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Short note

Critical assessment of the stability and convergence of the equations of multi-component diffusion

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1. Introduction

The transport phenomenon in many engineering applications is dominated by multi-component diffusion. Examples include low-pressure chemical vapor deposition, mass transport in gas diffusion layers in fuel cells, and transport of chemicals in biomedical devices. With increasing interest in small-scale devices, diffusion dominated (i.e., low Peclet number) transport is likely to become more important in engineering applications of the next generation.

Unlike in binary systems (consisting of two species), diffusion of a certain species in a multi-component system is dictated not only by its own concentration gradient but also by the concentration gradient of the other species in the system [1,2]. This results in a system of strongly coupled nonlinear second-order elliptic partial differential equations. In the case of binary systems, or in the case of dilute mixtures wherein a certain "reference" species constitute most of the mixture, these equations become segregated, or are only weakly coupled [1,2]. For concentrated non-binary mixtures, segregation of the governing equations cannot be performed naturally, and is performed artificially only to make the system of equations amenable to numerical solution.

Segregated solution of the governing equations, wherein only the self-diffusion operator is treated implicitly, while the diffusion due to the other species is treated explicitly, results in an iterative algorithm whose convergence depends on the strategy used to conserve overall mass. In this short note, it is shown that if the mass fraction summation criterion (i.e., mass fractions of species summing to unity) is imposed explicitly, and if the transport properties are not held constant, the convergence of this semi-implicit system of equations requires under-relaxation even for one-dimensional calculations. For multi-dimensional problems,

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Nomenclature

D_{kn}	ordinary multi-component diffusion coefficient tensor (m^2/s)
$\mathscr{D}_{kn}$	binary diffusion coefficient tensor (m^2/s)
$\mathbf{J}_k$	mass diffusion flux of *k*th species ($kg/m^2/s$)
M	mixture molecular weight (kg/kmol)
M_k	molecular weight of *k*th species (kg/kmol)
$\hat{\mathbf{n}}$	unit surface normal
N	number of species
N_C	number of cells (or finite volumes)
$\dot{S}_k$	production rate of the *k*th species due to chemical reaction ($kg/m^3/s$)
$\mathbf{U}$	fluid velocity vector (m/s)
X_k	mole fraction of *k*th species
Y_k	mass fraction of *k*th species
Greek	
α	under-relaxation factor
ρ	mixture density (kg/m^3)
Γ_{kn}	transformed diffusion coefficient tensor (m^2/s) (Eq. (8))

where the spatial operators have to be additionally split to enable use of iterative solvers, convergence is not guaranteed even with severe under-relaxation, and is dependent on the mesh size. It is also shown that indirect imposition of the mass fraction summation criterion by normalizing the calculated mass fractions by their sum results in an iterative algorithm that is stable. Since direct imposition of the mass fraction summation criterion is often desirable or necessary for more complex reacting flow calculations, a coupled fully implicit solution technique is proposed and demonstrated. It is shown that the new fully implicit procedure is unconditionally stable without under-relaxation even if the mass fraction summation constraint is imposed directly.

2. Governing equations

The equation governing the transport of species in a multi-component system is the generalized advection–diffusion species conservation equation [3]

$$\frac{\partial}{\partial t}(\rho Y_k) + \nabla \cdot (\rho \mathbf{U} Y_k) = -\nabla \cdot \mathbf{J}_k + \dot{S}_k \quad \forall k = 1, 2, \ldots, N, \tag{1}$$

where ρ is the mixture density, Y_k is the mass fraction of the *k*th species, $\mathbf{U}$ is mass-averaged bulk fluid velocity vector, $\mathbf{J}_k$ is the mass diffusion flux of the *k*th species, and $\dot{S}_k$ is the production rate of the *k*th species due to chemical reactions. In addition, overall mass conservation (or continuity) must be satisfied

$$\frac{\partial}{\partial t}(\rho) + \nabla \cdot (\rho \mathbf{U}) = 0 \tag{2}$$

Eq. (2) can be derived from Eq. (1) if and only if the following two constraints are satisfied:

$$\text{At any point in space}: \sum_{k=1}^{N} Y_k = 1, \tag{3}$$

$$\text{At any arbitrary cutting plane}: \sum_{k=1}^{N} \mathbf{J}_k \cdot \hat{\mathbf{n}} = 0, \tag{4}$$

where $\hat{\mathbf{n}}$ is the surface normal to the cutting plane in question. Eq. (3) is generally enforced either by solving only $N-1$ equations from the set in Eq. (1), and then using Eq. (3) directly to determine the mass fraction of the last species, or by normalizing the calculated mass fractions by their sum, resulting in an indirect correction strategy. Satisfaction of the second constraint, given in Eq. (4), is far more complex and requires further considerations.

In a binary system, consisting of species A and B, the diffusion flux is accurately described by the Fick's law of diffusion [1]

$$J_{\mathrm{A}} = -\rho \mathscr{D}_{\mathrm{AB}} \nabla Y_{\mathrm{A}}, \quad J_{\mathrm{B}} = -\rho \mathscr{D}_{\mathrm{BA}} \nabla Y_{\mathrm{B}}, \tag{5}$$

where $\mathscr{D}_{\mathrm{AB}}$ is the binary diffusion coefficient of species A into B, and is equal to $\mathscr{D}_{\mathrm{BA}}$, which is the binary diffusion coefficient of species B into A. Using the mass fraction summation constraint (Eq. (3)), it can be readily shown that $J_{\mathrm{A}} = -J_{\mathrm{B}}$, i.e., Eq. (4) is automatically obeyed. Thus, in a binary system, species diffusion is dictated by its own concentration gradient only, and the individual species transport equations can be easily segregated.

In a multi-component system, Eq. (4) cannot be satisfied by expressing the mass flux using Fick's law. In such systems, diffusion is best described by the Stefan–Maxwell equation [1], which implicitly relates molar fluxes of species to mole fraction gradients. This relationship has been formulated in such a manner that Eq. (4) is satisfied for an arbitrary multi-component system. For computational fluid dynamics (CFD) calculations, it is advantageous to recast the Stefan–Maxwell equations in terms of mass fraction since mass is conserved in the system. For a perfect mixture, the mass diffusion flux in multi-component systems is written as [2,4]

$$\mathbf{J}_k = -\rho \frac{M_k}{M^2} \sum_{n=1}^{N} M_n D_{kn} \nabla X_n, \tag{6}$$

where M is the mixture molecular weight, M_k is the molecular weight of the kth species, X_k is the mole fraction of the kth species, and D_{kn} is the ordinary multi-component diffusion coefficient tensor [1,2], which is different from the binary diffusion coefficient $\mathscr{D}_{kn}$. Specifically, while the binary diffusion coefficients are independent of the mole fractions, the ordinary multi-component diffusion coefficients are strong nonlinear functions of the mole fractions. Also, it is worth noting that $D_{kk} = 0$, but $D_{kn} \neq D_{nk}$. The ordinary multi-component diffusion coefficients can be computed using well-known relationships [2,5,6]. Using the conversion between mass and mole fraction, $Y_k = \frac{X_k M_k}{M}$, Eq. (6) may be recast [4] into a form where the dependent variable is not the mole fraction but the mass fraction

$$\mathbf{J}_k = -\rho \sum_{n=1}^{N} \Gamma_{kn} \nabla Y_n, \tag{7}$$

where Γ_{kn} is a new tensor, written as [4]

$$[\Gamma] = -\frac{1}{M^2}[M][D][M][C]. \tag{8}$$

In Eq. (8), $[M] = \mathrm{diag}[M_1, M_2, \ldots, M_N]$, $[D]$ is the matrix notation for the ordinary multi-component diffusion tensor D_{kn}, and $[C]$ the Jacobian of the transformation between mass and mole fraction, and is written as

$$C_{kn} = \left(\delta_{kn} - Y_k \frac{M}{M_k}\right) \frac{M}{M_n}, \tag{9}$$

where δ_{kn} is the Kronecker delta. In the absence of advection and reaction sources, Eq. (1), at steady-state, becomes

$$\nabla \cdot \mathbf{J}_k = -\nabla \cdot \left[\rho \sum_{n=1}^{N} \Gamma_{kn} \nabla Y_n\right] = 0 \quad \forall k = 1, 2, \ldots, N. \tag{10}$$

It is clear that Eq. (10) represents a system of coupled second-order partial differential equations. Furthermore, since Γ_{kn} and ρ are both functions of the mass fractions, this system of equations is nonlinear. The boundary conditions for Eq. (10) will depend on the problem at hand, and will be discussed further in later sections when specific examples are considered. It has been shown by Wangard et al. [4] that the properties of the tensor Γ_{kn} are such that the mass fraction summation criterion (Eq. (3)) is automatically satisfied provided Eq. (10) is solved exactly.

3. Analysis and results

One common approach for solving Eq. (10) is a semi-implicit approach, in which Eq. (10) is first rewritten as

$$\nabla \cdot [\rho \Gamma_{kk} \nabla Y_k] = -\nabla \cdot \left[\rho \sum_{\substack{n=1 \\ n \neq k}}^{N} \Gamma_{kn} \nabla Y_n\right]^* \quad \forall k = 1, 2, \ldots, N, \tag{11}$$

where it is seen that only the self-diffusion operator is retained on the left-hand side of the equation and treated implicitly, while the remaining terms are simply treated as sources, and explicitly calculated using old iteration values, as indicated by the superscript "*" on the right-hand side term. The resulting set of equations can be solved sequentially after appropriate spatial discretization, although iterations (so-called *outer* iterations) will be necessary to resolve the coupling between the mass fractions even if the properties (Γ_{kn} and ρ) are held constant and a direct solver is used. Wangard et al. [4] have shown using discrete Fourier analysis of the errors that the maximum eigenvalue of the iteration matrix, resulting from such a semi-implicit treatment, never exceeds unity, implying that the approach is unconditionally stable. Although not shown here for the sake of brevity, our calculations confirmed these findings. However, Wangard et al. [4] performed their analysis under the assumption that the properties are constant. Such an assumption not only linearizes the equations, but also changes the eigenvalues of the system because the properties are not allowed to vary spatially. In practice, as discussed earlier, both Γ_{kn} and ρ are strong functions of the mass-fractions, making the governing set of equations nonlinear. Under the circumstances, discrete Fourier analysis cannot be performed, and the behavior of the system of equations can only be investigated through trial-and-error. Wangard et al. [4] also noted that the segregated solution approach results in an error in the mass fraction sum (i.e., a deviation from unity), which, in a time-marching formulation with constant properties, scales as the time step used. Thus, despite the automatic mass conservation property of the tensor Γ_{kn} [4], the satisfaction of Eq. (3) is not automatically guaranteed using the semi-implicit segregated approach, and explicit strategies must be implemented in the overall numerical procedure to satisfy Eq. (3).

In order to test these practical numerical issues associated with the semi-implicit scheme, a simple one-dimensional test case was considered. The system consisted of three species, namely H_2, H_2O, and N_2. The one-dimensional domain considered was 0.1 m long, and the temperature of the domain was assumed to be uniform and fixed at 300 K. The prescribed mass fractions of the three species at the left boundary were [H_2, H_2O, N_2] = [0.6, 0.4, 0.0], while that at the right boundary were [H_2, H_2O, N_2] = [0.0, 0.6, 0.4]. The governing equations were discretized using a conservative finite-volume approach, in which central differencing on a uniform mesh was used to treat diffusion. The resulting discrete equations were solved using a direct tri-diagonal matrix solver. Two different strategies were used for overall mass correction (i.e., for enforcing Eq. (3)):

Strategy 1. Only $N - 1$ equations from the equation set shown in Eq. (11) were solved. The mass fraction of the final species was obtained using Eq. (3).

Strategy 2. All N equations from the equation set shown in Eq. (11) were solved. At each iteration, the mass fractions were corrected by scaling with their sum.

Using *Strategy 1*, it was impossible to obtain convergence with such a semi-implicit scheme (Fig. 1) without under-relaxing the species mass fractions (i.e., $Y = Y^* + \alpha\Delta Y$), where α is the under-relaxation factor, and ΔY is the change in mass fraction between the previous and current iteration. On the other hand, using *Strategy 2*, it was possible to attain convergence without the use of any under-relaxation (Fig. 1). Without the use of either of the above two strategies, although convergence was easily obtained (not shown), the summation of the mass fractions were found to be grossly erroneous, with errors larger than 100% at some spatial locations. Thus, the conservation properties of the tensor, Γ_{kn}, as discussed by Wangard et al. [4], is manifested only if the set of species conservation equations are solved simultaneously, rather than in segregated fashion.

In computations involving chemical reactions, scaling of the mass fractions may lead to undesirable gain or loss of reactants during the iteration process, leading to oscillations in the convergence and/or unphysical results. In such a scenario, direct imposition of Eq. (3) (*Strategy 1*) is preferable over scaling (*Strategy 2*). In order to achieve this goal, a coupled fully implicit procedure is proposed. In this fully implicit approach, finite-volume integration is directly performed in Eq. (10) without any additional rearrangement of the terms. For the simple one-dimensional case considered here, after finite-volume integration and discretization of the flux terms, the following equation is obtained:

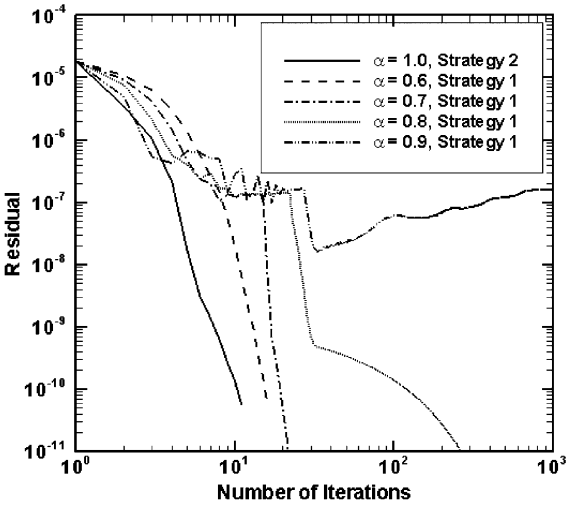

Fig. 1. Convergence of the multi-component diffusion equations for various under-relaxation factors using segregated solution. The residuals shown are for H_2. 80 cells were used for these computations. The residual of each species is defined as the $l2$norm of the mass imbalance of that species.

$$\sum_{n=1}^{N}\left[\left(\beta_{kn,\mathrm{e}}+\beta_{kn,\mathrm{w}}\right)Y_{n,\mathrm{O}}-\beta_{kn,\mathrm{e}}Y_{n,\mathrm{E}}-\beta_{kn,\mathrm{w}}Y_{n,\mathrm{W}}\right]=0 \quad \forall k=1,2,\ldots N-1, \tag{12}$$

where the subscripts "E", "W", "O", "e", and "w" carry their usual meanings, and $\beta_{kn}=\rho\Gamma_{kn}$. Eq. (12) represents a set of $N-1$ coupled equations. In conjunction with Eq. (3), it can be written in matrix form as

$$\begin{aligned}
&-\begin{bmatrix}\beta_{11,\mathrm{e}} & \beta_{12,\mathrm{e}} & \cdots & \beta_{1N,\mathrm{e}}\\ \vdots & \vdots & \vdots & \vdots\\ \beta_{N-1,1,\mathrm{e}} & \cdots & \cdots & \beta_{N-1,N,\mathrm{e}}\\ 0 & \cdots & \cdots & 0\end{bmatrix}\begin{bmatrix}Y_{1,\mathrm{E}}\\ Y_{2,\mathrm{E}}\\ \vdots\\ Y_{N,\mathrm{E}}\end{bmatrix}-\begin{bmatrix}\beta_{11,\mathrm{w}} & \beta_{12,\mathrm{w}} & \cdots & \beta_{1N,\mathrm{w}}\\ \vdots & \vdots & \vdots & \vdots\\ \beta_{N-1,1,\mathrm{w}} & \cdots & \cdots & \beta_{N-1,N,\mathrm{w}}\\ 0 & \cdots & \cdots & 0\end{bmatrix}\begin{bmatrix}Y_{1,\mathrm{W}}\\ Y_{2,\mathrm{W}}\\ \vdots\\ Y_{N,\mathrm{W}}\end{bmatrix}\\
&+\begin{bmatrix}\beta_{11,\mathrm{e}}+\beta_{11,\mathrm{w}} & \beta_{12,\mathrm{e}}+\beta_{12,\mathrm{w}} & \cdots & \beta_{1N,\mathrm{e}}+\beta_{1N,\mathrm{w}}\\ \vdots & \vdots & \vdots & \vdots\\ \beta_{N-1,1,\mathrm{e}}+\beta_{N-1,1,\mathrm{w}} & \cdots & \cdots & \beta_{N-1,N,\mathrm{e}}+\beta_{N-1,N,\mathrm{w}}\\ 1 & \cdots & \cdots & 1\end{bmatrix}\begin{bmatrix}Y_{1,0}\\ Y_{2,0}\\ \vdots\\ Y_{N,\mathrm{O}}\end{bmatrix}=\begin{bmatrix}0\\ \vdots\\ 0\\ 1\end{bmatrix}
\end{aligned} \tag{13}$$

Eq. (13) represents a block tri-diagonal system of equations for the cells [1, 2, ..., N_C], where each element of the tri-diagonal matrix is a $N\times N$ matrix itself. These element matrices are shown explicitly in Eq. (13) for a representative interior node, O. In the case where the transport coefficient, β_{kn}, is independent of the mass fractions, a single inversion of this tri-diagonal block matrix system will yield the final solution for all species and all cells. In the actual case, where β_{kn} is dependent on the mass fractions, iterations will still be necessary, since the governing equation is nonlinear. One other point of importance is the fact that the mass fraction summation criterion (Eq. (3)) is in-built into the coupled solver, thereby enforcing it at each cell and each iteration. It is to be noted that in this formulation, unlike the segregated solution approach, the choice of the species for which the governing equation is not solved is arbitrary, and does not affect either the accuracy or the convergence (not shown). This is because Eq. (3) is implemented implicitly within the solver rather than as an explicit correction step after the governing equations for all the other species are solved.

Computations were performed using the coupled fully implicit solver, and in each case, regardless of mesh size, convergence was obtained within 10 global (outer) iterations. The insensitivity of the convergence to mesh size is consistent with the fact that a direct solver is being used for this one-dimensional problem. A summary of the comparison between the fully implicit (coupled) method and the semi-implicit (segregated) method using both strategies, mentioned earlier, is shown in Table 1. For the semi-implicit method using *Strategy 1*, the best possible convergence results, which were obtained after several trial-and-error runs, are shown only.

Two-dimensional calculations were undertaken next to further investigate relative strengths and weaknesses of the various methods. For two-dimensional calculations, the use of direct solvers is prohibitive due to memory considerations, and the spatial operators in the independent directions have to be split (for both

Table 1
Comparison of performance of the semi-implicit (segregated) and fully implicit (coupled) solution approach for a one-dimensional calculation

Number of cells	Iterations		
	Segregated solution (*Strategy 1* with optimized α)	Segregated solution (*Strategy 2*)	Coupled solution
20	16	13	9
40	16	12	8
80	16	11	7

methods) to enable use of iterative solvers. For this study, the alternating direction implicit (ADI) method is chosen. The ADI method is chosen because it is a popular iterative solver for block-structured meshes, and the formulation developed earlier for the fully implicit method is directly extensible to multi-dimensional geometry with the ADI method. The geometry and boundary conditions for the two-dimensional test problem are shown in Fig. 2. The chosen boundary conditions represent worst-case scenarios where the mass fraction of each species will vary over the full realizable composition space.

In the case of the semi-implicit segregated solution approach using *Strategy 1*, convergence could only be obtained within a reasonable number of iterations on a coarse 20×20 mesh when severe under-relaxation was used (Fig. 3(a)). For a 40×40 mesh, convergence could only be attained after 100,000 iterations with an under-relaxation factor of 0.08. For a 80×80 mesh, convergence could not be attained at all. Attempts at improving the convergence by adjusting the number of inner iterations for the individual equations, or by changing the order of solution of the species, did not succeed. In contrast, it was possible to attain smooth convergence with the segregated solution approach using *Strategy 2* (Fig. 3(b)), and the fully implicit coupled solver in all cases (Fig. 4). The distributions of the various species are shown in Fig. 5. The behavior of the convergence of the fully implicit coupled method is in direct agreement with the general convergence behavior of the ADI method for a single equation. Since the contributions of two out of the four neighboring nodes are treated explicitly, the spectral radius increases with an increase in the number of cells, and the convergence deteriorates. Several techniques, such as multi-grid methods and block correction [7], are available to remedy this situation, and can be applied over and above the proposed solution technique to improve the convergence on finer meshes. In particular, the adaptation of the block matrix ADI method to a multi-grid ADI procedure will require little effort.

The disadvantage of using the fully implicit coupled solution approach is that it requires more memory. If N_C is the number of cells in any one direction, the fully implicit procedure requires storage of $N_C \times 3 \times N \times N$ link coefficients if the ADI method is used. In contrast, the semi-implicit procedure requires storage of only $N_C \times 3$ link coefficients. A few comments are warranted in this regard. Firstly, since the storage scales as the number of cells in one direction only, the overall memory requirement is not very high even for large three-dimensional calculations. For example, a three-dimensional calculation with 100 nodes in each direction (i.e., 1 million total cells), and 20 species, will require storage of only $100 \times 3 \times 20 \times 20 = 1{,}200{,}000$ numbers, which is equivalent to storage of the mass fraction of a single species, i.e.,

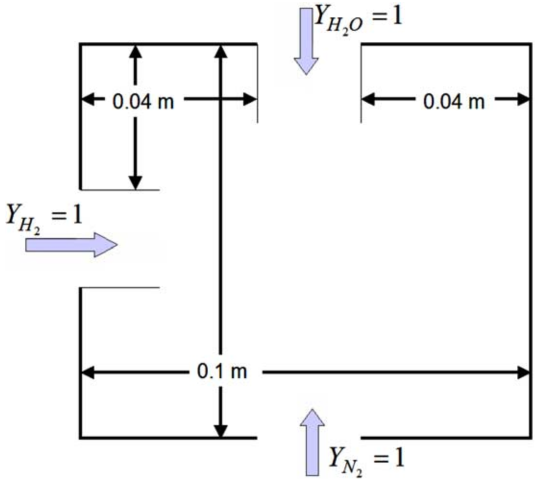

Fig. 2. Geometry and boundary conditions for the two-dimensional test problem.

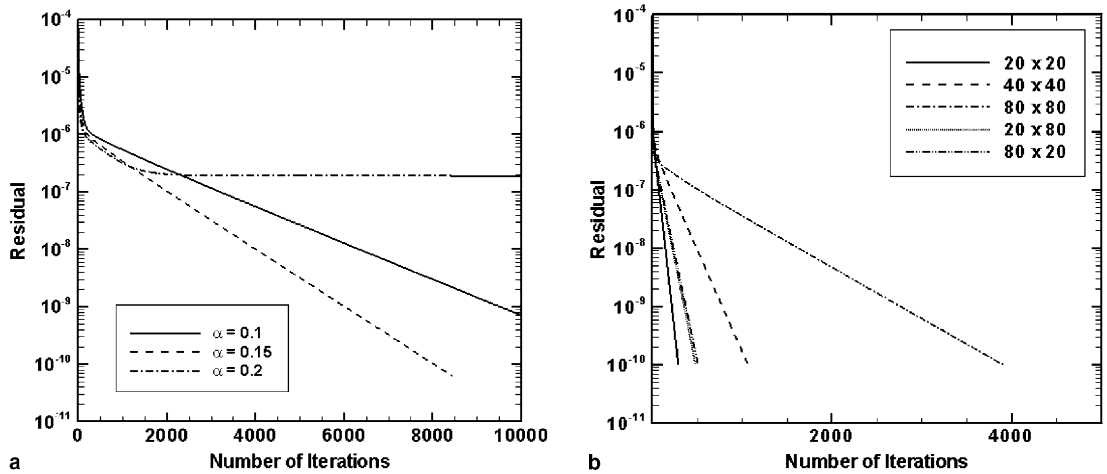

Fig. 3. Convergence of the semi-implicit segregated solution method. The residuals shown are for H_2: (a) *Strategy 1* on a 20×20 mesh with various under-relaxation factors; (b) *Strategy 2* for various mesh sizes with no under-relaxation.

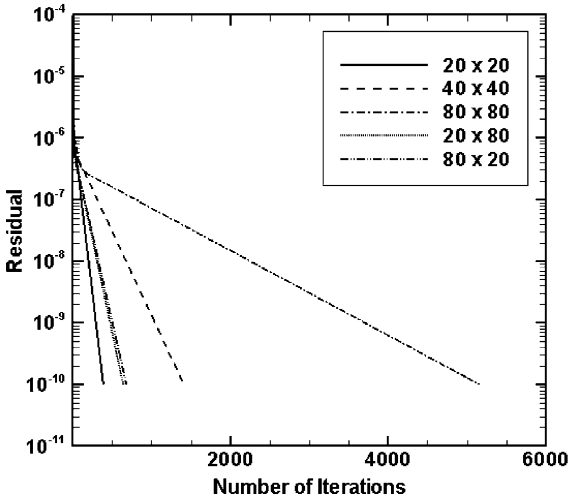

Fig. 4. Convergence of the fully implicit coupled solution method for several different mesh sizes and aspect ratios. The residuals shown are for H_2.

relatively insignificant. Secondly, although the link coefficients for all the other species are not stored simultaneously in the semi-implicit method, they must still be calculated to evaluate the right-hand side of Eq. (11). In other words, by not storing these link coefficients, computational effort is wasted since they have to be calculated repeatedly during the solution of the individual species equations. Thus, simultaneous storage of the link coefficients of all the species has additional benefits from the point of view of computational efficiency. Finally, in order to address the stiffness and nonlinearity, coupled solution of the species conservation equations is almost mandatory if complex finite-rate chemical reactions are considered, in which case, the proposed coupled solver requires no additional memory, while being still able to impose the mass conservation constraint directly.

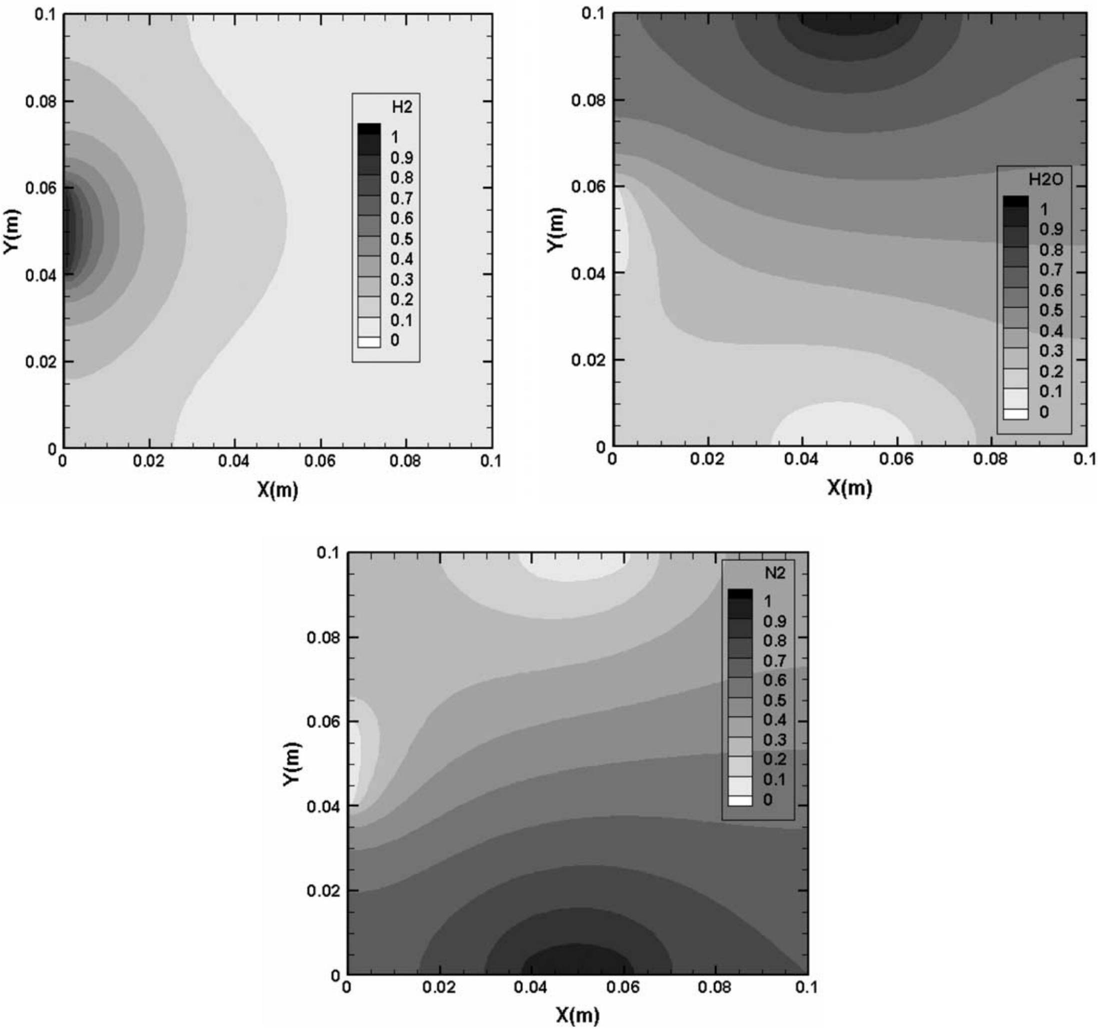

Fig. 5. Species mass fraction distributions for the two-dimensional test problem, computed on a 80 × 80 mesh.

4. Summary and conclusion

In a system consisting of more than two species, diffusion of a certain species is dictated not only by its own concentration gradient, but also by the concentration gradient of the other species in the system. This results in a set of strongly coupled nonlinear partial differential equations that cannot be segregated naturally. If only the self-diffusion operator is treated implicitly, the stability of the resulting equations depends on how the overall mass conservation constraint is imposed. If the mass conservation constraint (i.e., mass fractions summing to unity) is imposed directly to obtain the mass fraction of one of the species without solving its governing equation, the resulting algorithm is unstable. On the other hand, if the constraint is imposed indirectly by scaling the calculated mass fractions by their sum after every iteration, the resulting algorithm is stable, at least for the cases considered here. A fully implicit procedure has been presented to circumvent this fickleness in the numerical algorithm, and it is found to be unconditionally stable. The proposed fully implicit coupled procedure requires little additional memory and can be used for computations of complex reacting flows with little additional effort. The proposed method is expected to be useful for applications that involve low-speed (low Peclet number) reacting flows, as occurring in chemical vapor deposition reactors, fuel cells, and micro-scale devices.

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