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Analytical formulation of chemical derivatives in equilibrium plasma flows

Alessio Orsini[*]
AVIO Aerospace Propulsion, via I Maggio 99, 10040 Rivalta di Torino, Italy

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Chemical derivatives are used in the mathematical modeling of transport phenomena in equilibrium plasma flows when chemical element diffusion and mixing or demixing effects are accounted for. They measure the variation of mixture chemical composition in response to changes in element fractions, pressure, or temperature. Currently, these quantities are calculated numerically, using finite differences. This approach, other than being computationally expensive and prone to numerical error, does not provide any insight into flow physics. Our work is aimed at introducing a fully analytical method for the calculation of chemical derivatives which bypasses the computational cost. It also provides a simple means of estimating their order of magnitude.

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I. INTRODUCTION

High-temperature gases and plasmas are made of several chemical species each of them behaving with good approximation as a thermally perfect gas. Such mixtures are described as a continuum governed by the classical Navier-Stokes equations: conservation of mass, momentum, and energy. In the most general case, the mixture composition is given by a set of continuity equations, one for each species.

When chemical equilibrium occurs, the species continuity equations can be discarded and the composition is calculated from an algebraic system of equations [1]; local pressure, temperature, and chemical element fractions must be known. Element fractions (henceforth the term element will be used to denote a chemical element) either are assumed constant or, as we account for mixing and demixing phenomena, they are given by a set of continuity equations for the elements [2–5].

In both nonequilibrium and equilibrium plasma flows, transport phenomena occur [6]. Considering the transport of mass, a set of diffusion coefficients relate the species diffusion velocities with the gradients of pressure, temperature, and species molar fractions. Ern and Giovangigli [2] pointed out that, for a flow in chemical equilibrium, species diffusion coefficients can be replaced by a set of new coefficients which relate the diffusion velocities of elements with the gradients of pressure, temperature, and element molar fractions. Their derivation of the *elemental diffusion coefficients* is elegant and the physical interpretation of their work is appealing. A few years before, a simplified version of elemental diffusion coefficients was derived by Murphy in the special case of two homonuclear gases [4].

Both, Murphy before and Ern and Giovangigli later, introduced certain quantities which from now on will be named as *chemical derivatives*. Chemical derivatives provide a measure of the change in mixture composition with respect to a unit change in temperature, pressure or element fractions. In the two aforementioned works, the calculation of these quantities was not explicitly addressed; it was rather intended that they had to be calculated numerically by finite differences. This process is computationally expensive requiring to evaluate several times the mixture composition, moreover it is prone to numerical error.

Recently, Rini *et al.* [3] derived a set of coefficients equivalent to those of Ern and Giovangili without using chemical derivatives. Differently from the previous works, element mass fraction gradients were used in place of molar fraction gradients resulting in a different definition of the elemental diffusion coefficients. The method introduced by Rini *et al.* represents an advance over the previous works; however requires inversion of several matrices, therefore the computational cost remains high. In turn, the simplicity of the Ern and Giovangigli approach is lost and the physical interpretation of elemental diffusion coefficients is not as straightforward.

The present work provides a way to calculate the chemical derivatives accurately using a fully analytical method. Our derivation bypasses the computational cost, reducing the numerical errors and preserving mathematical simplicity. Moreover, by providing a simple means for estimating the order of magnitude of chemical derivatives, we open the possibility of evaluating the relevance of the different contributions (gradients in element fractions, pressure or temperature) to diffusion in equilibrium plasma flows.

It is worth mentioning that the reduction of species diffusion coefficients to element diffusion coefficients can be applied to both the symmetric formulation of species diffusion coefficients as introduced by Curtiss [7] and used by Ferziger and Kaper [8] and to the asymmetric formulation used by Hirschfelder, Curtiss, and Bird [9] and by Chapman and Cowling [10]. Chemical derivatives, as derived in this work, can be used for both formulations.

II. GAS MIXTURE PROPERTIES

This section is dedicated to presenting some properties which characterize a perfect gas composed of several chemical species. To simplify the exposition, we use high-temperature air as a reference mixture with a representative set of chemical species given by $\mathcal{S}=\{e^-,\mathrm{N},\mathrm{O},\mathrm{N}_2,\mathrm{O}_2,\mathrm{N}^+,\mathrm{O}^+\}$. The total number of species is n_s. All the quantities related to a given species are labeled using the subscripts i, j, k. Each species is obtained by combining n_e *elements* which, for this particular example, are $\mathcal{E}=\{e^-,\mathrm{N},\mathrm{O}\}$. Element properties are

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[*] alessio.orsini@gmail.com

identified by the greek indices α, β, γ. Chemical species are differentiated in n_e *independent species*, namely, $\mathcal{I}=\{e^-,\mathrm{N},\mathrm{O}\}$ (coincident with the elements) which are associated to the indices p, q, and n_r *dependent species*, $\mathcal{D}=\{\mathrm{N}_2,\mathrm{O}_2,\mathrm{N}^+,\mathrm{O}^+\}$, associated with the indices r, s. We also define each element of the *chemical matrix* $\phi_{\alpha i}$ as the number of particles of element α contained in the species i, for example, $\phi_{\mathrm{NN}_2}=2$, $\phi_{\mathrm{ON}}=0$, $\phi_{e^-\mathrm{O}^+}=-1$.

A. Species properties

The thermodynamic state of a mixture of perfect gases in thermal equilibrium is uniquely determined once temperature T, pressure P, and composition are specified. The composition is assigned by giving the species molar fractions x_i or mass fractions y_i:

$$x_i=\frac{n_i}{n},\quad y_i=\frac{\rho_i}{\rho}. \tag{1}$$

Species molar fractions represent the ratio between the number density of a given species n_i and the total number density of the mixture $n=\Sigma_i n_i$. Analogously, species mass fractions are defined as the ratio between the density of a given species ρ_i and the total density of the mixture $\rho=\Sigma_i\rho_i$. By definition, both molar and mass fractions satisfy the constraints $\Sigma_i x_i=1$ and $\Sigma_i y_i=1$. Introducing the species molar masses M_i, the molar and mass fractions relate as

$$x_i=\frac{y_i/M_i}{\sum_j y_j/M_j},\quad y_i=\frac{x_iM_i}{\sum_j x_jM_j}. \tag{2}$$

B. Element properties

Molar and mass fractions of elements are defined in analogy with the chemical species. Element molar fractions represent the ratio between the number of particles per unit volume of a given element and the total number of element particles per unit volume in the mixture. The same definition applies to element mass fractions when densities are considered. Element molar, and mass fractions are related to the corresponding species quantities by the chemical matrix:

$$x_\alpha=\frac{\sum_i \phi_{\alpha i}x_i}{\sum_{\beta,i}\phi_{\beta i}x_i},\quad y_\alpha=\sum_i \phi_{\alpha i}\frac{M_\alpha}{M_i}y_i. \tag{3}$$

Both these quantities are subjected to the usual constraints $\Sigma_\alpha x_\alpha=1$ and $\Sigma_\alpha y_\alpha=1$ (note that $\Sigma_\alpha\phi_{\alpha i}M_\alpha=M_i$). Relations similar to those relative to chemical species link element molar and mass fractions:

$$x_\alpha=\frac{y_\alpha/M_\alpha}{\sum_\beta y_\beta/M_\beta},\quad y_\alpha=\frac{x_\alpha M_\alpha}{\sum_\beta x_\beta M_\beta}. \tag{4}$$

Using Eqs. (3), the differentials of the element fractions are expressed as

$$\delta x_\alpha=\sum_i a_{\alpha i}\delta x_i,\quad \delta y_\alpha=\sum_i b_{\alpha i}\delta y_i. \tag{5}$$

Two new quantities named *chemical coefficients* are introduced here:

$$a_{\alpha i}=\frac{\phi_{\alpha i}-x_\alpha\sum_\beta\phi_{\beta i}}{\sum_{\beta,j}\phi_{\beta j}x_j},\quad b_{\alpha i}=\phi_{\alpha i}\frac{M_\alpha}{M_i}. \tag{6}$$

Due to the constraints on molar and mass fractions, the following relations hold:

$$\sum_i \delta x_i=0,\quad \sum_i \delta y_i=0,\quad \sum_\alpha \delta x_\alpha=0,\quad \sum_\alpha \delta y_\alpha=0. \tag{7}$$

III. CHEMICAL DERIVATIVES

The aim of this section is to derive an analytical expression for the *chemical derivatives* as used in Refs. [2,4]. When a reacting gas mixture is in local chemical equilibrium, its complete thermodynamic state is known at a given position if pressure, temperature, and element molar fractions (or mass fractions) are assigned at that position. All the remaining mixture properties, including the chemical composition, are functions of these quantities [1].

A. Molar fraction derivatives

From an operative point of view, the chemical composition is calculated by specifying a number of independent chemical reactions equal to the number of dependent species n_r. Since the choice of the reactions is arbitrary, the simplest set one can pick up is

$$X_r=\sum_p \phi_{pr}X_p. \tag{8}$$

Here the symbol X represents a generic species; we also used the short notation ϕ_{pr} in place of the more rigorous $(\phi_{\alpha r})_{\alpha=p}$. The mole fractions of chemical species obey the law of mass action:

$$\ln x_r=\sum_p \phi_{pr}\ln x_p+\ln\frac{P}{P_{\mathrm{ref}}}\sum_\gamma(\phi_{\gamma r}-1/n_e)+\ln K_r^P(P_{\mathrm{ref}},T). \tag{9}$$

The equilibrium constant K_r^P for the rth reaction is a function of the temperature only for any arbitrary choice of the reference pressure P_{ref}. By differentiating Eq. (9) with respect to the three independent variables (x_α,P,T) and applying the van't Hoff relation we obtain n_e+2 sets of n_r equations, one for each x_r:

$$\frac{\partial x_r}{\partial x_\alpha}=\sum_p \phi_{pr}\frac{x_r}{x_p}\frac{\partial x_p}{\partial x_\alpha}, \tag{10}$$

$$\frac{\partial x_r}{\partial P}=\sum_p \phi_{pr}\frac{x_r}{x_p}\frac{\partial x_p}{\partial P}+\frac{x_r}{P}\sum_\gamma(\phi_{\gamma r}-1/n_e), \tag{11}$$

$$\frac{\partial x_r}{\partial T} = \sum_p \phi_{pr} \frac{x_r}{x_p} \frac{\partial x_p}{\partial T} + \frac{x_r}{T} \frac{\Delta h_r}{\mathcal{R} T}. \tag{12}$$

Here $\mathcal{R}$ is the universal gas constant and $\Delta h_r = h_r - \Sigma_p \phi_{pr} h_p$ is the enthalpy of reaction per mole of products given as a linear combination of molar species enthalpies.

Expanding the differentials of species molar fractions, the first of Eqs. (5) gives

$$\begin{aligned}\delta x_\beta &= \sum_i a_{\beta i} \delta x_i \\ &= \sum_{\alpha,i} a_{\beta i} \frac{\partial x_i}{\partial x_\alpha} \delta x_\alpha + \sum_i a_{\beta i} \frac{\partial x_i}{\partial P} \delta P + \sum_i a_{\beta i} \frac{\partial x_i}{\partial T} \delta T \\ &= \sum_\alpha (\delta_{\beta\alpha} - x_\beta) \delta x_\alpha. \end{aligned} \tag{13}$$

The symbol $\delta_{\beta\alpha}$ is the Kronecker tensor. Because all the differentials appearing in Eq. (13) are arbitrary quantities, each term must vanish separately; $n_e + 2$ additional sets of n_e equations are therefore identified, one for each x_p:

$$\sum_i a_{\beta i} \frac{\partial x_i}{\partial x_\alpha} = \sum_p a_{\beta p} \frac{\partial x_p}{\partial x_\alpha} + \sum_r a_{\beta r} \frac{\partial x_r}{\partial x_\alpha} = \delta_{\beta\alpha} - x_\beta, \tag{14}$$

$$\sum_i a_{\beta i} \frac{\partial x_i}{\partial P} = \sum_p a_{\beta p} \frac{\partial x_p}{\partial P} + \sum_r a_{\beta r} \frac{\partial x_r}{\partial P} = 0, \tag{15}$$

$$\sum_i a_{\beta i} \frac{\partial x_i}{\partial T} = \sum_p a_{\beta p} \frac{\partial x_p}{\partial T} + \sum_r a_{\beta r} \frac{\partial x_r}{\partial T} = 0. \tag{16}$$

The presence of x_β in Eqs. (13) and (14) guarantees satisfaction of the additional constraints

$$\sum_{\beta,i} a_{\beta i} \frac{\partial x_i}{\partial x_\alpha} = \sum_\beta (\delta_{\beta\alpha} - x_\beta) = 0. \tag{17}$$

All these relations are valid also when the coefficients $a_{\alpha i}$ are replaced by $\hat{a}_{\alpha i} = a_{\alpha i} + \tau_\alpha$ with τ_α arbitrary quantities. This is demonstrated substituting $a_{\alpha i} = \hat{a}_{\alpha i} - \tau_\alpha$ in Eq. (13) and applying the first of identities (7). A convenient choice from a numerical point of view is $\tau_\alpha = \Sigma_{\beta,j} |a_{\beta j}| / (n_e n_s)$.

Combining Eqs. (10)–(12) with Eqs. (14)–(16) we obtain $n_e + 2$ sets of linear equations for the chemical derivatives of the independent species molar fractions:

$$\sum_p A_{\beta p} \frac{\partial x_p}{\partial x_\alpha} = \delta_{\beta\alpha} - x_\beta, \tag{18}$$

$$\sum_p A_{\beta p} \frac{\partial x_p}{\partial P} = -\frac{1}{P} \sum_r \hat{a}_{\beta r} x_r \sum_\gamma (\phi_{\gamma r} - 1/n_e), \tag{19}$$

$$\sum_p A_{\beta p} \frac{\partial x_p}{\partial T} = -\frac{1}{T} \sum_r \hat{a}_{\beta r} x_r \frac{\Delta h_r}{\mathcal{R} T}. \tag{20}$$

The matrix $A_{\beta p}$, common to the $n_e + 2$ linear systems (18)–(20), is given by

$$A_{\beta p} = \hat{a}_{\beta p} + \sum_r \hat{a}_{\beta r} \frac{x_r}{x_p} \phi_{pr}. \tag{21}$$

The solution of these equations is computationally inexpensive because it requires one only to invert the matrix $A_{\beta p}$ of dimensions $n_e \times n_e$. The use of $\hat{a}_{\alpha i}$ instead of $a_{\alpha i}$ ensures that $A_{\beta p}$ is nonsingular. The chemical derivatives of the dependent species molar fractions are calculated by substituting the values of $\partial x_p / \partial x_\alpha$, $\partial x_p / \partial P$, and $\partial x_p / \partial T$ in Eqs. (10)–(12).

We observe that, while $\partial x_i / \partial P$ and $\partial x_i / \partial T$ are unique for a given pressure, temperature, and element fractions, this is not true for the quantities $\partial x_i / \partial x_\alpha$. Due to the third of identities (7), these could be replaced in Eq. (13) by $\partial x_i / \partial x_\alpha + \tau_i$ with τ_i arbitrary quantities. Choosing $\tau_i = 0$ we satisfy the additional constraint $\Sigma_i \partial x_i / \partial x_\alpha = 0$.

B. Mass fraction derivatives

If chemical derivatives of mass fractions are required, they can be calculated by differentiating the second of Eqs. (2):

$$\delta y_i = \sum_j \chi_{ij} \delta x_j, \tag{22}$$

where we defined

$$\chi_{ij} = \frac{M_i \delta_{ij} - M_j y_i}{\sum_k M_k x_k}. \tag{23}$$

Using these relations one obtains

$$\frac{\partial y_i}{\partial y_\alpha} = \sum_j \chi_{ij} \frac{\partial x_j}{\partial y_\alpha} = \sum_{j,\beta} \chi_{ij} \frac{\partial x_j}{\partial x_\beta} \frac{\partial x_\beta}{\partial y_\alpha}, \tag{24}$$

$$\frac{\partial y_i}{\partial P} = \sum_j \chi_{ij} \frac{\partial x_j}{\partial P}, \tag{25}$$

$$\frac{\partial y_i}{\partial T} = \sum_j \chi_{ij} \frac{\partial x_j}{\partial T}. \tag{26}$$

The only unknown quantities $\partial x_\beta / \partial y_\alpha$ are given by the first of Eqs. (4):

$$\frac{\partial x_\beta}{\partial y_\alpha} = \frac{\delta_{\alpha\beta} - x_\beta}{M_\alpha \sum_\gamma y_\gamma / M_\gamma} = (\delta_{\alpha\beta} - x_\beta) x_\alpha / y_\alpha. \tag{27}$$

Chemical derivatives of mass fractions are therefore a linear combination of chemical derivatives of mole fractions. An equivalent derivation consists of writing Eq. (9) in terms of species mass fractions and repeating the same steps presented above for molar fractions.

IV. DIMENSIONAL ANALYSIS

As pointed out in the Introduction, chemical derivatives are used in the modeling of diffusion phenomena in equilibrium reacting flows when mixing and demixing effects are

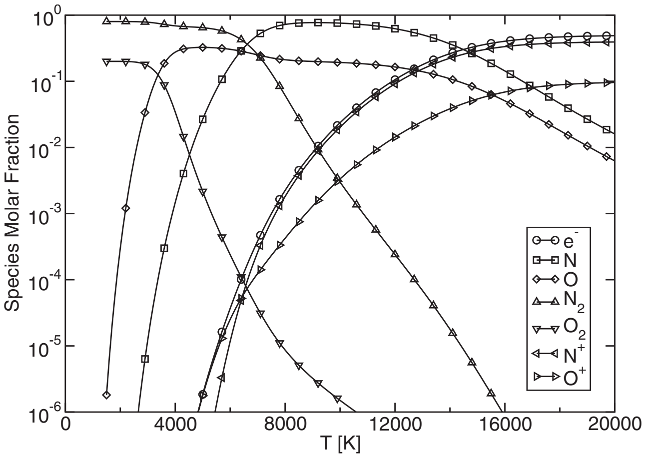

FIG. 1. Mixture equilibrium composition.

considered. Species diffusion is mainly driven by gradients in chemical composition (as well as the usual pressure diffusion and Soret effect). The gradients of species molar fractions can be expressed as a combination of gradients of element molar fractions, pressure, and temperature

$$\nabla x_i = \sum_\alpha \frac{\partial x_i}{\partial x_\alpha} \nabla x_\alpha + P\frac{\partial x_i}{\partial P} \nabla \ln P + T\frac{\partial x_i}{\partial T} \nabla \ln T. \quad (28)$$

To evaluate the relative weight of these three contributions to diffusion, we are now interested in estimating the order of magnitude of the coefficients multiplying the gradients in Eq. (28). Let us start by considering the quantities appearing in Eqs. (10)–(12) and (18)–(20). By definition, the molar fractions and the chemical matrix are of the order of 1: $x_i, x_\alpha, \phi_{\alpha i} = O(1)$. Also, from Eqs. (6) and (21), we have $\hat{a}_{\alpha i} = O(1)$ and $A_{\alpha p} = O(1)$ since these quantities are combinations of other quantities of order 1.

The term $\Delta h_r/\mathcal{R}T$ is also $O(1)$. This is shown by writing each species enthalpy as $h_i \approx h_i^f + \tilde{c}_{p,i}T$ where h_i^f is the formation enthalpy and $\tilde{c}_{p,i}$ is a suitable average specific heat per mole. For temperatures high enough [11] the term $h_i^f/\mathcal{R}T$ is small and $\tilde{c}_{p,i}/\mathcal{R} = O(1)$. Because Δh_r is a combination of h_i and $\phi_{\alpha i}$, our initial statement is demonstrated.

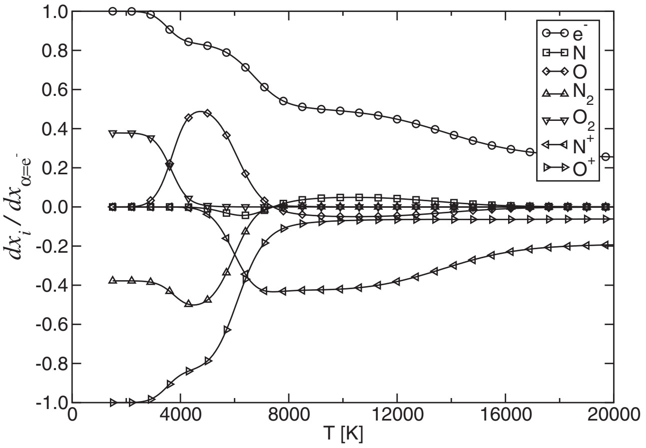

FIG. 2. Chemical derivatives of species molar fractions with respect to the molar fraction of element e^-.

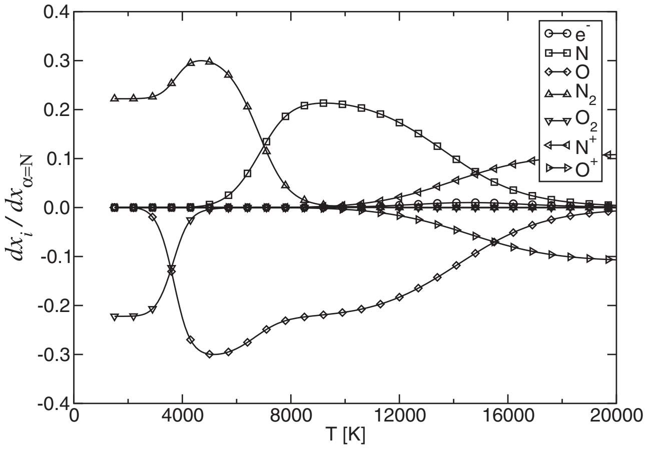

FIG. 3. Chemical derivatives of species molar fractions with respect to the molar fraction of element N.

Since both the matrix $A_{\alpha p}$ and the right hand side of Eqs. (18)–(20) are of order one (except for the terms $1/P$ and $1/T$), we assume that also the quantities $\partial x_p/\partial x_\alpha$, $P\partial x_p/\partial P$, $T\partial x_p/\partial T$ have the same order of magnitude. Analogous considerations applies to the chemical derivatives of the dependent species molar fractions (10)–(12) and to those relative to the mass fractions (24)–(26). We conclude that the terms ∇x_α, $\nabla \ln P$, and $\nabla \ln T$ in Eq. (28) should be directly compared while evaluating their contribution to diffusion since their coefficients have the same order of magnitude.

V. AN ILLUSTRATIVE EXAMPLE

To provide a simple numerical example, the chemical derivatives for the mixture considered in Sec. II are calculated. We choose a reference pressure of 1 atm giving the full set of chemical derivatives for species molar fractions as a function of the temperature. The molar fractions of the elements $\{e^-, \mathrm{N}, \mathrm{O}\}$ are assumed $\{0.0, 0.8, 0.2\}$. In performing our calculations, the thermodynamic database provided by Burcat and

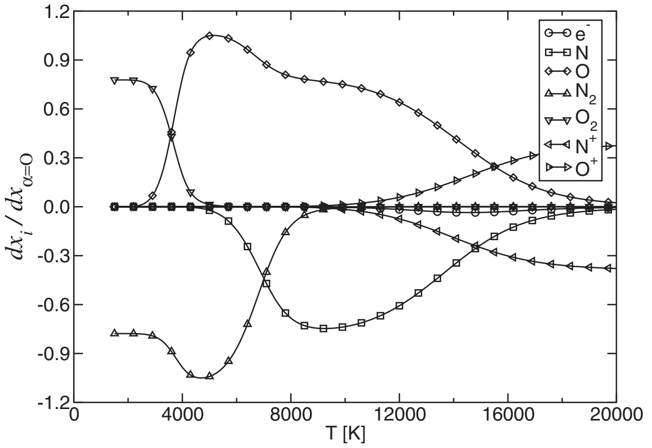

FIG. 4. Chemical derivatives of species molar fractions with respect to the molar fraction of element O.

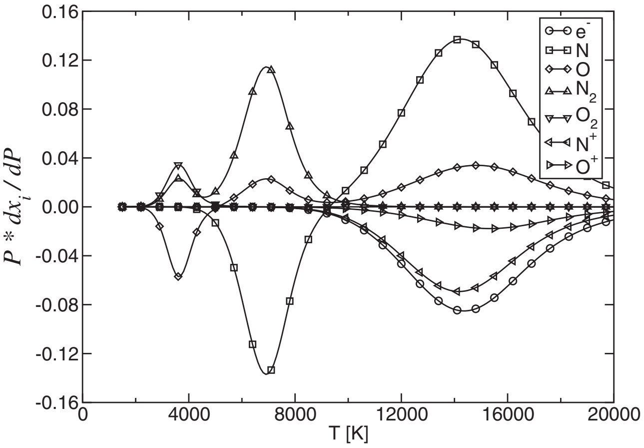

FIG. 5. Chemical derivatives of species molar fractions with respect to pressure.

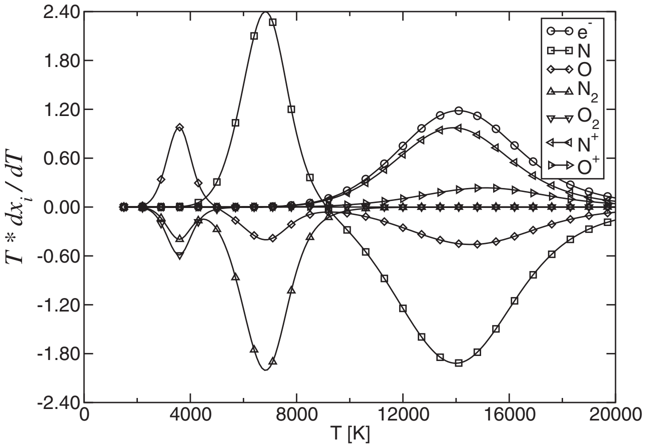

FIG. 6. Chemical derivatives of species molar fractions with respect to temperature.

Ruscic [12] is used; results are converged with a relative error of 10^{-12}.

In Fig. 1 the mixture equilibrium composition is given for a temperature up to 20 000 K. Figures 2–4 show the chemical derivatives of the species molar fractions with respect to the molar fractions of the elements. In Figs. 5 and 6 the chemical derivatives of the species molar fractions with respect to pressure and temperature are shown. The order of magnitude estimation provided in the previous section is confirmed by all the plots (values are all within ± 2.4).

Looking at the chemical composition, three transition points can be identified. The first one, around 3500 K, corresponds to the temperature at which the atomic population of oxygen exceeds the molecular population. Analogously, the second transition point corresponds to the nitrogen dissociation: around 6500 K the atomic nitrogen population becomes greater then the population of molecular nitrogen. Finally, the last transition point is located around 14 500 K when the electron population becomes dominant respect to the neutral species. The three points identified are reflected by the peaks and valleys of Figs. 5 and 6. This correspondence highlights the strong dependence of chemical derivatives on mixture composition.

VI. CONCLUSIONS

This research was aimed at identifying analytical expressions for certain quantities named as chemical derivatives which are used in the modeling of diffusion in equilibrium plasma flows. Our analytical expressions, other than being computationally inexpensive and free from numerical errors, offer the possibility to gain some insights into the physics of the problem. This is partly achieved by performing a dimensional analysis, supported by numerical evidence, which allowed us to predict the order of magnitude of the chemical derivatives. The dimensional analysis gives the possibility of estimating in advance which are the main drivers for diffusion: gradients in element fractions, pressure, or temperature.

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