar{D}_{AB}^E \mathbf{E} - \bar{D}_{AB}^T \nabla \ln T \end{aligned} \quad (32)$$

Substituting this into equation (27) gives

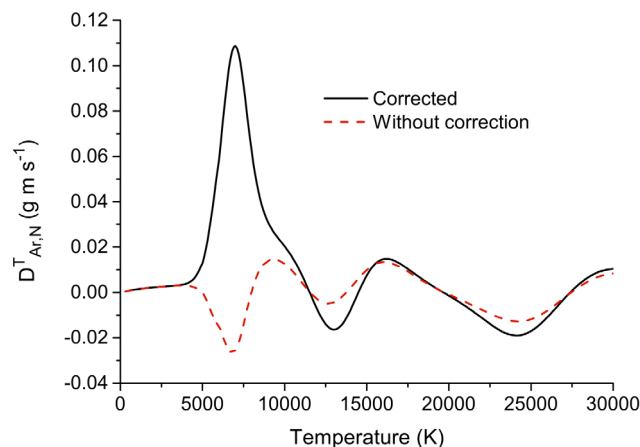
$$\begin{aligned} \frac{\partial \rho \bar{Y}_A}{\partial t} + \nabla \cdot (\rho \mathbf{v} \bar{Y}_A) = & \nabla \cdot \left( \rho \frac{\bar{m}_A \bar{m}_B}{\bar{M}_A \bar{M}} \bar{D}_{AB}^x \nabla \bar{Y}_A \right) \\ & + \nabla \cdot \left[ \rho \frac{\bar{m}_A \bar{m}_B}{\bar{M}^2} \bar{D}_{AB}^x \bar{Y}_A \nabla \left( \frac{\bar{M}}{\bar{M}_A} \right) \right] \\ & - \nabla \cdot \left( \rho \frac{\bar{m}_A \bar{m}_B}{\bar{M}^2} \bar{D}_{AB}^p \ln P \right) - \nabla \cdot \left( \rho \frac{\bar{m}_A \bar{m}_B}{\bar{M}^2} \bar{D}_{AB}^E \mathbf{E} \right) \\ & + \nabla \cdot \left( \bar{D}_{AB}^T \nabla \ln T \right) + S_A \end{aligned} \quad (33)$$

The first term on the right-hand side is the diffusion term, while the second, third, fourth and fifth terms on the right-hand side are not in  $\nabla \bar{Y}_A$ , and therefore have to be treated as source terms.

## Discussion

The following points related to the combined diffusion coefficients have been clarified.

1. Different expressions for the combined diffusion coefficients, arising from different definitions for the stoichiometric coefficients that assign the electrons to the two gases, have been shown to be equivalent;
2. An approach to dealing with the partial differential terms for which the mole fractions of the gases are held constant, which have to be calculated in determining the combined temperature and pressure diffusion coefficients, has been presented;
3. A method for the application of the combined diffusion coefficients in computational models that, as is usually the case, require diffusion to be expressed in terms of mass fraction gradients, has been described.



**Figure 1 | Combined temperature diffusion coefficient for a mixture of equal parts argon and nitrogen by mole fraction at 1 atm.** The ‘without correction’ curve was calculated including only the first term on the right-hand side of equation (25), while the ‘corrected’ curve was calculated using the full expression.

The first point is an important consideration in the consistent definition of the combined diffusion coefficients, and the correct choice of stoichiometric coefficients becomes critical when diffusion driven by external electric fields is taken into account.

The second point has to be understood and implemented to correctly calculate the combined temperature and pressure diffusion coefficients. In particular, very large errors are introduced in the calculation of the combined temperature diffusion coefficient if this point is neglected.

Finally, the third point provides an approach to implement the combined diffusion coefficients into standard computational models of thermal plasmas.

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## Author contributions

A.B.M. performed all the research presented, prepared the figure, and wrote the manuscript.

## Additional information

**Competing financial interests:** The authors declare no competing financial interests.

**How to cite this article:** Murphy, A.B. Calculation and application of combined diffusion coefficients in thermal plasmas. *Sci. Rep.* **4**, 4304; DOI:10.1038/srep04304 (2014).



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