

Closed form for the equations of chemically reacting flows under local thermodynamic equilibrium

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We present a closed form for the governing equations of chemically reacting flows under local thermodynamic equilibrium, which rigorously takes into account effects of elemental (de)mixing. To this end, we show that when chemistry is fast, the diffusion fluxes of elements and species enthalpies can be expressed as explicit linear functions of gradients of elemental mass fractions and temperature. Our formulation is a natural extension of classical work on local equilibrium flows by other authors and yields results equivalent with a recent fully rigorous mathematical theory in a straightforward and physically appealing manner. The obtained set of equations is well-suited for numerical implementations and does not require the computationally expensive evaluation of thermodynamic derivatives using finite differences. The new transport coefficients that appear in the equations allow quantitative predictions and help to gain deeper insight into the physics of chemically reacting flows at and near local equilibrium.

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I. INTRODUCTION

The physics of collision-dominated chemically reacting flows is described by an extended Navier-Stokes system, consisting of the following equations [1]:

- (1) global continuity, momentum, and total energy;
- (2) a separate continuity equation for each species, including finite-rate chemistry;
- (3) if thermal nonequilibrium occurs, an energy equation for each additional mode of freedom (vibrational, rotational, and electronic energies).

This formalism has several drawbacks. First, the equations are costly to implement and solve numerically. Second, many physical parameters essential for the modeling of chemistry and energy relaxation processes are usually missing. Third, even when a numerical solution is obtained, it is by no means obvious to interpret the vast amount of information obtained (e.g., concentration fields of a large number of chemical species). For these reasons, when chemistry and energy exchanges are fast, it is usually preferable to solve the more elegant and less uncertain local thermodynamic equilibrium (LTE) form of the aforementioned set of equations.

A major breakthrough in the field of LTE flow modeling was made by Butler and Brokaw [2,3], who showed that, assuming vanishing diffusive fluxes of chemical elements, the diffusive transport of species reaction enthalpies in the energy equation could be incorporated in a straightforward manner by introducing a coefficient of “thermal reactive conductivity” λ_R :

$$\sum_{s=1}^{N_{sp}} \mathbf{w}_s h_s = -\lambda_R \nabla T. \quad (1)$$

One often makes use of this result to reduce the full set of nonequilibrium equations to a system formally equivalent to the “conventional” Navier-Stokes equations (continuity, momentum, and energy), complemented by a modified equation of state $\rho(p, T)$ computed from statistical mechanics assuming a fixed elemental composition in the flow. For instance, Vasil’evskii *et al.* [4] successfully used this classical LTE formalism to simulate high-pressure air inductively coupled plasma flows, imposing a 21/79 volumetric ratio of oxygen and nitrogen elements throughout the flow field.

While appealing because of its simplicity, it is important to understand that this approach is approximate at best, since in general the elemental composition varies significantly in chemically reacting flows:

(1) *Mixing*: consider, e.g., low-speed diffusion flames, in which fuel and air are injected through different inlets and gradually mix.

(2) *Demixing*: consider, e.g., a thermal arc or inductive plasma torch. The kinetic theory of gases in general predicts nonzero elemental diffusion fluxes whenever the composition of the mixture varies due to chemical reactions. Thus variations in elemental composition appear even when the inflow elemental composition is uniform [5,6].

We know of no mixture containing more than a single element that can simultaneously satisfy the constraints of uniform elemental composition and vanishing elemental fluxes when chemical reactions occur.

Over the past four decades, several LTE formulations accounting for (de)mixing effects have been proposed.

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As pointed out by Murphy [5], a first quantitative explanation of demixing effects was presented in a series of papers by Frie and Maecker, in which they classified and discussed the significance of the different processes that drive demixing [7–10], and in a paper by Richter [11], who measured the degree of demixing in arcs in mixtures of argon, nitrogen, helium, and hydrogen, and explained his results in a manner similar to Frie and Maecker.

Suslov *et al.* [12] presented a general theoretical description of mixtures of chemically reacting gases under chemical equilibrium where (de-)mixing is taken into account by solving a set of elemental continuity equations. Although valid for any mixture of partially ionized gases, the proposed theory does not provide any explicit relation between elemental diffusion fluxes and temperature, pressure, or elemental concentration gradients and requires the solution of the Stefan-Maxwell equations [13,14] for given concentration gradients of species in the gas mixture. This formulation, which has been further improved in two more recent papers due to G. A. Tirskey [15,16], is in our opinion the most complete and accurate available description of LTE flows at present. While the formulation presented here is mathematically equivalent to the work of these references, it has the advantage of leading to a more physically appealing explicitly closed formalism that is obtained using a considerably more straightforward mathematical derivation.

Vasil'evskii and Tirskey analyzed the influence of elemental separation within equilibrium air boundary layers [17] near heat-shields of atmospheric (re-)entry capsules, and observed volumetric oxygen concentrations varying between 0.15 and 0.3 (when the far-field value is 0.23). In a successive study [18], Vasil'evskii investigated the influence of these effects on wall heat flux and observed variations of 3–10% depending on the wall boundary conditions.

Kovalev and Suslov investigated diffusive separation of chemical elements on a catalytic surface in Ref. [19]. Using an asymptotic expansion of the solution of the boundary layer equations for a multicomponent air mixture in chemical nonequilibrium for large Schmidt numbers, it was shown that an excess of a mixture element can be observed on the body under certain outer flow conditions.

Murphy [5,20–22] has investigated effects of elemental demixing in thermal arc-plasmas and points out that demixing occurs regardless of the degree of nonequilibrium in the plasma. Thus, even in the LTE case, an additional continuity equation needs to be included for the mass fraction of each element in the gas mixture. He presents an LTE model which allows computation of demixing in binary mixtures of homonuclear gases, which do not mutually react. While rigorous, his model cannot be applied to the more general case when species composed of various nuclei appear. For instance, an air plasma, which consists of nitrogen and oxygen nuclei, will contain mixed species such as NO which cannot be described by this theory. The appearance of explicit thermodynamic derivatives in his theory is troublesome from a numerical point of view: their evaluation by means of finite differences is in general very costly because for each finite difference the mixture composition needs to be recomputed using a Newton iterative solver. In the particular case of a mixture containing only two elements, the computational

cost can be reduced by computing the thermodynamic derivatives only once and storing the data in tabular form. Then, in the framework of computation fluid dynamics (CFD) codes, the tabulated coefficients can be accessed and interpolated as required. However, when the number of elements present in the mixture increases beyond two, this approach requires multidimensional interpolations, whose cost rapidly increases with the number of elements. In spite of the limitations of his theory, Murphy should be given credit for having presented the first closed LTE formulation and for having introduced the concept of elemental combined and thermal diffusion coefficients.

Ern and Giovangigli [23] introduced the concept of elemental multicomponent diffusion coefficients for general nonionized gas mixtures under LTE using two different approaches: (1) by deriving the Navier-Stokes equations directly from the LTE form of the Boltzmann equation or (2) by considering the Navier-Stokes equations for flows under chemical nonequilibrium and letting chemical reactions approach equilibrium. They point out that the reduced sets of equations obtained are formally similar but contain different transport coefficients. The abstract mathematical framework underlying their theory is its strength and weakness at once: while the mathematical rigor of the model is impressive, the proposed analysis is accessible only to those with a strongly mathematical mind-set and no particular effort is made to explain the physical implications of the model. As in Murphy's work, explicit thermodynamic derivatives remain in the final expressions. The paper remains at a theoretical level and no numerical values of elemental transport coefficients are computed; rather, it is concluded that it is more advantageous to retain the species diffusion velocities in the governing equations, which leads us back to an open formulation essentially equivalent to the one proposed by Suslov *et al.* [12]. We disagree with this conclusion and will argue that computing the LTE transport coefficients (Figs. 2–5) is not only more advantageous from a numerical point of view but also reveals a lot of interesting physics.

Van der Heijden [24] has proposed an alternative LTE model in his study of demixing in a Hg/Na/I metal halide lamp. His formulation is based upon a Fick-type diffusion model, which can only be applied when a minority species diffuses with respect to a background species, which is present in overwhelming quantities (mercury, in his case).

The present authors have recently performed calculations of air and carbon dioxide flows under LTE [6,25,26] using an open formulation similar to the one of Suslov *et al.* [12], valid for partially ionized gases [6]. For sufficiently high pressures, the LTE formulation is found to be as accurate as a full nonequilibrium Navier-Stokes solution.

The motivation of the present contribution is threefold.

(1) The restriction to mixtures of homonuclear gases in Murphy's theory strongly limits its field of application. In this contribution, this restriction is removed and a general formulation equivalent to the model of Ern and Giovangigli is provided. Contrary to their model, however, we have tried to reduce the mathematical complexity as much as possible and rely upon physical arguments where possible. The obtained formulation is well-suited for numerical implementation. In particular, the expressions for the LTE transport co-

efficients are readily available and do not require the computationally expensive evaluation of thermodynamic derivatives using finite differences.

(2) Our closed form for the elemental diffusion fluxes allows one to determine a more general expression for the LTE heat flux vector than the one proposed by Butler and Brokaw. Indeed, in this contribution a correction to λ_R is introduced, together with the concept of elemental heat transfer coefficients. The final formulation of the heat flux vector presented in this work is not formally identical to the results proposed in previous models; it will be shown that this is necessary to correctly analyze heat transfer phenomena in chemically reacting flows, in particular when interpreting measurements of thermal conductivity coefficients.

(3) As will become clear from the numerical results given at the end of this paper, this formulation provides a useful tool to analyze diffusion phenomena in mixtures under chemical equilibrium and in those which slightly depart from that condition.

In the following sections, we will concentrate only on neutral mixtures, referring the extension to ionized conditions to a future publication. Although we will focus on the particular case of air mixtures, well-suited for Earth entry applications (our particular field of research), we wish to point out that the presented LTE formulation is applicable to any chemically reacting flow near LTE and in particular the hydrocarbon-air mixtures used for combustion.

II. SPECIES ORDERING AND NOMENCLATURE

To make this text more accessible, we find it useful to first introduce some important concepts and symbols.

We represent mixtures of perfect gases by means of a finite set of N_{sp} species \tilde{S} , amongst which we furthermore distinguish between N_c “independent species” \tilde{E} consisting of pure elements (as such as in their stable form) and N_r “combined species” \tilde{R} , for instance:

5-species air $\tilde{E}=\{O, N\}$, $\tilde{R}=\{O_2, N_2, NO\}$, and $\tilde{S}=\tilde{R} \cup \tilde{E}$, valid for LTE mixtures at pressures above 0.01 atm and for temperatures between 300 and 8000 K.

We accordingly define the three sets of indexes $\mathcal{R}=\{1, \dots, N_r\}$, $\mathcal{E}=\{N_r+1, \dots, N_{sp}\}$, and $\mathcal{S}=\mathcal{R} \cup \mathcal{E}$. We characterize the chemical composition of the mixture in terms of mole fractions $x_s=n_s/n$, where n_s and n stand for the molar densities of individual species and of the entire mixture. Alternatively, we can also characterize the mixture composition by means of the mass fraction $y_s=\rho_s/\rho$, where ρ_s and ρ stand for the mass densities of the individual species, respectively, the full mixture.

We will indicate the number of atoms of element e contained in a species s by ϕ_s^e , for instance, for NO, $\phi_3^2=1$ while for O₂, $\phi_1^4=2$. This enables us to define the mole fractions X^e and mass fractions Y^e of elements in the mixture as follows:

$$X^e = \frac{\sum_{s \in \mathcal{S}} \phi_s^e x_s}{\sum_{e \in \mathcal{E}} \sum_{s \in \mathcal{S}} \phi_s^e x_s}; \quad Y^e = \sum_{s \in \mathcal{S}} \phi_s^e y_s \frac{M_e}{M_s}, \quad (2)$$

where M_s is the molar mass of species s , related to the mixture molar mass $M=\sum_{s \in \mathcal{S}} x_s M_s$.

We introduce the diffusion velocity \mathbf{V}_s with respect to the mass-averaged velocity of the mixture \mathbf{u} . The molar and mass fluxes of species s are then given by, respectively, $\mathbf{W}_s=n_s \mathbf{V}_s$ and $\mathbf{J}_s=M_s n_s \mathbf{V}_s$. The mole and mass fluxes of element e are then given by

$$\mathbf{N}_e = \sum_{s \in \mathcal{S}} \phi_s^e \mathbf{W}_s; \quad \mathbf{J}_e = M_e \mathbf{N}_e \quad (e \in \mathcal{E}). \quad (3)$$

We use bold type fonts to indicate vectors in the physical space. With “bar notation,” we refer to arrays containing species, elemental, or reactive properties, with respective lengths of N_{sp} , N_c , and N_r . For instance, the array of length N_c containing the mass diffusive fluxes of elements is written

$$\bar{\mathbf{J}} = \begin{bmatrix} \mathbf{J}_{N_r+1} \\ \mathbf{J}_{N_r+2} \\ \vdots \\ \mathbf{J}_{N_r+N_c} \end{bmatrix}. \quad (4)$$

III. COMPUTATION OF COMPOSITION UNDER LTE

A. Species continuity equations

We consider the commonly encountered flow regime in which chemical reactions are relatively rare with respect to elastic collisions, such that they do not play an important role in the thermalization of species in the flow (unlike the “kinetic chemical equilibrium regime” considered in the first part of Ref. [23], for which chemical reactions and elastic collisions are treated on the same level). The concentration of each species may then be determined from a respective species continuity equation [1]:

$$\partial_t(\rho y_s) + \nabla \cdot (\rho y_s \mathbf{u}) + \nabla \cdot (M_s \mathbf{W}_s) = \dot{\omega}_s, \quad (5)$$

where \mathbf{u} stands for the mass-averaged velocity of the mixture and $\dot{\omega}_s$ is the mass production/destruction term [27] of species s due to chemical reactions. The number fluxes of species respect the mass conservation constraint

$$\sum_{s \in \mathcal{S}} M_s \mathbf{W}_s = 0 \quad (6)$$

and obey the Stefan-Maxwell equations [13,14]

$$S \bar{\mathbf{W}} = \begin{bmatrix} \nabla x_1 \\ \vdots \\ \nabla x_{N_{sp}} \end{bmatrix} = \bar{\mathbf{d}} \quad (7)$$

where

$$S_{ij} = \frac{M}{\rho} \frac{x_i}{D_{ij} f_{ij}(L)} \quad (i \neq j),$$

$$S_{ij} = - \frac{M}{\rho} \sum_{k \neq i} \frac{x_k}{D_{ik} f_{ik}(L)} \quad (i = j), \quad (8)$$

for $i, j, k \in \mathcal{S}$. Herein, $\bar{\mathbf{d}}_i = \mathbf{d}_i = \nabla x_i$ is the i th vector of driving forces. To keep the analysis as simple as possible, we have

neglected effects of pressure and thermal diffusion; note, however, that these could be included without any particular problem. The binary diffusion coefficients \mathcal{D}_{ij} are symmetric $\mathcal{D}_{ij}=\mathcal{D}_{ji}$ and the symmetric factor $f_{ij}(L)$ takes into account the contribution of Laguerre-Sonine polynomials [14,28–30] of order $L \geq 2$ with the definition $f_{ij}(1)=1$ [increasing the order L of the Laguerre-Sonine polynomials yields higher accuracy of the spectral method used to define the transport systems (7)].

The binary diffusion coefficients can be further expressed as

$$\mathcal{D}_{ij} = \frac{3}{16n} \sqrt{\frac{2\pi k_B T}{m_{ij}}} \frac{1}{\bar{\Omega}_{ij}^{11}}, \quad (9)$$

where k_B is Boltzmann’s constant and the reduced mass of the particle pair ij is written as $m_{ij}=m_i m_j / (m_i + m_j)$ [in kg]. Readers eager to implement the results derived in this paper may find detailed curve fits for the collision integrals $\bar{\Omega}_{ij}^{11}(T)$ of air mixtures in Ref. [31].

B. Stoichiometric matrix

When chemistry is sufficiently fast with respect to other macroscopic processes in the flow (convection, diffusion, ...), we may compute the chemical composition from statistical mechanics for given values for the pressure, temperature, and elemental mass fractions [31] instead of solving Eqs. (5). To this end, we need to specify N_r independent reactions

$$\sum_{s \in \mathcal{S}} \nu_s^r A_s = 0 \quad (r \in \mathcal{R}) \quad (10)$$

where the stoichiometric coefficients are normalized such that $\nu_r^r=1$ and A_s is a symbolic notation for species s . The mole fractions $x_s=n_s/n$ obey the following relations:

$$\sum_{s \in \mathcal{S}} \nu_s^r \ln x_s = \ln K_x^r \quad (r \in \mathcal{R}), \quad (11)$$

where $K_x^r(T, p)$ is the equilibrium constant in terms of mole fractions, linked to the equilibrium constant in terms of partial pressures $K_p^r(T)$ by

$$\ln K_x^r = \ln K_p^r - \ln p \sum_{s \in \mathcal{S}} \nu_s^r.$$

In addition, we should fix the local elemental composition

$$\sum_{s \in \mathcal{S}} \phi_s^e y_s \frac{M_e}{M_s} = Y^e \quad (e \in \mathcal{E}) \quad (12)$$

where the mass fraction of elements Y^e is computed from the solution of a set of suitable advection-diffusion equations to be presented shortly [Eq. (18)].

For further mathematical convenience, we gather the ν_s^r and ϕ_s^e into a “stoichiometric matrix” \mathcal{M} :

$$\mathcal{M}_{rs} = \nu_s^r \quad (r \in \mathcal{R}, s \in \mathcal{S}),$$

$$\mathcal{M}_{es} = \phi_s^e \quad (e \in \mathcal{E}, s \in \mathcal{S}).$$

Following Butler and Brokaw [2], we note that \mathcal{M} has the following structure for the chosen ordering of species:

$$\mathcal{M} = \begin{bmatrix} I & -B^T \\ B & I \end{bmatrix} \quad (13)$$

where

$$B_{e-N_r, r} = \phi_r^e \quad (r \in \mathcal{R}, e \in \mathcal{E}).$$

As an example, for a five species air mixture, \mathcal{M} should be

	O ₂	N ₂	NO	O	N
O ₂	1	0	0	-2	0
N ₂	0	1	0	0	-2
NO	0	0	1	-1	-1
O	2	0	1	1	0
N	0	2	1	0	1

(14)

The particular structure of the stoichiometric matrix leads to several useful results. For instance, if we multiply the upper part of \mathcal{M} by the array of species enthalpies \bar{h} , we find the array of reaction enthalpies Δh :

$$[I \quad -B^T] \bar{h} = \overline{\Delta h}, \quad (15)$$

where $\overline{\Delta h}_r = \sum_{s \in \mathcal{S}} \nu_s^r h_s$ for $r \in \mathcal{R}$. Moreover, by multiplying the lower part of \mathcal{M} by the species diffusion fluxes, we obtain the array of elemental diffusion fluxes:

$$[B \quad I] \bar{W} = \bar{N}. \quad (16)$$

We can exploit the above result to express the array of species diffusive fluxes \bar{W} in terms of the diffusive fluxes of combined species \bar{W}_R and independent species \bar{N} . By using the following trivial factorization of the identity matrix I , we see that

$$\bar{W} = \underbrace{\begin{bmatrix} I & 0 \\ -B & I \end{bmatrix}}_{=I} \begin{bmatrix} I & 0 \\ B & I \end{bmatrix} \bar{W} = \begin{bmatrix} I & 0 \\ -B & I \end{bmatrix} \begin{bmatrix} \bar{W}_R \\ \bar{N} \end{bmatrix}. \quad (17)$$

The reader should keep in mind this relation, which will be used repeatedly in the analysis that ensues. Practical details on how to efficiently determine the equilibrium composition from Eqs. (10)–(12) can be found in an earlier publication [31].

C. Elemental continuity equations for neutral mixtures

As pointed out by Murphy, we need to solve additional element advection-diffusion equations to determine the elemental composition of the mixture [21,26]. To obtain these equations, we multiply Eqs. (5) by $\phi_s^e M_e / M_s$ and sum over all species. Since no elements are created in the considered chemical reactions, the mass fraction of any element e obeys the following equation:

$$\partial_t(\rho Y^e) + \nabla \cdot (\rho \mathbf{u} Y^e) + \nabla \cdot \mathbf{J}_e = 0 \quad (e \in \mathcal{E}). \quad (18)$$

In what follows, we will show that under LTE conditions, the mass diffusion flux of elements \mathbf{J}_e can be expressed in terms of gradients of elemental mass fractions and temperature. For simplicity, we consider flows at constant pressure, consistent with the neglect of pressure diffusion in Eqs. (7). Once again, we remark that this does not imply any fundamental limitation and pressure diffusion could be included easily if needed. The reader may note that Eqs. (18) are expressed in terms of element mass fractions, whereas previous models were based upon mole fractions or number densities of elements. We believe this to be more advantageous for two main reasons:

(1) *mathematical elegance*: The element mass fraction appears in a natural manner in the right-hand side of Eqs. (12); the mathematical analysis hence turns out to be easier if one continues to work in terms of this variable.

(2) *numerical convenience*: Many existing flow solvers allow one to easily add advection-diffusion equations for a generic scalar quantity ϕ ; the formalism proposed here [Eqs. (18)–(30)] fits nicely within such a numerical framework. In addition, by using the global continuity equation, Eqs. (18) may be cast under a nonconservative form

$$\rho \partial_t Y^e + (\rho \mathbf{u} \cdot \nabla) Y^e + \nabla \cdot \mathbf{J}_e = 0 \quad (e \in \mathcal{E}), \quad (19)$$

which tends to be much more robust from a numerical point of view.

D. Elemental diffusion coefficients

Proposition 1. In a flow of reacting mixtures under LTE and at constant pressure, the elemental fluxes are in general nonzero and can be explicitly expressed as a function of the gradients of temperature and elemental composition, i.e.,

$$\mathbf{J}_e = -\rho D_e^T(T, p, \bar{Y}) \nabla T - \sum_{f \in \mathcal{E}} \rho D_{ef}(T, p, \bar{Y}) \nabla Y^f \quad (e \in \mathcal{E}). \quad (20)$$

Proof. From Eqs. (6) and (7) the species diffusion fluxes can be expressed as a linear combination of species concentration gradients

$$\bar{\mathbf{W}} = S^{-1} \bar{\nabla} \mathbf{x} = -n \bar{D} \bar{\nabla} \mathbf{x} \quad (21)$$

where $\bar{D}_{sm} = \bar{D}_{sm}(T, p, \bar{Y})$ for $s, m \in \mathcal{S}$.

From Eqs. (10)–(12), since $x_s = x_s(T, p, \bar{Y})$, it follows that

$$\nabla x_s = \left. \frac{\partial x_s}{\partial T} \right|_{Y^e, p} \nabla T + \sum_{f \in \mathcal{E}} \left. \frac{\partial x_s}{\partial Y^f} \right|_{T, p} \nabla Y^f \quad (s \in \mathcal{S}, e \in \mathcal{E}). \quad (22)$$

Therefore from Eqs. (3), (21), and (22), Eq. (20) can be easily retrieved.

The explicit determination of the functions D_e^T and D_{ef} requires a deeper analysis presented in the remaining part of this section and detailed in the Appendix.

Considering the gradient of Eq. (11) written in matrix form, making use of Eqs. (7) and introducing Eq. (17), one has

$$[\tilde{A} \quad \tilde{B}^T] S \begin{bmatrix} I & 0 \\ -B & I \end{bmatrix} \begin{bmatrix} \bar{\mathbf{W}}_R \\ \bar{\mathbf{N}} \end{bmatrix} = \frac{\nabla T}{R_u T^2} \begin{bmatrix} \Delta h_1 \\ \vdots \\ \Delta h_{N_r} \end{bmatrix} \equiv \bar{\theta}, \quad (23)$$

where $\tilde{A}_{ij} = \delta_{ij}/x_j$, $\tilde{B}_{ij}^T = -B_{ij}^T/x_j$. Moreover, in Eq. (23) we make use of van't Hoff's relation [27] $d \ln K_p^r / dT = \Delta h_r / (R_u T^2)$, as suggested in Ref. [2], and we make the assumption of constant pressure, consistent with the neglect of pressure diffusion. This leads to the definition of the components of $\bar{\theta}$ as

$$\bar{\theta}_r = \frac{\Delta h_r}{R_u T^2} \nabla T \quad (r \in \mathcal{R}), \quad (24)$$

where $\Delta h_r = \sum_{s \in \mathcal{S}} \nu_s^r h_s$ is the enthalpy of reaction r already introduced in Eq. (15) and R_u is the universal gas constant. From Eq. (23) and after some straightforward algebra, we easily find the following expression relating the number flux of elements $\bar{\mathbf{N}}$ and of the combined species $\bar{\mathbf{W}}_R$:

$$\mathcal{Y} \bar{\mathbf{W}}_R + \mathcal{Z} \bar{\mathbf{N}} = \bar{\theta}, \quad (25)$$

where the expressions of $\mathcal{Y}(N_r \times N_r)$ and $\mathcal{Z}(N_r \times N_c)$ are given in the Appendix, Sec. II. Following a similar strategy for the lower part of the equilibrium system [Eq. (12)] we have that

$$[\mathcal{B} \quad \mathcal{C}] S \begin{bmatrix} I & 0 \\ -B & I \end{bmatrix} \begin{bmatrix} \bar{\mathbf{W}}_R \\ \bar{\mathbf{N}} \end{bmatrix} = \begin{bmatrix} \nabla Y^1 \\ \vdots \\ \nabla Y^{N_c} \end{bmatrix} \equiv \bar{\psi}, \quad (26)$$

where $\bar{\psi}_e = \nabla Y^e$ for $e \in \mathcal{E}$. The two matrices $\mathcal{B}(N_c \times N_r)$ and $\mathcal{C}(N_c \times N_c)$ are determined expressing the mass fraction gradients in terms of the species mole fraction gradients, directly related to the driving forces for diffusion phenomena (see the Appendix, Sec. 2). After some more straightforward algebra, we transform the above result into an additional relation between $\bar{\mathbf{W}}_R$ and $\bar{\mathbf{N}}$:

$$\mathcal{T} \bar{\mathbf{W}}_R + \mathcal{K} \bar{\mathbf{N}} = \bar{\psi}, \quad (27)$$

where the components of $\mathcal{T}(N_c \times N_r)$ and $\mathcal{K}(N_c \times N_c)$ are again given in the Appendix, Sec. 2. Replacing $\bar{\mathbf{W}}_R$ from Eq. (25) in Eq. (27), the number fluxes of elements follow from the solution of the linear system (28):

$$\mathcal{S} \bar{\mathbf{N}} = -\mathcal{T}^{-1} \bar{\theta} + \bar{\psi}, \quad (28)$$

where $\mathcal{S} = (\mathcal{K} - \mathcal{T}^{-1} \mathcal{Z})$. Equations (25) and (27) are still equivalent to the original singular system (7), but with a particular right-hand side, valid only under LTE. As a consequence, the system (28) inherits the singular character of Eqs. (7) and an additional mass conservation constraint is still needed to regularize the problem:

$$\bar{\alpha}^T \bar{\mathbf{N}} = 0 \quad (29)$$

where $\bar{\alpha}_e = M_e$ for $e \in \mathcal{E}$.

The solution of the system [Eqs. (28) and (29)] represents the last step for the determination of the expression of the

elemental multicomponent diffusion coefficients D_{ef} and thermal demixing coefficients D_e^T , for which detailed expressions may be found in the Appendix, Sec. 4. By inverting \mathcal{S} , accounting for Eq. (29) [see the Appendix, Sec. 3], we easily find that

$$\mathbf{J}_e = - \sum_{f \in \mathcal{E}} \rho D_{ef} \nabla Y^f - \rho D_e^T \nabla T. \quad (30)$$

The second term in the right-hand side of the above result will in general generate nonzero elemental diffusion fluxes even when the initial elemental composition is uniform.

IV. DIFFUSIVE TRANSPORT OF ENTHALPY

In reacting flows, the diffusion of species affects the mixture energy balance through the heat flux term:

$$\mathbf{q}_d = \sum_{s \in \mathcal{S}} \mathbf{W}_s h_s. \quad (31)$$

In a general nonequilibrium case, to compute \mathbf{q}_d , one should determine all the \mathbf{W}_s as a solution of Eq. (7) and then compute the above linear combination, as done in the methodology of Refs. [12,23,26]. On the other hand, under thermochemical equilibrium, Eq. (31) can be cast under a particular form which avoids the computation of the \mathbf{W}_s . A first step in this direction was made by Butler and Brokaw [2], who showed that, under the assumption of vanishing elemental fluxes, the diffusive heat flux takes the form of Eq. (1). In this section, we extend the work of Butler and Brokaw to the more general case when elemental fluxes are nonzero.

Proposition 2. For a mixture of reacting gases under thermochemical equilibrium, at constant pressure, the diffusive heat flux is proportional to both temperature and elemental concentration gradients, and can be expressed as

$$\sum_{s \in \mathcal{S}} \mathbf{W}_s h_s = - (\lambda_R + \lambda_D) \nabla T - \sum_{e \in \mathcal{E}} \lambda_{EL}^e \nabla Y^e. \quad (32)$$

Proof. Observing that the product $\bar{W}^T \bar{h}$ takes the following shape in matrix form:

$$\begin{aligned} \bar{W}^T \bar{h} &= \bar{W}^T \left(\underbrace{\begin{bmatrix} I & -B^T \\ 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & B^T \\ 0 & I \end{bmatrix}}_{=I} \right) \bar{h} \\ &= \bar{W}^T \begin{bmatrix} I & -B^T \\ 0 & 0 \end{bmatrix} \bar{h} + \bar{W}^T \begin{bmatrix} 0 & B^T \\ 0 & I \end{bmatrix} \bar{h} \\ &= \bar{W}^T \begin{bmatrix} I & -B^T \\ 0 & 0 \end{bmatrix} \bar{h} + \bar{h}^T \begin{bmatrix} 0 & 0 \\ B & I \end{bmatrix} \bar{W}, \end{aligned}$$

the diffusive heat flux can be easily split into a contribution due to the transport of reaction enthalpies [Eq. (15)] by combined species and of formation enthalpies of elements [Eq. (16)]:

$$\bar{W}^T \bar{h} = \bar{h}^T \bar{W} = \bar{\Delta h}^T \bar{W}_R + \bar{h}_{EL}^T \bar{N}, \quad (33)$$

where $\bar{h}_{EL}^T = \bar{h}_e^T$ for $e \in \mathcal{E}$. Using Eq. (25), we easily find that

$$\bar{W}^T \bar{h} = -\lambda_R \nabla T - (\bar{\Delta h}^T \mathcal{Y}^{-1} \mathcal{Z} - \bar{h}_{EL}^T) \bar{N}, \quad (34)$$

where $\bar{\Delta h}^T \mathcal{Y}^{-1} \bar{\theta} = -\lambda_R \nabla T$. Next, expressing the terms proportional to \bar{N} in terms of ∇T and ∇Y^e using Eqs. (28) and (29), we easily retrieve Eq. (32). Detailed expressions for λ_R , λ_D , and the λ_{EL}^e may be found in the Appendix, Sec. 5.

We see that in an LTE flow, the diffusive heat flux vector consists of three different part.

(1) The ‘‘thermal reactive conductivity’’ coefficient λ_R is identical to the well-known results by Butler and Brokaw [2,3] and takes into account diffusive transfer of species enthalpies in the absence of elemental diffusion.

(2) The ‘‘thermal demixing conductivity’’ coefficient λ_D corrects for the additional diffusive heat transfer that occurs due to nonzero elemental diffusive fluxes when elemental mass fraction gradients are zero [see the remark below Eq. (30)].

(3) Finally, the ‘‘elemental heat transfer coefficients’’ λ_{EL}^e take into account heat transfer due to elemental demixing driven by gradients in elemental composition.

At this point, it is interesting to comment on the well-known thermal conductivity measurements by Asinovsky *et al.* [32] and Devoto *et al.* [33]. In their experiments, the total LTE thermal conductivity λ_{Tot} is determined from the radial energy balance in a steady, axisymmetric arc plasma of very large ratio of length over diameter. One might wonder which of the above three terms is actually being measured. Because flow velocities and axial variations in the plasma are very small, the elemental continuity equations (18) reduce to the simple statements that the radial fluxes of elements vanish:

$$\frac{\partial r J^e}{\partial r} = 0 \Rightarrow \mathbf{N}_e = \text{const} = \mathbf{0} \quad (e \in \mathcal{E})$$

since no elements go into the isolated walls of the arc. From Eq. (34), we then see that the measured thermal conductivity coefficient λ_{Tot} takes into account only the conventional thermal conductivity coefficient λ and the thermal reactive conductivity: $\lambda_{\text{Tot}} = \lambda + \lambda_R$; the λ_D and the λ_{EL}^e do not play a role. Similarly, it would appear that in steady thermal boundary layers, only λ_R effectively contributes to the heat flux to the wall. This important physical observation has been the motivation for splitting the thermal conductivity coefficients unlike in previous LTE formulations.

V. CLOSED FORM OF THE GOVERNING EQUATIONS

Thanks to the results of Secs. III D and IV, the full system of the governing equations of chemically reacting gases under LTE can hence be reduced to the system (35) below, formally equivalent to the ‘‘conventional’’ Navier-Stokes equations extended with a set on N_c additional advection-diffusion equations for each of the mixture elements:

$$\begin{aligned} \partial_t(\rho Y^e) + \nabla \cdot (\rho \mathbf{u} Y^e) \\ = \nabla \cdot \left(\rho D_e^T \nabla T + \sum_{f \in \mathcal{E}} \rho D_{ef} \nabla Y^f \right) (e \in \mathcal{E}) \end{aligned} \quad (35a)$$

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{u}) = 0, \quad (35b)$$

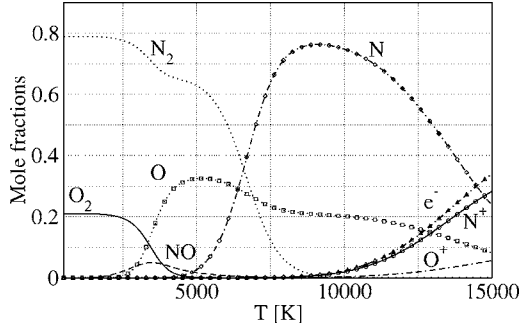


FIG. 1. Composition of an 11 species LTE air mixture at 1 atm ($Y^O=0.23$) [$O_2, N_2, O, N, NO, O^+, N^+, e^-$] (the concentrations of diatomic ions are negligible and hence do not appear).

$$\partial_t(\rho \mathbf{u}) + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) + \nabla p = \nabla \cdot \hat{\tau}, \quad (35c)$$

$$\begin{aligned} & \partial_t[\rho(e + \mathbf{u}^2/2)] + \nabla \cdot [\rho \mathbf{u}(h + \mathbf{u}^2/2)] \\ &= \nabla \cdot \left[(\lambda + \lambda_R + \lambda_D) \nabla T + \sum_{e \in \mathcal{E}} \lambda_{EL}^e \nabla Y^e \right] + \nabla \cdot (\mathbf{u} : \hat{\tau}). \end{aligned} \quad (35d)$$

Herein, e and h are, respectively, the mixture energy and enthalpy per unit mass, p stands for the static pressure, and $\hat{\tau}$ represents the tensor of viscous stresses:

$$\hat{\tau}_{ij} = \mu \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \nabla \cdot \mathbf{u} \right)$$

computed using Stokes' hypothesis of negligible bulk viscosity effects. Practical details on how to determine the thermodynamic properties e, h, ρ and the conventional transport properties μ and λ needed to solve the system (35) can be found in [30,31,34]. Expressions of the LTE transport properties $D_e^T, D_{eq}, \lambda_R, \lambda_D$, and λ_{EL}^e may be found back in the Appendix.

By writing the governing equations of chemically reacting flows under LTE as proposed in the system (35), the species diffusion fluxes and the enthalpy fluxes depend in an explicit manner on the solution unknowns, which is advantageous for their implementation in an implicit CFD code. Moreover, the physical effects leading to (de)mixing and its influence on the mixture energetic behavior clearly show up.

VI. AN ILLUSTRATIVE EXAMPLE

To present the application of the concepts introduced in the previous sections, we select as an example the mixture defined in Sec. II. The results presented below have been obtained extending the existing thermodynamics and transport library MUTATION [30] and using a second-order Laguerre- Sonine approximation for the computation of the elements of the matrix S in Eq. (8). To define a range of validity of the choice of species previously presented, we show in Fig. 1 the composition of an 11 species air mixture as a function of temperature for a reference pressure and elemental composition. We wish to stress the dependence of composition on elemental fraction [Eq. (12)] whose influ-

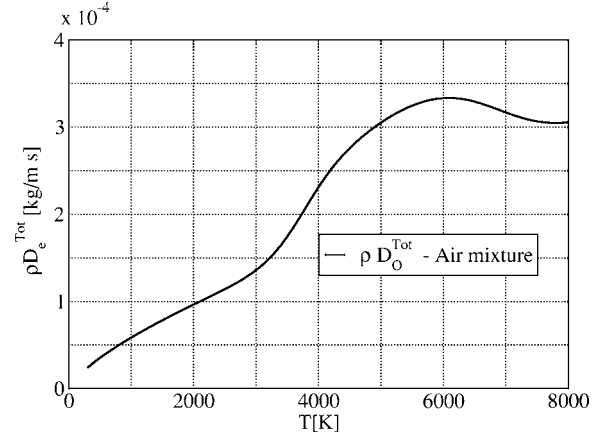


FIG. 2. Elemental total multicomponent diffusion coefficients for a five species air LTE mixture (this graph applies to both N and O due to the identity $D_N^{Tot} = D_O^{Tot}$).

ence on mixture composition is discussed in details in Ref. [26]. From the species evolution visible in the figure and from previous studies on the influence of species choice on mixture energetic behavior [31], we indicate 8000 K as the upper limit of the temperature range in which the transport properties previously introduced should be computed.

We now turn our attention to the evolution of the elemental multicomponent diffusion coefficients D_{eq} . For the particular case of a binary mixture, considering the expressions given in the Appendix, the diagonal elements are seen to be both equal to a common value D while the off-diagonal elements are equal to $-D$. For more general mixtures containing three or more elements, the elemental diffusion coefficient matrix will in general no longer have this elegant symmetric form. As observed by Murphy [20], for binary mixtures, the mass conservation constraint allows one to collect the diagonal and off-diagonal coefficients to form only one "total" elemental multicomponent coefficient for each element. Although our formulation is valid for mixtures of an arbitrary number of elements, we will here use this simplification to analyze demixing for the considered air mixture.

Since $\nabla Y^O = -\nabla Y^N$ in the air mixture, the oxygen and nitrogen diffusion fluxes read

$$\mathbf{J}_O = -\rho D_O^{Tot} \nabla Y^O - \rho D_O^T \nabla T, \quad (36a)$$

$$\mathbf{J}_N = -\rho D_N^{Tot} \nabla Y^N - \rho D_N^T \nabla T, \quad (36b)$$

where $D_O^{Tot} = D_N^{Tot} = 2D$. The presence of negative off-diagonal diffusion coefficients does not pose problems since D_O^{Tot} and D_N^{Tot} themselves are positive, as shown in Fig. 2. This result implies that the first term in the right-hand side of Eq. (36) will tend to smooth out variations of elemental mass fractions caused by temperature gradients. In Fig. 3 we show the thermal demixing coefficients plotted as a function of temperature. As for the total elemental multicomponent diffusion coefficients, the thermal demixing coefficients are not independent and as a consequence of mass conservation [Eq. (29)], $D_O^T = -D_N^T$. We observe a highly nonlinear behavior of these coefficients including the presence of a maximum just

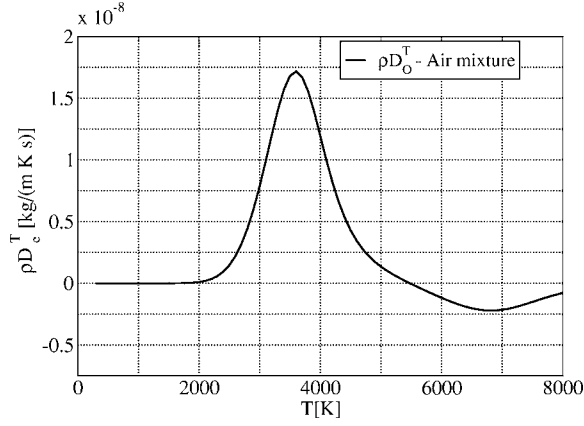


FIG. 3. Elemental thermal demixing coefficients for a five species air LTE mixture (this graph applies to both N and O due to the identity $D_N^T = -D_O^T$).

before 4000 K and a minimum one around 7000 K. The maximum and the minimum correspond to the dissociation of O_2 and N_2 and we observe that around 5500 K a change in sign takes place in D_O^T . This shows that, at low temperatures, oxygen will be driven in the direction opposite to the temperature gradient, while in higher temperature regions, the inverse phenomenon will take place. Figures 2 and 3 are obviously much more useful to predict and analyze diffusion phenomena in flows under LTE than the original set of Eqs. (5). A further step in the prediction of the effects of diffusion on the behavior of equilibrium mixtures is done by analyzing the diffusive transport of enthalpy. In the following pictures we present the thermal reactive conductivities introduced in Sec. IV. To clarify the analysis and discussion of the results we introduce the following notation:

λ' : represents the sum between the thermal reactive and demixing conductivities defined as $\lambda' = \lambda_R + \lambda_D$.

λ_{SM} : represents the ratio between the diffusive heat flux computed as $\sum_{s \in \mathcal{S}} \mathbf{W}_s h_s$ and a unity temperature gradient, where \mathbf{W}_s is the solution of Eq. (7) obtained as suggested in Ref. [30] in the absence of elemental concentration gradients.

λ_{BB} : represents the reactive conductivity computed using the formula of Ref. [3].

From Fig. 4 we see that there is a perfect match between (1) λ' and λ_{SM} and (2) λ_R and λ_{BB} , indeed from their definitions $\lambda' = \lambda_{SM}$ and $\lambda_R = \lambda_{BB}$. On the other hand, 20% differences between these respectively reactive conductivities due to demixing are visible (see Fig. 5) The sign of λ_D depends on temperature, showing that demixing may increase or decrease the heat flux depending on the local temperature in the mixture.

We now come to the last concept introduced in Sec. IV which deals with elemental heat transfer coefficients. As already observed for the elemental multicomponent diffusion coefficients, in the particular case of a binary mixture we can introduce a total elemental heat transfer coefficient λ_{EL}^{Tot} which will lead to the following heat flux contribution:

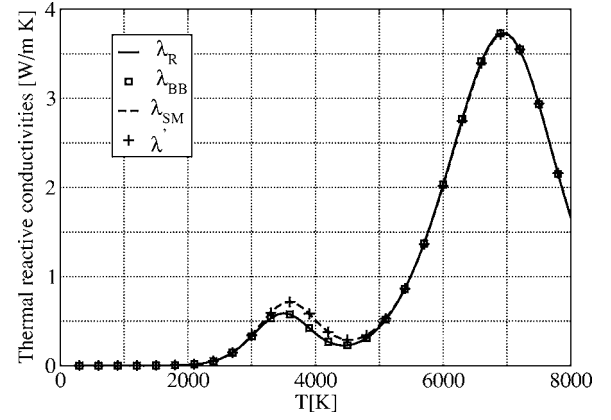


FIG. 4. Thermal reactive conductivities for a five species air LTE mixture.

$$-\sum_{e \in \mathcal{E}} \lambda_{EL}^e \nabla Y^e = -\lambda_{EL}^{Tot} \nabla Y^O, \quad (37)$$

where $\lambda_{EL}^{Tot} = \lambda_{EL}^O - \lambda_{EL}^N$. As a consequence of the definition of the elemental multicomponent diffusion coefficients, in the particular case of a binary elemental mixture, the elemental heat transfer coefficients are equal and opposite in sign [see the Appendix Sec. 5] giving rise to the λ_{EL}^{Tot} depicted in Fig. 6. There we see the λ_{EL}^{Tot} to be positive until around 8000 K, showing that the presence of an oxygen elemental gradient will give rise to an energy flux in the opposite direction for the considered neutral mixtures up to that temperature; beyond this temperature the effect is reversed.

VII. CONCLUSIONS

In this paper, we have shown that under conditions of LTE, the equations of chemically reacting flows can be reduced to an elegant system consisting of the conventional Navier-Stokes equations (mass, momentum, energy) complemented by an advection-diffusion equation for the mass fraction of each chemical element in the mixture. The obtained formalism is closed in the sense that diffusive fluxes are directly expressed in terms of gradients of the solution unknowns, unlike other formulations in which these fluxes are

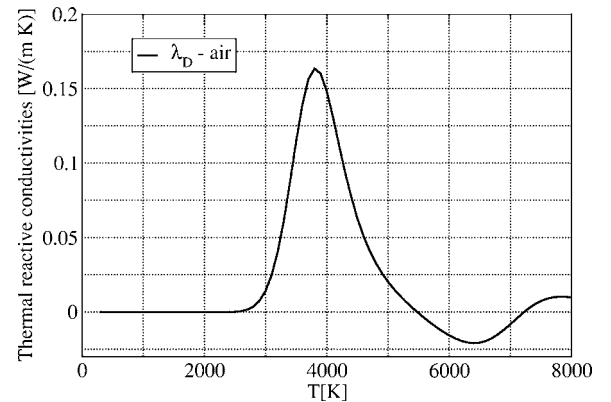


FIG. 5. Thermal demixing conductivity for a five species air LTE mixture.

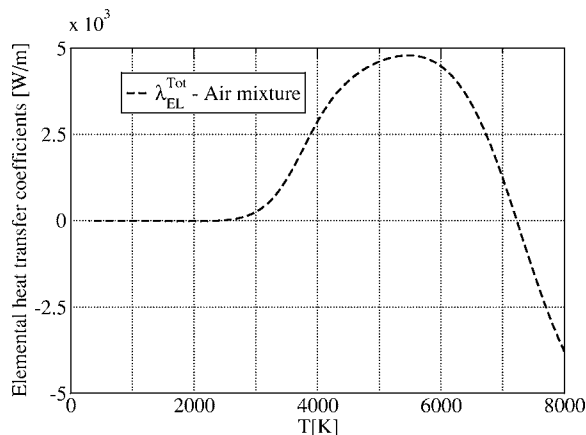


FIG. 6. Elemental total heat transfer coefficients for a five species air LTE mixture.

obtained in an implicit manner, by solving the full system of Stefan-Maxwell equations.

Our derivation is rigorous, up to the approximations of negligible pressure and thermal diffusion; as said, this is not a fundamental restriction and the reader may easily add these effects if desired. Several new LTE transport coefficients appear.

(1) The elemental advection-diffusion equations contain N_c^2 elemental multicomponent and N_c thermal demixing coefficients. While the matrix of elemental multicomponent diffusion coefficients takes a particularly simple form for the binary mixtures considered in the application, it is in general nonsymmetric.

(2) In the energy equation, the well-known thermal reactive conductivity coefficient (due to Butler and Brokaw) takes into account diffusive transport of species enthalpies in the absence of elemental demixing. An additional demixing thermal conductivity coefficient and a set of N_c elemental heat transfer coefficients correct for the additional flow of heat due to elemental demixing caused by temperature respectively elemental fraction gradients.

Detailed expressions of the LTE transport coefficients have been included in the Appendix; their implementation on a computer is straightforward.

From a numerical point of view, we believe that our closed formulation is considerably more advantageous than other existing LTE formalisms for two reasons:

(1) The solution unknowns and their derivatives appear explicitly in the equations. Hence when performing a finite-element or finite-difference discretization, the Picard Jacobian of the discrete equations can be obtained analytically without difficulty. This is not the case for open LTE formulations, in which the Jacobian of the diffusive fluxes can only be computed numerically by means of finite-differences.

(2) The formulas given in the Appendix do not require numerical computation of finite-differences of thermodynamic variables; doing so is computationally very expensive because for each finite-difference step, the mixture composition needs to be recomputed using a Newton iterative solver.

From a physical point of view, the derived transport coefficients provide a useful tool for the qualitative and quantitative understanding of diffusive phenomena in chemically

reacting flows at and near LTE. For instance,

(1) graphs such as those presented in this paper can be used to make an estimate of the degree of demixing to be expected in a chemically reacting flow prior to a numerical calculation. Based upon this knowledge, one may then decide whether or not to include the effect of demixing in the calculation.

(2) Full nonequilibrium calculations tend to yield excessively large amounts of information. If the flow is not too far from LTE, then graphs of LTE transport properties may be used to obtain a qualitative understanding of the computed species and temperature fields.

We hope that our results will be of use to other researchers working on the simulation of chemically reacting flows, in particular in the field of combustion modeling. We are currently developing an extension to ionized flows of the theory presented herein, which we intend to apply to model thermal arc and inductively coupled plasmas of considerably chemical complexity.

ACKNOWLEDGMENTS

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APPENDIX: DETAILED DERIVATION

In this section we provide detailed derivations of results derived in Secs. III and IV and used to obtain the numerical values presented in Sec. VI. These derivations can also be used as guidelines for the practical implementation.

1. Species diffusion

The species diffusion fluxes obey the Stefan-Maxwell equations introduced in Sec. III A and recalled hereafter:

$$\frac{M}{\rho} \sum_{j \in S} \left(\frac{x_i \mathbf{W}_j}{\mathcal{D}_{ijf_{ij}}} - \frac{x_j \mathbf{W}_i}{\mathcal{D}_{ijf_{ij}}} \right) = \nabla x_i = \mathbf{d}_i \quad (i \in S). \quad (\text{A1})$$

In matrix form, the previous equation reads

$$S \bar{\mathbf{W}} = \bar{\mathbf{d}} \quad (\text{A2})$$

where

$$S_{ij} = x_i M / [\rho \mathcal{D}_{ijf_{ij}}] \quad (i \neq j)$$

$$S_{ij} = \sum_{\ell \in S \setminus \{i\}} -x_\ell M / [\rho \mathcal{D}_{i\ell f_{i\ell}}] \quad (i = j).$$

For mathematical convenience, we split the matrix S into four components, defined as follows:

$$S = \begin{bmatrix} S_1 & S_2 \\ S_3 & S_4 \end{bmatrix}, \quad (\text{A3})$$

where $S_{1_{ij}} = S_{ij}$ ($i, j \leq N_r$), $S_{2_{i,j-N_r}} = S_{ij}$ ($i \leq N_r; N_r < j \leq N_s$), $S_{3_{i-N_r,j}} = S_{ij}$ ($N_r < i \leq N_s; j \leq N_r$), and $S_{4_{i-N_r,j-N_r}} = S_{ij}$ ($N_r < i, j \leq N_s$).

2. Matrix assembly

The first part of the system defining the equilibrium condition for each of the N_r reactions [Eqs. (10) and (11)] reads

$$\sum_{s \in \mathcal{S}} \nu_s^r \ln x_s = \ln K_p^r - \ln p \sum_{s \in \mathcal{S}} \nu_s^r \quad (r \in \mathcal{R}). \quad (\text{A4})$$

Taking the gradient of the previous equation, assuming constant pressure, and using the van't Hoff's relation, we have that

$$\sum_{s \in \mathcal{S}} \frac{\nu_s^r}{x_s} \nabla x_s = \frac{\Delta h^r}{R_u T^2} \nabla T \quad (r \in \mathcal{R}). \quad (\text{A5})$$

Substituting the Stefan-Maxwell equations [Eq. (A2)] into the matrix form of Eq. (A5), we obtain that

$$[\tilde{A} \quad \tilde{B}^T] \bar{d} = [\tilde{A} \quad \tilde{B}^T] S \bar{W} = \bar{\theta},$$

where $\tilde{A}_{ij} = \delta_{ij}/x_j$ and $\tilde{B}^T = -B_{ji}/x_j$. Introducing the unit matrix I and highlighting the structure of S , the previous relation reads

$$\begin{aligned} \bar{\theta} &= [\tilde{A} \quad \tilde{B}^T] \begin{bmatrix} S_1 & S_2 \\ S_3 & S_4 \end{bmatrix} \underbrace{\begin{bmatrix} I & 0 \\ -B & I \end{bmatrix} \begin{bmatrix} I & 0 \\ B & I \end{bmatrix}}_{=I} \bar{W} \\ &= [\tilde{A} \quad \tilde{B}^T] \begin{bmatrix} S_1 & S_2 \\ S_3 & S_4 \end{bmatrix} \begin{bmatrix} I & 0 \\ -B & I \end{bmatrix} \begin{bmatrix} \bar{W}_R \\ \bar{N} \end{bmatrix} \\ &= [\tilde{A} \quad \tilde{B}^T] \begin{bmatrix} S_1 - S_2 B & S_2 \\ S_3 - S_4 B & S_4 \end{bmatrix} \begin{bmatrix} \bar{W}_R \\ \bar{N} \end{bmatrix}. \end{aligned} \quad (\text{A6})$$

From Eq. (A6) one easily verifies the validity of Eq. (25) introduced in Sec. III D, recalled hereafter:

$$\mathcal{Y} \bar{W}_R + \mathcal{Z} \bar{N} = \bar{\theta} \quad (\text{A7})$$

where $\mathcal{Y} = \tilde{A}(S_1 - S_2 B) + \tilde{B}^T(S_3 - S_4 B)$ and $\mathcal{Z} = \tilde{A}S_2 + \tilde{B}^T S_4$. Note that \mathcal{Y} is symmetric; it may be shown that $\tilde{A}S_1$ and $\tilde{B}^T S_4 B$ are symmetric and $\tilde{A}S_2 B = -[\tilde{B}^T S_3]^T$.

The lower part of the equilibrium system, needed to impose the elements mass conservation [Eq. (12)], reads

$$\sum_{s \in \mathcal{S}} \phi_s^e y_s \frac{M_e}{M_s} = Y^e \quad (e \in \mathcal{E}).$$

Taking the gradient of the previous equation, we have that

$$M_e \sum_{s \in \mathcal{S}} \phi_s^e \frac{\nabla y_s}{M_s} = \nabla Y^e. \quad (\text{A8})$$

We now introduce the matrix \mathcal{F} representing the link between $\nabla(y_s/M_s)$ and ∇x_s . Species mass fractions are related to the respective mole fractions by means of the following relation:

$$y_s = \frac{\rho_s}{\sum_{i \in \mathcal{S}} \rho_i} = \frac{M_s n_s}{\sum_{i \in \mathcal{S}} M_i n_i} = \frac{M_s x_s}{\sum_{i \in \mathcal{S}} M_i x_i}.$$

The gradient of the previous relation reads

$$\begin{aligned} \frac{\nabla y_s}{M_s} &= \frac{\nabla x_s}{\sum_{i \in \mathcal{S}} M_i x_i} - \frac{x_s}{(\sum_{i \in \mathcal{S}} M_i x_i)^2} \sum_{i \in \mathcal{S}} M_i \nabla x_i \\ &= \frac{\nabla x_s}{M} - \frac{x_s}{M^2} \sum_{i \in \mathcal{S}} M_i \nabla x_i \\ &= \sum_{i \in \mathcal{S}} \mathcal{F}_{si} \nabla x_i, \end{aligned} \quad (\text{A9})$$

where M is the mixture molar mass, and the elements of the matrix \mathcal{F} are defined as

$$\mathcal{F}_{si} = \begin{cases} (1 - y_s)/M & \text{if } s = i \\ -x_s M_i / M^2 & \text{if } s \neq i. \end{cases} \quad (\text{A10})$$

Introducing the matrices $\hat{B}_{eq} = B_{eq} M_e$ and $\hat{C}_{e\ell} = \delta_{e\ell} M_e$ for $e, \ell \in \mathcal{E}$, and $q \in \mathcal{R}$, and making use of the matrix \mathcal{F} to express Eq. (A8) in matrix form, we have that

$$\begin{aligned} \bar{\psi} &= [\hat{B} \quad \hat{C}] \begin{bmatrix} \mathcal{F}_1 & \mathcal{F}_2 \\ \mathcal{F}_3 & \mathcal{F}_4 \end{bmatrix} \bar{d} = [\hat{B} \quad \hat{C}] \begin{bmatrix} \mathcal{F}_1 & \mathcal{F}_2 \\ \mathcal{F}_3 & \mathcal{F}_4 \end{bmatrix} S \bar{W} \\ &= [\hat{B} \quad \hat{C}] \begin{bmatrix} \mathcal{F}_1 & \mathcal{F}_2 \\ \mathcal{F}_3 & \mathcal{F}_4 \end{bmatrix} \begin{bmatrix} S_1 & S_2 \\ S_3 & S_4 \end{bmatrix} \begin{bmatrix} I & 0 \\ -B & I \end{bmatrix} \begin{bmatrix} \bar{W}_R \\ \bar{N} \end{bmatrix} \\ &= [\mathcal{B} \quad \mathcal{C}] \begin{bmatrix} S_1 & S_2 \\ S_3 & S_4 \end{bmatrix} \begin{bmatrix} I & 0 \\ -B & I \end{bmatrix} \begin{bmatrix} \bar{W}_R \\ \bar{N} \end{bmatrix} \\ &= [\mathcal{B} \quad \mathcal{C}] \begin{bmatrix} S_1 - S_2 B & S_2 \\ S_3 - S_4 B & S_4 \end{bmatrix} \begin{bmatrix} \bar{W}_R \\ \bar{N} \end{bmatrix}, \end{aligned} \quad (\text{A11})$$

where $\mathcal{B} = \hat{B} \mathcal{F}_1 + \hat{C} \mathcal{F}_3$ and $\mathcal{C} = \hat{B} \mathcal{F}_2 + \hat{C} \mathcal{F}_4$. From Eq. (A11) one easily verifies the validity of Eq. (27) introduced in Sec. III D, recalled hereafter

$$T \bar{W}_R + \mathcal{K} \bar{N} = \bar{\psi}, \quad (\text{A12})$$

where $T = \mathcal{B}(S_1 - S_2 B) + \mathcal{C}(S_3 - S_4 B)$ and $\mathcal{K} = \mathcal{B} S_2 + \mathcal{C} S_4$.

3. Linear systems solution

To obtain expressions for the elemental multicomponent diffusion coefficients, we now solve Eqs. (A7) and (A12) using straightforward Gaussian elimination, although other techniques based upon iterative solvers are also possible.

First we solve the system (A7) with respect to \bar{W}_R and then substitute the solution in Eq. (A12) which will be finally solved for \bar{N} by computing \mathcal{Y}^{-1} . Then the element number fluxes follow from the solution of the system (A13):

$$\mathcal{S}\bar{N} = -\mathcal{T}\mathcal{Y}^{-1}\bar{\theta} + \bar{\psi} \quad (\text{A13})$$

where $\mathcal{S} = (\mathcal{K} - \mathcal{T}\mathcal{Y}^{-1}\mathcal{Z})$. Because of the singular character of \mathcal{S} , inherited from the matrix S , the mass conservation constraint

$$\bar{\alpha}^T \bar{N} = 0, \quad (\text{A14})$$

where $\alpha_e = M_e$ for $e \in \mathcal{E}$, must still be applied to regularize \mathcal{S} [13]. This can be easily done by solving the following non-singular linear system equivalent to Eqs. (A13) and (A14) [30,35]:

$$(\mathcal{S} + \zeta \bar{\alpha} \otimes \bar{\alpha}) \bar{N} = \bar{\beta}, \quad (\text{A15})$$

where $\bar{\beta} = -\mathcal{T}\mathcal{Y}^{-1}\bar{\theta} + \bar{\psi}$. Indeed the matrix \mathcal{S} ($N_c \times N_c$) is such that the null spaces of \mathcal{S} and \mathcal{S}^T are, respectively, spanned by the vectors $\bar{R} \in \mathbb{R}^{N_c}$ and $\bar{L} \in \mathbb{R}^{N_c}$ satisfying the conditions $\bar{R}^T \bar{\alpha} \neq 0$ and $\bar{L}^T \bar{\alpha} \neq 0$. Therefore, for any nonzero parameter ζ (with dimensions [moles m/(kg s)]), $\exists \mathcal{D} = (\mathcal{S} + \zeta \bar{\alpha} \otimes \bar{\alpha})^{-1}$ such that for a vector $\bar{\beta} \in \mathbb{R}^{N_c}$ and in the range of \mathcal{S} , the solution of the system (A15) is

$$\bar{N} = -\mathcal{D}\mathcal{T}\mathcal{Y}^{-1}\bar{\theta} + \mathcal{D}\bar{\psi}, \quad (\text{A16})$$

where \bar{N} satisfies both Eqs. (A13) and (A14). From a practical point of view we suggest using ζ such that the regularization term has the same order of magnitude as the elements of the matrix \mathcal{S} , for example, $\zeta = \sum_{i,j \in \mathcal{E}} |\mathcal{S}_{ij}| / (N_c^2 M^2)$.

4. Elemental diffusion coefficients

To identify the elemental multicomponent and thermal demixing diffusion coefficients, we just need to extract the components of \bar{N} from Eq. (A16) and put them in the form of Eq. (20), recalled hereafter

$$\mathbf{J}_e = M_e \mathbf{N}_e = -\rho D_e^T \nabla T - \sum_{f \in \mathcal{E}} \rho D_{ef} \nabla Y^f. \quad (\text{A17})$$

The elemental multicomponent coefficients D_{ef} are related to the elements of the matrix \mathcal{D} , which are functions of $\zeta \in \mathbb{R}$. To eliminate this indeterminacy, characteristic of the solution technique used, we correct the matrix components as follows:

$$\mathcal{D}_{P_{ef}} = \mathcal{D}_{ef} - \frac{\sum_{h \in \mathcal{E}} \mathcal{D}_{eh}}{N_c}. \quad (\text{A18})$$

The reader may easily verify that for any physically acceptable right-hand side vector $\bar{\beta}$ such that $\sum_{e \in \mathcal{E}} \bar{\beta}_e = \bar{L}^T \bar{\beta} = 0$, $\bar{L} = [1, \dots, 1]^T$ being the member of the null space of \mathcal{S}^T . In addition, we have that $\mathcal{D}_P \bar{L} = 0$. Any vector $\bar{k} \in \mathbb{R}^{N_c}$ can be

written as the sum of a part parallel to and a part normal to \bar{L} : $\bar{k} = \bar{k}_{\parallel} + \bar{k}_{\perp}$. From the above, it follows that $\mathcal{D}_P \bar{k}$ is unique for any \bar{k} . In particular, $\mathcal{D}_P \bar{e}_i$ (where $\bar{e}_i = [0, \dots, 1, \dots, 0]^T$) is unique and hence all columns of \mathcal{D}_P are independent of ζ . Finally the elemental multicomponent diffusion coefficients read

$$\rho D_{ef} = -M_e \mathcal{D}_{P_{ef}} \quad (e, f \in \mathcal{E}). \quad (\text{A19})$$

The elemental thermal demixing coefficients can be easily computed by assembling the following expression and extracting the N_c components of the result:

$$\rho D_e^T = \frac{M_e}{R_u T^2} (\mathcal{D}_P \mathcal{T} \mathcal{Y}^{-1} \bar{\Delta} h)_e \quad (e \in \mathcal{E}). \quad (\text{A20})$$

5. Diffusive transport of enthalpy

The diffusive transport of enthalpy defined in Eq. (31) is recalled hereafter

$$\mathbf{q}_d = \sum_{s \in \mathcal{S}} \mathbf{W}_s h_s = \bar{\Delta} h^T \bar{W} + \bar{h}_{EL}^T \bar{N}. \quad (\text{A21})$$

Substituting Eqs. (A16) and (A18) into Eq. (A12) an expression for \bar{W}_R is found:

$$\bar{W}_R = \mathcal{Y}^{-1} \bar{\theta} - \mathcal{Y}^{-1} \mathcal{Z} \bar{N} = (\mathcal{Y}^{-1} + \mathcal{Y}^{-1} \mathcal{Z} \mathcal{D}_P \mathcal{T} \mathcal{Y}^{-1}) \bar{\theta} - \mathcal{Y}^{-1} \mathcal{Z} \mathcal{D}_P \bar{\psi}. \quad (\text{A22})$$

Substituting Eqs. (A22), (A16), and (A18) in Eq. (A21), the expression of the different contributions to the diffusive heat flux are retrieved. The computation of λ_R , λ_D , and λ_{EL}^e results from the straightforward application of the equations (A23)–(A25) below, which require the computation of several matrix products:

(1) The thermal reactive conductivity reads

$$\lambda_R = -\frac{1}{R_u T^2} \bar{\Delta} h^T \mathcal{Y}^{-1} \bar{\Delta} h. \quad (\text{A23})$$

(2) The thermal demixing conductivity is given by

$$\lambda_D = -\frac{1}{R_u T^2} (\bar{\Delta} h^T \mathcal{Y}^{-1} \mathcal{Z} \mathcal{D}_P \mathcal{T} \mathcal{Y}^{-1} \bar{\Delta} h - \bar{h}_{EL}^T \mathcal{D}_P \mathcal{T} \mathcal{Y}^{-1} \bar{\Delta} h). \quad (\text{A24})$$

(3) The elemental heat transfer coefficients are obtained as the components of the array

$$\bar{\lambda}_{EL}^T = \bar{\Delta} h^T \mathcal{Y}^{-1} \mathcal{Z} \mathcal{D}_P - \bar{h}_{EL}^T \mathcal{D}_P. \quad (\text{A25})$$

While they may appear tedious in analytical form, these matrix products can be easily implemented in an efficient manner on a computer.

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