IMPACT OF COMPUTING IN SCIENCE AND ENGINEERING 3, 244–276 (1991)

# Convergent Iterative Methods for Multicomponent Diffusion

VINCENT GIOVANGIGLI

*Centre de Mathématiques Appliquées, URA 756 du CNRS, Ecole Polytechnique, 91128 Palaiseau Cedex, France*

Received November 19, 1990

Vincent Giovangigli, Convergent Iterative Methods for Multicomponent Diffusion, *IMPACT of Computing in Science and Engineering* 3, 244–276 (1991).

We investigate iterative methods for solving consistent linear systems arising from the kinetic theory of gases and for providing multicomponent diffusion coefficients for gaseous mixtures. Various iterative schemes are proved to be convergent by using the properties of matrices with convergent powers and the properties of nonnegative matrices. In particular, we investigate Stefan–Maxwell diffusion equations and we express the multicomponent diffusion matrix as a symmetric convergent series. We also rigorously justify the accuracy of Hirschfelder–Curtiss approximations with mass correctors often used to approximate diffusion velocities in gas mixtures. © 1991 Academic Press, Inc.

## 1. INTRODUCTION

The species governing equations of multicomponent gaseous laminar reacting flows are derived from the kinetic theory of gases and are given in terms of the species diffusion velocities. More specifically, the species mass conservation equations in these flows can be written in the form [1–5]

$$\frac{\partial(\rho Y_k)}{\partial t} + \nabla\cdot(\rho v Y_k) = -\nabla\cdot(\rho Y_k V_k) + W_k\omega_k, \qquad k \in [1, n],$$

where $\rho$ is the density, $Y_k$ the mass fraction of the $k$th species, $t$ the time, $v$ the mass averaged flow velocity, $V_k$ the diffusion velocity of the $k$th species, $W_k\omega_k$ the mass production rate of the $k$th species, and $[1, n]$ the set of species indices, and the species boundary conditions at a reactive wall can be written as

$$\rho Y_k(v + V_k)\cdot\nu = \rho v\cdot\nu Y_k^0 + W_k\tilde{\omega}_k, \qquad k \in [1, n],$$



0899-8248/91 $3.00

where $\nu$ denotes the outward unit normal at the wall boundary, $Y_k^0$ the specified mass flux fraction, and $W_k\tilde{\omega}_k$ the surface mass production rate of the $k$th species. In order to render these governing equations soluble, the diffusion velocities $V_k$ appearing in these equations must therefore be determined. These velocities, on the other hand, can be expressed as [1–3]

$$V_k = -\sum_{l\in[1,n]} D_{kl}G_l, \qquad k\in[1, n], \tag{1.1}$$

where $D = (D_{kl})$ is the multicomponent diffusion coefficient matrix and where $G_k$ is the diffusion driving force of the $k$th species. The vectors $G_k$ incorporate the effects of various state variable gradients and external forces and can be written in the form

$$G_k = \nabla X_k + (X_k - Y_k)\frac{\nabla p}{p} + \frac{\rho}{p}\sum_{l\in[1,n]} Y_kY_l(f_l - f_k), \qquad k\in[1, n],$$

where $X_k$ denotes the mole fraction of the $k$th species, $p$ the pressure, and $f_k$ the external force per unit mass of the $k$th species. Note here that thermal diffusion is not considered in this paper. Only the driving forces $G_k$ such that $\sum_{k\in[1,n]} G_k = 0$ and the velocities $V_k$ such that $\sum_{k\in[1,n]} Y_kV_k = 0$ are of physical interest. A consequence of these expressions is that detailed modeling of the species diffusion velocities $V_k$ requires evaluating accurately the multicomponent diffusion coefficients $D_{kl}$ which are functions of the state variables $T$, $p$ and $Y_1, \ldots, Y_n$, i.e., $D_{kl} = D_{kl}(T, p, Y_1, \ldots, Y_n)$, where $T$ denotes the absolute temperature.

These diffusion coefficients, however, are not explicitly known from the kinetic theory. Evaluating the $D_{kl}$ requires solving large linear systems, namely of size $j*n$ when $j$ terms are retained in the Sonine polynomial expansions of the species perturbed distribution functions [1, 3]. A dual formulation of (1.1) can still be obtained and written in the form

$$G_k = -\sum_{l\in[1,n]} \Delta_{kl}V_l, \qquad k\in[1, n], \tag{1.2}$$

where $\Delta = (\Delta_{kl})$ is the dual multicomponent diffusion coefficient matrix and where the coefficients $\Delta_{kl}$ are function of the state variables $\Delta_{kl} = \Delta_{kl}(T, p, Y_1, \ldots, Y_n)$ [1, 6]. In principle, the diffusion velocities could be obtained from the dual relations and the mass conservation constraint $\sum_{k\in[1,n]} Y_kV_k = 0$. However, the dual diffusion coefficients are not explicitly known when $j \geqslant 2$. Indeed, they require eliminating $j-1$ blocks of size $n$ in a linear system of size $j*n$ as exemplified in [6]. However, they are explicitly known when $j = 1$, i.e., when only one term is retained in the Sonine polynomial expansions. In this situation, the relations (1.2) can be written in the form

$$G_k = \sum_{\substack{l\in[1,n]\\ l\neq k}} \frac{X_k X_l}{\mathcal{D}_{kl}} V_l - \left( \sum_{\substack{l\in[1,n]\\ l\neq k}} \frac{X_k X_l}{\mathcal{D}_{kl}} \right) V_k, \qquad k \in [1, n], \tag{1.3}$$

where $\mathcal{D}_{kl}$ denotes the usual binary diffusion coefficient for the species pair $(k, l)$ which depends only on temperature and pressure, $\mathcal{D}_{kl} = \mathcal{D}_{kl}(T, p)$ [1, 4–6]. These relations (1.3), which are referred as Stefan–Maxwell diffusion equations in the literature and which must be completed by the mass constraint $\sum_{k\in[1,n]} Y_k V_k = 0$ in order to define uniquely the diffusion velocities, may now be inverted to yield the velocities $V_k$. It is also possible to use a modified formulation of the Stefan–Maxwell diffusion equations

$$G_k = \sum_{\substack{l\in[1,n]\\ l\neq k}} \left( \frac{X_k X_l}{\mathcal{D}_{kl}} - \beta Y_k Y_l \right) V_l - \left( \sum_{\substack{l\in[1,n]\\ l\neq k}} \frac{X_k X_l}{\mathcal{D}_{kl}} + \beta Y_k Y_k \right) V_k,$$

$$k \in [1, n], \tag{1.4}$$

where $\beta$ is a positive constant. This system defines uniquely the diffusion velocities $V_k$ and yields that $-\beta(\sum_{k\in[1,n]} Y_k) \sum_{k\in[1,n]} Y_k V_k = \sum_{k\in[1,n]} G_k$. In particular $\sum_{k\in[1,n]} Y_k V_k$ is zero as long as $\sum_{k\in[1,n]} G_k$ is zero so that this system automatically handles mass conservation constraints as opposed to (1.3) where the mass constraint $\sum_{k\in[1,n]} Y_k V_k = 0$ is explicitly needed. This modified formulation has been introduced by the author in order to suppress artificial singularities in Jacobian matrices of discretized governing equations which may occur when all mass fractions are considered as independent unknowns [7].

However, inverting the Stefan–Maxwell diffusion equations (1.3), completed with the proper mass constraint, or their modified formulation (1.4), may be computationally expensive. Indeed, such inversions have generally to be performed at each time step—for unsteady problems—and at each computational cell. It is therefore interesting to use iterative techniques to invert these linear systems. Iterative methods are also a convenient way to define approximated diffusion coefficients, e.g., by truncating convergent series. Iterative schemes have been introduced in particular by Oran and Boris [8] and Jones and Boris [9] and accurate approximated solutions for diffusion velocities have also been considered by Coffee and Heimerl [10], Kee, Warnatz, and Miller [11], and Warnatz [12]. In this paper, we investigate—from a mathematical and numerical point of view—various iterative techniques for solving these systems. We first introduce a mathematical framework needed to prove rigorously that iterative methods are convergent. We state the properties of the matrices $D$ and $\Delta$ and show that they are generalized inverses of each other [7]. We also show that the matrices $\Delta$ corresponding to the Stefan–

Maxwell diffusion equations (1.3) satisfy the general properties required from the kinetic theory. We then prove that various iterative schemes, corresponding to regular splittings for $\Delta$, are convergent. Similarly, various iterative schemes for (1.4) are considered and we also study the case of vanishing species mass fractions by investigating the iterative solution of the species fluxes $F_k = Y_k V_k$ in terms of the diffusion driving forces $G_k$. In particular, new algorithms are proposed and proved to be convergent and a rigorous proof of the convergence of Oran–Boris–Jones type algorithms is also obtained. Our results are based on the properties of matrices for which the powers converge and on the properties of nonnegative matrices. Finally, we also justify rigorously the accuracy of Hirschfelder–Curtiss approximated diffusion velocities with mass correctors defined by

$$V_k = -\frac{D_k^*}{X_k} G_k + V_c, \qquad D_k^* = (1 - Y_k) / \sum_{\substack{l \in [1,n] \\ l \neq k}} (X_l / \mathcal{D}_{kl}), \qquad (1.5)$$

where $D_k^*$ is the diffusion coefficient of the $k$th species in the mixture and where the species independent correction velocity $V_c$ is chosen such that the mass constraint $\sum_{k \in [1,n]} Y_k V_k = 0$ is satisfied. We indeed prove that these diffusion velocities correspond to the first term of a convergent series.

In Section 2, we introduce a set of notations which will be used throughout this paper. Several results on generalized inverses and on iterative methods for singular systems are also summarized. In Section 3, we introduce a mathematical framework needed to investigate iterative methods. Various iterative schemes for the Stefan–Maxwell diffusion equations are then proved to be convergent in Section 4 where the case of vanishing mass fractions is also considered. Finally, numerical experiments are presented in Section 5 and a summary of practical results is given in Section 6.

## 2. Notations and Preliminaries

We shall consider the various diffusion matrices of a given multicomponent gas mixture with temperature $T$, pressure $p$, and species mass fractions $Y_1, \ldots, Y_n$. We shall denote by $n$ the number of species, by $[1, n] = \{1, \ldots, n\}$ the set of species indices, and we assume in the following that $n \geqslant 2$. Since the linear relations (1.1)–(1.5) between the various vectors $V_1, \ldots, V_n$ and $G_1, \ldots, G_n$, normally in $\mathbb{R}^3$, and involving the $n*n$ diffusion matrices $D$ and $\Delta$, may be decomposed on the canonical basis of $\mathbb{R}^3$, it will be sufficient to consider the case of scalar diffusion velocities $V_1, \ldots, V_n$ and scalar diffusion driving forces $G_1, \ldots, G_n$.

For a vector $x \in \mathbb{R}^n$ we denote by $x = (x_1, \ldots, x_n)$ its components and by $\mathbb{R}x$ the subspace $\operatorname{span}(x) = \{\lambda x; \lambda \in \mathbb{R}\}$. For $x, y \in \mathbb{R}^n$, we denote by $\langle x, y \rangle$ the scalar product $\langle x, y \rangle = \sum_{k \in [1,n]} x_k y_k$. For $x \in \mathbb{R}^n$, $x \neq 0$, we denote by $x^\perp$ the subspace $x^\perp = \{y \in \mathbb{R}^n; \langle x, y \rangle = 0\}$. Finally, if each component of a vector $x \in \mathbb{R}^n$ is nonnegative (positive) we write $x \geqslant 0$ ($x > 0$).

We use the notations $U = (1, \ldots, 1)$ and $Y = (Y_1, \ldots, Y_n)$ for the mass fractions. Unless explicitly stated, it will be assumed in the following sections that $Y > 0$, i.e., that the species mass fractions are positive. In the case of vanishing mass fractions we assume only that $Y \geqslant 0$ and $Y \neq 0$. Note also that for any physical mixture one has the relation $\sum_{k \in [1,n]} Y_k = \langle Y, U \rangle = 1$. However, this relation will not be needed in the following. Moreover, omitting factors such as $\langle Y, U \rangle$ when expressing diffusion velocities may modify Jacobian matrices of discretized systems when all mass fractions are considered as independent unknowns [7]. We shall thus keep these factors in various formulas and not assume a priori that $\langle Y, U \rangle = 1$. Finally we denote by $V$, $G$, and $F$ the vectors $V = (V_1, \ldots, V_n)$, $G = (G_1, \ldots, G_n)$, and $F = (F_1, \ldots, F_n)$ where $F_k = Y_k V_k$, $k \in [1, n]$.

We denote by $\mathbb{R}^{n,n}$ the set of $n*n$ square matrices. For $A \in \mathbb{R}^{n,n}$, we write $A = (A_{kl})$ the coefficients of the matrix $A$, $N(A)$ and $R(A)$ the nullspace and the range of $A$, respectively, and $A^T$ the transpose of $A$. Let $a, b \in \mathbb{R}^n$, then $a \otimes b$ denotes the matrix $a \otimes b = (a_k b_l)$. The identity matrix is denoted by $I$ and $\operatorname{diag}(\lambda_1, \ldots, \lambda_n)$ is the diagonal matrix with diagonal elements $\lambda_1, \ldots, \lambda_n$. In particular, we use the notation $\mathcal{Y} = \operatorname{diag}(Y_1, \ldots, Y_n)$. The projection matrix on a subspace $S_1$ along a complementary subspace $S_2$, i.e., $S_1 \oplus S_2 = \mathbb{R}^n$, is denoted by $P_{S_1,S_2}$. For $A \in \mathbb{R}^{n,n}$, $\sigma(A)$ and $\rho(A)$ denote the spectrum and the spectral radius of $A$ and we also define $\gamma(A) = \max\{|\lambda|; \lambda \in \sigma(A), \lambda \neq 1\}$. If each coefficient of a matrix $A \in \mathbb{R}^{n,n}$ is nonnegative (positive) we write $A \geqslant 0$ ($A > 0$). Finally, for $A \in \mathbb{R}^{n,n}$, we denote by $\|A\|$ its Frobenius norm defined by $\|A\| = (\sum_{k,l \in [1,n]} A_{kl}^2)^{1/2}$.

Let $A \in \mathbb{R}^{n,n}$ and let $T$, $S$ be two subspaces of $\mathbb{R}^n$ such that $N(A) \oplus S = \mathbb{R}^n$ and $R(A) \oplus T = \mathbb{R}^n$; then there exists a unique matrix $Z$ such that $AZA = A$, $ZAZ = Z$, $N(Z) = T$, and $R(Z) = S$ [13, p. 58]. This matrix $Z$ is called the generalized inverse of $A$ with prescribed range $S$ and nullspace $T$. In this situation the matrix $Z$ also satisfies $AZ = P_{R(A),T}$ and $ZA = P_{S,N(A)}$ [13, p. 58]. Similarly, let $A \in \mathbb{R}^{n,n}$ be such that $N(A) \oplus R(A) = \mathbb{R}^n$. Then there exists a unique matrix $Z$ such that $AZA = A$, $ZAZ = Z$, and $AZ = ZA$ [13, p. 162]. The matrix $Z$ is called the group inverse of $A$ and is denoted $A^\#$. In this situation one also has the properties $N(A) = N(A^\#)$, $R(A) = R(A^\#)$, and $AA^\# = A^\# A = P_{R(A),N(A)}$ [13, p. 162]. The group inverse is also the generalized inverse with prescribed range $R(A)$ and prescribed nullspace $N(A)$. Finally, we also consider the set $Z^{n,n} = \{A \in \mathbb{R}^{n,n}; A_{kl} \leqslant 0 \text{ for } k \neq l\}$ and a matrix $A \in Z^{n,n}$ is called an $M$-matrix if $A$ can be split into $A = sI - B$ where $s \geqslant \rho(B)$ and $B \geqslant 0$ [14].

A matrix $T \in \mathbb{R}^{n,n}$ is said to be convergent when the limit

$$\lim_{k \to +\infty} T^k$$

exists, not necessarily being zero. Note here that we are using the terminology of Neumann and Plemmons [14] rather than the more conventional one. It is well known that the powers of a matrix $T$ converge to zero if and only if $\rho(T) < 1$. More generally, $T$ is convergent if and only if either $\rho(T) < 1$ or $\rho(T) = 1$, $1 \in \sigma(T)$, $\gamma(T) < 1$, and $(I - T)^{\#}$ exists, i.e., $T$ has only elementary divisors corresponding to the eigenvalue 1 [14–17]. Next, for a matrix $A \in \mathbb{R}^{n,n}$, the decomposition

$$A = M - Z \tag{2.1}$$

is a splitting if $M$ is nonsingular. The splitting is said to be regular if $M^{-1} \geqslant 0$ and $Z \geqslant 0$. In order to solve the system

$$Ax = b, \tag{2.2}$$

where $b \in \mathbb{R}^n$, the splitting (2.1) induces the iterative scheme

$$x_i = Tx_{i-1} + M^{-1}b, \qquad i = 1, 2, \ldots, \tag{2.3}$$

where $T = M^{-1}Z$. If $A$ is nonsingular, then the sequence of iterates (2.3) converges for every $x_0$ to the unique solution of (2.2) if and only if $\rho(T) < 1$ [18–19]. If $A$ is singular and if the system (2.2) consistent, i.e., $M^{-1}b \in R(I - T)$, then the sequence of iterates converges for every $x_0$ if and only if the matrix $T$ is convergent [14–15]. In this situation, the solution $x_\infty$ to which the sequence of iterates converges depends on the initial solution $x_0$ and we have

$$\lim_{i \to \infty} x_i = (I - T)^{\#} M^{-1} b + E x_0,$$

where $E = I - (I - T)(I - T)^{\#}$. The asymptotic convergence rate is also $-\log \gamma(T)$. We refer to Neumann and Plemmons [14], Berman and Plemmons [16], and Keller [15] for an introduction to the solution of singular consistent linear systems by iteration techniques.

## 3. Diffusion Matrices

In this section, we introduce the various diffusion matrices of a gas mixture. We first state the general properties of $D$ and $\Delta$ and show that they are generalized inverses of each other. We then derive the properties of the matrices $\Delta$ arising from the Stefan–Maxwell diffusion equations. Finally we introduce the corresponding matrices $C$ and $\Gamma$ relating the diffusion fluxes $F = (Y_1 V_1, \ldots, Y_n V_n)$ to the diffusion driving forces $G$ which will be needed in the case of vanishing mass fractions.

### 3.1. *The Matrices D and* $\Delta$

We first consider the multicomponent diffusion matrix $D = D(T, p, Y_1, \ldots, Y_n)$ of a given mixture. Using the notations $V = (V_1, \ldots, V_n)$ and $G = (G_1, \ldots, G_n)$ we may write the linear relations (1.1) in the form

$$V = -DG, \tag{3.1}$$

keeping in mind that only the case where $V \in \mathbb{R}^n$ and $G \in \mathbb{R}^n$ is now considered. The diffusion coefficient matrix $D = (D_{kl})$ is assumed to have the properties

$$D = D^T, \tag{3.2}$$

$$DY = 0, \tag{3.3}$$

$$D \text{ is positive definite on } U^\perp . \tag{3.4}$$

Concerning these assumptions (3.2)–(3.4) we make the following remarks. First note from (3.2) that the matrix $D$ is symmetric. Symmetric diffusion coefficients have indeed been considered by Waldmann [3], Chapman and Cowling [1], Ferziger and Kaper [2], and Curtiss [20] and are consistent with Onsager reciprocal relations of thermodynamics of irreversible processes [2, 21]. An alternate definition, due to Hirschfelder, Curtiss, and Bird [4, 12, 22–23], imposes the constraint $D_{kk} = 0$, for $k \in [1, n]$, instead of (3.3), and unnecessarily breaks the symmetry of the diffusion process [2, 20, 21]. The property (3.3) corresponds to the mass conservation constraint and implies that $\sum_{k\in[1,n]} Y_k V_k = 0$, i.e., that $V \in Y^\perp$ for all $G \in \mathbb{R}^n$ [1–3]. Finally the property (3.4) corresponds to the positiveness of the entropy production quadratic form $-(p/T)\langle V, G\rangle$ on the physical hyperplane $\{ G \in \mathbb{R}^n; \sum_{k\in[1,n]} G_k = 0\} = U^\perp$ [2–3].

Similarly, we consider the dual diffusion coefficient matrix $\Delta = \Delta(T, p, Y_1, \ldots, Y_n)$ and write the dual relations in the form

$$G = -\Delta V, \tag{3.5}$$

where $G \in \mathbb{R}^n$ and $V \in \mathbb{R}^n$. The matrix $\Delta$ is assumed to satisfy

$$\Delta = \Delta^T, \tag{3.6}$$

$$\Delta U = 0, \tag{3.7}$$

$$\Delta \text{ is positive definite on } Y^\perp, \tag{3.8}$$

and it is assumed that the following relation holds between $D$ and $\Delta$:

$$\begin{cases} V = -DG, \\ G \in U^\perp, \end{cases} \quad \Leftrightarrow \quad \begin{cases} G = -\Delta V, \\ V \in Y^\perp. \end{cases} \tag{3.9}$$

Here again, the properties (3.6)–(3.8) correspond respectively to the symmetry of the dual diffusion matrix $\Delta$, the mass conservation constraints $G \in U^\perp$, for all $V \in \mathbb{R}^n$, and the positiveness of the entropy production quadratic form $-(p/T)\langle V, G\rangle$ on the physical hyperplane $\{V \in \mathbb{R}^n;\ \sum_{k\in[1,n]} Y_k V_k = 0\} = Y^\perp$. Finally the property (3.9) states that the restriction of $D$ to the physical hyperplane $U^\perp$ is a one to one mapping of $U^\perp$ onto $Y^\perp$ whose inverse is the restriction of $\Delta$ to $Y^\perp$ and conversely.

The relation between the matrices $D$ and $\Delta$ can be clarified by using the theory of generalized inverses [13]. We first derive some consequences of (3.1)–(3.9).

LEMMA 1. *If properties* (3.2)–(3.4) *hold, then we have* $N(D) = \mathbb{R}Y$ *and* $R(D) = Y^\perp$ *and denoting by* $\lambda_1 \leqslant \cdots \leqslant \lambda_n$ *the eigenvalues of* $D$, *we have* $\lambda_1 = 0$ *and* $\lambda_k > 0$, *for* $2 \leqslant k \leqslant n$. *Similarly, if properties* (3.6)–(3.8) *hold, then we have* $N(\Delta) = \mathbb{R}U$ *and* $R(\Delta) = U^\perp$ *and denoting by* $\mu_1 \leqslant \cdots \leqslant \mu_n$ *the eigenvalues of* $\Delta$, *we have* $\mu_1 = 0$ *and* $\mu_k > 0$, *for* $2 \leqslant k \leqslant n$. *Finally, if properties* (3.2)–(3.4), (3.6)–(3.8), *and* (3.9) *hold, then* $D\Delta D = D$ *and* $\Delta D \Delta = \Delta$.

*Proof.* From (3.2)(3.3) there exists an orthonormal basis consisting of eigenvectors of $D$ and $0 \in \sigma(D)$ since $DY = 0$. Let now $\lambda \in \sigma(D)$ and $e \in Y^\perp$ such that $De = \lambda e$ and $\langle e, e\rangle = 1$. Then there exists $x \neq 0$ such that $x \in U^\perp \cap (\mathbb{R}Y \oplus \mathbb{R}e)$ since $\dim(U^\perp) = n - 1$ and $\dim(\mathbb{R}Y \oplus \mathbb{R}e) = 2$. Now from (3.4) we have $\langle Dx, x\rangle > 0$ since $x \in U^\perp$ and $x \neq 0$ and a straightforward calculation yields $\langle Dx, x\rangle = \lambda\langle x, e\rangle^2$. This shows that $\lambda > 0$ and thus all eigenvalues of $D$ with eigenvectors in $Y^\perp$ are positive, and therefore $R(D) = Y^\perp$ and $N(D) = \mathbb{R}Y$. The properties of the matrix $\Delta$ can be obtained in a similar way. Now if $x \in \mathbb{R}^n$ then $Dx \in Y^\perp$ so that if we let $V = Dx$ and $G = -\Delta V$ then from (3.9) we get $V = -DG = D\Delta V = D\Delta Dx = Dx$ and thus $D\Delta D = D$ and the proof of $\Delta D\Delta = \Delta$ is similar.

Noting that $\mathbb{R}U \oplus Y^{\perp} = \mathbb{R}^n$ and $\mathbb{R}Y \oplus U^{\perp} = \mathbb{R}^n$, since $\langle U, Y \rangle \neq 0$, we now deduce from Lemma 1 and the definition of generalized inverses with prescribed range and nullspace, the following important corollary.

COROLLARY 2. *Assume that properties* (3.2)–(3.4), (3.6)–(3.8), *and* (3.9) *hold. Then* $\Delta$ *is the generalized inverse of* $D$ *with prescribed range* $U^{\perp}$ *and nullspace* $\mathbb{R}U$ *and* $D$ *is the generalized inverse of* $\Delta$ *with range* $Y^{\perp}$ *and nullspace* $\mathbb{R}Y$.

Using Corollary 2, we can then deduce the properties of $D$ from the properties of $\Delta$ and vice versa.

PROPOSITION 3. *Let* $D$ *be a matrix such that* (3.2)–(3.4) *hold and let* $\Delta$ *be the generalized inverse of* $D$ *with prescribed range* $U^{\perp}$ *and nullspace* $\mathbb{R}U$. *Then properties* (3.6)–(3.8) *and* (3.9) *hold.*

PROPOSITION 4. *Let* $\Delta$ *be a matrix such that* (3.6)–(3.8) *hold and let* $D$ *be the generalized inverse of* $\Delta$ *with prescribed range* $Y^{\perp}$ *and nullspace* $\mathbb{R}Y$. *Then properties* (3.2)–(3.4) *and* (3.9) *hold.*

*Proof.* Only the proof of Proposition 4 is given. The proof of Proposition 3 would be exactly similar. Let $D$ be the generalized inverse of $\Delta$ with prescribed range $Y^{\perp}$ and nullspace $\mathbb{R}Y$. By definition we have $D\Delta D = D$ and $\Delta D \Delta = \Delta$. Transposing these relations and using the symmetry of $\Delta$ we deduce that $D^T \Delta D^T = D^T$ and $\Delta D^T \Delta = \Delta$. Moreover $R(D^T) = (N(D))^{\perp}$ implies that $R(D^T) = Y^{\perp}$ and $N(D^T) = (R(D))^{\perp}$ yields $N(D^T) = \mathbb{R}Y$. From the uniqueness of the generalized inverse with prescribed range and nullspace we deduce that $D = D^T$ and (3.2) is proved. We also have (3.3) by construction since $N(D) = \mathbb{R}Y$. Now, for $x \in U^{\perp}$, $x \neq 0$, we have $\langle Dx, x \rangle = \langle D\Delta Dx, x \rangle = \langle \Delta Dx, Dx \rangle$ since $D = D^T$. Since $N(D) = \mathbb{R}Y$ by construction and $x \in U^{\perp}$, $x \neq 0$, we also have $Dx \neq 0$ because $\langle U, Y \rangle \neq 0$. Thus $\langle \Delta Dx, Dx \rangle > 0$ from (3.8) and thus $\langle Dx, x \rangle > 0$ and (3.4) is established. Finally, to prove (3.9), assume that $V = -DG$ and $G \in U^{\perp}$. Since $R(D) = Y^{\perp}$ by construction, we have $V \in Y^{\perp}$ and $\Delta V = -\Delta DG$. Now from Lemma 1 we have $R(\Delta) = U^{\perp}$. Thus if $G \in U^{\perp}$, there exists $z \in \mathbb{R}^n$ such that $\Delta z = G$. Therefore $\Delta V = -\Delta D \Delta z = -\Delta z = -G$. Conversely, if $V \in Y^{\perp}$ and $G = -\Delta V$, then from Lemma 1 we have $R(\Delta) = U^{\perp}$ so that $G \in U^{\perp}$, and since $V \in Y^{\perp}$ we have $V \in R(D)$ and there exists $z \in \mathbb{R}^n$ such that $V = Dz$. Thus $DG = -D\Delta V = -D\Delta Dz = -Dz = -V$ and the proof is complete.

From the properties of generalized inverses [13] we now deduce the following important expressions for the matrices $D\Delta$ and $\Delta D$ [7].

COROLLARY 5. *Assume that properties* (3.2)–(3.4), (3.6)–(3.8), *and* (3.9) *hold. Then the matrices* $\Delta D$ *and* $D\Delta$ *are projector matrices with ranges* $U^{\perp}$ *and* $Y^{\perp}$ *and nullspaces* $\mathbb{R}Y$ *and* $\mathbb{R}U$, *respectively, which can be written*

$$\Delta D = P_{U^{\perp},\mathbb{R}Y} = I - \frac{Y \otimes U}{\langle U, Y \rangle} \tag{3.10}$$

*and*

$$D\Delta = P_{Y^{\perp},\mathbb{R}U} = I - \frac{U \otimes Y}{\langle U, Y \rangle}. \tag{3.11}$$

As an immediate consequence of Corollary 5, we have the following very useful result [7].

PROPOSITION 6. *Assume that properties* (3.2)–(3.4), (3.6)–(3.8), *and* (3.9) *hold. Let* $\alpha$ *and* $\beta$ *be positive constants such that* $\alpha\beta\langle U, Y\rangle^2 = 1$. *Then the matrices*

$$\tilde{D} = D + \alpha U \otimes U$$

*and*

$$\tilde{\Delta} = \Delta + \beta Y \otimes Y$$

*are symmetric, positive definite, inverses of each other,*

$$(\Delta + \beta Y \otimes Y)(D + \alpha U \otimes U) = (D + \alpha U \otimes U)(\Delta + \beta Y \otimes Y) = I, \tag{3.12}$$

*and coincide respectively with* $D$ *and* $\Delta$ *on the physical hyperplanes* $U^{\perp}$ *and* $Y^{\perp}$.

*Proof.* First, the symmetry of $\tilde{D}$ and $\tilde{\Delta}$ is obvious. Now the quadratic forms defined by $D$ and $\alpha U \otimes U$ are both nonnegative and positive definite on $U^{\perp}$ and $\mathbb{R}U$, respectively, so that their sum is positive definite, and the same argument can be applied to $\tilde{\Delta}$. Finally, the formula (3.12) is a direct consequence of (3.3)(3.7) and (3.10)(3.11) since for $a, b, c, d \in \mathbb{R}^n$ and $A \in \mathbb{R}^{n,n}$ one has $a \otimes b\, c \otimes d = \langle b, c\rangle a \otimes d$, $a \otimes bA = a \otimes (A^T b)$ and $Aa \otimes b = (Aa) \otimes b$.

Note here that by using the matrices $\tilde{D}$ and $\tilde{\Delta}$ instead of $D$ and $\Delta$, one can suppress artificial singularities arising in Jacobian matrices of discretized governing equations when all mass fractions are considered as independent unknowns [7].

3.2. *Stefan–Maxwell Diffusion Equations*

A motivation for introducing the dual relations (3.5) is that when only one term is retained in the Sonine polynomial expansions of the species perturbed distribution functions, then the matrix $\Delta$ is explicitly known and can be written [1, 4–6]

$$\Delta_{kk} = \sum_{\substack{l\in[1,n]\\ l\neq k}} \frac{X_k X_l}{\mathcal{D}_{kl}}, \qquad k\in[1,n], \tag{3.13a}$$

$$\Delta_{kl} = -\frac{X_k X_l}{\mathcal{D}_{kl}}, \qquad k,l\in[1,n], \qquad k\neq l, \tag{3.13b}$$

where $\mathcal{D}_{kl}$ denotes the usual binary diffusion coefficient for the species pair $(k, l)$ which depends only on temperature and pressure, $\mathcal{D}_{kl} = \mathcal{D}_{kl}(T, p)$, and where $X_k$ denotes the mole fraction of the $k$th species. The mole fractions $X = (X_1, \ldots, X_n)$ can be expressed in terms of the mass fractions $Y$ by the formulas [1–5]

$$X_k = \frac{Y_k W}{W_k}, \qquad k\in[1,n], \tag{3.14a}$$

where $W_k$ is the molecular weight of the $k$th species and $W$ the molecular weight of the mixture. The molecular weights of the species $W_k$, $k\in[1,n]$, are simply positive constants and the molecular weight of the mixture $W$ is given by [7]

$$\Big(\sum_{k\in[1,n]} Y_k\Big)/W = \sum_{k\in[1,n]} Y_k/W_k. \tag{3.14b}$$

Since the mass fractions $Y$ have been assumed to be positive, it is easy to check that the corresponding mole fractions $X$ are positive. Moreover, binary diffusion coefficients are always positive numbers and are symmetric, i.e., $\mathcal{D}_{kl} = \mathcal{D}_{lk}$ for $k\neq l$. From these assumptions, we now prove that properties (3.6)–(3.8) hold.

PROPOSITION 7. *Let $W_k$, $k\in[1,n]$, be positive numbers, let $\mathcal{D}_{kl}$ be positive numbers defined for $k, l\in[1,n]$, $k\neq l$, and symmetric, and assume that $Y > 0$. Then the matrix $\Delta$ defined as in* (3.13)(3.14) *satisfies properties* (3.6)–(3.8). *Moreover, this matrix is irreducible, is diagonally dominant, and is an M-matrix.*

*Proof.* The symmetry of $\Delta$ is obvious from definition (3.13) and the properties of the binary diffusion coefficients $\mathcal{D}_{kl}$. Similarly, the relation $\Delta U = 0$ is a consequence of (3.13). A straightforward computation also yields that for $x \in \mathbb{R}^n$ we have

$$\langle \Delta x, x \rangle = \sum_{\substack{k,l \in [1,n] \\ k \neq l}} \frac{X_k X_l}{2\mathcal{D}_{kl}} (x_k - x_l)^2,$$

so that $\langle \Delta x, x \rangle \geqslant 0$ and $\langle \Delta x, x \rangle = 0$ implies $x \in \mathbb{R}U$ since $X > 0$. Therefore $\Delta$ is positive definite on $Y^\perp$ since $U \notin Y^\perp$. The graph of $\Delta$ is also strongly connected since $\Delta_{kl} \neq 0$ for all $k, l \in [1, n]$ so that $\Delta$ is irreducible [18, p. 20] and the diagonal dominance [18, p. 23] is obvious. Now let $s \in \mathbb{R}$ be such that $s \geqslant \Delta_{kk}$, for $k \in [1, n]$, and define $B = sI - \Delta$. Then $B \geqslant 0$ from the definitions of $\Delta$ and $s$. Applying then the Gershgorin theorem [18, p. 16] to $B$ yields that $|\lambda| \leqslant s$ for $\lambda \in \sigma(B)$ since $\sum_{l \in [1,n]} B_{kl} = s$ for $k \in [1, n]$, so that $\Delta$ is an $M$-matrix.

We can similarly derive some of the properties of the matrix $\tilde{\Delta} = \Delta + \beta Y \otimes Y$.

PROPOSITION 8. *Keep the assumptions of Proposition 7 and let $\beta$ be a positive constant. Then the matrix $\tilde{\Delta} = \Delta + \beta Y \otimes Y$ is symmetric and positive definite. Moreover, if $0 < \beta \leqslant \beta^*$, where $\beta^*$ is defined by*

$$\beta^* = W^2 / \max\{W_k W_l \mathcal{D}_{kl};\ k, l \in [1, n],\ k \neq l\}, \qquad (3.15)$$

*then $\tilde{\Delta}$ is strictly diagonally dominant, is an M-matrix, and $\tilde{D} = \tilde{\Delta}^{-1} \geqslant 0$. Finally, if $0 < \beta < \beta^*$, then $\tilde{\Delta}$ is irreducible and $\tilde{D} = \tilde{\Delta}^{-1} > 0$.*

*Proof.* From Propositions 6 and 7 we deduce that $\tilde{\Delta}$ is symmetric and positive definite. Then, if $0 < \beta \leqslant \beta^*$, we have

$$\tilde{\Delta}_{kl} = -Y_k Y_l \left( \frac{W^2}{W_k W_l \mathcal{D}_{kl}} - \beta \right) \leqslant -Y_k Y_l (\beta^* - \beta) \leqslant 0,$$

$$k, l \in [1, n],\ k \neq l,$$

so that $\tilde{\Delta} \in Z^{n,n}$, and if $0 < \beta < \beta^*$, then $\tilde{\Delta}_{kl} \neq 0$ for $k, l \in [1, n]$ so that $\tilde{\Delta}$ is irreducible [18, p. 20]. Now let $s$ be such that $s \geqslant \tilde{\Delta}_{kk}$, for $k \in [1, n]$, and define $B = sI - \tilde{\Delta}$. Then $B \geqslant 0$ for $0 < \beta \leqslant \beta^*$ and $B > 0$ for $0 < \beta < \beta^*$ and applying the Gershgorin theorem to $B$ yields that $|\lambda| < s$ for $\lambda \in \sigma(B)$ since $\sum_{l \in [1,n]} B_{kl} = s - \beta Y_k \sum_{l \in [1,n]} Y_l$ for $k \in [1, n]$. Therefore $\tilde{D} = \tilde{\Delta}^{-1} = s^{-1} \sum_{k \geqslant 0} (B/s)^k$ and $\tilde{D} \geqslant 0$ for $0 < \beta \leqslant \beta^*$ whereas $\tilde{D} > 0$ for $0 < \beta < \beta^*$. Finally, proving the strict diagonal dominance is straightforward.

### 3.3. *The Case of Vanishing Mass Fractions*

In this section we assume only that $Y \geqslant 0$ and $Y \neq 0$. Some of the mass fractions are thus allowed to vanish and the mole fractions $X$, given by (3.14), are then such that $X_k = 0$ if and only if $Y_k = 0$. In the limit of vanishing mass fractions, the diffusion matrix $D$ and the diffusion velocities $V$ are no more defined and the matrix $\Delta$ becomes singular on $Y^{\perp}$. Nevertheless, the quantities that are needed to formulate the multicomponent laminar reacting flow governing equations are the mass fluxes $F = (Y_1 V_1, \ldots, Y_n V_n)$. Therefore, in this situation, we must solve for the fluxes $F$ in terms of $G$ and only the fluxes $F$ such that $\sum_{k \in [1,n]} F_k = 0$, i.e., $F \in U^{\perp}$, are of physical interest. We are thus led to introduce the matrix $\Gamma = (\Gamma_{kl})$ such that

$$\Gamma_{kk} = \frac{W}{W_k} \sum_{\substack{l \in [1,n] \\ l \neq k}} \frac{X_l}{\mathcal{D}_{kl}}, \qquad k \in [1, n], \tag{3.16a}$$

$$\Gamma_{kl} = -\frac{W}{W_l} \frac{X_k}{\mathcal{D}_{kl}}, \qquad k, l \in [1, n], \qquad k \neq l, \tag{3.16b}$$

and given $G \in U^{\perp}$, we want to find $F \in U^{\perp}$ such that

$$G = -\Gamma F. \tag{3.17}$$

Denoting by $\mathcal{Y}$ the diagonal matrix $\mathcal{Y} = \operatorname{diag}(Y_1, \ldots, Y_n)$, note that we have the relation $\Delta = \Gamma \mathcal{Y}$. In the following proposition, we derive the properties of the matrix $\Gamma$ and of its group inverse $C$.

PROPOSITION 9. *Let $W_k$, $k \in [1, n]$, be positive numbers, let $\mathcal{D}_{kl}$ be positive numbers defined for $k, l \in [1, n]$, $k \neq l$, and symmetric, i.e., $\mathcal{D}_{kl} = \mathcal{D}_{lk}$, for $k \neq l$, and assume that $Y \geqslant 0$ and $Y \neq 0$. Then the matrix $\Gamma$ defined by (3.16)(3.14) is such that $N(\Gamma) = \mathbb{R}Y$ and $R(\Gamma) = U^{\perp}$ and thus admits a group inverse $C = \Gamma^{\#}$. The matrix $C = \Gamma^{\#}$ is such that $N(C) = \mathbb{R}Y$ and $R(C) = U^{\perp}$ and we have*

$$C\Gamma = \Gamma C = I - \frac{Y \otimes U}{\langle U, Y \rangle}. \tag{3.18}$$

*Moreover we have the relation*

$$\begin{cases} F = -CG, \\ G \in U^{\perp}, \end{cases} \quad \Longleftrightarrow \quad \begin{cases} G = -\Gamma F, \\ F \in U^{\perp}, \end{cases} \tag{3.19}$$

*and $\Gamma$ is an M-matrix. Finally, when all mass fractions are positive, then $C = \mathcal{Y} D$ and $\Gamma = \Delta \mathcal{Y}^{-1}$.*

*Proof.* When all mass fractions are positive, the matrix $\mathcal{Y}$ is invertible and from $\Delta = \Gamma\mathcal{Y}$ we deduce that $\Delta\mathcal{Y}^{-1} = \Gamma$ and thus that $N(\Gamma) = \mathcal{Y}(N(\Delta)) = \mathbb{R}Y$ and that $R(\Gamma) = R(\Delta) = U^{\perp}$. In the case of vanishing mass fractions, we may assume, without loss of generality, that the species have been ordered such that $Y_k > 0$, for $1 \leqslant k \leqslant p$, and $Y_k = 0$, for $p+1 \leqslant k \leqslant n$, for some $1 \leqslant p < n$. Using the partitioning $[1, n] = [1, p] \cup [p+1, n]$, we may decompose each $x \in \mathbb{R}^n$ into $x = (x^+, x^0)$ where $x^+ \in \mathbb{R}^p$ and $x^0 \in \mathbb{R}^{n-p}$. Correspondingly we decompose each matrix $A \in \mathbb{R}^{n,n}$ into the blocks $A^{++} \in \mathbb{R}^{p,p}$, $A^{+0} \in \mathbb{R}^{p,(n-p)}$, $A^{0+} \in \mathbb{R}^{(n-p),p}$, and $A^{00} \in \mathbb{R}^{(n-p),(n-p)}$ in such a way that $y = Ax$ if and only if $y^+ = A^{++}x^+ + A^{+0}x^0$ and $y^0 = A^{0+}x^+ + A^{00}x^0$. A straightforward calculation then shows that the matrix $\Gamma$ admits the block decomposition

$$\Gamma = \begin{bmatrix} \Gamma^{++} & \Gamma^{+0} \\ \Gamma^{0+} & \Gamma^{00} \end{bmatrix} = \begin{bmatrix} \Gamma_{11} & \cdots & \Gamma_{1p} & \Gamma_{1(p+1)} & \cdots & \Gamma_{1n} \\ \vdots & & \vdots & \vdots & & \vdots \\ \Gamma_{p1} & \cdots & \Gamma_{pp} & \Gamma_{p(p+1)} & \cdots & \Gamma_{pn} \\ 0 & \cdots & 0 & \Gamma_{(p+1)(p+1)} & & 0 \\ \vdots & & \vdots & & \ddots & \\ 0 & \cdots & 0 & 0 & & \Gamma_{nn} \end{bmatrix}, \tag{3.20}$$

so that $\Gamma^{0+} = 0$ and $\Gamma^{00}$ is diagonal with positive elements $\Gamma_{(p+1)(p+1)}, \ldots, \Gamma_{nn}$. Let then $x = (x^+, x^0) \in \mathbb{R}^n$ such that $\Gamma x = 0$. From (3.20) we get that $\Gamma^{00}x^0 = 0$ so that $x^0 = 0$ and $\Gamma^{++}x^+ = 0$. Now, if $p \geqslant 2$, $\Gamma^{++}$ is exactly the matrix $\Gamma^{[p]}$ that would be obtained from (3.16)(3.14) by considering only the first $p$ species with positive mass fractions $Y^+ = (Y_1, \ldots, Y_p)$. In particular we have, with obvious notations, $\Gamma^{++}\mathcal{Y}^{++} = \Delta^{++}$ and thus, from Proposition 7 and Lemma 1, $N(\Gamma^{++}) = \mathcal{Y}^{++}(\mathbb{R}U^+) = \mathbb{R}Y^+$. The same result trivially holds if $p = 1$ since then $\Gamma^{++}$ is the zero $1 * 1$ matrix and $N(\Gamma^{++}) = \mathbb{R}Y^+$ where $Y^+ = (Y_1)$. Therefore $\Gamma x = 0$ if and only if for some $\lambda \in \mathbb{R}$ we have $x = (x^+, x^0) = (\lambda Y^+, 0) = \lambda(Y^+, 0) = \lambda Y$ so that $N(\Gamma) = \mathbb{R}Y$. Moreover from (3.16) we have $R(\Gamma) \subset U^{\perp}$ and thus $R(\Gamma) = U^{\perp}$. Now $N(\Gamma) \oplus R(\Gamma) = \mathbb{R}^n$ because $Y \notin U^{\perp}$ and thus $\Gamma$ admits a group inverse which satisfies $C\Gamma = \Gamma C = P_{R(\Gamma),N(\Gamma)}$ which can be written $C\Gamma = \Gamma C = I - (Y \otimes U)/\langle U, Y\rangle$. The relations (3.19) are then easily shown as in the proof of Proposition 4. Let then $s$ such that $s \geqslant \Gamma_{kk}$, for $k \in [1, n]$, and define $B = sI - \Gamma$. Then $B \geqslant 0$ and applying the Gershgorin theorem [18, p. 16] to $B^T$ yields that $|\lambda| \leqslant s$ for $\lambda \in \sigma(B) = \sigma(B^T)$ since $\sum_{k \in [1,n]} B_{kl} = s$ for $l \in [1, n]$, so that $\Gamma$ is an $M$-matrix. Finally, when all mass fractions are positive, we deduce from Propositions 7 and 4 that there exists a generalized inverse $D$ of $\Delta$ with $R(D) = Y^{\perp}$ and $N(D) = \mathbb{R}Y$. Then from $\Delta = \Gamma\mathcal{Y}$ we get that $\Gamma = \Delta\mathcal{Y}^{-1}$ and we also have $N(\mathcal{Y}D) = N(D) = \mathbb{R}Y$ and $R(\mathcal{Y}D) = \mathcal{Y}(R(D)) = U^{\perp}$. Moreover we deduce from $D\Delta D = D$ and $\Delta D\Delta = \Delta$ that $(\mathcal{Y}D)(\Delta\mathcal{Y}^{-1})(\mathcal{Y}D) = \mathcal{Y}D$

and $(\Delta\mathcal{Y}^{-1})(\mathcal{Y}D)(\Delta\mathcal{Y}^{-1}) = \Delta\mathcal{Y}^{-1}$ so that $C = \mathcal{Y}D$ from the uniqueness of the generalized inverse with prescribed range and null space and the proof is complete.

In the next proposition we establish some of the properties of the modified matrices $\tilde{C}$ and $\tilde{\Gamma}$ from which we deduce the smoothness of the matrix $C$ as a function of the mass fractions $Y$.

PROPOSITION 10. *Keeping the notations of Proposition 9, let $\alpha$ and $\beta$ be positive constants such that $\alpha\beta\langle U, Y\rangle^2 = 1$. Then the matrices*

$$\tilde{C} = C + \alpha Y \otimes U$$

*and*

$$\tilde{\Gamma} = \Gamma + \beta Y \otimes U$$

*are inverses of each other,*

$$(\Gamma + \beta Y \otimes U)(C + \alpha Y \otimes U) = (C + \alpha Y \otimes U)(\Gamma + \beta Y \otimes U) = I, \quad (3.21)$$

*and coincides with $C$ and $\Gamma$ respectively on the physical hyperplane $U^{\perp}$. Moreover, if $0 < \beta \leqslant \beta^*$, then $\tilde{\Gamma}$ is an M-matrix and $\tilde{C}$ is nonnegative, i.e., $\tilde{C} \geqslant 0$. Finally, the coefficients of the matrix $C$ are smooth rational functions of the mass fractions in the physical domain $\{Y \in \mathbb{R}^n;\ Y \geqslant 0,\ \langle U, Y\rangle = 1\}$.*

*Proof.* Since $R(C) = R(\Gamma) = U^{\perp}$, we have $N(C^T) = N(\Gamma^T) = \mathbb{R}U$ and thus $C^T U = \Gamma^T U = 0$ and we also have $CY = \Gamma Y = 0$. From these relations and from (3.18) we now easily obtain (3.21) as in the proof of Proposition 6. From this relation, we deduce that $C = (\Gamma + \beta Y \otimes U)^{-1} - \alpha Y \otimes U$. Now for any fixed positive value of $\beta$ the matrix $\Gamma + \beta Y \otimes U$ is invertible on $\{Y \in \mathbb{R}^n;\ Y \geqslant 0, \langle U, Y\rangle = 1\}$. Moreover it is well known that the set of invertible matrices $\mathcal{J}$ is open in $\mathbb{R}^{n,n}$ and that the application $M \to M^{-1}$ from $\mathcal{J}$ to $\mathbb{R}^{n,n}$ is smooth. This shows that the coefficients of $C$ are smooth functions of the mass fractions in the domain $\{Y \in \mathbb{R}^n;\ Y \geqslant 0,\ \langle U, Y\rangle = 1\}$. Moreover these functions are rational since $\Gamma$ is a rational function of $Y$ and since for $M \in \mathcal{J}$ one has $M^{-1} = \mathrm{adj}(M)/\det(M)$—with obvious notations—which is a rational function of $M$. Finally, for $0 < \beta \leqslant \beta^*$, $\tilde{\Gamma}$ can be shown to be an $M$-matrix and $\tilde{C} \geqslant 0$ as in the proof of Proposition 9.

The next proposition gives the behavior of the matrices $\Gamma$ and $C$ when some of the mass fractions are vanishing. Without loss of generality, we assume, as in the proof of Proposition 9, that the species have been ordered such that the nonzero mass fractions are $Y_1, \ldots, Y_p$ for some $1 \leqslant p < n$. Using again the partitioning $[1, n] = [1, p] \cup [p + 1, n]$, we decompose each $x \in \mathbb{R}^n$ into

$x = (x^+, x^0)$, where $x^+ \in \mathbb{R}^p$, $x^0 \in \mathbb{R}^{n-p}$, and similarly we decompose each matrix $A \in \mathbb{R}^{n,n}$ into the blocks $A^{++} \in \mathbb{R}^{p,p}$, $A^{+0} \in \mathbb{R}^{p,(n-p)}$, $A^{0+} \in \mathbb{R}^{(n-p),p}$, and $A^{00} \in \mathbb{R}^{(n-p),(n-p)}$ in such a way that $y = Ax$ if and only if $y^+ = A^{++}x^+ + A^{+0}x^0$ and $y^0 = A^{0+}x^+ + A^{00}x^0$.

PROPOSITION 11. *Assume that, for some $1 \leqslant p < n$, we have $Y_k > 0$, for $1 \leqslant k \leqslant p$, and $Y_k = 0$, for $p + 1 \leqslant k \leqslant n$. Then the corresponding block decompositions of the matrices $C$ and $\Gamma$,*

$$C = \begin{bmatrix} C^{++} & C^{+0} \\ C^{0+} & C^{00} \end{bmatrix}, \qquad \Gamma = \begin{bmatrix} \Gamma^{++} & \Gamma^{+0} \\ \Gamma^{0+} & \Gamma^{00} \end{bmatrix}, \tag{3.22}$$

*are such that $C^{0+} = \Gamma^{0+} = 0$, $C^{00}$ and $\Gamma^{00}$ are diagonal and inverse of each other, i.e., $C^{00} = \operatorname{diag}(\delta_{p+1}, \ldots, \delta_n)$, $\Gamma^{00} = \operatorname{diag}(\Gamma_{(p+1)(p+1)}, \ldots, \Gamma_{nn})$, and $\delta_k \Gamma_{kk} = 1$, for $k \in [(p+1), n]$, and $C^{++}$ and $\Gamma^{++}$ are exactly the matrices $C^{[p]}$ and $\Gamma^{[p]}$ that would be obtained by considering only the mixture of $p$ nonzero mass fractions $Y^+ = (Y_1, \ldots, Y_p)$, with the convention that $C^{[1]}$ and $\Gamma^{[1]}$ are the zero $1 * 1$ matrices. In particular, whenever $Y_k = 0$, we have*

$$F_k = -\delta_k G_k, \qquad \delta_k = \frac{W}{W_k} \Big/ \sum_{\substack{l \in [1,n] \\ l \neq k}} \frac{X_l}{\mathcal{D}_{kl}},$$

*so that the mass flux $F_k$ is proportional to $G_k$.*

*Proof.* From (3.16)(3.14) we first get that $\Gamma^{++} = \Gamma^{[p]}$, $\Gamma^{0+} = 0$ and $\Gamma^{00}$ is diagonal with positive elements $\Gamma_{(p+1)(p+1)}, \ldots, \Gamma_{nn}$. From the relation $\Gamma C = I - (Y \otimes U)/\langle U, Y \rangle$ and the block decomposition (3.22) we then deduce that $\Gamma^{00} C^{0+} = 0$ so that $C^{0+} = 0$ and $\Gamma^{00} C^{00} = I$ since $Y^0 = 0$. Now let $z^+ \in \mathbb{R}^p$ such that $z^+ \in R(C^{++})$; then $z^+ = C^{++}x^+$ for some $x^+ \in \mathbb{R}^p$. Letting now $z = (z^+, 0)$ and $x = (x^+, 0)$ we get $z = Cx$ and thus $z \in R(C) = U^\perp$. Therefore $\langle U, z \rangle = \langle U^+, z^+ \rangle = 0$ and $z^+ \in (U^+)^\perp$. Conversely if $z^+ \in (U^+)^\perp$ then for $z = (z^+, 0)$ we have $z \in U^\perp = R(C)$ and thus $z = Cx$ for some $x \in \mathbb{R}^n$. Now since $C^{0+} = 0$ and $C^{00}$ is invertible we get that $z^0 = C^{00}x^0 = 0$ so that $x^0 = 0$ and $x = (x^+, 0)$, $z^+ = C^{++}x^+$ and $z^+ \in R(C^{++})$. We have thus shown that $R(C^{++}) = (U^+)^\perp$ and since $CY = 0$ we deduce that $C^{++}Y^+ = 0$ and thus $N(C^{++}) = \mathbb{R}Y^+$. On the other hand we get from (3.18) that $C^{++}\Gamma^{++} = \Gamma^{++}C^{++} = I - (Y^+ \otimes U^+)/\langle U, Y \rangle$. Finally, multiplying this equality by $C^{++}$ and $\Gamma^{++}$ we obtain that $C^{++}\Gamma^{++}C^{++} = C^{++}$ and $\Gamma^{++}C^{++}\Gamma^{++} = \Gamma^{++}$ and thus $C^{++}$ is the group inverse of $\Gamma^{++} = \Gamma^{[p]}$. Therefore, if $p \geqslant 2$, $C^{++}$ is exactly the diffusion matrix $C^{[p]}$ that would be obtained by considering the $p$ species mixture $Y^+ = (Y_1, \ldots, Y_p)$, whereas if $p = 1$, $C^{++}$ is the zero $1 * 1$ matrix.

We now investigate the limit of the coefficients $D_{kl}$, $k$, $l \in [1, n]$, when some mass fractions are vanishing. From Proposition 9, we know that for $Z \in \mathbb{R}^n$, $Z > 0$, we have $D_{kl}(Z) = C_{kl}(Z)/Z_k$, $k$, $l \in [1, n]$. Let then $Y \in \mathbb{R}^n$ with $Y = (Y^+, Y^0)$, $Y^+ \in \mathbb{R}^p$, $Y^0 \in \mathbb{R}^{n-p}$, $Y^+ > 0$ and $Y^0 = 0$. Keeping in mind that the matrix $C$ is a smooth function of $Z$, from Proposition 10, and that $C_{kl}(Y) = 0$ for $p + 1 \leqslant k \leqslant n$ and $k \neq l$, from Proposition 11, we can pass to the limit in the latter relations to obtain that

$$\lim_{\substack{Z\to Y\\ Z>0}} D_{kl}(Z) = \frac{C_{kl}(Y)}{Y_k}, \qquad k \in [1, p], \qquad l \in [1, n],$$

$$\lim_{\substack{Z\to Y\\ Z>0}} D_{kl}(Z) = \frac{\partial C_{kl}}{\partial Y_k}(Y), \qquad k \in [p+1, n], \qquad l \in [1, n], \qquad k \neq l,$$

and

$$\lim_{\substack{Z\to Y\\ Z>0}} Z_k D_{kk}(Z) = C_{kk}(Y) > 0, \qquad k \in [p+1, n].$$

This shows that, in the case of vanishing mass fractions, all diffusion coefficients $D_{kl}$ have finite limits, excepted the diagonal coefficients $D_{kk}$, $p + 1 \leqslant k \leqslant n$, corresponding to the vanishing mass fractions species, which are blowing up.

### 3.4. *Miscellaneous*

In the preceding sections, we have considered the linear relations between the diffusion velocities $V$ and diffusion driving forces $G$ which are given in terms of the gradients of the mole fractions $\nabla X_k$. However, the mass fractions are often chosen as the fundamental unknowns—together with the density $\rho$, the mass average velocity $v$ and the temperature $T$—for solving the multicomponent laminar reacting flow governing equations. In particular, an especially interesting situation is the approximation $G_k = \nabla X_k$, for which it becomes possible to express the diffusion velocities in terms of the gradients of the mass fractions $H_k = \nabla Y_k$ only. It is therefore interesting to investigate the corresponding linear relations between $V$ and $H$ where $H = (H_1, \ldots, H_n)$. Under the approximation $G_k = \nabla X_k$, $k \in [1, n]$, the linear relation between $G$ and $H$ is easily deduced from (3.14) and can be written in the form

$$G = EH,$$

with $E = (E_{kl})$ given by

$$E_{kk} = \frac{W}{W_k} + \frac{X_k}{\langle U, Y\rangle}\left(1 - \frac{W}{W_k}\right), \qquad k \in [1, n],$$

$$E_{kl} = \frac{X_k}{\langle U, Y\rangle}\left(1 - \frac{W}{W_l}\right), \qquad k, l \in [1, n], \qquad k \neq l.$$

Since this matrix $E$ is regular [7] it is therefore immediate to deduce the properties of the matrices $D' = DE$ and $\Delta' = E^{-1}\Delta$, which are such that $V = -D'H$ and $H = -\Delta' V$, by simply rewriting the corresponding properties of $D$ and $\Delta$. For instance we deduce from Lemma 1 that $N(D') = \mathbb{R}M$ and $N(D') = Y^{\perp}$, where $EM = Y$. We shall thus not consider these matrices any more in the next sections. Remark however that some of the properties of $D$ and $\Delta$ do not hold for $D'$ and $\Delta'$. For instance $D'$ and $\Delta'$ are not symmetric in general and the matrix $\Delta'$ is not always in the set $Z^{n,n}$.

Because of the considerable simplifications that may result, we now investigate the situations where the diffusion process can be represented by a diagonal matrix. In other words, we want to identify the cases where the matrix $D$ coincides with a diagonal matrix on the physical hyperplane $U^{\perp}$. Remark that this situation differs from the usual excess species approximation for which $D$ is approximated by a diagonal matrix on a subspace $S$ of dimension $n - 1$ which differs from $U^{\perp}$. We first consider the case where the velocities $V$ are expressed in terms of the diffusion driving forces $G$ and we then consider the case where the velocities $V$ are expressed in terms of the gradients of the mass fractions $H$.

PROPOSITION 12. *The matrix D coincides with a diagonal matrix on the subspace $U^{\perp}$ if and only if the numbers $W_k W_l \mathcal{D}_{kl}$, $k, l \in [1, n]$, $k \neq l$, are equal. In this situation we have*

$$D = \mathcal{D}\left(\mathcal{Y}^{-1} - \frac{U \otimes U}{\langle U, Y\rangle}\right), \tag{3.23}$$

*where $\mathcal{D}$ denotes the common value of the $W_k W_l \mathcal{D}_{kl}/(W^2\langle U, Y\rangle)$ for $k \neq l$.*

PROPOSITION 13. *The matrix DE coincides with a diagonal matrix on the subspace $U^{\perp}$ if and only if the numbers $\mathcal{D}_{kl}$, $k, l \in [1, n]$, $k \neq l$, are equal. In this situation we have*

$$DE = \mathcal{D}\left(\mathcal{Y}^{-1} - \frac{Z \otimes U}{\langle U, Y\rangle}\right), \tag{3.24}$$

*where $\mathcal{D}$ denotes the common value of the $\mathcal{D}_{kl}/\langle U, Y\rangle$ for $k \neq l$ and $Z = \mathcal{Y}^{-1}E^{-1}Y$.*

*Proof.* Only the proof of Proposition 13 is given. The proof of Proposition 12 would be similar. By assumptions there exists a diagonal matrix $\Phi = \mathrm{diag}(\phi_1, \ldots, \phi_n)$ such that $U^\perp \subset N(DE - \Phi)$. Thus there exists a vector $C$ such that $DE - \Phi = C \otimes U$. By transposing this relation, we also obtain that $E^T D - \Phi = U \otimes C$. Next from $DY = 0$ and the latter relations we deduce that $\phi_k Y_k = -\langle C, Y \rangle$ and that $\phi_k M_k = -C_k \langle M, U \rangle$, where we have introduced $M = E^{-1} Y$. Noting now that $\langle Y, U \rangle = \langle EM, U \rangle = \langle M, E^T U \rangle$ we also obtain that $\langle Y, U \rangle = \langle M, U \rangle$, since $E^T U = U$. Therefore, defining $\mathcal{D} = -\langle C, Y \rangle$, we can write, after a little bit of algebra, that $DE = \mathcal{D}(\mathcal{Y}^{-1} - Z \otimes U / \langle U, Y \rangle)$, where we have introduced $Z$ such that $Z = \mathcal{Y}^{-1} E^{-1} Y$. Multiplying on the right by $E^{-1}$ we then get $D = \mathcal{D}((E\mathcal{Y})^{-1} - Z \otimes U / \langle U, Y \rangle)$ since for $a, b \in \mathbb{R}^n$ and $A \in \mathbb{R}^{n,n}$ one has $a \otimes bA = a \otimes (A^T b)$ and since $(E^{-1})^T U = U$. By using this expression of $D$, the relation $D\Delta = I - U \otimes Y / \langle U, Y \rangle$, and the fact that $\Delta^T U = \Delta U = 0$, we then deduce that $\Delta = (1/\mathcal{D}) E\mathcal{Y}(I - U \otimes Y / \langle U, Y \rangle)$. Keeping in mind that for $a, b \in \mathbb{R}^n$ and $A \in \mathbb{R}^{n,n}$ one has $Aa \otimes b = (Aa) \otimes b$, and using then the properties $E\mathcal{Y}U = EY = X$ and $E\mathcal{Y} = \mathcal{X} + X \otimes (Y - X) / \langle U, Y \rangle$, where $\mathcal{X} = \mathrm{diag}(X_1, \ldots, X_n)$, we finally obtain that $\Delta = (1/\mathcal{D})(\mathcal{X} - X \otimes X / \langle U, Y \rangle)$. Therefore, all the binary diffusion coefficients $\mathcal{D}_{kl}$, $k, l \in [1, n]$, $k \neq l$, are equal to $\mathcal{D}\langle U, Y \rangle$.

Conversely, assume that all binary diffusion coefficients are equal. In this situation, one can easily check that $\Delta = (1/\mathcal{D})(\mathcal{X} - X \otimes X / \langle U, Y \rangle)$, where $\mathcal{D}\langle U, Y \rangle$ denotes the common value of the binary diffusion coefficients and where $\mathcal{X} = \mathrm{diag}(X_1, \ldots, X_n)$. Using then the relations $X = EY$ and $\mathcal{X} = E\mathcal{Y} - X \otimes (Y - X) / \langle U, Y \rangle$ we thus get that $\Delta = (1/\mathcal{D}) E(\mathcal{Y} - Y \otimes Y / \langle U, Y \rangle)$. Multiplying this expression on the right by $D$ and using the identities $\Delta D = I - Y \otimes U / \langle U, Y \rangle$ and $D^T Y = DY = 0$ we thus get that $D = \mathcal{D}(E\mathcal{Y})^{-1}(I - Y \otimes U / \langle U, Y \rangle)$. Multiplying on the right by $E$ and using $E^T U = U$ we finally obtain (3.24) so that $DE$ is diagonal on $U^\perp$ and the proof is complete.

Proposition 13 shows that a generalized Fick's law of the type $F_k = Y_k V_k = -\alpha_k H_k$, where $\alpha_k$ is a scalar, cannot be used for all the species, $k \in [1, n]$, unless all the proportionality coefficients $\alpha_k$, $k \in [1, n]$, are equal, i.e., $\alpha_1 = \cdots = \alpha_n$. In this situation, all the binary diffusion coefficients $\mathcal{D}_{kl}$, $k, l \in [1, n]$, $k \neq l$, are also equal.

## 4. Iterative Methods for Multicomponent Diffusion

### 4.1. *Iterative Methods for Diffusion Velocities*

In this section, we investigate the convergence of iterative methods for the Stefan–Maxwell diffusion equations (3.5), where $\Delta$ is given by (3.13)(3.14).

More specifically, for a given vector $G \in U^{\perp}$, we want to solve the consistent singular system $G = -\Delta V$ by iteration techniques and we want to obtain the only solution $V$ which is in $Y^{\perp}$, i.e., $V = -DG$. We assume here that $Y > 0$. We now state the main result of this section.

THEOREM 14. *Let $\Delta$ be as in (3.13)(3.14) and keep the assumptions of Proposition 7. Let $M = \operatorname{diag}(M_1, \ldots, M_n)$ be such that $M_k > \Delta_{kk}$, for $k \in [1, n]$, so that the splitting $\Delta = M - Z$ is regular. Denote $P = P_{Y^{\perp}, \mathbb{R}U}$, $Q = P_{U^{\perp}, \mathbb{R}Y}$, and $T = M^{-1}Z = I - M^{-1}\Delta$; let $x_0 \in \mathbb{R}^n$, $y_0 = Px_0$, and $G \in U^{\perp}$; and define also*

$$x_{i+1} = Tx_i + M^{-1}(-G), \qquad i \geqslant 0, \tag{4.1}$$

$$y_{i+1} = PTy_i + PM^{-1}(-G), \qquad i \geqslant 0. \tag{4.2}$$

*Then $y_i = Px_i$, for all $i \geqslant 0$, $\rho(T) = 1$, $\rho(PT) < 1$ and*

$$V = P(\lim_{i\to\infty} x_i) = \lim_{i\to\infty} y_i, \tag{4.3}$$

*where $V$ is the unique solution of $\Delta V = -G$ in the subspace $Y^{\perp}$. Moreover, if $D$ is the generalized inverse of $\Delta$ with prescribed range $Y^{\perp}$ and nullspace $\mathbb{R}Y$, then we have*

$$D = \sum_{k=0}^{\infty} (PT)^k PM^{-1}Q, \tag{4.4}$$

*and each partial sum $D_i = \sum_{k=0}^{i} (PT)^k PM^{-1}Q$ of this series is symmetric, satisfies $D_iY = 0$, and is positive definite on $U^{\perp}$.*

*Proof.* Since $M_k > \Delta_{kk}$, for $k \in [1, n]$, it is easy to check that $\Delta = M - Z$ is a regular splitting. Denoting $T = M^{-1}Z$, first note that we have $T > 0$ because $Z > 0$ and from $\Delta U = 0$ we also obtain $TU = U$. This shows that $\sum_{k\in[1,n]} T_{kl} = 1$, for $l \in [1, n]$. From the Gershgorin theorem [18, p. 16] we thus get that $\rho(T) \leqslant 1$ and thus $\rho(T) = 1$ since $TU = U$. However $T$ is a primitive matrix because $T > 0$ [18, p. 40] and thus $T$ has only one eigenvalue of maximum modulus and this eigenvalue is $\rho(T)$ [18, p. 35] and therefore $\gamma(T) < 1$. Since $I - T = M^{-1}\Delta$, we also deduce from Lemma 1 that $N(I - T) = \mathbb{R}U$ and $R(I - T) = M^{-1}(U^{\perp}) = (MU)^{\perp}$ since $M = M^T$. We thus obtain that $N(I - T) \cap R(I - T) = \{0\}$ because $\langle MU, U\rangle > 0$ and thus $(I - T)^{\#}$ exists and the matrix $T$ is convergent. We now prove that $\rho(PT) < 1$. Let $P'$ denote the projection on the join of all root subspaces of $T$ associated with the eigenvalues other than 1 along the eigenspace of $T$ associated with the eigenvalue 1, i.e., $\mathbb{R}U$. By definition of $\gamma(T)$, we have the relation

$\gamma(T) = \rho(TP')$ and it is well known that $P'$ commutes with $T$. One can also easily check that $PP' = P$ and $P'P = P'$. Keeping in mind that for any $A$, $B \in \mathbb{R}^{n,n}$, $\rho(AB) = \rho(BA)$, we now obtain that [14, Theorem 2]

$$\gamma(T) = \rho(TP') = \rho(TP'P) = \rho(PTP') = \rho(PP'T) = \rho(PT)$$

so that $\rho(PT) < 1$. Since $T$ is convergent and $M^{-1}(-G) \in R(I - T)$, we deduce that the sequence $\{x_i;\, i \geq 0\}$ is convergent and since $\rho(PT) < 1$ we deduce that the sequence $\{y_i;\, i \geq 0\}$ is also convergent. Denoting $x_\infty$ and $y_\infty$ the corresponding limits, we get from (4.1) that $\Delta(x_\infty - V) = 0$ so that $x_\infty - V \in \mathbb{R}U$. Therefore we have $P(x_\infty - V) = 0$ and thus $V = Px_\infty$ since $PV = V$. Moreover a direct calculation yields that $PT = PTP$ since $TU = U$ and $PU = 0$. Therefore from $x_{i+1} = Tx_i + M^{-1}(-G)$ we deduce that $Px_{i+1} = PTx_i + PM^{-1}(-G)$ and thus $Px_{i+1} = PT(Px_i) + PM^{-1}(-G)$ and a straightforward induction shows that $y_i = Px_i$ for all $i \geq 0$ and thus $y_\infty = Px_\infty = V$. Finally, since $\rho(PT) < 1$, we know that the series in (4.4) converges in $\mathbb{R}^{n,n}$ [18, p. 82]. Moreover, for $x \in U^\perp$, we have $Qx = x$ and from (4.2)(4.3) we deduce that the images of $x$ under both members of (4.4) are identical. Moreover the same is true if $x \in \mathbb{R}Y$ since then both images are zero and thus (4.4) holds since $\mathbb{R}Y \oplus U^\perp = \mathbb{R}^n$. Now from $PT = PTP$, one easily deduces by induction that $PT^k = (PT)^k P$ for $k \geq 0$ and this implies that $(PT)^k PM^{-1}Q$ is symmetric since $Q = P^T$ and $PT^k M^{-1}Q = P(M^{-1}Z)^k M^{-1}P^T$ is symmetric for all $k \geq 0$ because $M^{-1}$ and $Z$ are symmetric. Therefore $D_i$ is symmetric and of course $D_i Y = 0$ by construction since $QY = 0$. Furthermore, after a little bit of algebra, one may check that for $k = 2l$, $l \geq 0$, we have

$$\langle (PT)^k PM^{-1}Qx, x\rangle = \langle Mz, z\rangle$$

and

$$\langle (PT)^k PM^{-1}Qx, x\rangle + \langle (PT)^{k+1} PM^{-1}Qx, x\rangle = \langle (2M - \Delta)z, z\rangle,$$

where $z = T^l M^{-1}Qx$. On the other hand, for $x \in \mathbb{R}^n$, we obtain that

$$\langle (2M - \Delta)x, x\rangle = \sum_{k\in[1,n]} 2(M_k - \Delta_{kk})x_k^2 + \frac{1}{2} \sum_{\substack{k,l\in[1,n]\\ k\neq l}} |\Delta_{kl}|(x_k + x_l)^2,$$

so that $2M - \Delta$ is positive definite. Therefore we have for $l \geq 0$ and $x \in \mathbb{R}^n$

$$\langle (2M - \Delta)M^{-1}Qx, M^{-1}Qx\rangle = \langle D_1 x, x\rangle \leq \langle D_{(2l+1)}x, x\rangle \leq \langle D_{(2l+2)}x, x\rangle,$$

whereas $\langle D_0 x, x\rangle = \langle MQx, Qx\rangle$. This shows that all the matrices $D_i$, $i \geqslant 0$, are positive definite on $U^\perp$ and the proof is complete.

Remark here that the proof of Theorem 14 is based on the properties of matrices with convergent powers and the properties of nonnegative matrices. However, some of the results established in this proof can also be deduced from the properties of singular $M$-matrices [14] or symmetric positive semidefinite matrices [15]. First, it is shown in [14] that if $\Delta$ is monotone on a subspace $S$ complementary to $N(\Delta)$, then, for any regular splitting $\Delta = M - Z$, we have $\rho(T) \leqslant 1$ and $(I - T)^{\#}$ exists [14, Theorem 1]. Considering however $Y^\perp$, which is a complementary space to $N(\Delta) = \mathbb{R}U$, then $\Delta$ is monotone on $Y^\perp$. Indeed, if $x \in Y^\perp$ and $\Delta x \geqslant 0$ then we have $\tilde{\Delta}x = \Delta x \geqslant 0$. But for any fixed value of $\beta$ such that $0 < \beta \leqslant \beta^*$ we have $\tilde{D} \geqslant 0$. Therefore $\tilde{D}\tilde{\Delta}x \geqslant 0$ and thus $x \geqslant 0$. The fact that $\rho(PT) < 1$ is also a consequence of the results of Neumann and Plemmons [14, Theorem 2]. On the other hand, it is shown by Keller in [15] that if $A$ is a symmetric matrix and $A = M - Z$ a splitting such that $M + Z^T$ is positive definite, then the matrix $T = M^{-1}Z$ is convergent if and only if $A$ is positive semidefinite [15, Theorem 2]. However, in our situation, we have $A = \Delta$ which is positive semidefinite from Proposition 7 and $M + Z^{\mathrm{T}} = 2M - \Delta$ which has already been shown to be positive definite and thus $T = M^{-1}Z$ is a convergent matrix.

It is interesting to note that the splitting

$$M_k = \frac{\Delta_{kk}}{1 - Y_k/\langle Y, U\rangle} = \frac{X_k}{D_k^*}, \qquad D_k^* = \left(1 - \frac{Y_k}{\langle Y, U\rangle}\right) \Big/ \sum_{\substack{l \in [1,n] \\ l \neq k}} \frac{X_l}{\mathcal{D}_{kl}},$$

is well defined and satisfies the hypotheses of Theorem 14 since $Y > 0$ and thus $0 < 1 - (Y_k/\langle Y, U\rangle) < 1$ and $0 < \Delta_{kk} < M_k$. For this particular splitting, the vector $M^{-1}(-G)$ corresponds to the so called Hirschfelder–Curtiss approximated diffusion velocities $V$ [24] and the vector $PM^{-1}(-G)$ exactly corresponds to the Hirschfelder–Curtiss approximated velocities with a species independent mass correction velocity [10–11]. This shows that the widely used approximations $V \simeq PM^{-1}(-G)$ for $V$, which have formerly been considered as ad hoc approximations, have indeed a rigorous justification. Note that for $G \in U^\perp$, the latter approximations can be written in the symmetric form $PM^{-1}Q(-G)$. Remark also that a justification for choosing this particular splitting is, for instance, to substitute the approximation $D \simeq M^{-1}$ into the relation (3.10) and to identify the corresponding diagonals. For this particular splitting, the iterative scheme (4.1) has been introduced by Oran and Boris [8] and Jones and Boris [9]. To the author's knowledge, the projected algorithm (4.2), the asymptotic expansion (4.4), and the convergence results are new. Note also that the components in $\mathbb{R}U$, according to the direct sum

$\mathbb{R}U \oplus R(I - T) = \mathbb{R}^n$, of $x_0$ and of successive roundoff errors remain undamped with the algorithm (4.1) [15], at variance with the algorithm (4.2) for which $\rho(PT) < 1$. Finally, for this particular splitting, it is easy to show, by a straightforward calculation, that the iteration matrix $PT = P(I - M^{-1}\Delta)$ is zero if and only if the numbers $W_k W_l \mathcal{D}_{kl}$, $k, l \in [1, n]$, $k \neq l$, are equal.

We now investigate the convergence of iterative methods for the modified Stefan–Maxwell diffusion equations. More specifically, for a given vector $G \in U^\perp$, we want to solve the regular system $G = -\tilde{\Delta}V$, where $\tilde{\Delta} = \Delta + \beta Y \otimes Y$, by iteration techniques. From the definition of $\tilde{\Delta}$, this solution $V$ is in $Y^\perp$ since $U^\perp = \tilde{\Delta}(Y^\perp)$. As an immediate corollary of Theorem 14 we deduce the following very useful result.

COROLLARY 15. *Keep the assumptions and notations of Theorem* 14, *let* $\alpha$ *and* $\beta$ *be positive numbers such that* $\alpha\beta\langle Y, U\rangle^2 = 1$, *and let* $\tilde{D} = \tilde{\Delta}^{-1}$. *Then we have*

$$\tilde{D} = \sum_{k=0}^{\infty} (PT)^k PM^{-1}Q + \alpha U \otimes U, \tag{4.5}$$

*and each partial sum* $\tilde{D}_i = \sum_{k=0}^{i} (PT)^k PM^{-1}Q + \alpha U \otimes U$ *of this series is symmetric, satisfies* $\tilde{D}_i(U^\perp) = Y^\perp$, *and is positive definite.*

The first approximation $\tilde{D}_0 = PM^{-1}Q + \alpha U \otimes U$ has been used by the author in [7] (without the $Q$ factor) in order to suppress artificial singularities due to mass conservation constraints when all mass fractions are considered as independent unknowns. On the other hand, it is also possible to obtain convergence results for different splittings of $\tilde{\Delta}$ which rely on more classical results for regular $M$-matrices. It is well known for instance that for $A \in \mathbb{R}^{n,n}$, if $A = M - Z$ is a regular splitting, $A$ is invertible, and $A^{-1} \geqslant 0$, then $\rho(M^{-1}Z) < 1$ [18, p. 89]. We may therefore state:

THEOREM 16. *Let* $\tilde{\Delta}$ *be as in Proposition* 8 *and assume that* $\beta \in (0, \beta^*]$. *Let also* $M = \operatorname{diag}(M_1, \ldots, M_n)$ *be such that* $M_k \geqslant \tilde{\Delta}_{kk}$, *for* $k \in [1, n]$. *Then the splitting* $\tilde{\Delta} = M - Z$ *is regular and* $\rho(M^{-1}Z) < 1$. *There exist also a unique value of* $\beta$ *in* $(0, \beta^*]$ *and a unique splitting* $\tilde{\Delta} = M - Z$ *which yields a minimum value for the spectral radius* $\rho(M^{-1}Z)$ *of the iteration matrix* $M^{-1}Z$. *This value is* $\beta = \beta^*$ *and the splitting is* $M = \operatorname{diag}(\tilde{\Delta}_1, \ldots, \tilde{\Delta}_n)$.

*Proof.* First, the convergence statements are consequences of well known results on regular $M$-matrices [18, p. 89] since for $\beta \in (0, \beta^*]$ we have $\tilde{D} \geqslant 0$. Assume then that $\beta \in (0, \beta^*)$ is fixed and let us denote by $M^*$ the matrix $M^* = \operatorname{diag}(\tilde{\Delta}_1, \ldots, \tilde{\Delta}_n)$ constituted by the main diagonal of $\tilde{\Delta}$. Let then $M = \operatorname{diag}(M_1, \ldots, M_n)$ be such that $M^* \leqslant M$ and $M^* \neq M$. Then, denoting $Z^* = M^* - \tilde{\Delta}$ and $Z = M - \tilde{\Delta}$, we have $0 \leqslant Z^* \leqslant Z$ and $Z^* \neq Z$. Now since $\tilde{D} > 0$ for $\beta \in (0, \beta^*)$, a classical comparison theorem [18, p. 90] yields that $\rho((M^*)^{-1}Z^*) < \rho(M^{-1}Z) < 1$ so that the asymptotic rate of convergence is minimized for the splitting $\Delta = M^* - Z^*$. Let now consider this splitting $\Delta = M^* - Z^*$ and its iteration matrix $T^* = (M^*)^{-1}Z^*$. The diagonal coefficients of $T^*$ are zero and its off diagonal coefficients are given by

$$T^*_{kl} = \frac{|\Delta_{kl}| - \beta Y_k Y_l}{|\Delta_{kk}| + \beta Y_k Y_k}$$

and thus are positive decreasing functions of $\beta$ since $Y > 0$. On the other hand, it is easy to check that $T^*$ is irreducible because $T^*_{1k} \neq 0$ and $T^*_{k1} \neq 0$ for $k \in [2, n]$ so that the graph of $T^*$ is strongly connected. However, it is well known that the spectral radius of an irreducible nonnegative matrix if a decreasing function of its coefficients [18, p. 30]. Therefore we have $\rho(T^*(\beta')) < \rho(T^*(\beta))$ for $0 < \beta < \beta'$, with obvious notations. Using the continuity of the spectral radius and passing to the limit $\beta \to \beta^*$ we deduce that the minimum spectral radius is obtained for $\beta = \beta^*$ and the proof is complete.

The approximated diffusion matrices corresponding to the iterative schemes of Theorem 16 will be shown to be of limited interest because the corresponding partial sums $\hat{D}_i = \sum_{k=0}^{i} T^k M^{-1}$ actually converge slower than the $\tilde{D}_i$ of Corollary 15. Moreover these partial sums do not satisfy the mass constraint $\hat{D}_i(U^\perp) = Y^\perp$ for $i \geq 1$.

### 4.2. *Iterative Methods for Diffusion Fluxes*

In this section, we investigate the convergence of iterative methods for the equations (3.17), where $\Gamma$ is given by (3.16)(3.14). More specifically, for a given vector $G \in U^\perp$, we want to solve the consistent singular system $G = -\Gamma F$ by iteration techniques and we want to obtain the only solution $F$ which is in $U^\perp$, i.e., $F = -CG$. We now assume only that $Y \geq 0$ and $Y \neq 0$. The following theorem is the main result of this section.

THEOREM 17. *Let $\Gamma$ be as in (3.16),(3.14) and keep the assumptions of Proposition 9. Let $L = \text{diag}(L_1, \ldots, L_n)$ be such that $L_k > \Gamma_{kk}$, if $Y_k > 0$, and $L_k \geq \Gamma_{kk}$, if $Y_k = 0$, for $k \in [1, n]$, so that the splitting $\Gamma = L - Z$ is regular. Denote $Q = P_{U^\perp, \mathbb{R}Y}$ and $S = L^{-1}Z = I - L^{-1}\Gamma$; let $x_0 \in \mathbb{R}^n$, $y_0 = Qx_0$, and $G \in U^\perp$; and define also*

$$x_{i+1} = Sx_i + L^{-1}(-G), \qquad i \geq 0, \tag{4.6}$$

$$y_{i+1} = QSy_i + QL^{-1}(-G), \qquad i \geq 0. \tag{4.7}$$

*Then $y_i = Qx_i$, for all $i \geq 0$, $\rho(S) = 1$, $\rho(QS) < 1$, and*

$$F = Q(\lim_{i\to\infty} x_i) = \lim_{i\to\infty} y_i, \tag{4.8}$$

*where $F$ is the unique solution of $\Gamma F = -G$ in the subspace $U^{\perp}$. Moreover, if $C$ is the group inverse of $\Gamma$, then we have*

$$C = \sum_{k=0}^{+\infty} (QS)^k Q L^{-1} Q. \tag{4.9}$$

*Proof.* Since $L_k \geqslant \Gamma_{kk}$, for $k \in [1, n]$, it is easy to check that $Z = L - \Gamma \geqslant 0$. Arguing now by contradiction, assume that for some $k$ we have $L_k = 0$. This implies that $L_k = \Gamma_{kk} = 0$ and thus that $Y_l = 0$, for $l \in [1, n]$, $l \neq k$. But since $Y \neq 0$ we deduce that $Y_k > 0$ and thus that $L_k > \Gamma_{kk}$ by assumption, an obvious contradiction. Thus $L_k > 0$, for $k \in [1, n]$, and $\Gamma = L - Z$ is a regular splitting. In order now to prove that $\gamma(S) < 1$, assume first that the mass fractions are positive, i.e., $Y > 0$. Then we have $S > 0$ so that $S$ is a primitive matrix. Furthermore from $\Gamma Y = 0$ we deduce that $SY = Y$ and $1 \in \sigma(S)$. Let now $\lambda \in \sigma(S)$. Then, noting that we have $\sigma(S) = \sigma(S^{\mathrm{T}}) = \sigma(Z^{\mathrm{T}} L^{-1})$ and $\sigma(Z^{\mathrm{T}} L^{-1}) = \sigma(L^{-1} Z^{\mathrm{T}})$, we deduce, from the Gershgorin Theorem, that $|\lambda| \leqslant 1$ since for $A = L^{-1} Z^{\mathrm{T}}$ we have $A \geqslant 0$ and $\sum_{l \in [1,n]} A_{kl} = 1$. Therefore $\rho(S) = 1$ and since $S$ is primitive we have $\gamma(S) < 1$. In the case of vanishing mass fractions, we may again assume, without loss of generality, that the nonzero mass fractions are $Y_1, \ldots, Y_p$ for some $1 \leqslant p < n$. Introducing then the partitioning $[1, n] = [1, p] \cup [p + 1, n]$, we decompose each vector of $\mathbb{R}^n$ and each matrix of $\mathbb{R}^{n,n}$ as in Proposition 11. It is easy to check then that $S^{0+} = 0$ and $S^{00} = \mathrm{diag}(\mu_{p+1}, \ldots, \mu_n)$ where $0 \leqslant \mu_k = 1 - (\Gamma_{kk}/L_k) < 1$ since $0 < \Gamma_{kk} \leqslant L_k$ for $k \in [p + 1, n]$. Therefore, if $\mu = \max_{k \in [p+1,n]} \mu_k$, then we have $\gamma(S) = \max(\gamma(S^{++}), \mu)$. Now, if $p \geqslant 2$, $S^{++}$ is exactly the matrix that would be obtained by considering only the mixture constituted of the $p$ nonzero mass fractions, for which we already know that $\gamma(S^{++}) < 1$, whereas if $p = 1$, then $S^{++}$ is the unity $1 * 1$ matrix and thus $\gamma(S^{++}) = 0$. This shows that $\gamma(S^{++}) < 1$ and thus that $\gamma(S) < 1$. Since $I - S = L^{-1}\Gamma$, we deduce from Proposition 9 that $N(I - S) = \mathbb{R}Y$ and $R(I - S) = L^{-1}(U^{\perp}) = (LU)^{\perp}$ since $L = L^{\mathrm{T}}$. We thus obtain that $N(I - S) \cap R(I - S) = \{0\}$ because $\langle LU, Y \rangle > 0$, keeping in mind that $Y \neq 0$, $Y \geqslant 0$ and $L_k > \Gamma_{kk} \geqslant 0$ whenever $Y_k > 0$ by assumption, and thus $(I - S)^{\#}$ exists and the matrix $S$ is convergent. Moreover, proceeding as in the proof of Theorem 14, one can easily prove that $\gamma(S) = \rho(QS)$, so that $\rho(QS) < 1$. Now since $S$ is convergent and $L^{-1}(-G) \in R(I - S)$, we deduce that the sequence $\{x_i; i \geqslant 0\}$ is convergent and since $\rho(QS) < 1$ we deduce that the sequence $\{y_i; i \geqslant 0\}$ is also convergent. Denoting by $x_\infty$ and $y_\infty$ the corresponding limits, we get from (4.6) that $\Gamma(x_\infty - F) = 0$ so that $x_\infty - F \in \mathbb{R}Y$. Therefore we have $Q(x_\infty - F) = 0$ and thus $F = Qx_\infty$ since $QF = F$. A direct calculation also yields that $QS = QSQ$ which in turn implies that $y_i = Qx_i$, for $i \geqslant 0$, and thus that $y_\infty = Qx_\infty = F$. Finally, the formula (4.9) is obtained as in the proof of Theorem 14.

Assume now that there are at least two nonzero mass fractions, i.e., $p \geqslant 2$. Then the usual splitting

$$L_k = \frac{\Gamma_{kk}}{1 - Y_k/\langle Y, U\rangle} = \frac{W}{W_k}\frac{1}{D_k^*}, \qquad D_k^* = \left(1 - \frac{Y_k}{\langle Y, U\rangle}\right) \Big/ \sum_{\substack{l\in[1,n]\\ l\neq k}} \frac{X_l}{\mathcal{D}_{kl}},$$

is well defined since $0 < 1 - (Y_k/\langle Y, U\rangle)$, for $k \in [1, n]$, and satisfies the hypotheses of Theorem 17 since $1 - (Y_k/\langle Y, U\rangle) < 1$ if and only if $Y_k > 0$, and thus $0 < \Gamma_{kk} < L_k$, if $Y_k > 0$, and $0 < \Gamma_{kk} = L_k$, if $Y_k = 0$. Here again the vector $L^{-1}(-G)$ corresponds to the Hirschfelder–Curtiss approximated diffusion fluxes $F$ and, for $G \in U^\perp$, the vector $QL^{-1}(-G)$ exactly corresponds to the Hirschfelder–Curtiss approximations with mass correction fluxes proportional to the mass fractions $Y$. This shows that the widely used approximations $F \simeq QL^{-1}(-G)$ for $F$ also have a rigorous justification, even in the case of vanishing mass fractions, provided there are at least two nonzero mass fractions in the mixture. On the other hand, in the case of a pure species state of the mixture $Y = (1, 0, \ldots, 0)$, we have $\Gamma_{11} = 0$, and it is easy to check that any splitting $\Gamma = L - Z$ such that $L = \mathrm{diag}(\Upsilon, \Gamma_{22}, \ldots, \Gamma_{nn})$, where $\Upsilon > 0$ is arbitrary, leads to a one step convergence of the sequence (4.7). Although the coefficients $D_k^*$, $k \in [1, n]$, do not provide such a splitting, because then $D_1^*$ is undefined, an interesting numerical procedure for evaluating these mixture diffusion coefficients has been introduced by Kee, Warnatz, and Miller [11]. It consists in evaluating perturbed coefficients $D_k^*(\epsilon)$ defined by

$$D_k^*(\epsilon) = \sum_{\substack{l\in[1,n]\\ l\neq k}} \frac{W_l(X_l + \epsilon)}{W\langle Y, U\rangle} \Big/ \sum_{\substack{l\in[1,n]\\ l\neq k}} \frac{(X_l + \epsilon)}{\mathcal{D}_{kl}}, \tag{4.10}$$

where $\epsilon$ is a small positive constant, typically smaller than the machine precision. Now for a pure species state $Y = (1, 0, \ldots, 0)$, this formula yields $D_k^*(\epsilon) = D_k^* + O(\epsilon)$, for $k \in [2, n]$, whereas it gives an arbitrary but positive $D_1^*(\epsilon) > 0$, for $k = 1$. Defining now $L_k = W/(W_k D_k^*(\epsilon))$, for $k \in [1, n]$, we obtain a regular splitting, and thus a one step convergence of the algorithm (4.7), with an arbitrary but positive $L_1 = \Upsilon > 0$. Finally, to the author's knowledge, the algorithms (4.6) and (4.7), the asymptotic expansion (4.9), and the convergence results are new.

We now investigate the convergence of iterative methods for the modified fluxes equations. More specifically, for a given vector $G \in U^\perp$, we want to solve the regular system $G = -\tilde{\Gamma}F$ by iteration techniques. From the definition of $\tilde{\Gamma}$, this solution $F$ is in $U^{\perp}$ since $U^{\perp} = \tilde{\Gamma} U^{\perp}$. As an immediate consequence of Theorem 17 we deduce the following very useful result.

COROLLARY 18. *Keep the assumptions and notations of Theorem* 17, *let* $\alpha$ *and* $\beta$ *be positive numbers such that* $\alpha\beta\langle Y, U\rangle^2 = 1$, *and let* $\tilde{C} = \tilde{\Gamma}^{-1}$. *Then we have the identity*

$$\tilde{C} = \sum_{k=0}^{\infty} (QS)^k Q L^{-1} Q + \alpha Y \otimes U. \tag{4.11}$$

Different algorithms could also be used to invert $\tilde{\Delta}$ and, as in the preceding sections, one may indeed prove the following theorem whose proof is omitted.

THEOREM 19. *Let* $\tilde{\Gamma}$ *be as in Proposition* 10, *assume that* $\beta \in (0, \beta^*]$, *and let* $L = \mathrm{diag}(L_1, \ldots, L_n)$ *be such that* $L_k \geqslant \tilde{\Gamma}_{kk}$, *for* $k \in [1, n]$. *Then the splitting* $\tilde{\Gamma} = L - Z$ *is regular and* $\rho(L^{-1}Z) < 1$. *Moreover, assuming that there are at least two nonzero mass fractions, there exists a unique value of* $\beta \in (0, \beta^*]$ *and a unique splitting* $\tilde{\Gamma} = L - Z$ *which yields a minimum value for the spectral radius* $\rho(L^{-1}Z)$ *of the iteration matrix* $L^{-1}Z$ *and a one step convergence for the velocities* $V_k$ *corresponding to the vanishing mass fractions species. This value is* $\beta = \beta^*$ *and the splitting is simply* $M = \mathrm{diag}(\tilde{\Gamma}_1, \ldots, \tilde{\Gamma}_n)$.

## 5. NUMERICAL EXPERIMENTS

In this section, we test numerically the iterative schemes introduced in the preceding sections. Numerical tests are performed for a 9-species mixture used for hydrogen–air flame chemistry [25] and a 26-species mixture used for methane–air flame chemistry [26], at temperature $T = 1000$ K and pressure $p = 1$ atm conditions. The binary diffusion coefficients $\mathcal{D}_{kl}$ have been taken in the form

$$\mathcal{D}_{kl} = \frac{3}{16} \frac{\sqrt{2\pi k_B^3 T^3 / \mu_{kl}}}{p\pi\sigma_{kl}^2 \Omega^{(1,1)*}}, \tag{5.1}$$

where $\mu_{kl}$ is the reduced mass of the species pair $(k, l)$, $\sigma_{kl}$ the collision diameter of the species pair $(k, l)$, $k_B$ the Boltzmann constant, and $\Omega^{(1,1)*}$ a reduced collision integral. The reduced collision integrals $\Omega^{(1,1)*}$ depend on the reduced temperature $T_{kl}^* = k_B T / \epsilon_{kl}$, where $\epsilon_{kl}$ is the Lennard–Jones potential well depth of the species pair $(k, l)$, and on various other molecular parameters. The Chemkin and Transport packages have been used to evaluate these binary diffusion coefficients [11, 23, 27]. The mixture used for hydrogen–air flame chemistry [25] is constituted of the $n = 9$ species $H_2$, $O_2$, $N_2$, $H_2O$, H, O, OH, $HO_2$, and $H_2O_2$ and will be refered as "the hydrogen mixture." The mixture used for methane–air flame chemistry [26] is constituted of the $n = 26$ species $CH_4$, $CH_3$, $CH_2$, CH, $N_2$, $H_2$, $O_2$, $H_2O$, H, O, OH, $HO_2$, $H_2O_2$, $C_2H_6$, $C_2H_5$, $C_2H_4$, $C_2H_3$, $C_2H_2$, $C_2H$, $CH_2O$, $CH_3O$, $CH_2CO$, CHO, $CO_2$, CO, and $C_2HO$ and will be refered as "the methane mixture."

First, for each state $Y$ that we have considered and such that $Y > 0$ and $\langle Y, U \rangle = 1$, we have evaluated the first terms of the sequences of matrices $\{D_i; i \geqslant 0\}$, $\{\tilde{D}_i; i \geqslant 0\}$ and $\{\hat{D}_i; i \geqslant 0\}$ defined by

$$D_i = \sum_{k=0}^{i} (PT)^k PM^{-1}Q, \tag{5.2}$$

$$\tilde{D}_i = \sum_{k=0}^{i} (PT)^k PM^{-1}Q + \alpha U \otimes U, \tag{5.3}$$

and

$$\hat{D}_i = \sum_{k=0}^{i} \hat{T}^k \hat{M}^{-1}, \tag{5.4}$$

where $M = \text{diag}(M_1, \ldots, M_n)$, $M_k = \Delta_{kk}/(1 - Y_k)$, $T = I - M^{-1}\Delta$, $P = P_{Y^\perp, \mathbb{R}U}$, $Q = P_{U^\perp, \mathbb{R}Y}$, $\alpha = 1/\beta^*$, $\hat{M} = \text{diag}(\hat{M}_1, \ldots, \hat{M}_n)$, $\hat{M}_k = \tilde{\Delta}_{kk}$, $\hat{T} = I - \hat{M}^{-1}\tilde{\Delta}$, and $\tilde{\Delta} = \Delta + \beta^* Y \otimes Y$. For these sequences, which converge respectively to $D$, $\tilde{D}$, and $\tilde{D}$ from Theorem 14, Corollary 15 and Theorem 16, we have evaluated the corresponding reduced errors

$$e(D_i) = \|D - D_i\| / \|D\|,$$

$$e(\tilde{D}_i) = \|\tilde{D} - \tilde{D}_i\| / \|\tilde{D}\|,$$

and

$$e(\hat{D}_i) = \|\tilde{D} - \hat{D}_i\| / \|\tilde{D}\|,$$

where for any matrix $A \in \mathbb{R}^{n,n}$, $\|A\|$ denotes its Frobenius norm.

Similarly, for each state $Y$ that we have considered and such that $Y \geqslant 0$, $\langle Y, U \rangle = 1$, and $Y$ is not a pure species state, we have evaluated the first terms of the sequences of matrices $\{C_i; i \geqslant 0\}$, $\{\tilde{C}_i; i \geqslant 0\}$, and $\{\hat{C}_i; i \geqslant 0\}$ defined by

$$C_i = \sum_{k=0}^{i} (QS)^k QL^{-1}Q, \tag{5.5}$$

$$\tilde{C}_i = \sum_{k=0}^{i} (QS)^k QL^{-1}Q + \alpha Y \otimes U, \tag{5.6}$$

and

$$\hat{C}_i = \sum_{k=0}^{i} \hat{S}^k \hat{L}^{-1}, \tag{5.7}$$

where $L = \mathrm{diag}(L_1, \ldots, L_n)$, $L_k = \Gamma_{kk}/(1 - Y_k)$, $S = I - L^{-1}\Gamma$, $Q = P_{U^\perp, \mathbb{R}Y}$, $\alpha = 1/\beta^*$, $\hat{L} = \mathrm{diag}(\hat{L}_1, \ldots, \hat{L}_n)$, $\hat{L}_k = \tilde{\Gamma}_{kk}$, $\hat{S} = I - \hat{L}^{-1}\tilde{\Gamma}$, and $\tilde{\Gamma} = \Gamma + \beta^* Y \otimes U$. For these sequences, which converge respectively to $C$, $\tilde{C}$, and $\tilde{C}$ from Theorem 17, Corollary 18, and Theorem 19, we have evaluated the corresponding reduced errors

$$e(C_i) = \|C - C_i\| / \|C\|,$$

$$e(\tilde{C}_i) = \|\tilde{C} - \tilde{C}_i\| / \|\tilde{C}\|,$$

and

$$e(\hat{C}_i) = \|\tilde{C} - \hat{C}_i\| / \|\tilde{C}\|.$$

The errors $e(D_i)$, $e(\tilde{D}_i)$, $e(\hat{D}_i)$, $e(C_i)$, $e(\tilde{C}_i)$, and $e(\hat{C}_i)$, for $i = 0, \ldots, 4$, corresponding to the hydrogen and methane mixtures in the equimolar state, i.e., $X_k = 1/n$, $k \in [1, n]$, are given in Tables I and II respectively. These tables clearly indicate that the iterates (5.3) and (5.6) converge faster than (5.4) and (5.7), respectively, so that they are significantly more accurate. We also observe that the convergence behavior of the iterative schemes (5.2) and (5.5), and thus of (5.3) and (5.6), is excellent and is about the same for these two mixtures. On the other hand, in the case of vanishing concentrations, we have considered the hydrogen mixture in the two states $X_{H_2} = X_{O_2} = \frac{1}{2}$ and $X_{H_2} = X_{O_2} = X_{N_2} = \frac{1}{3}$, with all the other mole fractions set to zero,

TABLE I
REDUCED FROBENIUS ERRORS: HYDROGEN MIXTURE IN THE EQUIMOLAR STATE

| $i$ | $e(D_i)$ | $e(\tilde{D}_i)$ | $e(\hat{D}_i)$ | $e(C_i)$ | $e(\tilde{C}_i)$ | $e(\hat{C}_i)$ |
|---|---|---|---|---|---|---|
| 0 | 3.91E−2 | 3.65E−2 | 1.75E−1 | 2.92E−2 | 2.52E−2 | 2.45E−1 |
| 1 | 2.37E−3 | 2.22E−3 | 7.27E−2 | 1.02E−3 | 8.87E−4 | 7.86E−2 |
| 2 | 1.47E−4 | 1.38E−4 | 3.05E−2 | 4.19E−5 | 3.61E−5 | 2.88E−2 |
| 3 | 9.43E−6 | 8.82E−6 | 1.29E−2 | 2.13E−6 | 1.84E−6 | 1.02E−2 |
| 4 | 6.00E−7 | 5.61E−7 | 5.45E−3 | 1.19E−7 | 1.03E−7 | 3.68E−3 |

TABLE II
REDUCED FROBENIUS ERRORS: METHANE MIXTURE IN THE EQUIMOLAR STATE

| $i$ | $e(D_i)$ | $e(\tilde{D}_i)$ | $e(\hat{D}_i)$ | $e(C_i)$ | $e(\tilde{C}_i)$ | $e(\hat{C}_i)$ |
|---|---|---|---|---|---|---|
| 0 | 1.21E−2 | 1.14E−2 | 2.11E−1 | 1.62E−2 | 1.42E−2 | 3.15E−1 |
| 1 | 2.63E−4 | 2.48E−4 | 1.35E−1 | 4.57E−4 | 4.01E−4 | 1.98E−1 |
| 2 | 6.97E−6 | 6.55E−6 | 8.74E−2 | 1.46E−5 | 1.28E−5 | 1.24E−1 |
| 3 | 2.15E−7 | 2.02E−7 | 5.63E−2 | 4.79E−7 | 4.20E−7 | 7.86E−2 |
| 4 | 6.95E−9 | 6.53E−9 | 3.63E−2 | 1.58E−8 | 1.39E−8 | 4.95E−2 |

and the methane mixture in the state where all mole fractions are equal to $1/(n-2)$ excepted that of the light species H and $H_2$ which are set to zero and in the state where all mole fractions are equal to $1/(n-1)$ excepted that of the last species $C_2HO$ which is again set to zero. The errors $e(C_i)$, for $i = 0, \ldots, 4$, corresponding to these four states of the hydrogen and methane mixtures are given in Table III, in columns one to four respectively. This table again indicates that the convergence behavior is about the same as in the case of positive mass fractions. Note also the two step convergence for the 9-species hydrogen mixture in the state where only two mass fractions are nonzero. Finally, in the case of a pure species state, we have tested the modified expressions (4.10) with $\epsilon = 10^{-20}$ and we have observed a one step convergence up to the machine precision.

## 6. A SUMMARY OF PRACTICAL RESULTS

In this section, we summarize some practical aspects of the theoretical results obtained in the preceding sections.

Let us first consider a mixture in a state $Y$ such that $Y > 0$. The results obtained in Proposition 4, Proposition 6, and Proposition 7 then show that the Stefan–Maxwell diffusion matrix $\Delta$, defined as in (3.13), satisfies the

TABLE III
REDUCED FROBENIUS ERRORS: HYDROGEN AND METHANE MIXTURES WITH VANISHING MASS FRACTIONS

| $i$ | $e(C_i)$ | $e(C_i)$ | $e(C_i)$ | $e(C_i)$ |
|---|---|---|---|---|
| 0 | 6.78E−2 | 5.64E−2 | 1.61E−2 | 1.11E−2 |
| 1 | 8.01E−17 | 5.85E−3 | 4.36E−4 | 2.15E−4 |
| 2 | — | 3.66E−4 | 1.34E−5 | 4.86E−6 |
| 3 | — | 3.80E−5 | 4.24E−7 | 1.17E−7 |
| 4 | — | 2.38E−6 | 1.35E−8 | 2.88E−9 |

properties required from the kinetic theory and that the multicomponent diffusion matrix $D$ is given by

$$D = (\Delta + \beta Y \otimes Y)^{-1} - \alpha U \otimes U,$$

where $\alpha$ and $\beta$ are positive constants such that $\alpha\beta\langle U, Y\rangle^2 = 1$. This matrix $D$ is symmetric, satisfies $DY = 0$, so that mass is conserved, and gives a positive entropy production on the physical hyperplane of zero-sum gradients. The matrices $D$ and $\Delta$ also satisfy the properties (3.9), (3.10), and (3.11).

Define now $M = \mathrm{diag}(M_1, \ldots, M_n)$ with $M_k = \Delta_{kk}/(1 - Y_k/\langle U, Y\rangle)$ and $T = M^{-1}(M - \Delta) = I - M^{-1}\Delta$ and let $P = I - U \otimes Y/\langle U, Y\rangle$ and $Q = I - Y \otimes U/\langle U, Y\rangle$. Then the sequence of iterates

$$D_i = \sum_{k=0}^{i} (PT)^k PM^{-1}Q,$$

is convergent, that is to say the spectral radius $\rho(PT)$ of $PT$ is lower than unity, $\rho(PT) < 1$, and converges towards the multicomponent diffusion matrix $D$. Moreover, these iterates satisfy the same properties as the matrix $D$, namely symmetry, mass conservation, and positiveness of the entropy production on the physical hyperplane of zero-sum gradients. The first iterate $D_0 = PM^{-1}Q$ also coincides, on the hyperplane of zero-sum gradients $U^\perp$, with $D_0 = PM^{-1}$, since $QG = G$ for $G \in U^\perp$, and $-PM^{-1}G$ corresponds to the Hirschfelder–Curtiss approximated diffusion velocities with species independent mass correctors, often used to evaluate diffusion velocities in gas mixtures. Further note that for a given vector $G$, the numerical evaluation of $D_iG$ requires no matrix multiplications. Only products between matrices and vectors have to be performed, giving a computational cost of order $O(n^2)$. Although evaluating $D_i$ requires in general $O(n^3)$ operations, one can still evaluate $D_0$ and $D_1$ in $O(n^2)$ operations since $P$ and $Q$ are rank-one perturbations of the identity matrix $I$ and since $M$ is diagonal. Finally, the modified iterates

$$\tilde{D}_i = D_i + \alpha U \otimes U$$

may also be used when all mass fractions are considered as independent unknowns, in order to avoid artificial singularities [7].

When some mass fractions are allowed to vanish, the diffusion matrix $D$ is no longer defined. More specifically, the diagonal coefficients of the matrix $D$, corresponding to the vanishing mass fractions, blow up. In this situation, it is necessary to use the flux formulation $F = -CG$ instead of the velocity formulation $V = -DG$, where $F_k = Y_kV_k$, $k \in [1, n]$. Let us thus consider a mixture in a state $Y$ such that $Y \geqslant 0$ and $Y \neq 0$. The results obtained in Proposition 9 and Proposition 10 then show that the Stefan–Maxwell flux equations are well defined and that the multicomponent flux matrix $C$ is given by

$$C = (\Gamma + \beta Y \otimes U)^{-1} - \alpha Y \otimes U,$$

where $\Gamma$ is defined as in (3.16) and where $\alpha$ and $\beta$ are positive constants such that $\alpha\beta\langle U, Y\rangle^2 = 1$. The matrices $C$ and $\Gamma$ also satisfy the properties (3.18) and (3.19). Further note that if $Y > 0$, then $C = \mathcal{Y}D$ and $\Gamma = \Delta\mathcal{Y}^{-1}$ so that considering $C$ and $\Gamma$ instead of $D$ and $\Delta$ corresponds to factoring $\mathcal{Y} = \mathrm{diag}(Y_1, \ldots, Y_n)$ and eliminating the associated singularities.

Define now $L = \mathrm{diag}(L_1, \ldots, L_n)$ with $L_k = \Gamma_{kk}/(1 - Y_k/\langle U, Y\rangle)$ and $S = L^{-1}(L - \Gamma) = I - L^{-1}\Gamma$ and let $Q = I - Y \otimes U/\langle U, Y\rangle$. Then the sequence of iterates

$$C_i = \sum_{k=0}^{i} (QS)^k QL^{-1}Q,$$

is convergent, that is to say the spectral radius $\rho(QS)$ of $QS$ is lower than unity, $\rho(QS) < 1$, and converges towards the multicomponent flux diffusion matrix $C$. The computational costs associated with these iterates $C_i$ are the same as for the iterates $D_i$. The modified iterates

$$\tilde{C}_i = C_i + \alpha Y \otimes U,$$

may also be used when all mass fractions are considered as independent unknowns, in order to avoid artificial singularities [7]. Note again that if $Y > 0$, then, with the above definitions of $M$ and $L$, we have $L = M\mathcal{Y}^{-1}$, $Q = \mathcal{Y}P\mathcal{Y}^{-1}$, and $S = \mathcal{Y}T\mathcal{Y}^{-1}$, so that $C_i = \mathcal{Y}D_i$ and $\tilde{C}_i = \mathcal{Y}\tilde{D}_i$ for all $i \geq 0$.

Finally, rather than evaluating the coefficients $L_k = \Gamma_{kk}/(1 - Y_k/\langle U, Y\rangle)$, one may evaluate $L_k = W/(W_k D_k^*(\epsilon))$, where the modified formulation (4.10) is used to automatically handle pure species states of the mixture. In this situation, the modified coefficients yield a well defined splitting matrix $L$ and give a one step convergence, i.e., $C = C_0 = QL^{-1}Q$, for pure species states of the mixture.

## REFERENCES

1. S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases.* Cambridge Univ. Press, Cambridge (1970).
2. J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases.* North-Holland, Amsterdam (1972).
3. L. Waldmann, Transporterscheinunungen in Gasen von mittlerem druck. *In* S. Flügge (Ed.), *Handbuch der Physik,* Vol. 12, pp. 295–514. Springer-Verlag, Berlin (1958).
4. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids.* Wiley, New York (1954).

5. F. A. Williams, *Combustion Theory*, 2nd ed. Benjamin/Cummings, Menlo Park, CA (1985).
6. L. Monchick, R. J. Munn, and E. A. Mason, Thermal diffusion in polyatomic gases: A generalized Stefan–Maxwell diffusion equation. *J. Chem. Phys.* **45**, 3051–3058 (1966).
7. V. Giovangigli, Mass conservation and singular multicomponent diffusion algorithms. *IMPACT Comput. Sci. Engrg.* **2**, 73–97 (1990).
8. E. S. Oran and J. P. Boris, Detailed modeling of combustion systems. *Prog. Energy Combust. Sci.* **7**, 1–72 (1981).
9. W. W. Jones and J. P. Boris, An algorithm for multispecies diffusion fluxes. *Comput. Chem.* **5**, 139–146 (1981).
10. T. P. Coffee and J. M. Heimerl, Transport algorithms for premixed, laminar steady-state flames. *Combust. Flame* **43**, 273–289 (1981).
11. R. J. Kee, J. Warnatz, and J. A. Miller, *A Fortran Computer Code Package for the Evaluation of Gas-Phase Viscosities, Conductivities, and Diffusion Coefficients.* SANDIA National Laboratories Report, SAND83-8209 (1983).
12. J. Warnatz, Influence of transport models and boundary conditions on flame structure. *In* N. Peters and J. Warnatz (Eds.), *Numerical Methods in Laminar Flame Propagation*, pp. 87–111. Vieweg Verlag, Braunschweig (1982).
13. A. Ben-Israel and T. N. E. Greville, *Generalized Inverses, Theory and Applications.* Wiley, New York (1974).
14. M. Neumann and R. J. Plemmons, Convergent nonnegative matrices and iterative methods for consistent linear systems. *Numer. Math.* **31**, 265–279 (1978).
15. H. B. Keller, On the solution of singular and semidefinite linear systems by iteration. *SIAM J. Numer. Anal.* **2**, 281–290 (1965).
16. A. Berman and R. J. Plemmons, *Nonnegative Matrices in the Mathematical Sciences.* Academic Press, New York (1979).
17. R. Oldenburger, Infinite powers of matrices and characteristic roots. *Duke Math. J.* **6**, 357–361 (1940).
18. R. S. Varga, *Matrix Iterative Analysis.* Prentice-Hall, Englewood Cliffs, NJ (1962).
19. G. H. Golub and C. F. Van Loan, *Matrix Computations.* Johns Hopkins Univ. Press, Baltimore (1983).
20. C. F. Curtiss, Symmetric gaseous diffusion coefficients. *J. Chem. Phys.* **49**, 2917–2919 (1968).
21. J. Van de Ree, On the definition of the diffusion coefficients in reacting gases. *Physica* **36**, 118–126 (1967).
22. G. Dixon-Lewis, Flame structure and flame reaction kinetics. II. Transport phenomena in multicomponent systems. *Proc. Roy. Soc. London Ser. A* **307**, 111–135 (1968).
23. R. J. Kee, G. Dixon-Lewis, J. Warnatz, M. E. Coltrin, and J. A. Miller, *A Fortran Computer Code Package for the Evaluation of Gas-Phase Multicomponent Transport Properties.* SANDIA National Laboratories Report, SAND86-8246 (1986).
24. J. O. Hirschfelder and C. F. Curtiss, Flame propagation in explosive gas mixtures. *In Third Symposium (International) on Combustion*, pp. 121–127. Reinhold, New York (1949).
25. V. Giovangigli and M. D. Smooke, Adaptive continuation algorithms with application to combustion problems. *Appl. Numer. Math.* **5**, 305–331 (1989).
26. V. Giovangigli and M. D. Smooke, Application of continuation techniques to plane premixed laminar flames. In preparation.
27. R. J. Kee, J. A. Miller, and T. H. Jefferson, *CHEMKIN: A General-Purpose, Problem-Independent, Transportable, Fortran Chemical Kinetics Code Package.* SANDIA National Laboratories Report, SAND80-8003 (1990).