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A Numerically Stable Method for Integration of the Multicomponent Species Diffusion Equations

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A diagonally implicit method is shown to be an effective method for integrating the multicomponent species conservation equations. The constitutive equation for multicomponent diffusion is recast into a form analogous to that for binary diffusion, except that the diffusion coefficient is replaced with a matrix of effective multicomponent diffusion coefficients. The resulting matrix has properties that allow the diagonal terms to be integrated implicitly and the off-diagonal terms to be integrated explicitly. Numerical experiments show the integration procedure is stable for time steps much larger than the diffusion equation time step condition. © 2001 Elsevier Science

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1. INTRODUCTION

Diffusive transport is very important to many scientific disciplines, particularly in situations where pressure is low, temperature is high, or forced convection is negligible. Examples of such systems include chemical vapor deposition, plasma etching, and low-pressure combustion. Often, mass diffusion is treated as an analogy to heat conduction: as heat flux is proportional to the temperature gradient, diffusion mass flux of a species in a mixture is proportional solely to its own concentration gradient. This is called Fick's Law. The use of Fick's Law to predict species diffusion in multicomponent mixtures with more than two species is inappropriate, because it does not ensure that the sum of the species diffusion fluxes equals zero.

There are several approaches for solving multicomponent diffusion problems. The diffusion fluxes can be solved for directly in terms of the mole fraction gradients and other

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driving forces, or by solving the Stefan–Maxwell formulation [1]. The Stefan–Maxwell equations are a special case of the rigorous multicomponent formulation, in which a linear system is solved for the diffusion velocities. In the rigorous multicomponent formulation, the diffusion coefficients are obtained by the solution of linear systems [2, 3], whereas the diffusion fluxes are obtained by matrix multiplication.

The Stefan–Maxwell multicomponent formulation has the advantage that the coefficients to form the linear system involve quantities that are straightforward to evaluate, for example, the binary mass diffusion coefficient pairs. Convergent iterative schemes have been used to compute the diffusion velocities using the Stefan–Maxwell equations [4–6]. One potential disadvantage of the Stefan–Maxwell equations arises when considering a transient problem, since an iterative procedure is required to obtain convergence of the diffusion velocities consistent with the composition field within each time step.

The rigorous multicomponent formulation is described in detail in a number of reference texts [2, 7]. One main difference between the diffusion matrices presented in these works is that the diffusion coefficients in [7] are formulated to obey the Onsager reciprocity relations; that is, the diffusion coefficient matrix is symmetric. In [2], this symmetry is artificially destroyed, but the coefficients are still rigorously correct. It has been shown that the mass diffusion flux is a linear combination of the gradients of the mole fractions of the species [2, 8, 9].

When solving unsteady, diffusion-dominated problems it is often desirable to integrate the equations using an implicit or trapezoidal rule. In such cases, to avoid the iterations within each time step required to achieve convergence for the diffusion fluxes based on the composition field, it is useful to express the diffusion flux as a linear combination of the mass fraction gradients. If the diffusion equations are integrated explicitly, the variables used to compute the diffusion flux are known, and the standard formulation is adequate. Also, if the molar form of the species conservation equations is used, as in [5], then the standard formulation is more convenient; however, in many nonisothermal, reacting flows, the mass fraction form of the species conservation equation is often preferred [10, 11].

In the present work an approach is presented for solving the equations governing laminar diffusion of multicomponent fluids (gas or liquid). The rigorous model for multicomponent mass diffusion is recast into a mathematical form analogous to that for binary diffusion. This formulation uses the matrix of ordinary multicomponent diffusion coefficients [2, 12, 13] to compute a matrix of effective ordinary diffusion coefficients, which act on the vector of mass fraction gradients. This formulation for multicomponent diffusion is analogous to the formulation generally used for binary diffusion, except that the diffusion coefficient is replaced by a matrix. In addition, the unsteady formulation is expressed in terms of consistent primitive variables, the species mass fractions.

A scheme for integrating the multicomponent diffusion equations is presented whereby the diagonal portion of the diffusion matrix is integrated implicitly and off-diagonal parts are integrated explicitly. This formulation has several advantages. First, it allows the individual species equations to be decoupled, since the coefficient matrix includes only the terms from the diagonal part of the diffusion matrix. Second, the numerical integration procedure is shown to have improved stability properties; a von Neumann analysis is performed on a linearized, one-dimensional system with constant coefficients, and it is shown that the iteration matrix has a maximum eigenvalue of unity, indicating that none of the Fourier modes will grow without bound.

The principal advantage of the diagonally implicit scheme over that of a fully implicit scheme is that the size of the coefficient matrix is reduced. Assuming that a numerical solution is desired on a grid with N grid points, for a mixture of M species, and assuming a discrete operator stencil size S, the fully implicit coefficient matrix would be approximately size $M^2 \times S^2 \times N$, assuming a sparse matrix representation. The proposed scheme reduces the problem to a set of M solves, each with a coefficient matrix size $S \times N$.

The proposed scheme is tested by integrating the multicomponent diffusion equations for an isothermal system consisting of several species that are initially perturbed from their equilibrium concentrations. It is shown that the proposed scheme yields solutions that are stable for time steps greater by several orders of magnitude than the time step imposed by the stability criterion for a fully explicit scheme.

Finally, it is noted that the constitutive equation used for multicomponent species transport is rigorously valid only for gases at low densities, but the theory is often applied to gas mixtures at high densities, and even liquid mixtures [2].

2. MULTICOMPONENT DIFFUSION EQUATIONS

2.1. Species Continuity

The governing equations describing the transport of fluid species in a mixture are known as the species continuity (or mass transfer) equations. There is a separate governing equation for each of the M species in the mixture [10],

$$\rho \frac{\partial \psi_m}{\partial t} + \rho \mathbf{v} \cdot \nabla \psi_m = -\nabla \cdot \mathbf{j}_m + r_m, \quad \text{for } m = 1, 2, \ldots, M, \tag{1}$$

where ρ is the mixture density, ψ_m is the mass fraction of species m, $\mathbf{v}$ is the mass average velocity of the mixture, $\mathbf{j}_m$ is the diffusion flux of species m, and r_m is the net mass rate of production of species m by homogeneous chemical reaction.

The definition of the diffusion flux requires that this phenomenon be completely random. As such, the diffusion fluxes of the individual species in a mixture must satisfy a mass conservation constraint:

$$\sum_{m=1}^{M} \mathbf{j}_m = \mathbf{0}. \tag{2}$$

The continuity equation above is written in terms of reference velocity $\mathbf{v}$, which is the mass average velocity defined in [1, 2, 14]. An alternative approach is to define the continuity equation in terms of the molar average velocity. Then, the constraint equation above would be written in terms of the molar diffusion flux. Equations for the molar forms of these equations are given in [1]. Both representations are equally valid, but the mass average form is generally preferred since total mass, not moles, is always conserved, and it is this velocity, rather than the molar average velocity, that appears in the continuity equation and in Navier–Stokes equations.

2.2. Constitutive Equations for the Diffusion Flux

2.2.1. *Binary Diffusion*

When only two species are present in a fluid phase, the constitutive equation relating diffusion flux and composition gradients is known as Fick's Law;

$$\mathbf{j}_A = -\rho D_{AB} \nabla \psi_A, \tag{3}$$

where D_{AB} is the binary diffusion coefficient of species A in B, and this expression in Eq. (3) can be cast in either molar or mass units.

Writing a similar equation for the diffusion flux of species B and using Eq. (2), it can readily be shown that, since $\nabla \psi_A = -\nabla \psi_B$,

$$D_{BA} = D_{AB}. \tag{4}$$

2.2.2. *Multicomponent Diffusion*

The rigorous kinetic theory of dilute gas mixtures [2] results in a constitutive equation for multicomponent diffusion flux that is more complex than Fick's law for binary mixtures. While it is known that diffusion flux depends on not only composition gradients but also temperature and pressure gradients, as well as externally applied body forces, for the purpose of demonstrating the reformulation of the constitutive equation, these effects will be neglected. In this case, the form of the constitutive equation for multicomponent diffusion flux is given as [2]

$$\mathbf{j}_m = \rho \frac{w_m}{\tilde{w}^2} \sum_{n=1}^{M} w_n D_{mn} \nabla \chi_n, \tag{5}$$

where w_m is the molecular weight of species m, $\tilde{w}$ is the mean molecular weight of the mixture, D_{mn} is the mnth element of the matrix of ordinary multicomponent diffusion coefficients, $\mathbf{D}$, and χ_n is the mole fraction of species n. The mass conservation constraint, Eq. (2), requires that, by definition, $D_{mm} \equiv 0$. It can be shown that Eq. (5) reduces to Fick's Law when $M = 2$.

Under certain conditions, multicomponent diffusion can be modeled with reasonable accuracy using a Fickian model, where an effective, or mixture diffusivity is applied instead of binary diffusion coefficients. Such a Fickian model would yield a diagonal diffusion matrix. A conservative procedure with diagonal diffusion matrices has been presented for integrating the transient, multicomponent diffusion equations for multicomponent systems [15]. This situation arises when all species have comparable binary diffusion coefficients, when all species save one are present in trace amounts, or when only one species in a multicomponent mixture is diffusing. In systems where the species have similar molecular weights and sizes, or a diluent or bath gas is present in great excess, the use of Fick's law with an effective diffusivity can yield reliable results. However, in general, application of the effective diffusion model can lead to errors as large as 10%.

The constitutive equation for multicomponent diffusion flux, Eq. (5), can be written in block-diagonal matrix form as

$$\begin{Bmatrix} j_{x_1} \\ \vdots \\ j_{x_M} \\ j_{y_1} \\ \vdots \\ j_{y_M} \\ j_{z_1} \\ \vdots \\ j_{z_M} \end{Bmatrix} = \frac{\rho}{\tilde{w}^2} \begin{bmatrix} \mathbf{WDW} & & \\ & \mathbf{WDW} & \\ & & \mathbf{WDW} \end{bmatrix} \begin{Bmatrix} \frac{\partial \chi_1}{\partial x} \\ \vdots \\ \frac{\partial \chi_M}{\partial x} \\ \frac{\partial \chi_1}{\partial y} \\ \vdots \\ \frac{\partial \chi_M}{\partial y} \\ \frac{\partial \chi_1}{\partial z} \\ \vdots \\ \frac{\partial \chi_M}{\partial z} \end{Bmatrix}, \tag{6}$$

where $\mathbf{W} = \text{diag}[w_1, w_2, \ldots, w_M]$.

It may be shown that [2]

$$\sum_{m=1}^{M} w_m D_{mn} w_n = \mathcal{A} \quad \text{for all } n, \tag{7}$$

where $\mathcal{A}$ is a constant.

A simplified notation for the above matrix expression may be introduced. Nothing that **WDW** operates on each of the spatial components of the M vector of mole fraction gradients and returns that same spatial component of diffusion fluxes, it may be written

$$\mathbf{j}^l = \frac{\rho}{\tilde{w}^2} \mathbf{WDW} \nabla^l \chi, \tag{8}$$

where it is assumed that l is one of the spatial components of the diffusion flux or the gradient operator.

2.3. Reformulation of the Constitutive Equation

In numerical analysis it is common to cast the species continuity equations, Eqs. (1), in mass form (as opposed to molar) because mass is a conserved quantity. Further, Eq. (1) is often solved in conjunction with the Navier–Stokes equations, which are themselves based on mass quantities. However, the diffusion flux constitutive equation, Eq. (5), is derived in terms of mole fractions gradients. To incorporate Eq. (5) into Eq. (1), the constitutive equation will be reformulated in terms of mass fractions gradients. The resulting expression will look mathematically similar to Fickian diffusion, except that the diffusion coefficient in Eq. (3) will be replaced with a matrix of diffusion coefficients. In the sections that follow it will be shown that this matrix has properties that allow it to be solved using a diagonally implicit procedure.

To reformulate the multicomponent constitutive equation, a conversion formula from mole fraction to mass fraction is used:

$$\psi_m = \frac{\chi_m w_m}{\tilde{w}} = \frac{\chi_m w_m}{\sum_{n=1}^{M} \chi_n w_n}. \tag{9}$$

Differentiating this expression using the chain rule yields

$$\nabla^l \chi = \mathbf{C} \nabla^l \psi, \tag{10}$$

where $\mathbf{C}$ is the Jacobian matrix of the conversion formula. The mnth element of $\mathbf{C}$ is

$$C_{mn} = \left(\delta_{mn} - \psi_m \frac{\tilde{w}}{w_n} \right) \frac{\tilde{w}}{w_m}, \tag{11}$$

where δ_{mn} is the Kronecker delta. Equation (11) can also be written

$$C_{mn} = (\delta_{mn} - \chi_m) \frac{\tilde{w}}{w_n}, \tag{12}$$

using Eq. (9) and the properties of the Kronecker delta. It can be shown that the columns of $\mathbf{C}$ sum to zero using Eq. (12) as the starting point:

$$\begin{aligned} \sum_{m=1}^{M} C_{mn} &= \sum_{m=1}^{M} (\delta_{mn} - \chi_m) \frac{\tilde{w}}{w_n}, \\ &= \frac{\tilde{w}}{w_n} \left(1 - \sum_{m=1}^{M} \chi_m \right), \\ &= 0. \end{aligned} \tag{13}$$

Substituting Eq. (10) into the constitutive equation yields

$$\mathbf{j}^l = -\rho \Gamma \nabla^l \psi, \tag{14}$$

where

$$\Gamma \equiv -\frac{1}{\tilde{w}^2} \mathbf{WDWC}. \tag{15}$$

The columns of Γ also sum to zero. This is demonstrated by substituting Eq. (12) into Eq. (15);

$$\Gamma = \mathbf{ABW}^{-1}, \tag{16}$$

where

$$\mathbf{A} \equiv -\frac{1}{\tilde{w}} \mathbf{WDW}, \tag{17}$$

and

$$\mathbf{B} \equiv I - \mathbf{X}. \tag{18}$$

The tensor $\mathbf{X}$ is the $M \times M$ matrix whose columns are formed by the vector of mole fractions,

$$\mathbf{X} = \overbrace{\lceil \chi \ \chi \cdots \chi \rceil}^{M}. \tag{19}$$

The mnth element of Γ is

$$\Gamma_{mn} = \sum_{k=1}^{M} A_{mk} B_{kn} \frac{1}{w_n}. \tag{20}$$

The column sum of Γ is

$$\sum_{m=1}^{M} \Gamma_{mn} = \sum_{m=1}^{M} \sum_{k=1}^{M} A_{mk} B_{kn} \frac{1}{w_n} = \frac{1}{w_n} \sum_{k=1}^{M} B_{kn} \sum_{m=1}^{M} A_{mk} = \frac{1}{w_n} \mathcal{A} \sum_{k=1}^{M} B_{kn} = 0, \tag{21}$$

since the columns of $\mathbf{B}$ sum to zero and also using Eq. (7). The columns of Γ sum to zero due to the properties of the transformation matrix. Also, since the transformation matrix is singular, so is Γ.

The singular nature of Γ is important when applying Neumann or mixed boundary conditions on the mass fractions. Since Γ is singular, the boundary fluxes cannot be directly inverted to obtain the surface gradients. There are standard ways of solving this problem, and this situation poses no insurmountable difficulties [16].

The diffusion flux given by

$$\mathbf{j}^l = -\rho \Gamma \nabla^l \psi \tag{22}$$

is guaranteed to satisfy the constraint that the diffusion fluxes sum to zero. The proof is obtained summing $\mathbf{j}_i$ over all i species and using the fact that the column sum of Γ is zero.

In its present form, Eq. (14) appears analogous to the diffusion flux expression for binary mixtures, except that the binary diffusion coefficient in Eq. (3) is replaced with a matrix of diffusion coefficients. Further, for the case where there are only two species present, Eq. (14) reduces identically to Eq. (3). This result may be demonstrated by applying Eq. (14) to a system containing only two species:

$$\begin{aligned} \mathbf{j}_1 &= -\rho \Gamma_{11} \nabla \psi_1 - \rho \Gamma_{12} \nabla \psi_2, \\ \mathbf{j}_2 &= -\rho \Gamma_{21} \nabla \psi_1 - \rho \Gamma_{22} \nabla \psi_2. \end{aligned} \tag{23}$$

Since $\nabla \psi_1 = -\nabla \psi_2$, these expressions may be written as

$$\mathbf{j}_1 = -\rho (\Gamma_{11} - \Gamma_{12}) \nabla \psi_1, \tag{24}$$

$$\mathbf{j}_2 = -\rho (\Gamma_{22} - \Gamma_{21}) \nabla \psi_2. \tag{25}$$

Evaluating Γ,

$$\begin{aligned} \Gamma &= -\frac{1}{\tilde{w}^2} \mathbf{WDWC}, \\ &= -\frac{1}{\tilde{w}^2} \begin{bmatrix} C_{21} w_1 D_{12} \tilde{w}_2 & C_{22} w_1 D_{12} \tilde{w}_2 \\ C_{11} \tilde{w}_2 D_{21} \tilde{w}_1 & C_{12} w_2 D_{21} \tilde{w}_1 \end{bmatrix}, \end{aligned} \tag{26}$$

since $D_{11} = D_{22} \equiv 0$. Finally, it is necessary to show that $\Gamma_{11} - \Gamma_{12} = D_{12}$. Using Eq. (11),

$$\begin{aligned}
\Gamma_{11} - \Gamma_{12} &= -\frac{w_1 D_{12} w_2}{\tilde{w}^2}(C_{21} - C_{22}), \\
&= -\frac{w_1 D_{12} \tilde{w}_2}{\tilde{w}^2}\left[\frac{\tilde{w}}{w_2}\left(-\psi_2 \frac{\tilde{w}}{w_1}\right) - \frac{\tilde{w}}{w_2}\left(1 - \psi_2 \frac{\tilde{w}}{w_2}\right)\right], \\
&= -\frac{w_1 D_{12} w_2}{\tilde{w}^2}\left[-\chi_2 \frac{\tilde{w}}{w_1} - \frac{\tilde{w}}{w_2}\chi_1\right], \\
&= \frac{D_{12}}{\tilde{w}}[\chi_2 w_2 + \chi_1 w_1], \\
&= D_{12}\ (=D_{AB}).
\end{aligned}$$

Interchanging the subscript and superscript "1" and "2," it is clear that $\Gamma_{22} - \Gamma_{21} = D_{21} = D_{BA}$. Thus, the expression for diffusion flux given by Eq. (14) reduces to Fick's law when applied to a binary system.

3. A DIAGONALLY IMPLICIT NUMERICAL INTEGRATION METHOD

In this section, a procedure for a finite difference integration procedure is presented, and it is shown that the maximum eigenvalue of the linearized iteration matrix is unity, indicating that none of the Fourier modes will grow without bound.

To demonstrate how this approach is applied and to illustrate the main points of the implicit technique, a number of assumptions are made that simplify the form of the species continuity equation, Eq. (1): (1) the system is one dimensional; (2) mass transfer is dominated by diffusion and $\mathbf{v} \approx 0$; (3) no chemical reactions occur; (4) mixture density is constant; (5) the multicomponent diffusion coefficients are independent of spatial position; and (6) the nonlinearity in Γ is ignored. Using these approximations, the species continuity equation for the mth species may be written as

$$\frac{\partial \psi_m}{\partial t} - \sum_{n=1}^{M} \Gamma_{mn} \frac{\partial^2 \psi_n}{\partial x^2} = 0, \quad \text{for } m = 1, 2, \ldots, M. \tag{27}$$

If the one-dimensional computational grid contains K nodes, with an index running from 0 to $K - 1$, and the nodes are uniformly spaced, then the vertex of the kth grid point is $x = kh$, where h is the grid spacing. For a uniform discrete time step Δt, the total elapsed time is $t = s\Delta t$, where s is the time step index. Thus,

$$\psi_m(x, t) = \psi_m(kh, s\Delta t) = \psi_{m,k}^s. \tag{28}$$

At the kth grid point, finite difference approximations of the terms in the differential equation (27) may be written as

$$\frac{\partial \psi_{m,k}}{\partial t} = \frac{\psi_{m,k}^{s+1} - \psi_{m,k}^s}{\Delta t} + \mathcal{O}(\Delta t) \tag{29}$$

and

$$\frac{\partial^2 \psi_m}{\partial x^2} = \frac{\psi_{m,k+1} - 2\psi_{m,k} + \psi_{m,k-1}}{h^2} + \mathcal{O}(h^2). \tag{30}$$

If the mth species is integrated implicitly and all the other terms are integrated explicity, then the finite difference approximation to Eq. (27) is

$$\psi_{m,k}^{s+1} - \psi_{m,k}^{s} - R_{mm}\left(\psi_{m,k+1}^{s+1} - 2\psi_{m,k}^{s+1} + \psi_{m,k-1}^{s+1}\right) = \sum_{\substack{n=1 \\ n\neq m}}^{M} R_{mn}\left(\psi_{n,k+1}^{s} - 2\psi_{n,k}^{s} + \psi_{n,k-1}^{s}\right) + \mathcal{O}(\Delta t, h^2), \tag{31}$$

where $R_{mn} \equiv (\Delta t/h^2)\Gamma_{mn}$.

Assuming a discrete Fourier transform exists, the mass fractions at any grid point can be written as a linear combination of the Fourier modes,

$$\psi_{m,k}^{s} = \sum_{l=0}^{K-1} \xi_{m,l}^{s} e^{ilhk}, \tag{32}$$

where $\xi_{m,l}^{s}$ is the Fourier coefficient for species m at grid point l at time step s, $i = \sqrt{-1}$, and l is a summed over all grid points [17]. Substituting Eq. (32) into Eq. (31), collecting terms and eliminating the common summation results in the equation for the Fourier coefficients,

$$(1 + \beta_l R_{mm})\,\xi_{m,l}^{s+1} = \xi_{m,l}^{s} - \sum_{\substack{n=1 \\ n\neq m}}^{M} \beta_l R_{mn} \xi_{n,l}^{s}, \tag{33}$$

where $\beta_l = 4\sin^2(lh/2)$.

The subscript l on ξ indicates that this equation is evaluated at the lth grid point. The same equation applies to each grid point, so hereafter, the l subscript on ξ is omitted.

Because Eq. (33) may be written for each species at each grid point, the set of equations can be represented in matrix form. The matrix on the left-hand side of the resulting equation is diagonal and may be readily inverted. The resulting iteration matrix for the Fourier coefficients may thus be written as

$$\xi^{s+1} = \mathbf{F}\,\xi^{s}, \tag{34}$$

where the iteration matrix $\mathbf{F}$ is given by

$$\mathbf{F} = \begin{bmatrix} \frac{1}{1+\beta_l R_{11}} & \frac{-\beta_l R_{12}}{1+\beta_l R_{11}} & \frac{-\beta_l R_{13}}{1+\beta_l R_{11}} & \cdots \\ \frac{-\beta_l R_{21}}{1+\beta_l R_{22}} & \frac{1}{1+\beta_l R_{22}} & \frac{-\beta_l R_{23}}{1+\beta_l R_{22}} & \cdots \\ \frac{-\beta_l R_{31}}{1+\beta_l R_{33}} & \frac{-\beta_l R_{32}}{1+\beta_l R_{33}} & \frac{1}{1+\beta_l R_{33}} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{bmatrix}. \tag{35}$$

It can be shown that one of the eigenvalues of $\mathbf{F}$ is always unity. This is done by substituting $\lambda = 1$ into the characteristic equation for $\mathbf{F}$,

$$|\mathbf{F} - \mathbf{I}| = \frac{(\beta_l)^M}{\prod_{i=1}^{M}(1 + \beta_l R_{ii})}|\mathbf{R}|, \tag{36}$$

where **I** is the identity matrix. Since **R** has a zero eigenvalue, its determinant is zero, and the characteristic equation is satisfied.

Numerical investigation has shown that the maximum eigenvalue is unity in all cases encountered. Since the maximum eigenvalue is unity, none of the Fourier modes will grow without bound. Iteration matrices in singular systems such as these, having a unity eigenvalue, have been shown to be convergent [7, 18].

Lastly, it is noted that this integration scheme is not guaranteed to satisfy the constraint on the mass fractions. It is readily verified that the error in the sum of the mass fractions is $\mathcal{O}(\Delta t)$. This is due to the particular integration scheme chosen for this example. In practice, one may solve the integrations for the dilute species and then use the constraint equation to solve for the bulk species. Another possible correction is

$$\psi^*_{m,k} = \frac{\psi^{n+1}_{m,k}}{\sum_{m=1}^{M} \psi^{n+1}_{m,k}}, \tag{37}$$

where the $*$ represents a correction to the mass fraction of the mth species at the kth grid point at the $n+1$ time state such that the mass fraction constraint is satisfied exactly.

4. NUMERICAL EXAMPLE

In this example, transient one-dimensional diffusion is considered in a multicomponent gas mixture of a moderate number of species, commonly present during the combustion of hydrogen in air [19]. This diffusion problem might result, for example, as part of a splitting scheme for a more complex reaction–diffusion problem in combustion [20]. The mixture consists of eleven species: H_2, O_2, N_2, H, O, N, HO_2, H_2O, NO, H_2O_2, and OH. For convenience it is assumed that the first three species dominate the mixture and the remaining species are dilute.

The initial temperature and pressure of the mixture are 300 K and 1 atm. It is assumed that the three dominant species are perturbed from their equilibrium distributions as specified by the functions

$$\psi_{H_2}(x, 0) = 0.33(1 + 0.25 \sin 0.2\pi x)$$
$$\psi_{O_2}(x, 0) = 0.33(1 - 0.15 \sin 0.2\pi x)$$
$$\psi_{N_2}(x, 0) = 0.26 - 0.033 \sin 0.2\pi x,$$

and the initial composition of the remaining trace species is $\psi_m(x, 0) = 0.01$, where the species subscript m = H, O, N, HO_2, H_2O, NO, H_2O_2, and OH.

The simulations are run until equilibrium is established. The 1-D computational domain is 10 cm long and is divided into 33 equally spaced grid points for all simulations. The stability of the method is tested by solving Eq. (31) subject to four different time steps Δt.

The ordinary multicomponent diffusion coefficients, D_{mn}, are evaluated using the Chemkin Transport library [21]. These diffusion coefficients are functions of the local temperature, pressure, and gas composition, and are computed at each time step. Then Eq. (15) is used to compute Γ_{mn} at each point in the domain.

The time step used for each of the four experiments was a multiple of the explicit time step, Δt_e, where this quantity is the maximum allowable, that is, stable time step in a fully

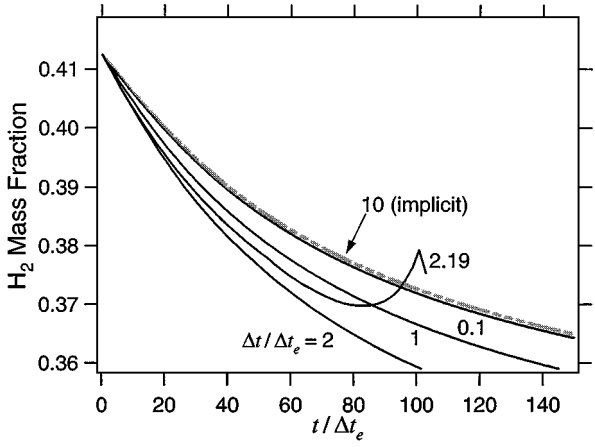

FIG. 1. The time evolution of hydrogen mass fraction at $x = 2.5$ cm for different values of the integration time step, Δt. Time has been normalized by the maximum stable explicit time step, Δt_e. The integration method is fully explicit for $\Delta t/\Delta t_e = 0.1$, 1.0, 2.0, and 2.19 (solid lines). The result from the diagonally implicit scheme is shown for $\Delta t/\Delta t_e = 10$ (dashed gray line).

explicit integration scheme. For numerical stability, Δt_e must satisfy

$$\frac{\Gamma_{max}\Delta t_e}{\Delta x^2} < \frac{1}{2}, \tag{38}$$

where Δx is the grid spacing. In this expression, it is assumed that the value of Γ_{max} is constant over the domain. Since this is in general not true, the above criterion can only be used to determine an approximate value of Δt_e. Simulations using a fully explicit integration scheme have been performed for various time step ratios, $\Delta t/\Delta t_e$, to determine the onset of numerical instability. Then, simulations using the proposed diagonally implicit integration scheme are performed for time step ratios of 10, 10^2, 10^3, and 10^4.

Computed results for the fully explicit scheme are represented by the solid black lines in Fig. 1. In this figure, the mass fraction of H_2 at $x = 2.5$ cm is plotted as a function of time normalized by Δt_e, for several values of the normalized integration time step $\Delta t/\Delta t_e$. In this particular system the solution of the fully explicit scheme converges only when $\Delta t/\Delta t_e < 2.19$. As expected, the stability boundary is encountered when $\Delta t/\Delta t_e = \mathcal{O}(1)$; the actual value is somewhat greater than unity because the stability criterion shown in Eq. (38) is approximate. Also plotted in Fig. 1 is the result from the diagonally implicit scheme with a time step ratio of $\Delta t/\Delta t_e = 10$. This result is represented by the dashed gray line. Note that the prediction of the diagonally implicit method for $\Delta t/\Delta t_e = 10$ is in close quantitative agreement with the fully explicit scheme solution obtained using a time step ratio of 0.1.

Figure 2 shows the results of the diagonally implicit scheme for time step ratios $\Delta t/\Delta t_e =$ 10, 10^2, and 10^3. As may be seen in the figure, all calculations converge. A calculation using a time step ratio of 10^4 also converges but is not included in the figure for purposes of clarity. To compare the steady state offset of the different calculations, the exact steady state solution—$\psi_{H_2} = 0.33$—is also shown in the figure.

In all cases studied, the steady state offset increases as Δt increases, but the order of the method was not rigorously computed. As stated previously, the error in the mass fraction

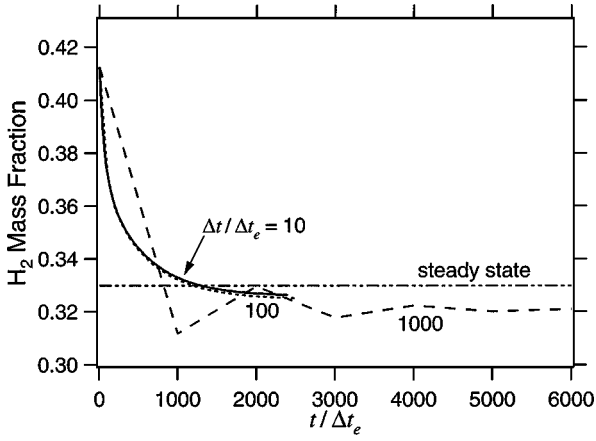

FIG. 2. The time evolution of hydrogen mass fraction at $x = 2.5$ cm for different values of the integration time step, Δt. Time has been normalized by the maximum stable explicit time step, Δt_e. The integration scheme is diagonally implicit for all calculations shown.

constraint is $\mathcal{O}(\Delta t)$. The accumulation of this error over time, in addition to the errors due to the spatial discretization, which are $\mathcal{O}(\Delta x^2)$, and roundoff result in the steady state offset.

5. CONCLUSION

It has been shown here that using Γ to reformulate the diffusion term in the species conservation equation results in a rigorous multicomponent expression that is mathematically analogous to the simple Fickian form applicable to binary systems. In addition, the properties of the matrix of effective ordinary diffusion coefficients allow the diffusion equation to be integrated using a diagonally implicit scheme with time steps much larger than the time step permitted with a fully explicit scheme. A linearized, one-dimensional analysis demonstrates that the scheme presented is unconditionally stable. In addition, the diagonalization of the diffusion problem, Eq. (31), decouples the species conservation equations, dramatically reducing the size of the coefficient matrix, making the problem more tractable for systems with very large numbers of species.

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