

## Simplified diffusion model for detailed and reduced reaction mechanisms

**Citation for published version (APA):**

Eggels, R. L. G. M., Somers, L. M. T., & Goey, de, L. P. H. (1997). Simplified diffusion model for detailed and reduced reaction mechanisms. In J. Warnatz, & F. Berendt (Eds.), *Proceedings of the third Workshop on Modelling of Chemically Reacting Systems*

**Document status and date:**

Published: 01/01/1997

**Document Version:**

Accepted manuscript including changes made at the peer-review stage

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

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# Simplified Diffusion Model for Detailed and Reduced Reaction Mechanisms

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## Abstract

A diffusion model is proposed, which simplifies the application of reduced reaction mechanisms considerably, whereas the results agree well with computations using a more detailed constant Lewis number diffusion model. Results are presented for one-dimensional premixed burner-stabilized flames using methane/air and hydrogen/air mixtures. The diffusion model is based on unit Lewis number assumptions for most of the species. Only for  $H$  and  $H_2$  non-unit Lewis numbers are applied. As a result, the mass fractions of the elements do not change in the flame, which implies that these element mass fractions do not have to be taken into account as additional degrees of freedom for reduced reaction mechanisms.

## 1 Introduction

A lot of effort has been devoted to the development of reduced reaction mechanisms recently [1,2]. The aim of the application of reduced mechanisms is to reduce the computational effort, without introducing large errors. The computational gain is largest in case of reduced reaction mechanism with low dimensions. Furthermore, if look-up tables are used, as is the case for Intrinsic Low-Dimensional Manifolds, the size of these tables increases fast with increasing dimension of the reduced mechanism. Therefore, accurate reduced reaction mechanisms are required, with a dimension as low as possible.

If non-unit Lewis numbers are applied, the element mass fractions may vary in the computational domain and have to be considered as additional degrees of freedom for the reduced reaction mechanism. Unit-Lewis number assumptions are therefore often used. Although the Lewis numbers for most of the species are close to one, the Lewis numbers for  $H$  and  $H_2$  deviate strongly from one (they are approximately equal to 0.18 and 0.3, respectively). It is well known that the unit Lewis number assumption for all species is not very accurate since the effects of preferential diffusion may be significant, for instance, on the adiabatic mass burning rate.

In order to describe the effects of preferential diffusion correctly and at the same time circumventing the increase of the number of degrees of freedom, the following diffusion model is proposed: for all species unit Lewis numbers are assumed, only for  $H$  and  $H_2$  non-unit Lewis numbers are applied. It will be shown that the element mass fractions remain constant for certain kinds of flames, if this model is used.

The proposed diffusion model will be applied to flat flames and the results are compared with a more detailed diffusion model (non-unit Lewis numbers for all species). The simplified diffusion model is applied to reduced reaction mechanisms, subsequently. The reaction mechanisms are reduced by application of the Mathematically Reduction Technique which determines Intrinsic Low-Dimensional Manifolds. The principle of the method is not treated here, as it is already explained extensively in [1,2,3].

## 2 Specific element mole numbers

In this section it will be shown briefly that, for certain kinds of flames, the specific element mole numbers remain constant in the domain if all Lewis numbers are equal to one except those of  $H$  and  $H_2$ . The specific mole numbers of the species are given by

$$\phi_i = Y_i/M_i, \quad (1)$$

with  $Y_i$  the mass fraction and  $M_i$  the molar mass of one of the  $n$  species denoted by the index  $i$ . The specific element mole numbers are defined similarly,

$$\chi_j = \frac{z_j}{W_j}, \quad (2)$$

where  $z_j$  indicates the mass fraction of element  $j$  and  $W_j$  the molar mass of element  $j$ . The specific element mole numbers are related to the specific mole numbers of the species by

$$\chi_j = \sum_{i=1}^n \mu_{ji} \phi_i, \quad (3)$$

with  $\mu_{ji}$  denoting the element composition coefficients. These element composition coefficients indicate the number of atoms of kind  $j$  in species  $i$ . Note that  $M_i = \sum_{j=1}^{n_e} \mu_{ji} W_j$ , where  $n_e$  is the number of elements.

First, it will be shown that a specific element mole number  $\chi_j$  does not vary in space and time if the Lewis numbers (defined by  $Le_i = \lambda/(\rho D_i c_p)$ ) of all species for which  $\mu_{ji} \neq 0$  are equal. The differential equations for the specific element mole numbers are derived from the differential equations of the species. The latter are given by:

$$\rho \frac{\partial \phi_i}{\partial t} + \rho \mathbf{v} \cdot \nabla \phi_i - \nabla \cdot (\rho D_i \nabla \phi_i) = \dot{\rho}_i / M_i. \quad (\text{for } i = 1, \dots, n). \quad (4)$$

When these equations are multiplied with  $\mu_{ji}$  and added, the following differential equation can be derived:

$$\rho \frac{\partial \chi_j}{\partial t} + \rho \mathbf{v} \cdot \nabla \chi_j = \sum_{i=1}^n \mu_{ji} \nabla \cdot (\rho D_i \nabla \phi_i) + \sum_{i=1}^n \mu_{ji} \dot{\rho}_i / M_i. \quad (5)$$

The term  $\sum_{i=1}^n \mu_{ji} \dot{\rho}_i / M_i$  is equal to zero because elements are conserved in chemical reactions. Next, using the definition of the Lewis numbers and the relation  $\sum_{i=1}^n \mu_{ji} \nabla \phi_i = \nabla \chi_j$ , we find:

$$\rho \frac{\partial \chi_j}{\partial t} + \rho \mathbf{v} \cdot \nabla \chi_j - \frac{1}{Le} \nabla \cdot \left( \frac{\lambda}{c_p} \nabla \chi_j \right) = \nabla \cdot \left( \frac{\lambda}{c_p} \sum_{i=1}^n \mu_{ji} \left( \frac{1}{Le_i} - \frac{1}{Le} \right) \nabla \phi_i \right). \quad (6)$$

Note that a source term appears in the right-hand-side of this equation, which is only zero if all Lewis numbers are equal ( $Le_i = Le$ ). Then, an effective diffusion coefficient given by  $\frac{1}{Le} \frac{\lambda}{\rho c_p}$  appears in the equation for the specific element mole numbers  $\chi_j$ .

It is obvious that the solution of this equation depends on the boundary conditions. If we assume that (1) the inner product of the gradient vector of the specific element mole numbers and the normal unit vector  $\mathbf{n}$  on the boundaries is equal to zero  $\nabla \chi_j \cdot \mathbf{n} = 0$  (i.e. no flux through the boundaries) and (2)  $\chi_j$  is constant at the inflow and (3) the system has an initial solution  $\chi_j(\mathbf{x}, t = 0) = \chi_j^0$ , then the solution of these equations is given by:  $\chi_j(\mathbf{x}, t) = \chi_j^0$ . This means that the specific element mole numbers remain constant in the entire domain if all Lewis numbers are equal. Note that for non-premixed flames, the specific element mole numbers are not equal at the various inlets and are therefore not constant in the domain.

Assuming that all above mentioned conditions are valid, it follows from equation (6) that  $\chi_j(\mathbf{x}, t)$  is constant in time and space for premixed flames, if  $Le_i = Le$  for the species  $i$  with  $\mu_{ji} \neq 0$ . Furthermore, it has to be realized that the specific element mole numbers cannot change independently. Since the mass fractions of all species add to one, the following relation for the specific element mole numbers can be derived:

$$\sum_{i=1}^n Y_i = \sum_{i=1}^n M_i \phi_i = \sum_{i=1}^n \sum_{j=1}^{n_e} \mu_{ji} W_j \phi_i = \sum_{j=1}^{n_e} W_j \chi_j = 1, \quad (7)$$

which states that the sum of the element mass fractions  $z_j = W_j \chi_j$  is conserved:

$$\sum_{j=1}^{n_e} z_j = 1. \quad (8)$$

From equation (7) it becomes clear that it is not possible that a single specific element mole number varies in space, if the others are constant in the complete flame domain. This implies that if  $Le_H \neq 1$  and  $Le_{H_2} \neq 1$  and  $Le_i = 1$  for all other species, all specific element mole numbers remain constant.

It should be noted that a consequence of the introduction of constant Lewis numbers is that the sum of diffusion fluxes is not equal to zero, in general. This problem can be circumvented by replacing the differential equation for nitrogen by the equation  $Y_{N_2} = 1 - \sum_{i=1, i \neq i_{N_2}}^N Y_i$  in mixtures with an abundant nitrogen part. Then, however, the specific element mole number of nitrogen is not conserved, in contradiction with eq. (6). This means that not both the conservation of diffusion fluxes and the conservation of elements can be conserved if constant Lewis numbers are introduced. To investigate this problem, we performed the following two computations. In one calculation the diffusion fluxes are conserved and for the second computation the specific element mole numbers were constant. From the fact that the differences between the results are very small ( $< 1\%$ ) it may be concluded that both approaches are valid. This is also supported by comparing results of computations with detailed transport and results of computations with constant Lewis numbers. Then, differences can hardly be observed. In the first case the sum of diffusion fluxes is zero, while this is not guaranteed if constant Lewis numbers are applied. From this numerical study we may conclude that the model is valid to model hydrocarbon flames with an abundant part of inert nitrogen.

Although all the specific element mole numbers are constant in the above mentioned diffusion model, variations in enthalpy due to preferential diffusion have to be taken into account. This becomes clear if the differential equation for the enthalpy is considered:

$$\rho \frac{\partial h}{\partial t} + \rho \mathbf{v} \cdot \nabla h - \nabla \cdot \left( \frac{\lambda}{c_p} \nabla h \right) = \nabla \cdot \left( \frac{\lambda}{c_p} \sum_{i=1}^n h_i \left( \frac{1}{Le_i} - 1 \right) \nabla \phi_i M_i \right). \quad (9)$$

This equation is similar to the equations of the specific element mole numbers and the source term is zero, if all Lewis numbers are equal to one. However, if all Lewis numbers are one, except those for  $H$  and  $H_2$ , it is seen from equation (9) that the source-term of the enthalpy equation is non-zero.

The Mathematical Reduction Technique is used for computing the reduced reaction mechanism and the application to flat flames are described in detail before [2,3]. The following equations for the control variables are used to model flat flames:

$$\begin{aligned} \rho u \frac{d\alpha_j}{dx} \sum_{i=1}^n \left( \frac{d\phi_i}{d\alpha_j} \right)^2 - \sum_{i=1}^n \left[ \left( \frac{d\phi_i}{d\alpha_j} \right)^2 \frac{d(\rho D_i)}{d\alpha_j} \left( \frac{d\alpha_j}{dx} \right)^2 + \frac{d\phi_i}{d\alpha_j} \rho D_i \frac{d^2 \phi_i}{d\alpha_j^2} \left( \frac{d\alpha_j}{dx} \right)^2 \right. \\ \left. + \left( \frac{d\phi_i}{d\alpha_j} \right)^2 \rho D_i \frac{d^2 \alpha_j}{dx^2} \right] - \rho \sum_{i=1}^n \frac{d\phi_i}{d\alpha_j} \rho_i / M_i = 0, \quad j = 1, \dots, n_c, \end{aligned} \quad (10)$$

where  $\alpha_j$  denotes the control variable and  $n_c$  the number of control variables. These equations are obtained by projecting the original differential equations of the species on the local tangential direction vector of the Intrinsic Low-Dimensional Manifold  $\frac{d\phi}{d\alpha_j}$  [2,3]. If the reduced reaction mechanism is applied to more dimensional flames the projection is more complicated. In eq. (10) the diffusion constants of all species appear. This shows that the diffusion coefficients of all species have an influence on the solution.

### 3 Results

In this section the simplified diffusion model is compared with a more detailed diffusion model, with non-unit Lewis numbers for all species. The simplified model is applied to the modelling of a flat burner-stabilized hydrogen/air flame first. The initial reaction mechanism includes eight species and is presented in Eggels et al. [3]. The results of this model are compared with a more detailed diffusion model, using constant Lewis numbers (obtained by fitting to mixture averaged results [4,5]). The mole fraction profiles of some species are presented in Figs. 1 and 2. It can be seen that the differences are small. The importance of preferential diffusion of  $H$  and  $H_2$  becomes clear by considering the adiabatic mass burning rate. If unit Lewis numbers are used for all species the mass burning rate is equal to  $0.127g/(cm^2s)$ , whereas it is  $0.206g/(cm^2s)$  if non-unit Lewis numbers are applied for all species and  $0.205g/(cm^2s)$  if non-unit Lewis numbers are applied for  $H$  and  $H_2$ , only. It may, therefore, be concluded that the most important preferential diffusion effects are well described by the proposed simplified diffusion model.

Next, the model is applied to an adiabatic methane/air flame ( $\Phi = 1$ ). As reaction mechanism the skeletal mechanism proposed by Smooke [4] is used. The results are presented in Figures 3 and

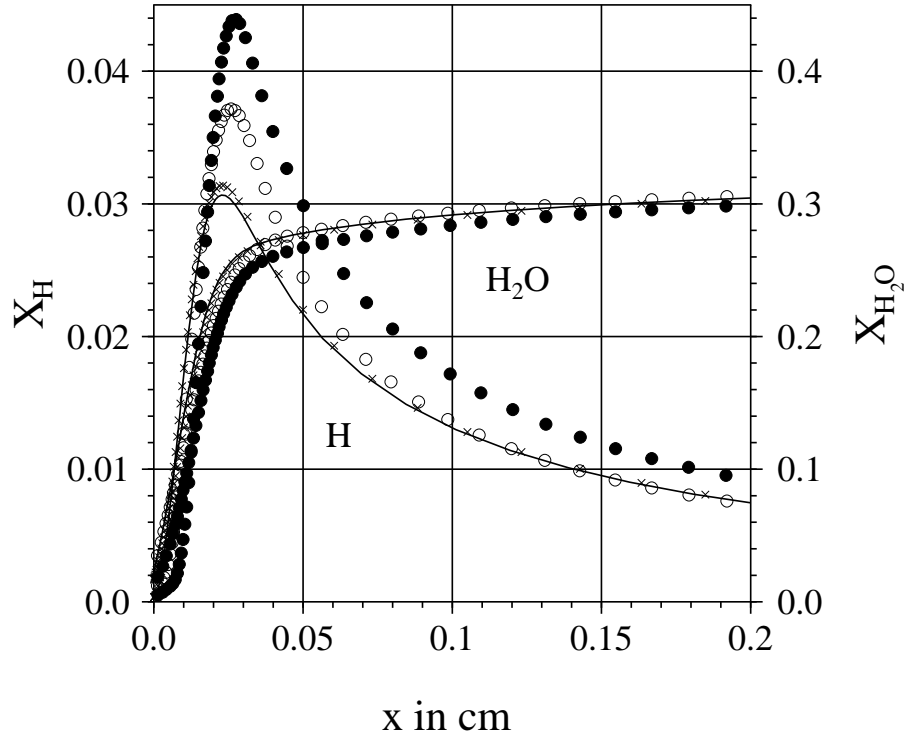


Figure 1: Detailed and reduced hydrogen/air computations using various transport models,  $\dot{M} = 0.14 \text{ gr/cm}^2/\text{s}$ ,  $\Phi = 1.0$ . The lines correspond to detailed computations using non-unit Lewis numbers for all species; the computations with unit Lewis numbers, except for  $H$  and  $H_2$  are denoted by markers. The  $\times$  symbols correspond to the detailed reaction mechanism, the circles to the two-step reduced reaction mechanism;  $\bullet$ : enthalpy variations due to preferential diffusion neglected,  $\circ$ : enthalpy variations included.

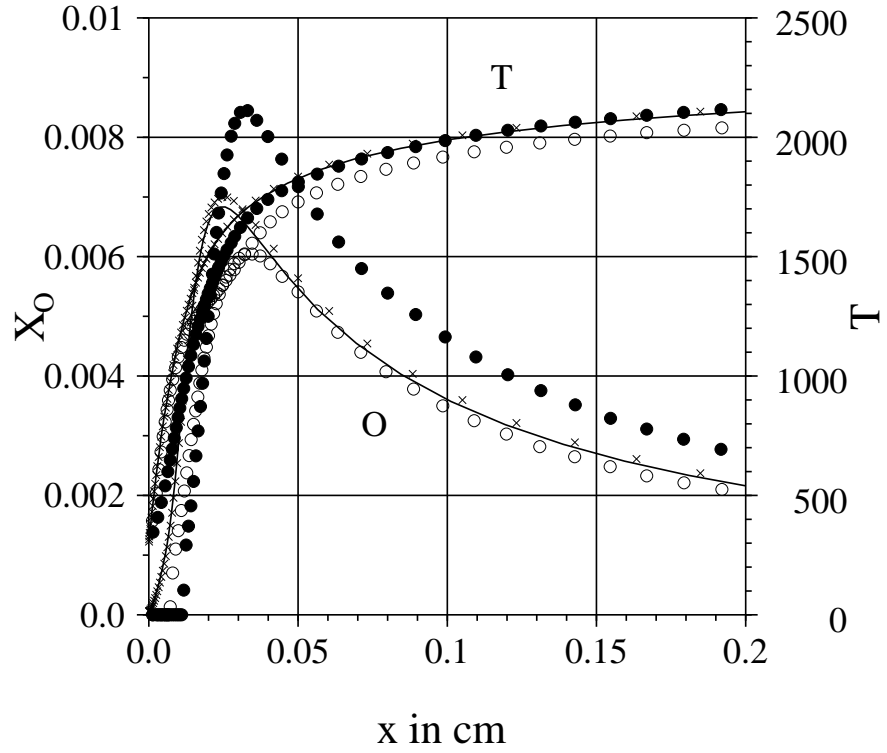


Figure 2: Detailed and reduced hydrogen/air computations using various transport models,  $\dot{M} = 0.14 \text{ gr/cm}^2/\text{s}$ ,  $\Phi = 1.0$ . The lines correspond to detailed computations using non-unit Lewis numbers for all species; the computations with unit Lewis numbers, except for  $H$  and  $H_2$  are denoted by markers. The  $\times$  symbols correspond to the detailed reaction mechanism, the circles to the two-step reduced reaction mechanism;  $\bullet$ : enthalpy variations due to preferential diffusion neglected,  $\circ$ : enthalpy variations included.

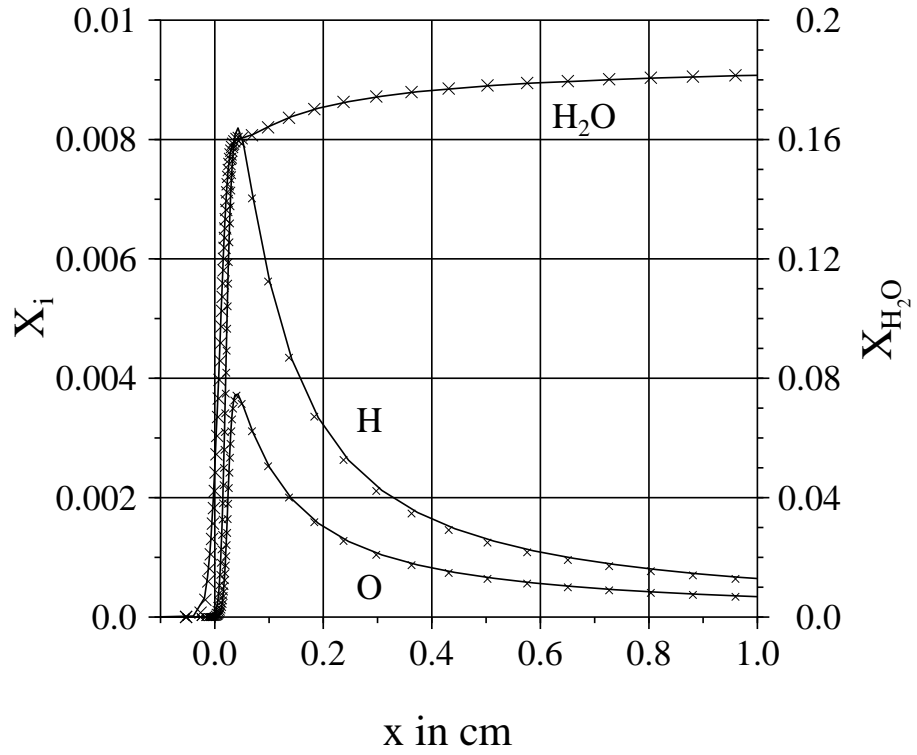


Figure 3: Detailed adiabatic methane/air computations using various transport models,  $\Phi = 1.0$ . The lines correspond to computations using non-unit Lewis numbers for all species, the markers to computations with unit Lewis numbers, except for  $H$  and  $H_2$ .

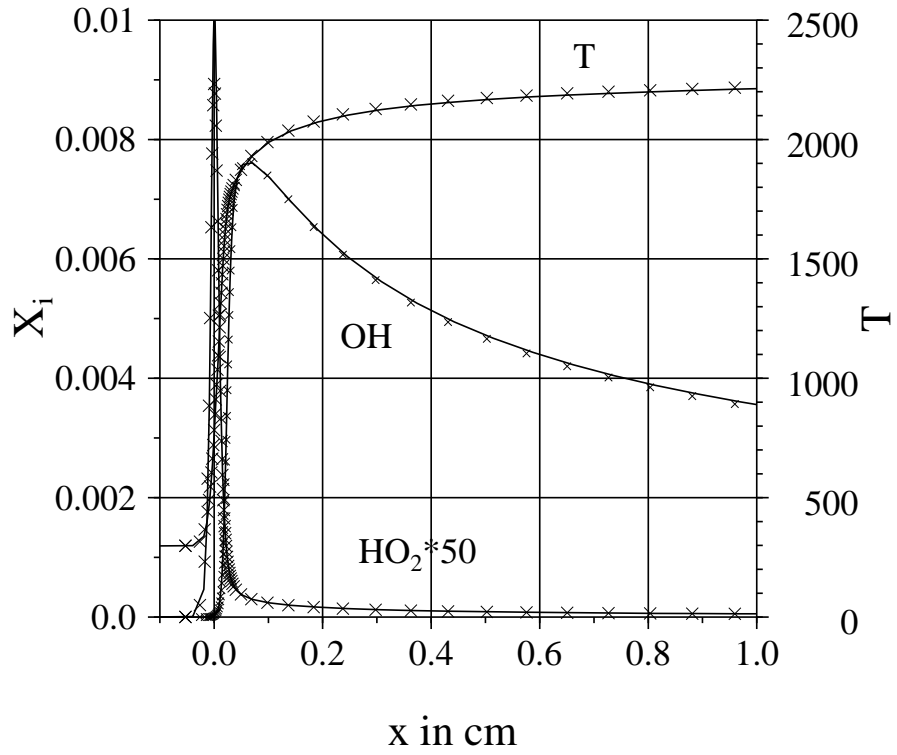


Figure 4: Detailed adiabatic methane/air computations using various transport models,  $\Phi = 1.0$ . The lines correspond to computations using non-unit Lewis numbers for all species, the markers to computations with unit Lewis numbers, except for  $H$  and  $H_2$ .



4. The adiabatic mass burning rate of the detailed diffusion model is equal to  $0.0466g/(cm^2s)$  and  $0.0436g/(cm^2s)$  for the simplified diffusion model. The figures indicate that the results of the simplified diffusion model agree well with those of the more detailed diffusion model. This implies that preferential diffusion effects are mainly caused by  $H$  and  $H_2$  in case of hydrogen and methane/air flames.

Finally, we focus on reduced reaction mechanisms. A two-step reduced mechanism for the above mentioned hydrogen mechanism is constructed by using the Mathematical Reduction Technique [2,3]. Since we consider a burner-stabilized flame the enthalpy is an additional degree of freedom on the manifold, so that the dimension of the manifold is three. In order to obtain an accurate manifold which is not too large, the manifold is locally refined. The method is applied to the hydrogen/air reaction mechanism only. Previous investigations [2] have shown that for the methane/air reaction mechanism at least a three-step reduced mechanism has to be applied. Since also the enthalpy has to be used as additional variable, the total dimension on the manifold is four. We are, however, not able to make such a four-dimensional manifold, yet. To investigate the influence of preferential diffusion on the enthalpy, additional computations with the reduced reaction mechanism are performed where enthalpy variations are neglected. These results, as well as the results where enthalpy variations due to preferential diffusion are included, are presented in Figs. 1 and 2, together with the detailed results. The results indicate that the influence of preferential diffusion on the enthalpy is significant. If enthalpy variations are included, the profiles of the major species agree well with the detailed computations. Some radicals show more deviations, but are never larger than 10%. If the enthalpy variations are neglected, the differences are larger. The results presented above indicate that the simplified diffusion model is accurate, whereas the computational effort for the application of reduced reaction mechanisms is reduced considerably.

## 4 Conclusion

A simplified diffusion model is presented, which is based on the assumption of unit Lewis numbers for most species. Non-unit Lewis numbers are applied for  $H$  and  $H_2$ . A comparison of this model with a more detailed model shows that the simplified model is accurate, indicating that the most important effects of preferential diffusion are caused by  $H$  and  $H_2$ . The advantage of this model is that the specific element mole numbers don't change in the computational domain of some premixed flames, which simplifies the application of reduced reaction mechanisms, such as the Mathematical Reduced Technique (ILDM).

## References

- [1] Maas, U., Pope, S.B., Simplifying Chemical Kinetics: Intrinsic Low-Dimensional Manifolds in Composition Space. *Combust. Flame*, **88**:239 (1992).
- [2] Eggels, R.L.G.M., Modelling of Combustion Processes and NO Formation with Reduced Reaction Mechanisms, *Ph.D. Thesis, Eindhoven University of Technology*, 1995.
- [3] Eggels, R.L.G.M., Goey de, L.P.H., Mathematically Reduced Reaction Mechanisms Applied to Adiabatic Flat Hydrogen/air Flames. *Combust. and Flame*, **100**:559 (1995).
- [4] Smooke, M.D., Reduced Kinetics Mechanisms and Asymptotic Approximations for Methane Air Flames, *Lecture Notes in Physics*, Springer Verlag, 1991.
- [5] Somers, L.M.T., The Simulation of Flat Flames with Detailed and Reduced Chemical Models. *Ph.D. Thesis, Eindhoven University of Technology*, 1994.