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Modeling of multicomponent diffusion in high temperature flows

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Abstract—Three methods for computing diffusive mass transfer in non-reactive high temperature flows are compared. Results show that the widely used effective binary approximation may lead to large errors (up to 70%) in the evaluation of the mass fluxes, reflecting, therefore, on the solution of the species conservation equations. Two other approaches, the consistent effective binary diffusion due to Ramshaw, hereafter called the Ramshaw's approximation, and the linearized method are shown to reproduce accurately the mass transfer obtained with the exact formulation for multicomponent high temperature flows in isotherm conditions. When temperature gradients are imposed, the linear approximation leads to important errors (up to 40%) on the mass flux calculation. © 1997 Elsevier Science Ltd.

INTRODUCTION

The modeling of high temperature flows is a challenging task, involving fluid mechanics, heat transfer and mass transfer. Relying largely on the CFD effort, much of the work in this field has been based on relatively simple formulations for the diffusion mass transfer, although it represents a key element in the models. Probably due to the computational complexity of the task, previous works in numerical simulation of reactive flows have paid little attention to multicomponent effects [1–6]. The availability of computers of higher capacity now permits the investigation of more complete formulations for mass transfer.

Recent numerical studies [2, 7, 8] reveal the importance of diffusion mass transfer in predicting realistic concentration profiles, particularly in situations where hydrogen or other low molecular weight species are present in the multicomponent mixture. Phenomena like flame tip-opening can be explained by preferential diffusion of heat and mass in laminar diffusion flames [2]. In CVD deposition of diamond where film uniformity is of great importance, one must consider reactive heating due to hydrogen diffusion to the substrate [7]. Important demixing effects induced by multicomponent effects can also be predicted in an electrical arc [8], where in addition to ordinary diffusion the effect of ambipolar diffusion has to be considered.

Some approaches have been proposed to consider multicomponent diffusion [9–11]. It is relevant to compare them when they are applied to a common diffusion problem, neglecting chemical reactions in a first step. The separate study of mass transfer is appropriate considering that the coupling effect of kinetics could hinder the analysis. Furthermore, such a comparison is believed to bring conclusions applicable more generally to reactive flows.

The present paper analyses the results of three different mass flux formulations used for the diffusion of various ideal gas mixtures in a high temperature tubular reactor, and compares them to an exact formulation. After a theoretical review and a brief presentation of the governing equations and of the boundary conditions, the results are discussed in relation to multicomponent effects. Two different gas mixtures are studied to assert the accuracy and the performance of the formulations considered. The main conclusions about the comparison of the different diffusional approaches are then drawn.

THEORETICAL

Effective binary diffusion method

The simplest way to consider multicomponent diffusion is through the use of an effective binary diffusion coefficient. This approach assumes that the rate of diffusion of a specific species depends only on the composition gradient of that species:

$$\mathbf{J}_i^* = -c_t D_{i,\text{eff}} \nabla x_i \quad i = 1, \ldots, n. \tag{1}$$

Many methods have been described to calculate $D_{i,\text{eff}}$. A popular way to implement this approach is found in the work of Wilke [9] who developed the calculation of an approximate diffusion coefficient when a gas diffuses in a mixture of $n-1$ stagnant gases:

$$D_{i,\text{eff}} = \frac{(1-x_i)}{\sum_{j \neq i} \frac{x_j}{D_{i-j}}}. \tag{2}$$

Widely used [1, 2, 12], this method is often unjusti-

NOMENCLATURE

c_p	specific heat of the mixture [J (kg K)$^{-1}$]
c_t	total concentration of the mixture [mol m^{-3}]
$[B]^{-1}$	matrix used in the Maxwell–Stefan formulation
D_{ij}	Fick's multicomponent diffusion coefficients [m^2 s^{-1}]
D_{i-j}	binary diffusion coefficients [m^2 s^{-1}]
$D_{i,\text{eff}}$	effective diffusivity of component i [m^2 s^{-1}]
$[D]$	Fick's matrix of diffusion coefficients
h_i	specific enthalpy of component i [J kg^{-1}]
J_i^*	molar flux of component i [mol (m^2 s)$^{-1}$]
j_i	mass flux of component i [kg (m^2 s)$^{-1}$]
k	ratio of radii ($k = r_1/R$)
L	length of the reactor [m]
M_i	molecular weight of component i [kg mol^{-1}]
$\bar{M}$	mean molecular weight of mixture [kg mol^{-1}]
P	pressure [Pa]
R	radius of the reactor modeled [m]
r	radial coordinate [m]
r_1	radius of inside tube [m]
T	temperature [K]
u	mass averaged mean velocity [m s^{-1}]
u^*	molar averaged mean velocity [m s^{-1}]
x_i	molar fraction of component i
z	axial coordinate [m].

Greek symbols

λ	conductivity of the mixture [W (m K)$^{-1}$]
μ	viscosity of the mixture [kg (m s)$^{-1}$]
ρ	density of the mixture [kg m^{-3}]
ρ_i	density of the component [kg m^{-3}].

Subscripts

1	relative to central injection
2	relative to peripheral injection
i	relative to component i
in	entrance conditions
j	relative to component j.

Superscripts

1	relative to central injection
2	relative to peripheral injection.

fiably broadened to treat the general case where the approximation of the stagnant $n-1$ gases is not valid [13]. As a major drawback, it lacks the essential condition of flux consistency, i.e. $\Sigma J_i^* \neq 0$. It is, however, simple to implement in a general CFD procedure, since it has a standard convection–diffusion form. The flux consistency can further be imposed by calculating the flux of the last species by:

$$J_n^* = -\sum_{i=1}^{n-1} J_i^*.$$

Consistent effective binary diffusion method

Ramshaw [11] improves the preceding approach by proposing a correction to be added to the binary velocities. The resulting mass fluxes are then forced to be consistent through the addition of a simple term:

$$\mathbf{J}_i^* = -c_t D_{i,\text{eff}} \nabla x_i + x_i c_t \sum_{j=1}^{n} D_{j,\text{eff}} \nabla x_j. \qquad (3)$$

This corrected formulation ensures that the diffusive fluxes relative to averaged fluid velocity properly sum up to zero. It thus combines the simplicity of the effective binary diffusion approach with flux consistency.

Linearized theory method

The third multicomponent approximation studied in this work starts with the more rigorous Fick's formulation for ideal gases:

$$\mathbf{J}_i^* = -\sum_{j=1}^{n-1} c_t D_{ij} \nabla x_j \quad i = 1, \ldots, n-1 \qquad (4)$$

or, in matrix notation

$$[\mathbf{J}^*] = -c_t [D][\nabla x].$$

Comparing with the generalized Maxwell–Stefan equations for multicomponent diffusion in ideal gases:

$$[\mathbf{J}^*] = -c_t [B]^{-1} [\nabla x] \qquad (5)$$

with

$$B_{ii} = \frac{x_i}{D_{i-n}} + \sum_{k=1, i\neq k}^{n} \frac{x_k}{D_{i-k}} \quad \text{and}$$

$$B_{ij} = -x_i \left(\frac{1}{D_{i-j}} - \frac{1}{D_{i-n}} \right)$$

$[D] = [B]^{-1}$ can be deduced. Using this last relation, calculation of the full matrix formulation of multicomponent diffusion is then possible. The matrix $[B]^{-1}$

is a known function of concentration and Maxwell–Stefan diffusion coefficients. Furthermore, these coefficients can be precisely determined by the Chapman–Enskog theory, the Maxwell–Stefan coefficients being equivalent to binary diffusion coefficients in an ideal mixture. However, it is important to emphasize that such a relation between Fick's matrix of diffusion coefficients and Maxwell–Stefan formulation is only possible when a molar basis is considered.

One way to consider this rigorous formulation comes from the linearized theory of Toor [14] which simplifies the problem by considering a constant matrix of diffusion coefficients, evaluated at the mean concentration of the mixture. This linearizes the species conservation equations that can further be diagonalized by a matrix transformation [15]. The strength of this simplification comes from the possibility of using the available solution of binary diffusion systems obtained with similar conditions.

Exact method

Considering the variation of $[D]$, it is possible to model mass fluxes in their complete Fick's form. This approach, which is based on an exact and, thus, consistent flux formulation, is also used by Valerio and Vanni [16] for modeling interfacial mass transfer in a two phases chemical system. The exact method was also validated by simulating a Loschmidt tube with the experimental conditions of Arnold and Toor [17]. While the accuracy of this formulation, as the other ones, lies on the numerical scheme of resolution used, no more assumptions are considered. Because of its completeness, this last approach is chosen as a basis of comparison for the discussion of the results.

GOVERNING EQUATIONS

The geometry of the physical system modeled is shown in Fig. 1 and an axisymmetric configuration is adopted. The following assumptions are used throughout the development of the model:

- steady-state, laminar and axisymmetric flow;
- inlet pressure is atmospheric;
- diffusive species are chemically inert, i.e. no chemical reaction is considered.

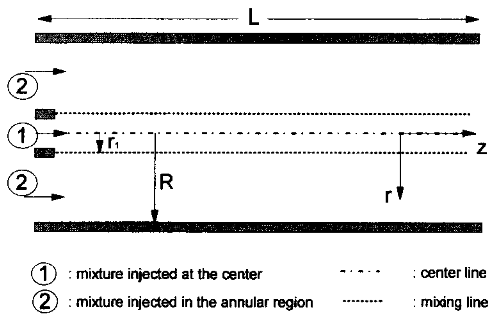

Fig. 1. Setup of the chemical reactor modeled.

The governing equations to be solved are the continuity, momentum, energy and species (diffusion) conservation equations for multicomponent fluid mixture.

- Continuity equation:

$$\nabla\cdot(\rho\,\mathbf{u}) = 0. \tag{6}$$

- Momentum equation:

$$\nabla\cdot(\rho\,\mathbf{uu}) = -\nabla P + \nabla\cdot(\mu\nabla\mathbf{u}). \tag{7}$$

- Energy equation:

$$\rho c_p(\mathbf{u}\cdot\nabla T) = \nabla\cdot(\lambda\nabla T) - \sum_{i=1}^{n}(\mathbf{j}_i\cdot\nabla h_i). \tag{8}$$

- Diffusion equations (molar basis):

$$\nabla\cdot(c_t\mathbf{u}^* x_i) = -\nabla\cdot\mathbf{J}_i^* \quad i = 1,\ldots,n. \tag{9}$$

Because the constitutive relations for the multicomponent diffusion fluxes are in a molar basis, the continuity equations must be solved with respect to mole fraction. This situation implies the use of a molar averaged mean velocity, u^*, that can be computed from the more common mass averaged mean velocity, u:

$$\mathbf{u}^* = \mathbf{u} + \sum_{i=1}^{n}\frac{x_i}{\rho_i}\mathbf{j}_i \tag{10}$$

with

$$\mathbf{j}_i = M_i\mathbf{J}_i^* - \frac{x_i M_i}{\bar{M}}\sum_{k=1}^{n} M_k\mathbf{J}_k^*.$$

Equations (6)–(9) are solved simultaneously by the control volume based numerical procedure Simpler [18]. Transport properties (μ, λ, D_{i-j}) are evaluated using the Chapman–Enskog theory with Lennard–Jones potentials.

BOUNDARY CONDITIONS

Equations (6)–(9) are submitted to the following boundary conditions:

- Entrance ($z = 0$): $v = 0 \quad T = T_{\text{in}}$

$$0 < r < r_1 \quad u = u_{\max 1}\left[1-\left(\frac{r}{R}\right)^2\right] \quad x_i = x_i^1 \tag{11}$$

$$r_1 < r < R \quad u = u_{\max 2}\left[1-\left(\frac{r}{R}\right)^2 + \frac{1-k^2}{\ln\left(\frac{1}{k}\right)}\ln\left(\frac{r}{R}\right)\right]$$

$$x_i = x_i^2. \tag{12}$$

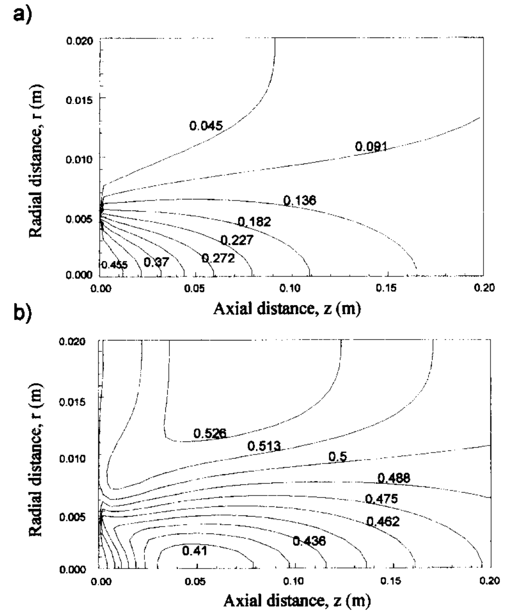

Fig. 2. Molar fraction isocontours in a ternary flow configuration: (a) CH_4 (injected centrally); (b) Ar (initially uniform).

- Exit ($z = L$): $v = 0$, axial gradients $= 0$ for u, T and x_i.
- Centerline ($r = 0$) $v = 0$, radial gradients $= 0$ for u, T and x_i.
- Wall ($r = R$) $u = v = 0$, $T = T_w$ and radial gradients $= 0$ for x_i.

RESULTS AND DISCUSSION

In order to evaluate the methods for calculating diffusive fluxes, two different chemically inert systems are considered. The first one consists of a ternary mixture of gaseous methane, hydrogen and argon. While the central part of the reactor is fed with an equimolar mixture of CH_4 and Ar (10 l min^{-1}), the outer flow (40 l min^{-1}) is composed of an equimolar mixture of H_2 and Ar. Thus, at the beginning of the reactor, the only diffusing species are CH_4 (Fig. 2a) and H_2. As the diffusion process starts, demixing of Ar is observed (Fig. 2b). This multicomponent effect is caused by the peculiar influence of each diffusing species exerting a specific force over the initially uniform species, Ar.

The other system studied involves 10 diffusing species: CH_4, CO, C_2H_6, C_3H_8, CO_2, H_2, H_2O, N_2, NH_3 and Ar. A similar configuration is used with an argon molar fraction of 0.50 in the central injection as well as in the annular flow. Molar feed rates are kept constant for all simulations. As with the ternary system, Ar demixing is also predicted, again due to the interaction of this initially uniform gas with other diffusing species. Nevertheless, the number of components is higher resulting in lower initial concentration gradients as a consequence of the fact that

$$\sum_{i=1}^{n} x_i = 1.0.$$

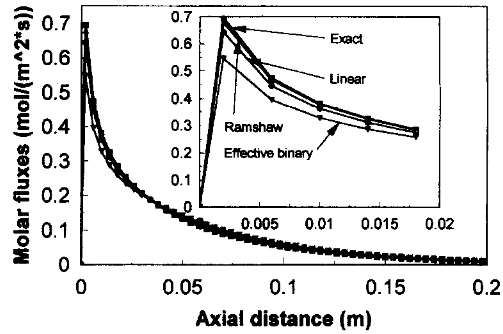

Fig. 3. Radial molar fluxes of methane in isothermal ternary mixture as function of axial distance.

Since axial Peclet number exceeds 10^2, the axial diffusion is far less important than convection. Thus, in order to compare the different flux formulations presented, the focus is rather made on radial mixing by considering radial molar fluxes at the mixing line (cf. Fig. 1), where radial Peclet number approaches 10^0.

For the first system analyzed, where ternary diffusion takes place, the radial molar flux of a diffusing species, CH_4, is presented in Fig. 3 where the maximum flux is naturally found at the beginning of the reactor. Here, the three mass flux approximations compare qualitatively well to the exact formulation. However, while the linear and Ramshaw's approximation follow the exact curve inside a 5% error, effective binary approach may underestimate or overestimate CH_4 radial flux with an error up to 20%, found at the inlet.

It is also interesting to analyze the radial molar flux of argon at the mixing line. In the first part of the reactor, this flux corresponds to more than half of the CH_4 flux, thus illustrating the multicomponent feature of the flow. Figure 4 shows the results obtained from the different approximations. Again, the three approximations predict the general features of the exact curve, though the linear method gives better results. Ramshaw's method leads to good overall

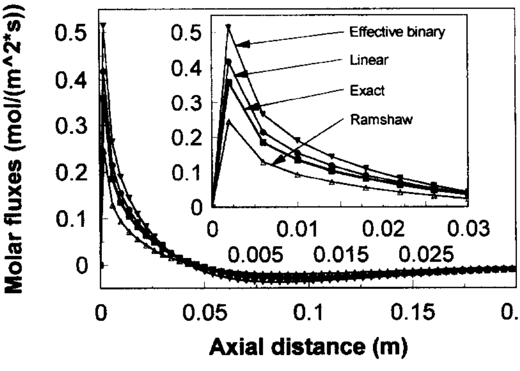

Fig. 4. Radial molar fluxes of argon in isothermal ternary mixture as function of axial distance.

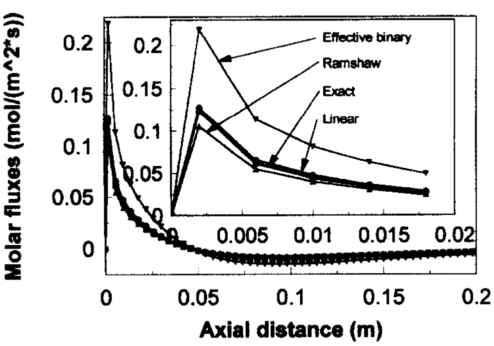

Fig. 5. Radial molar fluxes of argon in isothermal mixture of 10 constituents: CH_4, CO, C_2H_6, C_3H_8, CO_2, H_2, H_2O, N_2, NH_3 and Ar.

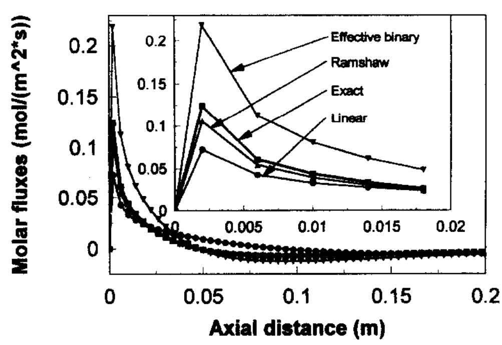

Fig. 7. Radial molar fluxes or argon in non isothermal mixture of 10 constituents: CH_4, CO, C_2H_6, C_3H_8, CO_2, H_2, H_2O, N_2, NH_3 and Ar.

results but errors up to 30% can be found at the beginning of the reactor.

Strictly speaking, the effective binary approach does not present the demixing effect due to multicomponent nature of the diffusion, the flux of argon in this case being solely related to its own concentration gradient which is zero. The calculated flux of the Fig. 4 comes from the restriction imposed for local mass conservation. Argon being the dependent species, its flux is computed from the other ones. Thus, it is not surprising to note errors as high as 40% on the radial molar flux when compared to the exact one.

Concentration fields calculated for the 10 diffusing species cases are similar to the ones found in the ternary flow. The only difference comes from the initial concentration gradients which cannot be as high as the ternary ones. In order to compare results obtained with these two different systems, argon molar fraction in feed flows is kept at 0.5.

Again, the diffusion of species presenting initial composition gradients drives the demixing of argon, resulting in non-negligible radial molar flux of this species at the mixing line. Figures 5 and 6 present comparative results obtained with the different methods. Figure 5 shows radial molar flux of Ar at the mixing line. Figure 6 shows two isocontours of Ar molar fraction ([Ar] = 0.47, 0.51). While the linear and Ramshaw's computed fluxes are very close to the exact ones, this is not the case for the effective binary method where a relative error of about 76% can be calculated on the radial molar flux at the beginning of the reactor.

Reactive flows such as flames often present strong temperature gradients. It is, therefore, pertinent to assess the effect of such gradients on the accuracy of the different diffusion formulations. Numerical simulations are thus repeated, this time with inlet temperature (T_{in} = 1200 K) higher than wall temperature (T_w = 300 K). Results obtained with the 10 species system (cf. Figs 7 and 8) show the sensitivity of the linear method with respect to the presence of temperature gradients. This sensitivity can be explained by the assumed constant matrix of diffusion. While the effective binary approach is clearly inappropriate to model argon demixing, Ramshaw's method predicts the exact fluxes quite accurately in this case.

This comparative study reveals the weaknesses of the popular effective binary approach in modeling multicomponent diffusion in a non-reactive flow. The calculation of diffusion flux of one species based only on the concentration gradient of that same species, this method cannot reflect demixing effects like the one observed here with argon, unless flux consistency is imposed. Nevertheless, it is the simplest and the cheapest formulation to implement in a CFD code.

The approach based on the linearization of the mass

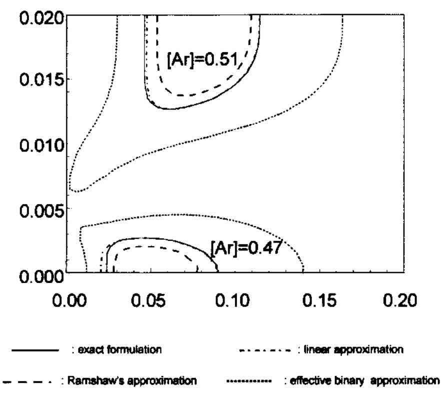

Fig. 6. Isocontours of Ar molar fraction for the diffusion methods studied. Isothermal case.

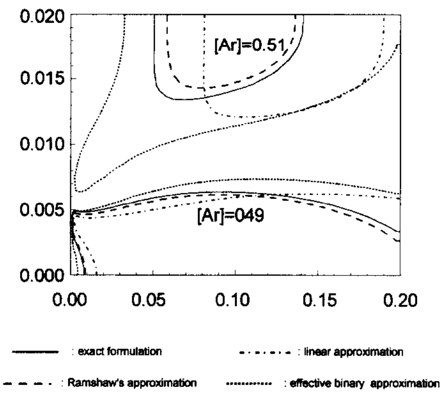

Fig. 8. Isocontours of Ar molar fraction for the diffusion methods studied. Temperature gradient case.

conservation equations responds quite well in isotherm situations. Its sensitivity to temperature gradients and its complexity of implementation limit its applicability. In fact, this method requires almost the same computing effort as the exact one. Ramshaw's improvement of the effective binary approximation gives the best results. Consistent, this method also reflects multicomponent effects in an advantageous way, even in presence of temperature gradients. Its implementation is almost as direct as the effective binary approach, a correction term based on the local mass conservation distinguishing the two approximations. Clearly, it represents the best compromise between the accuracy and the computing effort needed.

CONCLUSIONS

Three different diffusion flux formulations have been compared to an exact approach in order to evaluate their strengths and limits. The objective pursued was to get a better understanding of multicomponent mass transfer when coupled with fluid mechanics and heat transfer. A common diffusion problem has been used as a benchmark. Results reveal that the effective binary method presents some inherent deficiencies for the computation of the inert flows considered. The linear and Ramshaw's approximations reflect well the multicomponent features of these flows in isotherm situations. However, Ramshaw's approach appeared more adequate to model diffusion fluxes especially in the context of flames where important temperature gradients are present. Furthermore, it has the simplicity of the effective binary method, while not requiring much supplementary computing effort.

Future work should include chemical reactions in the present model and look at the importance of a precise diffusion calculation for a representative sample of chemical systems. The degree of complexity in the treatment of diffusion may depend on the problem considered. If the kinetics is controlling, for example, then the effective binary formulation may provide sufficiently precise mass flux calculations. The study of high temperature reactive flows like thermal plasmas should also include the treatment of ionized species by considering ambipolar diffusion.

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