Chemical Derivatives and Elemental Transport Coefficients in Plasma Flows Near Local Equilibrium

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Abstract. Elemental transport coefficients are extensively used for modeling chemically reacting and plasma flows when the proximity to local equilibrium is exploited to combine the ordinary transport coefficients into a few elemental coefficients. A deeper insight into the physics of chemically reacting flows near local equilibrium can be achieved by looking only at a reduced number of relevant parameters in the expression of the flow transport properties.

A new technique to calculate chemical derivatives using an analytical method which strongly reduces computational effort and numerical errors is introduced. A general formalism for elemental diffusion velocities, heat flux and electric current for plasma flows near local equilibrium is then derived. An order of magnitude analysis shows how to identify the main contributions to the transport fluxes among: elemental fractions gradients, pressure or temperature gradients, electric field. The resulting theoretical framework is particularly suitable for numerical implementation.

The present contribution aims to provide a summary of the theoretical framework described above. Numerical examples of chemical derivatives and elemental transport coefficients are given. Results are presented for a carbon dioxide mixture of practical interest for aerospace applications and atmospheric entry problems.

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BACKGROUND

High temperature gases are made of several chemical species each one behaving with good approximation as a thermally perfect gas. Under strong non-equilibrium conditions (SNE) [1, 2], such mixtures are described as a continuum governed by an extended Navier-Stokes system of equations including: global continuity, momentum and total energy equations, a continuity equation for each chemical species, an energy equation for each internal energy mode. For numerical calculations, this formalism has three major drawbacks: the number of equations is large, the species and energy equations include stiff source terms, the reaction rates and energy relaxation rates are affected by considerable uncertainties.

In many practical circumstances, one deals with weak deviations from equilibrium, or weak non-equilibrium (WNE) [1]. When the flow locally approaches the thermodynamic equilibrium, the equations for the species and internal energy modes can be discarded; only the global energy equation is retained together with global continuity and momentum equations. In the Euler approximation of an inviscid non-conducting flow, the chemical composition is calculated from an algebraic system [3, 4] requiring knowledge of the local pressure, temperature and fractions of chemical elements. In this case, the elemental fractions remain constant along a trajectory. In the viscous gas approximation, we should account for mixing and demixing phenomena, and therefore solve a continuity equation for each element containing the corresponding diffusion velocity [4, 5, 6].

The transport terms appearing in the WNE governing equations are: elemental diffusion velocities, heat flux, electric current and viscous stress. Except the last one, these quantities are related to the gradients of pressure, temperature, and molar fractions of chemical elements. In the recent years, several methods have been proposed to calculate the elemental transport terms in a manner which is fully consistent with the WNE formalism [4, 5, 6, 7, 8, 9, 10]. Some authors use certain quantities named chemical derivatives. Chemical derivatives provide a measure of the change in mixture composition with respect to variations in temperature, pressure or elemental fractions.

Recently a new technique to calculate the chemical derivatives using an analytical method was introduced [11]. This technique strongly reduces the computational effort and improves the numerical accuracy. The general framework of elemental transport properties in WNE reacting flows was then simplified and rearranged [12] to reflect the one used by the transport theory in the SNE case [2] or in the case of frozen chemical reactions [13]. Furthermore, the order

of magnitude analysis in [12] shows how to properly compare the factors driving the transport fluxes (gradients in elemental fractions, pressure or temperature gradients, electric field); identifying the most relevant contributions might suggest some simplifications in the numerical analysis. The resulting theoretical framework is particularly suitable for the numerical implementation since several computational codes accounting for the chemical species transport properties already exist.

METHODOLOGY

Each reacting gas mixture contains a set of n_s *chemical species*. For example, a simplified representation of high temperature air is given by $\{e^-, N, O, NO, N_2, O_2, N^+, O^+, NO^+\}$. Each species is obtained by combining n_e *chemical elements* which, for this particular example, are $\{e^-, N, O\}$. Among the chemical species, one can select a subset of *independent species* which usually correspond to the chemical elements. The remaining species are the *dependent species*. Hereafter, all the quantities related to a chemical species are labeled with the subscripts i, j. Elemental properties are identified by the greek indices α, β, γ. Properties for independent and dependent species are denoted by the subscripts p and q, respectively.

Chemical Derivatives

The molar fractions of chemical elements and chemical species are related by $x_\alpha = \sum_i \phi_{\alpha i} x_i / \sum_{\beta, i} \phi_{\beta i} x_i$ where the quantities $\phi_{\alpha i}$ represent the number of elements α contained in the species i. The chemical derivatives of the independent species molar fractions x_p with respect to the elemental molar fractions x_α, pressure P and temperature T can be calculated analytically by solving the linear systems:

$$\sum_p A_{\beta p} \frac{\partial x_p}{\partial x_\alpha} = B_{\beta \alpha} \tag{1}$$

$$\sum_p A_{\beta p} P \frac{\partial x_p}{\partial P} = B_\beta^P \tag{2}$$

$$\sum_p A_{\beta p} T \frac{\partial x_p}{\partial T} = B_\beta^T \tag{3}$$

The solution of these equations is computationally inexpensive because it requires only to invert the matrix $A_{\beta p}$ of dimension $n_e \times n_e$, where usually $n_e \ll n_s$. The matrix $A_{\beta p}$, common to the $n_e + 2$ linear systems (1-3), reads:

$$A_{\beta p} = a_{\beta p} + \sum_q a_{\beta q} \frac{x_q}{x_p} \left[\phi_{\gamma q} \right]_{\gamma = p} \qquad a_{\beta p} = \frac{\phi_{\beta p} - x_\beta \sum_\gamma \phi_{\gamma p}}{\sum_{\gamma, j} \phi_{\gamma j} x_j} + \tau_\beta \tag{4}$$

where the τ_β are arbitrary quantities aimed to make the matrix $A_{\beta p}$ non singular. The detailed derivation of the above equations is given in [11]. The chemical derivatives of the dependent species molar fractions x_q are available from:

$$\frac{\partial x_q}{\partial x_\alpha} = \sum_p C_{qp} \frac{\partial x_p}{\partial x_\alpha} \tag{5}$$

$$P \frac{\partial x_q}{\partial P} = \sum_p C_{qp} P \frac{\partial x_p}{\partial P} + F_q^P \tag{6}$$

$$T \frac{\partial x_q}{\partial T} = \sum_p C_{qp} T \frac{\partial x_p}{\partial T} + F_q^T \tag{7}$$

The quantities $A_{\beta p}$, $B_{\beta \alpha}$, B_β^P, B_β^T, C_{qp}, F_q^P, F_q^T are simple functions of the local mixture composition. Pressure and temperature do not appear explicitly in the expression of these coefficients with exception of a weak explicit temperature dependence of B_β^T and F_q^T vanishing at high temperatures. Therefore, the chemical derivatives $\partial x_i / \partial x_\alpha$ and $P \partial x_i / \partial P$ depend explicitly only on the mixture composition. This is almost true also for $T \partial x_i / \partial T$. It can be

shown that all the chemical derivative are of the same magnitude. This observation allows to estimate the order of magnitude of the elemental transport coefficients introduced below. Explicit expressions for al the above coefficients can be found in [11].

Elemental Transport Coefficients

According to classical transport theory for non-reacting mixtures [13] and SNE flows with finite-rate chemistry [2], the species diffusion velocities are linearly related to the driving forces through the species diffusion coefficients. For non magnetized gas mixtures, the driving forces consist of species molar fractions gradients, pressure and temperature gradients and electric field.

The elemental diffusion velocities are traditionally calculated by linearly combining the species diffusion velocities:

$$\vec{v}_\alpha = \sum_i c_{\alpha i} \vec{v}_i \qquad c_{\alpha i} = \phi_{\alpha i} \frac{M_\alpha / y_\alpha}{M_i / y_i} \tag{8}$$

where M_i and M_α are the molar masses of chemical species and chemical elements respectively. In [12], we proposed an alternative expression for these quantities which reflects the formalism adopted for the species diffusion velocities:

$$\vec{v}_\alpha = -\sum_\beta D_{\alpha\beta} \vec{\nabla} x_\beta - D_\alpha^P \vec{\nabla} lnP - D_\alpha^T \vec{\nabla} lnT - D_\alpha^E \vec{\mathscr{E}} \tag{9}$$

The quantities $D_{\alpha\beta}, D_\alpha^P, D_\alpha^T, D_\alpha^E$, are the elemental diffusion coefficients obtained by combining the multicomponent species diffusion coefficients D_{ij} and the species diffusion ratios k_j^P, k_j^T, k_j^E with the chemical derivatives:

$$D_{\alpha\beta} = \sum_{i,j} c_{\alpha i} D_{ij} \frac{\partial x_j}{\partial x_\beta} \tag{10}$$

$$D_\alpha^P = \sum_{i,j} c_{\alpha i} D_{ij} \left(P \frac{\partial x_j}{\partial P} + k_j^P \right) \tag{11}$$

$$D_\alpha^T = \sum_{i,j} c_{\alpha i} D_{ij} \left(T \frac{\partial x_j}{\partial T} + k_j^T \right) \tag{12}$$

$$D_\alpha^E = \sum_{i,j} c_{\alpha i} D_{ij} k_j^E \tag{13}$$

$\vec{\mathscr{E}} = e\vec{E}/k_B T$ is the nondimensional electric field (e = elementary charge, $\vec{E}$ = electric field, k_B = Boltzmann constant).

Sometimes the species diffusion velocities are derived from the Stefan-Maxwell Equations [14]. In analogy with the species transport theory, the Stefan-Maxwell equations for the elemental diffusion velocities read:

$$\vec{d}_\alpha = \sum_\beta A_{\alpha\beta} \vec{v}_\beta \tag{14}$$

where the elemental driving forces are:

$$\vec{d}_\alpha = \vec{\nabla} x_\alpha + k_\alpha^P \vec{\nabla} lnP + k_\alpha^T \vec{\nabla} lnT + k_\alpha^E \vec{\mathscr{E}} \tag{15}$$

In the equations above $A_{\alpha\beta}$ are the elemental Stefan-Maxwell coefficients and can be obtained from the elemental diffusion coefficients as described in [12]. Similarly $k_\alpha^P, k_\alpha^T, k_\alpha^E$ are the diffusion ratios of the chemical elements, which are related to the diffusion coefficients by:

$$k_\alpha^{P/T/E} = -\sum_\beta A_{\alpha\beta} D_\beta^{P/T/E} \tag{16}$$

The classical relation between diffusion velocities and driving forces reads:

$$\vec{v}_\alpha = -\sum_\beta D_{\alpha\beta} \vec{d}_\beta \tag{17}$$

Also the heat flux vector can be expressed as a function of the elemental fractions, pressure and temperature gradients and of the electric field:

$$\vec{q} = -\sum_\alpha \lambda_\alpha \vec{\nabla} x_\alpha - \lambda^P \vec{\nabla} lnP - \left(\lambda^T + \lambda \, T\right) \vec{\nabla} lnT - \lambda^E \vec{\mathscr{E}} \tag{18}$$

As for the elemental diffusion coefficients, the new set of thermal conductivity coefficients λ_α, λ^P, λ^T, λ^E is introduced (λ is the usual mixture thermal conductivity).
Coherently with the equilibrium formalism, the electric current vector is given by:

$$\vec{J} = Q\vec{u} - \sum_\alpha \sigma_\alpha \vec{\nabla} x_\alpha - \sigma^P \vec{\nabla} lnP - \sigma^T \vec{\nabla} lnT - \sigma^E \vec{\mathscr{E}} \tag{19}$$

where suitable electric conductivity coefficients σ_α, σ^P, σ^T, σ^E are used (Q = mixture charge per unit volume, $\vec{u}$ = mean flow velocity).

All the elemental transport coefficients in this section are calculated by combining the species transport coefficients with the chemical derivatives as discussed in [12].
With a dimensional analysis [11, 12], it is possible to demonstrate that all the coefficients appearing in Eq. (9) have the same magnitude. An identical consideration apply to the thermal conductivity coefficients in Eq. (18) and to the electric conduction coefficients in Eq. (19). As a consequence, the terms $\vec{\nabla} x_\alpha$, $\vec{\nabla} lnP$, $\vec{\nabla} lnT$ and $\vec{\mathscr{E}}$ can be directly compared to assess their relative contribution as driving factors for mass, energy and charge diffusion. Identifying the most relevant terms might lead to relevant simplifications in the numerical analysis.

NUMERICAL EXAMPLE

As an example, the case of the neutral carbon dioxide mixture $\{C, O, CO_2, CO, O_2\}$ is presented here. The chemical derivatives and elemental transport coefficients are calculated at 1 atm from 2500K, when chemical reactions came into play, up to 8000K when the hypothesis of neutrality vanishes. The molar fractions of the elements $\{C, O\}$ are $\{0.4, 0.6\}$. The database provided by Burcat and Ruscic [15] is used for the thermodynamic properties of the chemical species. The collision integrals required for the computation of the species transport coefficients are calculated using the formulae proposed by Bzowski and coworkers [16].

Figure 1 shows the mixture equilibrium composition. If we consider the dominant species, three different regions can be identified. In the low temperature region all the species except the atomic carbon are present in a relevant amount; in the intermediate temperature region there is a significant presence of CO and O; the high temperature region is characterized by the presence of the atomic species C and O and carbon monoxide.

Figure 2 shows the chemical derivatives of the species molar fractions with respect to the molar fractions of the elements. In Figure 3, the pressure and temperature derivatives are shown. Since all the chemical derivatives depend explicitly on the mixture composition only (with the exception of $T \partial x_i / \partial T$), the chemical composition and chemical derivatives show the same trend. In particular, the derivatives in Figure 2 are non negligible only in the region where the corresponding species are present in a relevant amount. Moreover, the variation of the chemical derivatives in Figure 2 is strictly related to the change of the corresponding species molar fractions. The temperature chemical derivatives in Figure 3, by definition, reflect the slopes of the chemical composition lines in Figure 1. The pressure derivatives have an analogous behavior but opposite sign.

Figures 4 and 5 contain the elemental transport coefficients. Figure 4 shows the elemental diffusion coefficients (a) and Stefan-Maxwell coefficients (b). Finally in Figure 5 the elemental diffusion ratios (a) and thermal conductivities (b) are given. Since all the species are neutral, electric conductivities are zero. Elemental diffusion ratios behave similarly to the chemical derivatives, while the diffusion coefficients strongly increase with the temperature. The Stefan-Maxwell coefficients are the counterpart of the elemental diffusion coefficients, therefore they decrease with the temperature. A curious feature can be observed in Figure 5: the pressure diffusion ratios k_α^P are zero around 3500K and 7300K; approximately at the same temperatures, the thermal diffusion ratios k_α^T show a relative maximum or minimum. As for the thermal conductivities, there is a remarkable increase of λ^T at high temperatures, while the contribution related to the pressure gradient remains always small.
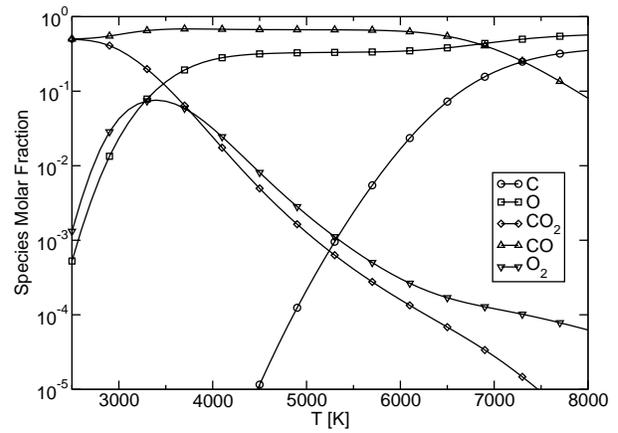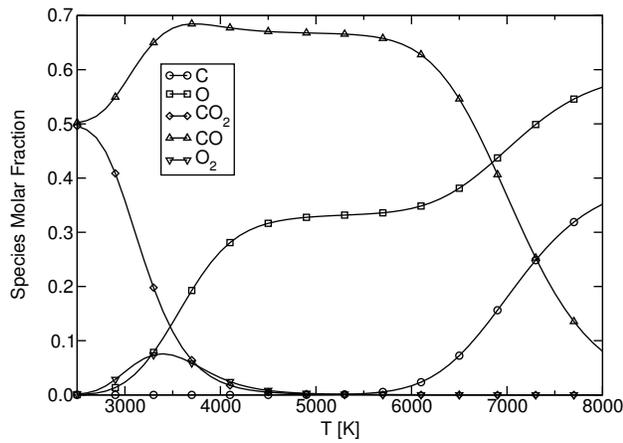
FIGURE 1. Equilibrium species molar fractions: (a) Linear scale. (b) Logarithmic scale.
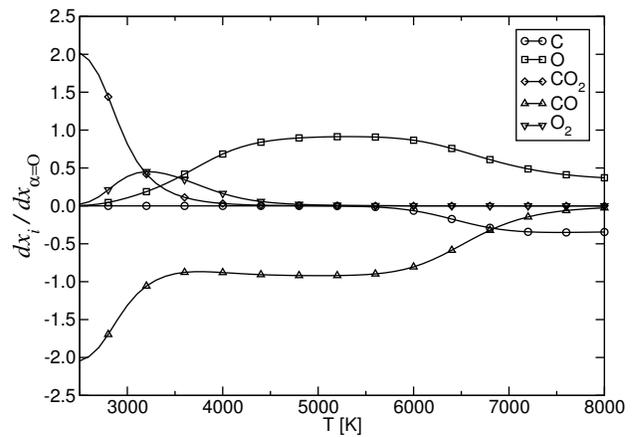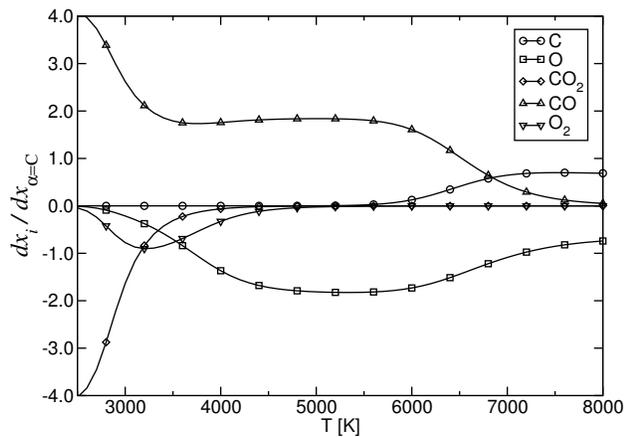
FIGURE 2. (a) Chemical derivatives relative to the element C. (b) Chemical derivatives relative to the element O.
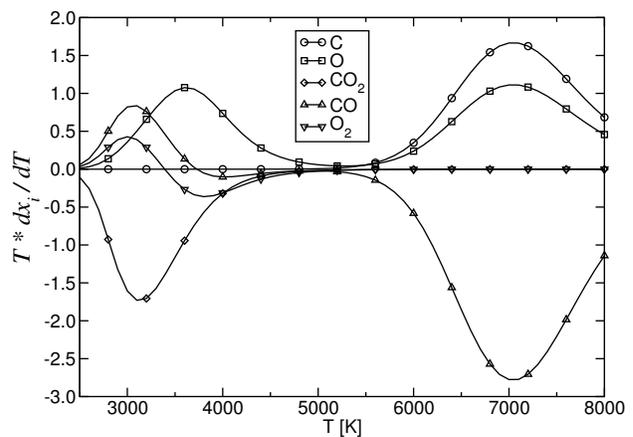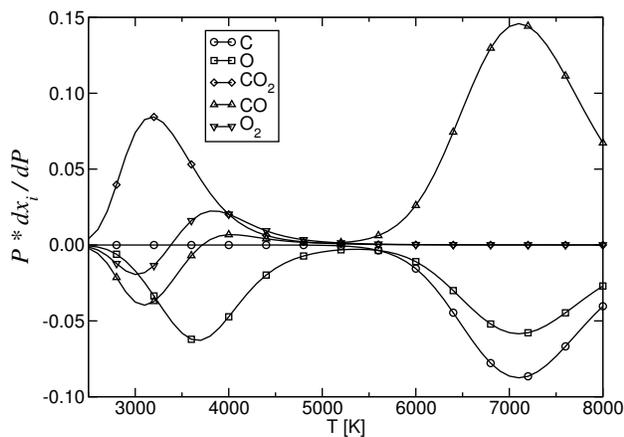
FIGURE 3. (a) Pressure chemical derivatives. (b) Temperature chemical derivatives.
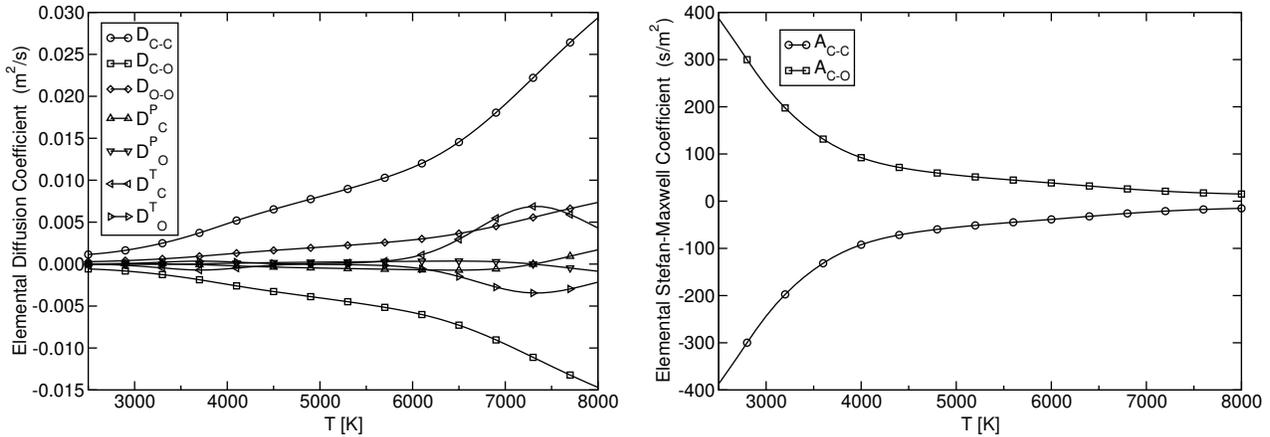
FIGURE 4. (a) Elemental diffusion coefficients ($D_{OC}=D_{CO}$). (b) Elemental Stefan-Maxwell coefficients ($A_{OC}=A_{CO}$; $A_{OO}=A_{CC}$).
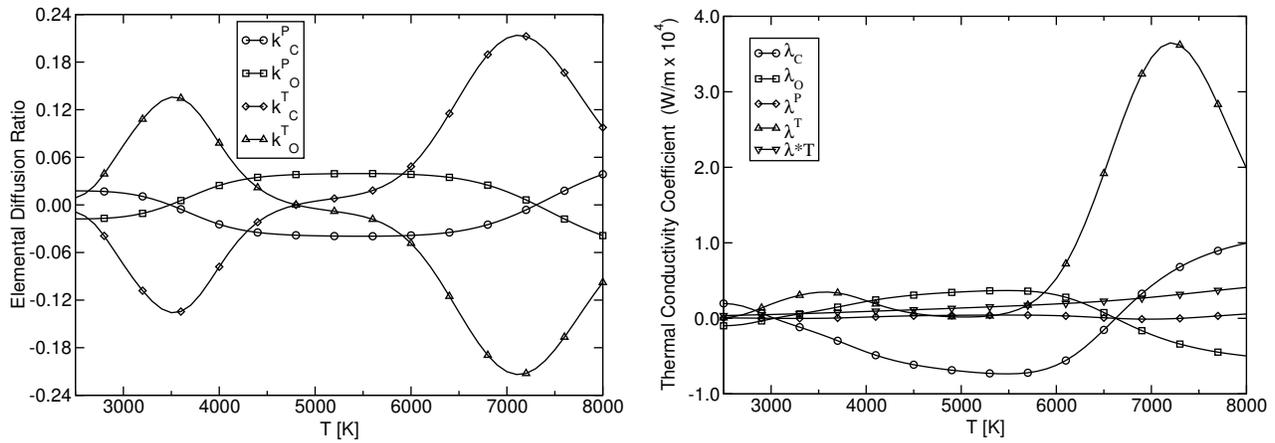
FIGURE 5. (a) Elemental diffusion ratios. (b) Thermal conductivity coefficients.

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