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The Simulation of Flat Flames
with
Detailed and Reduced
Chemical Models

PROEFSCHRIFT

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Chapter 1

General Introduction

1.1 Prologue

Combustion in general and flames in particular have played a major role in man's history. Some historians even point man's ability of employing fire at their own benefit as one of the first steps to a more advanced technological (crafts-making) age. The history of combustion science, however, has long been an experimental based science with the first experiments of Le Chatelier dating from 1883. In the late nineteenth and the early twentieth century theoretical treatments of combustion processes were introduced (Arrhenius (1889), Burke-Schumann (1921)). Nowadays, the theoretical basis of combustion science is well founded, at least for laminar gas-phase combustion processes [Hir54, Cha70, Wil85].

The physical basis of combustion processes is completely determined by the interaction between fluid dynamics and chemical reactions. Due to the nature of the governing equations, which is non-linear in both fluid-dynamical and chemical aspects, there is no analytical solution available even for the simplest problems in combustion science. It is due to the development in computer technology and advances in numerical methods in the last two decades that accurate detailed chemical models are available today.

In the first part of this century the chemistry was modelled in a simplified manner. Usually a one-step overall reaction yielding,

\[ \text{Fuel} + \text{Oxygen} \rightarrow \text{Products} \]

replaced the complex chemistry. Then, for some special cases (simplified geometries), like one-dimensional (flat) flames or rotationally symmetric co-flowing diffusion flames (Burke-Schumann geometry, with infinite-rate chemistry and simplified flow equations), analytical solutions can be found. More advanced techniques like AEA\(^1\) and RRA\(^2\) have become available only recently. The latter enable more complicated chemical models to be incorporated in analytical treatments. These treatments yield quantitative and qualitative good results for combustion of methane (\(C_2H_4\)).

\(^1\)Activation Energy Asymptotics
\(^2\)Reaction Rate Asymptotics
and some higher hydrocarbons in zero- and one-dimensional reactive systems, e.g., [Pet87, Ses90].

However, for detailed chemical models, an analytical solution is still not available. The only way to handle these large sets of non-linear equations is to employ computers. In fact, it is because of the growth of CPU-performance and availability of memory in the eighties, that the reaction rate data for methane chemistry has become as reliable as it is today. However, not only the increase in computer performance, also the development of sophisticated solution techniques has played a major role in the recent advances [Deu87]. The nature of the governing equations induce specific problems in the numerical simulation of flames. The most obvious problems arising in combustion modelling originate from the differences in time and geometry scales. The latter occur in both simple and complex reaction models, for the dimension of the chemically active layer is \( O(0.1 \text{mm}) \) while the total length of the physical domain may be \( O(10 \text{cm}) \) geometry. This difference in length scales\(^3\) is normally tackled with an adaptive gridding technique.

The difference in time-scales, which is more prominent in detailed chemical models, even makes higher demands on the numerical algorithm. This inherent stiffness\(^4\), present in the chemistry itself and in flow and chemistry as well, requires special attention [Smo93, Rog91, Dix68, Ora87]. These techniques, however, are very memory- and CPU-intensive and the first multi-dimensional\(^5\) laminar flame with detailed chemistry has been published only recently [Smo90]. The original calculation took approximately 150 hours on a Cray-2 supercomputer, which has been reduced to 15 hours recently, due to improved vectorization and recent advances in solution techniques for large linear systems [Smo92]. This illustrates that detailed chemical calculations in realistic burner geometries are still impractical at the moment.

The aim of the present research project at the Eindhoven University of Technology is to investigate the stability and structure of laminar gas-flames with respect to changes in gas composition. Due to governmental policy, nowadays many different gas-resources are used (Russian, Norwegian, Algerian), which do not only exhibit differences in caloric value but also show different burning behavior [Jes76]. Originally this project was initiated by the VEG-Gasinstituut\(^6\) in order to predict (and control) the effects of these known differences in gas compositions on burner behavior in domestic applications. However, it clearly is impractical (and even impossible for most practical burner geometries) to apply full detailed chemical models. Therefore, at first a one-step overall chemical model was chosen. An infinite-rate chemistry would certainly facilitate the treatment of this one step chemistry (Fuel + Oxygen \( \rightarrow \) Products), but would only apply to diffusion flames. The latest trend in modern domestic applications is to implement fully premixed burners.

\(^3\)Sometimes referred to as grid-stiffness.

\(^4\)The presence of many different orders of magnitude in timescales, in a problem.

\(^5\)It concerns a three-dimensional rotationally-symmetric co-flow diffusion flame which is easier to compute since the place of the flame front is determined by diffusion processes mainly.

\(^6\)Presently GASTEC N.V.
for environmental and constructional purposes, a finite-rate chemical model was introduced. Thus, an Arrhenius-like fuel mass consumption rate was postulated,

$$\dot{\rho}_{fu} = -A[Fu]^{\alpha}[Ox]^{\beta}T^{\gamma}e^{-E_a/RT},$$

where \([Fu]\) and \([Ox]\) represent the concentration of the fuel and oxidizer, respectively. The parameters \(A, \alpha, \beta\) and \(E_a\) depend on the gas to be burnt. The actual values for these parameters may be obtained from flat-flame experiments, conducted to give the adiabatic flame temperature and burning velocity as a function of the equivalence ratio. The parameters are then fitted to the experimental data. This approach has been tested for \(CH_4\)-air flames and performs quite well [Lan92]. The main advantage of this procedure is that it is readily applicable on natural gases as well. It is only a matter of performing the proper experiments with the mixture to be studied. Currently, based on this simple chemistry computational methods are available [Lan92] for one-dimensional, two-dimensional cartesian and three-dimensional rotationally-symmetric combustion problems. The results obtained by these methods describe the flame shape and the flash-back behavior induced by the interaction of flow and heat generated by the chemical reactions within at most 20%.

However, there are some fundamental drawbacks to this one-step chemical model. Certain instabilities in practical flames are due to complex transport effects (Lewis number effects, preferential diffusion) which are known to be important in some flame phenomena (cellular flames, stretch induced effects) and can be modelled to a limited extent only. Another drawback is related to environmental issues, which at present become more and more important. The exhaust level of certain pollutants (e.g. \(NO_x\), soot) nowadays place severe restrictions on new burner concepts. Some of the governmental regulations even demand limits close to their theoretically possible lower limits. The accurate predictions of these emissions, cannot be modelled accurately by this single-step chemistry. Even so-called ‘post-calculations’ need at least accurate values for some of the major components.

These arguments form the motivation of the research presented in this thesis. We want to incorporate more complex chemical models in the computational methods available in our group. The level of complexity, as pointed out earlier, ought to be kept in hand since ultimately realistic burner geometries are to be handled. Yet, for certain characteristics, like \(NO_x\)-emissions, accurate predictions for some species present in the flame are indispensable. The objective of the present study will therefore be: the application of more complex chemical schemes for the combustion of \(CH_4\)-air in particular geometries. Different levels of approximation in these more complex chemical schemes, will be compared with each other for certain characteristic flame phenomena.

The remainder of this chapter will deal with the physical and chemical background. The basic flow equations for reactive mixtures and transport properties for multi-component mixtures will be introduced, followed by an introduction of some general aspects of chemical reactions, present in both complex and systematically reduced schemes.

---

7 Flame lengths in premixed burners are much shorter than in partial premixed- or diffusion flame burners.

8 For post-processing calculations of \(NO\) one needs accurate values for \(O_2\), \(H_2O\) and \(H_2\) at least.
Chapter two deals with the modelling of complex chemistry and complex transport in one-dimensional premixed flames (flat-flame geometries). First, the governing equations will be treated and the reference complex chemical scheme, the so-called 'skeletal-mechanism' consisting of 25 reactions between 15 species, used for CH₄-combustion will be elucidated. The reason for not using standard available software [San85, Rog91] is twofold. First, we want to perform a systematic study into different levels of approximation (complex diffusion versus constant Lewis-numbers, constant $c_p$ and $\lambda$ versus mixture averaged properties.) on flame structure. Secondly, we want to implement more complex chemistry in the multidimensional computational methods available in our group. The numerical aspects, specific for complex chemical calculations, will be treated and the implementation chosen and used throughout this thesis will be presented. The main results using the 'skeletal mechanism' will be discussed with respect to different levels of approximation.

In chapter three, we will introduce a technique to reduce the number of species in the problem systematically [Pet87, Smo91]. The reason for a reduction strategy, in our case, stems from an engineering point of view. The advantage of such procedures is that it reduces the number of variables⁹ to be modelled while preserving quantitative and qualitative predictions of structure and stability phenomena. It should be noted that exactly this reduction of variables should make the application of more complex chemical models to complex geometries possible, within reasonable computing time. Furthermore, a technique will be presented to perform a systematical analysis of the reduced chemical model. It will be used to deduce and improve the presented (4-step) model for lean methane-air combustion. The results will be compared with results of full complex calculations.

Chapter four deals with the simulation of two-dimensional flames. Some aspects of the method developed by de Lange [Lan92] will be discussed and the numerical implementation is described. The extension of this method to the simulation of two-dimensional flames with detailed chemical models is treated. The numerical method used to solve the large set of equations will be presented. Finally, the method is used for the simulation of the small scale flame structure of a perforated plate flat-flame burner with the 'skeletal mechanism'. The results are compared with the results of a true one-dimensional flame.

⁹In a numerical implementation suitable for modelling complex chemistry laminar flames, the amount of 'work' is proportional with the squared number of variables.
1.2 Combustion and Fluid Flow

In this section the governing equations for modelling laminar flames and other types of reacting flows are presented. In the first subsection, the general set of equations is introduced. Subsequently, an approximated set is derived which is commonly used in laminar flame simulations. Transport and thermodynamical properties are presented in the final subsection.

1.2.1 General reactive flow equations

As in conventional fluid dynamics, the laws of overall conservation of mass, momentum and energy hold. Therefore, in modelling reactive flow phenomena the same starting set of equations is used. The continuity equation reads,

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{v}) = 0 ,$$

where $\rho$ is mass-density ($kg/m^3$) and $\vec{v}$ the mixture velocity. Conservation of momentum is covered by the Navier-Stokes equations,

$$\frac{\partial \rho \vec{v}}{\partial t} + \nabla \cdot (\rho \vec{v} \vec{v}) = -\nabla \cdot \vec{p} + \rho \vec{g} ,$$

where the tensor $\vec{p}$ is a short-hand notation for, $\vec{p} = \rho \vec{I} + \tau$. Here, $p$ is the hydrostatic pressure, $\vec{I}$ the unit tensor and $\tau$ the stress-tensor. It is worth mentioning that gravity is considered to be the only external force acting on the mixture. Finally, the equation for conservation of energy in the absence of an external heat source can be written as,

$$\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho \vec{v} u) = -\nabla \cdot \vec{q} - \nabla \cdot (\vec{p} \cdot \vec{v}) + \rho \vec{v} \cdot \vec{g}$$

with $u = \frac{1}{2} v^2 + \tilde{u}$ the total energy-density and $\vec{q}$ is the heat flux vector. The term $\tilde{u}$ represents the internal energy density and $\frac{1}{2} v^2$ the energy contained of the ordered fluid motion. The heat flux due to radiation will not be taken into account. For matters of convenience we will not use the above form of the energy conservation equation. Instead, the contribution of the kinetic energy of the ordered motion to the energy density is eliminated by subtracting the dot product of $\vec{v}$ with the momentum equation (1.2) from Eq. (1.3). This leads to

$$\frac{\partial \rho \tilde{u}}{\partial t} + \nabla \cdot (\rho \vec{v} \tilde{u}) = -\nabla \cdot \vec{q} - \vec{p} : (\nabla \vec{v}) .$$

In reactive flows this set does not provide enough equations for all observables. On one hand, if chemical reactions are to be considered at all, values of the chemical constituents are needed as function of place and time. On the other hand, concentrations of all constituents appear in the expressions for the heat flux and mixture properties (conductivity, viscosity etc.), as will be seen further on. The latter argument applies to inert mixtures as well and is not specific for the reactive aspects in combustion phenomena.
Therefore, for every species present in the mixture a mass-balance equation has to be introduced, which in reactive flows has the form,

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \vec{v}_i) = \dot{\rho}_i , \quad i = 1(1)N$$

(1.5)

with \( \rho_i \) and \( \vec{v}_i \) the mass density and specific velocity of each species \( i \), respectively. \( N \) equals the number of species, and Eq. (1.5) is thus a set of equations ranging from \( i = 1 \) to \( N \), shortly denoted with the convention \( i = 1(1)N \). The chemical source term \( \dot{\rho}_i \) is characteristic for the reactive nature and would not appear in inert mixtures.

For matters of convenience we introduce the diffusion velocity \( \vec{V}_i = \vec{v}_i - \vec{v} \) where \( \vec{v} \) is defined as the mass-averaged flow velocity

$$\rho \vec{v} = \sum_{i=1}^{N} \rho_i \vec{v}_i .$$

Using \( \rho \) and \( \vec{V}_i \), (1.5) is now rewritten in the form of the more commonly used convection-diffusion equation,

$$\frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho Y_i \vec{v}) + \nabla \cdot (\rho Y_i \vec{V}_i) = \dot{\rho}_i , \quad i = 1(1)N$$

(1.6)

where the definition for the mass-fraction \( Y_i = \rho_i / \rho \) is introduced. Since chemical reactions conserve mass, \( \sum_{i=1}^{N} \dot{\rho}_i = 0 \), the sum over \( i \) of (1.6) leads to the observation that the diffusive fluxes sum to zero,

$$\sum_{i=1}^{N} \rho Y_i \vec{V}_i = 0 .$$

The set of equations (1.1, 1.2, 1.4) and (1.6) is not closed. In the conservation equations for the four unknowns \( \rho, \vec{v}, \vec{V}_i \) and \( Y_i \), new quantities have been introduced. For these, being the pressure \( p \) and the stress-tensor \( \tau \) in the Navier-Stokes and the energy equation, the heat-flux \( \vec{q} \) in the energy equation and the diffusion velocity \( \vec{V}_i \) in the convection-diffusion equation, relations have to be formulated such that the number of equations is equal to the total number of unknowns. This closure is obtained by posing so-called constitutive relations.

In most combustion problems each species can be considered to behave as a perfect gas. The 'partial' pressure is then given by

$$p_i = n_i RT = n X_i RT$$

with \( R \) the universal gas constant and \( n_i \) the molar density (or concentration) of species \( i \). For later use the concentration fraction \( X_i \) is introduced, \( X_i = n_i / n \). It is simply related to the mass fraction, \( X_i = Y_i M / M_i \), where \( M \) is the average molar

---

\(^{10}\)It should be noted that if each component \( i \) in the mixture would experience a different external force, say \( \vec{g}_i \), e.g., ionized gases (plasmas) in an external electric field, the last term in the Navier-Stokes equation should read \( \sum_{i=1}^{N} \rho_i \vec{g}_i \).
mass and \( M_i \) the molar mass of species \( i \). The \( n \) is the number density, or molar density of the mixture (moles per volume).

According to Dalton's law the static pressure is equal to the sum of the partial pressures thus leading to,

\[
p = nRT, \tag{1.7}
\]

where the equality \( \sum_{i=1}^{N} X_i = 1 \) is used. This provides a unique relation between pressure and temperature. This relation can be used to relate all remaining constitutive relations to the set \((\rho, Y, T, \vec{v})\), as is mostly done in combustion modelling.

The stress tensor \( \tau \) of the mixture is identical with the expression for a single-component Newtonian fluid, i.e,

\[
\tau = -\eta[(\nabla \vec{v}) + (\nabla \vec{v})^T] + \frac{2}{3} \eta(\nabla \cdot \vec{v}) \mathbf{I} \tag{1.8}
\]

where \( \eta \) is the dynamic viscosity of the mixture. In fact, this expression is formally not correct since terms involving the gradients of the diffusion velocity, \( \vec{V}_i \), are neglected with respect to those of the average velocity \( \vec{v} \). Otherwise the assumption \( \eta = Y_i \eta_i \) with \( \eta_i \) the dynamic viscosity of species \( i \), has to be posed, to derive Eq. (1.8) rigorously [Buc82]. As shown by Hirschfelder et al. [Hir54] this stress-tensor equation is the first Chapman-Enskog approximation to the more complete expression.

The most accurate expression for the diffusion velocity, \( \vec{V}_i \), appearing in the convection-diffusion equation yields [Dix68],

\[
\vec{V}_i = -\frac{D_i^T}{\rho Y_i T} \nabla T + \frac{n}{X_i \rho} \sum_{j=1, j\neq i}^{N} M_j D_{ij} \vec{d}_j , \quad i = 1(1)N \tag{1.9}
\]

where the thermal diffusion coefficient \( D_i^T \) and the generalized diffusion coefficients \( D_{ij} \) are used. The first term denotes the effect on diffusion caused by temperature gradients (Soret-effect). The second term involves the quantity \( \vec{d}_j \) which takes the effect of concentration- and pressure gradients into account, i.e,

\[
\vec{d}_j = \nabla X_j + \left( \frac{1}{n} - \frac{M_j}{\rho} \right) \nabla p, \quad j = 1(1)N \tag{1.10}
\]

This expression is only valid within the perfect gas assumption mentioned earlier. More general expressions can be found in [Hir54, Cha70]. It should be noted that the pressure dependence disappears from (1.10) if all molar masses are equal.

Due to the multi-component nature of the medium, the expression for the heat flux \( \vec{q} \) becomes fairly complex,

\[
\vec{q} = -\lambda \nabla T + \rho \sum_{i=1}^{N} Y_i h_i \vec{V}_i - \rho T \sum_{i=1}^{N} \frac{D_i^T}{X_i M_i} \vec{d}_i . \tag{1.11}
\]

where \( h_i \) is the specific enthalpy of the \( i \)-th component, formally given by

\[
h_i(T) = h_i^0 + \int_{T_0}^{T} c_{pi}(T')dT' \tag{1.12}
\]
with \( h^0 \) the enthalpy at the reference temperature \( T_0 \). The specific heat capacity, \( c_{p,i}(T) \), of species \( i \) is assumed to be a function of temperature only. Pressure dependence is usually very small and will not be taken into account. The first term in Eq. (1.11) is the ordinary single-component fluid heat flux. It should be noted that in a mixture the conductivity, \( \lambda' \), will not be the proportionality factor measured with an experiment linking the temperature gradient to conduction only. In fact, the second term, which incorporates the enthalpy transport due to the mass diffusion, contains a term proportional to the temperature gradient as can be seen in the expression for the diffusion velocity (1.9). The last term in (1.11) is the direct effect of concentration- (Dufour-effect) and pressure gradients on the heat flux. In fact the Dufour-effect in the heat flux is the counterpart of the Soret-effect in the diffusive flux.

The only constitutive relation that has not been stated yet is the one relating internal energy to the primitive variables. Within the perfect gas assumption mentioned earlier, the internal energy density, \( \dot{\varepsilon}_i \) of species \( i \) is given by

\[
\dot{\varepsilon}_i = h_i - \frac{\rho_i}{\rho}
\]

with \( h_i \) the specific enthalpy. The total internal energy density, formally given by

\[
\dot{\varepsilon} = \sum_{i=1}^{N} Y_i \dot{\varepsilon}_i,
\]

then yields,

\[
\dot{\varepsilon} = \sum_{i=1}^{N} Y_i h_i - \frac{p}{\rho}
\]

(1.13)

where the pressure term evolves since the \( \sum_{i=1}^{N} Y_i p_{i}/\rho_i = p/\rho \).

In principle all constitutive relations are now determined and the problem is closed. Only the thermodynamical properties of the constituents, \( c_{p,i}, \lambda', D_{ij} \) and \( V_{ij} \), are unknown at this point. Formal expressions for these quantities can only be derived rigorously on a molecular theory based approach [Hir54, Cha70, Wil85]. Typically, these properties involve the evaluation of so-called collision integrals which is a very CPU-intensive job and should therefore be avoided in numerical simulations of reactive flow phenomena. Excellent treatments on the principles can be found in the latter citations or in [Dix68] where the expressions are extended to incorporate quantum-mechanical molecular states as well. However, we will use data tabulated in thermodynamical databases as they are provided with the CHEMKIN-package [San86, San89, San91]. These expressions will be treated in the last part of this chapter.

In the next section the formal set of equations introduced here are put in its final, approximated, form as used throughout the thesis.

### 1.2.2 Fluid Flow equations in Laminar Flames

Most authors do not use the formal set of equations presented in the preceding subsection. In most numerical treatments, though not absolutely necessary, the conservation equations are cast in a more tractable form.

---

1. Furthermore, there is very little accurate experimental data available to justify modelling it at all [Wil85].
2. Heat flux driven by concentration gradients vs. mass flux driven by temperature gradients (Onsager).
First substituting (1.13) in the energy Eq. (1.4) gives,

\[
\frac{\partial \rho}{\partial t} \left( \sum_{i=1}^{N} Y_i h_i \right) + \nabla \cdot (\rho \bar{u} (\sum_{i=1}^{N} Y_i h_i)) =
- \nabla \cdot \bar{q} - p \left( \nabla \bar{v} \right) + \frac{\partial p}{\partial t} + \nabla \cdot (p \bar{v}) .
\]  

(1.14)

where all terms involving the pressure are taken to the right hand side. For matters of convenience we will use the identity,

\[
p : (\nabla \bar{v}) - \nabla \cdot (p \bar{v}) = \tau : (\nabla \bar{v}) - \bar{n} \nabla p
\]  

(1.15)

and substitute the right-hand side in the Eq. (1.14), thus obtaining

\[
\frac{\partial \rho}{\partial t} \left( \sum_{i=1}^{N} Y_i h_i \right) + \nabla \cdot (\rho \bar{u} (\sum_{i=1}^{N} Y_i h_i)) =
- \nabla \cdot \bar{q} - \tau : (\nabla \bar{v}) + \frac{\partial p}{\partial t} + \bar{n} \cdot \nabla p.
\]  

(1.16)

Up to this point no additional assumptions have been made to the original set of equations. Usually in combustion modelling the Dufour-effect in (1.11) and the contribution of the stress-tensor to the energy equation, \( \tau : \nabla \bar{v} \), are neglected. Furthermore, typical flow velocities in laminar flames are subsonic, and it can then be shown that the pressure may be treated as a spatially constant \(^{13}\) in the energy equation [Buc85]. This is in the field of flame modelling mostly referred to as the Combustion Approximation, or isobaric approximation, which is essentially different from the constant density approximation used in some theoretical combustion studies ([Buc82, Buc85]).

The consequence of the assumptions is twofold. The most straightforward implication is that term involving the pressure gradient, \( \bar{n} \cdot \nabla p \), in (1.16) can be omitted. Furthermore, the pressure gradient in the heat flux vanishes, leading to a simpler expression for the heat flux,

\[
q' = -\lambda' \nabla T' + \rho \sum_{i=1}^{N} Y_i \bar{V}_i h_i ,
\]  

(1.17)

and \( \nabla \cdot q' \), which appears in the energy equation, becomes,

\[
\nabla \cdot q' = \nabla \left( \cdot \lambda' \nabla T' \right) + \sum_{i=1}^{N} (\rho Y_i \bar{V}_i \cdot \nabla h_i) + \sum_{i=1}^{N} (h_i \nabla \cdot \rho Y_i \bar{V}_i) .
\]  

Substituting this in Eq. (1.16) and realizing that both \( \partial / \partial t \) and \( \nabla \) are linear operators, we get,

\[
\rho \sum_{i=1}^{N} (Y_i \frac{\partial h_i}{\partial t}) + \rho \bar{V} \cdot \sum_{i=1}^{N} (Y_i \nabla h_i) =
\]  

\(^{13}\)Or equivalently, every spatial pressure variation is immediately wiped out by an acoustic wave.
\begin{align}
- \nabla \cdot ( \rho \nabla T ) + \rho \sum_{i=1}^{N} \left( Y_i \nabla V_i \cdot \nabla h_i \right) + \frac{\partial p}{\partial t} \quad (1.18) \\
- \sum_{i=1}^{N} h_i \left( \frac{\partial \rho Y_i}{\partial t} \right) + \nabla \cdot ( \rho Y_i \vec{v} ) + \nabla \cdot ( \rho Y_i \nabla V_i )
\end{align}

If multiplied with the specific enthalpies, the sum over the convection-diffusion Eq. (1.5) of all species yields,

\begin{align}
\sum_{i=1}^{N} h_i \left( \frac{\partial \rho Y_i}{\partial t} \right) + \nabla \cdot ( \rho Y_i \vec{v} ) + \nabla \cdot ( \rho Y_i \nabla V_i ) = \sum_{i=1}^{N} h_i \dot{\rho}_i, \quad (1.19)
\end{align}

Using this equality, the term

\begin{align}
\sum_{i=1}^{N} h_i \left( \frac{\partial \rho Y_i}{\partial t} \right) + \nabla \cdot ( \rho Y_i \vec{v} ) + \nabla \cdot ( \rho Y_i \nabla V_i )
\end{align}

which appears in (1.18), can be replaced by the right-hand side of (1.19). This leads to the form of the enthalpy equation as it is used in most combustion studies.

\begin{align}
\rho \sum_{i=1}^{N} \left( Y_i \frac{\partial h_i}{\partial t} \right) + \rho \dot{\rho}(\sum_{i=1}^{N} Y_i \nabla h_i) = \\
- \nabla \cdot \left( -\lambda' \nabla T \right) - \rho \sum_{i=1}^{N} \left( Y_i \nabla V_i \cdot \nabla h_i \right) + \frac{\partial p}{\partial t} - \sum_{i=1}^{N} h_i \dot{\rho}_i. \quad (1.20)
\end{align}

Note that this equation is exact within the Combustion Approximation, or equivalently in isobaric circumstances.

The last objective is to write (1.20) in terms of temperature \( T \) explicitly. This is a rather trivial procedure. Only basic algebra is used\(^{14}\) and gives a well-known representation of the enthalpy equation encountered in many combustion studies,

\begin{align}
\rho c_p \frac{\partial T}{\partial t} + p c_p \frac{\partial \rho}{\partial t} \cdot \nabla T - \nabla \cdot ( \rho c_p \nabla T ) = \frac{\partial p}{\partial t} + \sum_{i=1}^{N} h_i \dot{\rho}_i \quad (1.21)
\end{align}

The mixture heat capacity is introduced here, as being,

\begin{align}
c_p = \sum_{i=1}^{N} Y_i c_{p_i}, \quad (1.22)
\end{align}

which evolves as a natural consequence of the derivation presented above.

The energy equation is to a large extent equivalent to that for a single-component fluid. The only effect of the chemical reactions on the energy equation is contained in the term \( \sum_{i=1}^{N} h_i \dot{\rho}_i \). Note that not the formation enthalpies, \( \dot{h}_i^0 \), appear but the

\(^{14}\)The simple rule \( \frac{\partial}{\partial x} \left( \int_{x_0}^{x} f(y') \, dy' \right) = f(y) \frac{\partial}{\partial t} \), which is valid if \( f \) is not explicitly dependent on \( x \).
1.2. Combustion and Fluid Flow

which is in contrast with the formulation used by some authors [Lan92, Buc82]. The other term, which is \(-\sum_{i=1}^{N} \rho Y_i c_p V_i \cdot \nabla T\), is a small effect, but will be present even in an inert mixture. In laminar flame modelling it is often neglected. The \(\frac{\partial P}{\partial t}\) term is retained for matters of completeness but will not be considered in further applications of the thesis, since only steady phenomena are studied. The last part of this section will deal with the final form of the species convection-diffusion equation. In fact the derivation presented will concern the simplification of the expression for the diffusion velocity (1.9) only.

In the earlier mentioned Combustion Approximation the term due to pressure gradients may be neglected. Furthermore, thermal diffusion is normally very small as well and will be neglected\(^{15}\). However, the diffusion velocity of a constituent still depends on the concentration gradients of every other constituent which severely complicates the modelling of flames. Within the earlier assumptions, it can be shown that the expression (1.9) can be rearranged to yield [Muc58, Mon66, Dix68],

\[
\nabla X_i = \sum_{j=1}^{N} \frac{X_j X_{ij}}{D_{ij}} (\nabla j - \nabla i)
\]

(1.23)

which is commonly referred to as the Stefan-Maxwell equation. This expression is much simpler to evaluate since it involves the binary diffusion coefficients, \(D_{ij}\), which are virtually independent of the composition. For this reason only, the Stefan-Maxwell equation are to be preferred above the original expression for the diffusion velocity. The latter involves the generalized diffusion coefficients\(^{16}\) which depend explicitly on the composition in a complicated and CPU-intensive manner\(^{17}\).

For this reason in most laminar flame studies the diffusion flux is cast in a Fick-like expression,

\[
\vec{v}_i = -\frac{D_{im}}{X_i} \nabla X_i.
\]

(1.24)

where the so-called mixture-averaged diffusion coefficient, \(D_{im}\), describes the diffusivity of the species in the mixture.

An exact derivation of this equation does not exist. In fact, it can be derived only from the Stefan-Maxwell equations if it is assumed that all \(\vec{v}_j\) (\(j \neq i\)) take a common value \(\vec{v}\). Substituting this, and making use of the relation,

\[
Y_i \vec{v}_i + (1 - Y_i) \vec{v}
\]

which is then true by definition, the Stefan-Maxwell equations (1.23) can be rear-

\(^{15}\) Only for very light species (\(H_2, H\) or \(He\)) this can have a considerable contribution to the total diffusive flux \(\mathcal{O}(20\%)\).

\(^{16}\) The relation between the two is known and relatively simple for a ternary mixture

\[
D_{12} = D_{12} \left\{ 1 + \frac{X_2 (M_1/M_2) (D_{13} - D_{12})}{X_1 D_{23} + X_2 D_{12} + X_3 D_{13}} \right\}
\]

and similar relations for \(D_{21}, D_{23}, D_{31}, D_{32}, D_{33}\).

\(^{17}\) To first order the generalized diffusion coefficients involve a \((N \times N)\)-matrix inversion for every species thus leading to \(\mathcal{O}(N^3)\) operations per gridpoint [Gar84d].
ranged to yield,

\[ D_{im} = \frac{(1 - Y_i)}{\sum \phi_j X_j / D_{ij}} \]  

(1.25)

where the coefficients \( D_{ij} \) are the earlier mentioned binary diffusion coefficients. Strictly, in a multi-component flow this expression only applies\(^{18}\) for a trace species and is therefore often referred to as the trace-species approximation. In can be expected that this approximation applies quite well in atmospheric fuel-air flame modelling since approximately 80\% Nitrogen (N\(_2\)) is present under these circumstances.

Formally, if one wishes to write the species balance equation entirely in terms of mass-fractions the expression (1.24) is rewritten according to,

\[ Y_i \vec{V}_i = - \frac{M_i}{M} D_{im} \vec{v} X_i \]

\[ = - \frac{M_i}{M} D_{im} \vec{v} (Y_i \frac{M}{M_i}) \]

\[ = - D_{im} \left[ \vec{v} Y_i + Y_i \vec{v} \rho_l(M) \right] \]

where the identity \( Y_i / X_i = M_i / M \) has been used. The last term on the right-hand side is in \( C/II \) - air combustion negligible since the average molar mass is almost constant. Substitution of the trace species diffusive flux in the balance equation thus gives an expression for the species mass-fraction which is very similar to the temperature equation (1.21),

\[ \rho \frac{\partial Y_i}{\partial t} + \rho \vec{v} \cdot \vec{\nabla} Y_i - \vec{\nabla} \cdot (\rho \vec{V}_{im}) \vec{v} Y_i = \dot{\rho}_i. \]

(1.26)

In many theoretical studies this feature is used explicitly to simplify the solution considerably.

The latter equation together with the continuity equation (1.1), the Navier-Stokes equation (1.2), the energy equation (1.21) and the ideal gas law (1.7), summarized below,

\[ \frac{\partial p}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0 \]  

(1.27)

\[ \frac{\partial \rho \vec{v}}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v} \vec{v}) = - \vec{\nabla} \cdot (\rho \vec{v}) + \rho \vec{j} \]  

(1.28)

\[ \rho c_v \frac{\partial T}{\partial t} + \rho c_p \vec{V}_i \cdot \vec{\nabla} T - \vec{\nabla} \cdot \lambda \vec{\nabla} T = \frac{\partial p}{\partial t} - \sum_{i=1}^{N} \rho Y_i \vec{v}_i \cdot \vec{\nabla} \vec{T} \]  

(1.29)

\[ \rho = nRT \]  

(1.30)

will be the set of equations used in this thesis.

\(^{18}\) Or in a binary mixture, but that is trivial.
However, it should be noted that the diffusive fluxes no longer sum to zero due to the assumptions made. Formally, the continuity equation no longer holds. Some authors correct this deficiency by calculating the mean overall diffusion velocity according to \( \bar{V}_i = -\sum Y_i V_i^e \) and substitute each \( V_i^e \) by \( \bar{V}_i = V_i + \bar{V} \). Here, another commonly used correction will be used. The balance equation, (1.26), for the species which is most abundant is omitted (\( N_2 \) in our case) and mass conservation is used explicitly by taking \( Y_{Ni} = 1 - \sum_{i=1}^{N-1} Y_i \). Therewith the continuity equation is forced to hold.

### 1.2.3 Thermodynamical and transport properties

The evaluation of transport properties of any multi-component mixture is in general very complex, and is normally very CPU-intensive [Gar84d, Dix68]. Especially the latter argument is of major importance in flame simulation. Therefore, many formulations exist with a variety of approximation levels. In the early eighties some investigators have tested these formulations [Cof81, Ora81]. The expressions presented below are a compilation of the (semi-empirical) formulae used by many authors. They are believed to yield accurate results for the respective fluxes, and do not use excessive CPU time.

For the mixture averaged viscosity, \( \eta \), in most standard laminar flame packages (Sandia-codes), the semi-empirical formula of Wilke [Wil50] is used,

\[
\eta = \sum_{k=1}^{N} \frac{X_k \eta_k}{\sum_{j=1}^{N} X_j \Phi_{kj}}
\]

where \( \eta_k \) are the single species gas viscosities. The quantity \( \Phi_{kj} \) is given by,

\[
\Phi_{kj} = \frac{1}{\sqrt{8}} \left\{ 1 + \left( \frac{M_k}{M_j} \right)^{\frac{1}{2}} \right\} \left\{ 1 + \left( \frac{\eta_k}{\eta_j} \right)^{\frac{1}{2}} \left( \frac{M_k}{M_j} \right)^{-\frac{1}{2}} \right\}^2
\]

The mixture averaged conductivity, \( \lambda' \), can be put in a somewhat related form [Mas58],

\[
\lambda' = \sum_{k=1}^{N} \frac{\lambda_k}{1 + 1/X_k \sum_{i=1; i \neq k}^{N} (1.065 X_i \Phi_{ki})}
\]

which, however, is not used frequently in numerical combustion studies. Instead, a semi-empirical formulation is applied [Mat67],

\[
\lambda' = \frac{1}{2} \left\{ \sum_{i=1}^{N} X_i \lambda_i + \left( \sum_{i=1}^{N} X_i / \lambda_i \right)^{-1} \right\}
\]

which involves only the pure species conductivities. According to Coffee and Heimerl [Cof81] this gives results with errors in the range of a few percent. In a one-dimensional premixed geometry the latter expression is to be preferred because there the viscosities, and thus \( \Phi_{kj} \), do not need to be evaluated. In multi-dimensional
simulations there is no preference, since then the viscosity of the mixture will have to be evaluated anyway.

The properties, $D_{\text{m}}$, and $c_p$, are already introduced in the preceding sections, and are presented for matters of completeness only.

$$D_{\text{m}} = \frac{(1 - Y_i)}{\sum_{j \neq i} X_j / D_{ij}} \quad i = 1(1)N \quad (1.34)$$

$$c_p = \sum_{i=1}^{N} Y_i c_{p_i} \quad (1.35)$$

and complete the mixture averaged thermodynamical and transport properties.

The pure species quantities, $c_{p_i}$, that arise in the averaged formula, (1.35), and, $h_{ij}$, in the chemical source term of the energy equation (1.21) are well tabulated [San91]. The properties are cast in a polynomial form presented below,

$$\frac{c_{p_i}}{\mathcal{R}} = \sum_{n=1}^{5} c_{n; i} T^{n-1} \quad i = 1(1)N \quad (1.36)$$

$$\frac{h_{ij}}{\mathcal{R} T} = \sum_{n=1}^{5} \frac{c_{n; i}}{n} T^{n-1} + \frac{c_{6, i}}{T} \quad i = 1(1)N$$

with $\mathcal{R}$ the universal gas constant.

The binary diffusion coefficients are not tabulated because that would result in a database too large to be practical. This holds for the viscosities and the conductivities as well, since these are expressed in terms of binary diffusion coefficients. Instead, the Lennard-Jones potential data for each species, necessary to evaluate these properties, are tabulated in the STANJAN-tables [San86]. Then for a specific problem, appropriate fitting procedures, e.g. provided with the CHEMKIN-package [San86], are used to put them in a similar polynomial form yielding,

$$\ln(\lambda_i) = \sum_{n=1}^{\mu} a_{n, i} (\ln T)^{n-1} \quad i = 1(1)N$$

$$\ln(\eta_{ij}) = \sum_{n=1}^{\nu} b_{n, ij} (\ln T)^{n-1} \quad i = 1(1)N \quad (1.37)$$

$$\ln(D_{ij}) = \sum_{n=1}^{\mu} d_{n, ij} (\ln T)^{n-1} \quad i = 1(1)N, j = 1(1)N, j \neq i$$

This procedure has to be performed once for every mixture, in contrast with the coefficients in (1.36) which can be evaluated for every species once and for all.

Now, the set of equations describing reacting flows are almost in a closed form. The only terms not specified yet, are the chemical source terms $\dot{\rho}_c$. In the last section of this chapter, some general aspects are introduced, concerning chemical reaction schemes.
1.3 Chemical Aspects in Combustion

In the previous section the general reactive flow equations are introduced, but the chemical source terms appearing in the energy (1.21) and species balance equations (1.26) are not specified yet. In combustion of natural gas, these generally involve so-called chain-reactions, which means that the oxidation of the fuel is composed of many elementary steps. These steps, or elementary reactions, have a physical relation with microscopic processes, in contrast with overall chemical reactions where the reaction equations merely state the overall conversion ratios.

For methane-air mixtures the elementary steps are known and tabulated. Complete $\text{C}_4\text{H}_4$ chemical models consist of approximately 36 species and 210 reactions [Ego90]. Some general principles, present in these detailed chemical models, will be clarified in this section. These principles apply to all fields of reactive flows.

1.3.1 General elementary reactions

In general, any elementary reaction can be written in the form,

$$\nu'_1 A_1 + \nu'_2 A_2 + \ldots + \nu'_N A_N \rightarrow \nu''_1 A_1 + \nu''_2 A_2 + \ldots + \nu''_N A_N$$  \hspace{1cm} (1.38)

where $A_i$ represents one of the $N$ species present in the model and $\nu'_i - \nu''_i$ the number of molecules $A_i$ converted in the elementary reaction. Since neither nuclear fission, nor fusion processes will be considered, each reaction conserves the total number of elements ($\text{C}$, $\text{H}$, $\text{O}$ and $\text{N}$ in hydrocarbon air systems).

The formal reaction (1.38) implies that,

$$\frac{q_i}{(\nu'_i - \nu''_i)} = \frac{q_j}{(\nu'_j - \nu''_j)}$$

for any pair $i, j$ of particles in the reaction. Here, $q_i$ is defined as the net rate of increase of species $i$ (in moles per volume$^{19}$ per second). It's now common practice to define the reaction rate $q$, as being equal to the $q_i$ for a species when $(\nu'_i - \nu''_i)$ is equal to one. One then obtains,

$$q_j = (\nu'_j - \nu''_j)q.$$  \hspace{1cm} (1.39)

The phenomenological law of mass action now states that a reaction rate is proportional to the product of the concentrations, $n_i$, which leads for the formal reaction (1.38) to the expression,

$$q = k \prod_{i=1}^{N} n_i^\nu_i$$  \hspace{1cm} (1.40)

where the proportionality parameter $k$, sometimes is referred to as the specific reaction rate constant. The reverse reaction of (1.38) often plays an important role as well,

$$\nu''_1 A_1 + \nu''_2 A_2 + \ldots + \nu''_N A_N \rightarrow \nu'_1 A_1 + \nu'_2 A_2 + \ldots + \nu'_N A_N.$$  

$^{19}$The volume is not specified but in chemical literature often cm$^3$ is used.
Therefore, in flame modelling, it is convenient to rewrite the combination of both
to,

\[ \nu_1^r A_1 + \nu_2^r A_2 + \ldots \nu_N^r A_N \rightleftharpoons \nu_1^a A_1 + \nu_2^a A_2 + \ldots \nu_N^a A_N \]  

(1.41)

where the symbol \( \rightleftharpoons \) indicates the reversible nature. The net reaction rate of (1.41) is now given by,

\[ q = k_f^f \prod_{i=1}^{N} n_i^{\nu_i^f} - k_r^f \prod_{i=1}^{N} n_i^{\nu_i^r} \]  

(1.42)

The \( k_f^f \) and \( k_r^f \) are now the specific reaction rate constants of the forward and reverse reactions, respectively.

In a practical gas-phase combustion system the reaction order, \( \sum_{i=1}^{N} \nu_i \), of the reactions involved in the chain mechanism will not exceed three. At low densities, or pressures < 100 bar, the probability of a collision between four or more molecules is so small, that these higher order reactions may be neglected. The remaining three reaction types, (first, second and third order), are treated in the following subsections.

1.3.2 Bimolecular reactions

The most common and least complicated type of reaction is the so-called bimolecular reaction e.g.

\[ CH_4 + H = CH_3 + H_2 \]

where the methane molecule is attacked by an hydrogen radical to form a methyl radical and molecular hydrogen and reversely. The reaction rate is now given by,

\[ q = k_f^f [CH_4][H] - k_r^f [CH_3][H_2] \]

where \([\cdot] \) is an often used notation for the molar density \( n \). The specific reaction rate constants are generally not constant. As argued by Arrhenius (1889) an appropriate representation is given by,

\[ k = B_0 \exp\left(-\frac{E_a}{RT}\right) \]  

(1.43)

where the frequency factor \( B \) and the activation energy \( E_a \) do not depend on the temperature. However, some reactions show so-called non-Arrhenius behavior and extensive studies learn that the Arrhenius form cannot represent this behavior correctly[Zel79]. Therefore, usually a slightly modified form of the reaction rate constants is chosen according to,

\[ k = A T^{m_f \cdot \frac{E_a}{RT}} \]  

(1.44)

which will be used throughout this thesis. This extra \( T \) dependence is often attributed to effects of internal molecular orientation and internal molecular energy on the reaction probability.
1.3.3 Dissociation and Recombination Reactions

The two other important reaction types are the first-order and its 'counterpart' the third-order reaction. The first-order reaction\(^ {20} \) is often referred to as a dissociation reaction, e.g.,

\[
H_2 + M \rightarrow H + H + M \tag{1.45}
\]

These uni-molecular reactions are believed to follow the mechanism as proposed by Lindemann. This mechanism, in itself a chain-reaction, proceeds via two paths, being an excitation reaction \( I \),

\[
H_2 + M \rightarrow H_2^* + M \tag{1.46}
\]

which in fact is bimolecular reaction producing an intermediate, excited \( H_2 \) molecule, with specific reaction rates \( k_0^f \) and \( k_0^r \) for the reverse reaction (de-excitation reaction). The excited Hydrogen molecule then decomposes via a true uni-molecular reaction \( II \),

\[
H_2^* \rightarrow H + H \tag{1.47}
\]

with specific reaction rate \( k_{\text{exc}} \). Though the intermediate species \( (H_2^*) \) can have different, energetically excited states, it is common practice to treat all with the same reaction rate[Gar84b]. The overall reaction rate for the dissociation reaction 1.45 is now composed of two steps,

\[
q_{II} = k_0^f [H_2][M] - k_0^r [H_2^*][M] \]

\[
q_{II} = k_{\text{exc}} [H_2^*].
\]

The stoichiometric relations for both molecules now give,

\[
q_{H_2} = -q_{II}
\]

\[
q_{II} = q_{II} - q_{H_2},
\]

where it should be noted that \( q_{II} \) contains the \( H_2^* \) concentration explicitly. The application of a steady-state relation for the excited Hydrogen molecule, \( d[H_2^*]/dt = 0 \) eliminates the excited intermediate from the formal reaction rate. The dissociation rate for \( H_2 \) then yields,

\[
q_{H_2} = k_0^f [H_2]^\dagger \tag{1.46}
\]

with a formal specific reaction rate,

\[
k_0^f = k_0^f [M] \left( \frac{k_{\text{exc}}}{k_{\text{exc}} + k_0^r [M]} \right) \tag{1.47}
\]

independent of the excited Hydrogen molecule concentration.

A similar treatment for the recombination reaction,

\[
H + H + M \rightarrow H_2 + M
\]

\(^{20}\)Though not truly first order, like in particular dissociation reactions of a highly excited molecules \( H_2^* \rightarrow H + H \).
using the elementary steps $-1$ and $-II$,

\[
\begin{align*}
H + H & \rightarrow H_2 & -II \\
H_2^* + M & \rightarrow H_2 + M & -I
\end{align*}
\]

instead, yields for the recombination reaction,

\[
\eta_{II} = k^r[H][H]
\]

(1.48)

with the formal specific reaction rate now equal to,

\[
k^r = k^r_\infty \left( \frac{k^r_0[M]}{k^\infty_\alpha + k^r_0[M]} \right).
\]

(1.49)

The factors in brackets in both equations (1.47) and (1.49) indicate the probability that the reactions are completed after initiation\(^{21}\). An advantage of this formulation is that this definition of $k^r$ and $k^r_\infty$ follows the definition of chemical equilibrium,

\[
K = \frac{[H][H]}{[H_2]} = \frac{k^r}{k^r_\infty} = \frac{k^r_0}{k^\infty_\alpha k^r_0[M]}
\]

The $[M]$-dependence of the specific reaction rates $k^r$ and $k^r_\infty$ of these types of reactions is commonly referred to as the pressure dependence of dissociation and recombination reactions\(^{22}\). Two limiting cases can be recognized [Gar84b], one low pressure branch, $[M] \rightarrow 0$, yielding,

\[
\begin{align*}
k^r & = k^r_0[M] \\
k^r_\infty & = \frac{k^r_0}{k^\infty_\alpha} \frac{k^r_0}{k^r_0} \frac{k^r_0}{k^r_0} \frac{k^r_0}{k^r_0}
\end{align*}
\]

(1.50)

where the excitation reaction is thought to be rate-controlling. At high pressures, $[M] \rightarrow \infty$, the other limit is encountered,

\[
\begin{align*}
k^r & = \frac{k^r_0}{k^\infty_\alpha} \frac{k^r_0}{k^r_0} \frac{k^r_0}{k^r_0} \frac{k^r_0}{k^r_0} \\
k^r_\infty & = \frac{k^r_0}{k^\infty_\alpha}
\end{align*}
\]

(1.51)

as can be verified easily. Then the collisions between the 'third' particle and $H_2$ or $H_2^*$ are so frequent that the uni-molecular decomposition $I$ and the reversible process for the recombination case become rate-controlling. It's worth mentioning that the dissociation reaction switches from a uni-molecular to a bi-molecular behavior going from high to low pressures, whilst the recombination switches from tri-molecular to bi-molecular going from low to high pressures instead. Both limiting branches (1.50) and (1.51) are plotted in figure (1.1) with the dotted lines. Both relations (1.47) and (1.49) are indicated by the top solid line.

---

\(^{21}\)Being that $H_2 + M \rightarrow H_2^* + M$ is the initiation for dissociation and $H + H + M \rightarrow H_2 + M$ for recombination.

\(^{22}\)Though concentration or molar density dependence would be better.
fig. 1.1: Fall-off curves represented in the reduced coordinate. The dotted lines indicate the high, \((k_{\infty})\) and low pressure, \((k_0[M])\) limiting cases. The solid line indicated with \(F_{LH}(x)\) is the Lindemann-Hinshelwood expression. The extended expression (Eq. (1.53)) is shown with the second solid line indicated with \(F_{LH}(x) \cdot F'(x)\). A value of \(\log F_{\text{cent}} = 0.3\) (Eq. (1.54)) is used.

Generally the real behavior of the specific reaction rate, solid line in figure 1.1, is not equal to the earlier derived expressions. To incorporate this experimental observed behavior a compact representation of the fall-off curve, as it is often referred to, is mostly of practical importance. Therefore, usually the so-called 'center', \([M]_c\), of the fall-off curve located at the intersection of both limiting branches of \(k\). The reduced coordinate \(x = [M]/[M]_c = k_0/k_{\infty}\) offers a possibility to generate a compact expression for the reaction rate constant,

\[
\frac{k}{k_{\infty}} = \frac{x}{1 + x} \tag{1.52}
\]

where the latter is often abbreviated by \(F_{LH}(x)\) after Lindemann and Hinshelwood who first introduced this function. In fact \(F_{LH}\) is no more than a switching function between two limiting branches of the reaction rates indicated by a dashed curve in Fig (1.1) and equals the expression (1.47) and (1.49) as can be verified easily.

The fall-off curve is often broader than \(F_{LH}\) and theoretical analysis shows that this broadening effect can be accounted for reasonably by adding a factor \(F'(x)\), yielding,

\[
\frac{k}{k_{\infty}} = F_{LH}(x) F'(x) \tag{1.53}
\]

\(^{23}\)Bear in mind that \([M]_c = k_{\infty}/k_0\) per definition
The function, $F(x)$, is in good approximation determined by,

$$\log(F(x)) = \left( \frac{1}{1 + (\log x)\xi} \right) \log(F_{\text{cent}})$$

(1.54)

where $\log(F_{\text{cent}})$ is the depression from the real fall-off curve at the center of the Lindemann-Hinshelwood expression. It should be noted that more complex expressions are available that perform better in comparison with the observed behavior. These will not be used in this thesis, since they only offer minor modifications and do not have a large effect on the flame structure. An excellent survey can be found in [Car84b, Tro83].

So far no attention has been paid to the concentration of the inert species $M$, or so-called 'bath-gas'. It does not take part in the reaction ($\nu_i' = 0$) but is absolutely crucial as otherwise momentum and energy could not be conserved simultaneously. It can, however, be any particle present in the mixture. The concentration of the 'inert' particle will therefore, in the simplest case be given by $p/RT$. However, in most uni- and tri-molecular reactions the rate coefficient is different for every third body. Stated explicitly, for instance,

$$H_2 + H_2 \rightarrow H + H + H_2$$

will have a higher rate than,

$$H_2 + O_2 \rightarrow H + H + O_2.$$ 

On a molecular level this means that the collision probability of $H_2-H_2$ to form an excited Hydrogen molecule ($H_2^*$) is larger than of $H_2-O_2$ for this particular reaction. Instead of introducing a specific reaction rate for every collision partner, this effect is in most flame modelling studies incorporated by introducing so-called 'enhanced efficiencies' $\sigma_i$, which can have values ranging from 1.0 to 10.0 approximately. The 'concentration' of the third particle $M$ is than given by,

$$[M] = \sum_{i=1}^{N} \sigma_i X_i p/RT$$

(1.55)

which reduces to the appropriate value $p/RT$ when all $\sigma_i$ are equal to one. In the next chapter we will treat the modelling of complex chemical systems in a flat-flame geometry. All reaction types treated here are present in the actual chemical scheme used.
Chapter 2

Modelling of Flat Flames with Complex Chemistry

2.1 Introduction

In this chapter premixed laminar flat flames with detailed chemistry are treated. We will present the numerical approach used to deal with the specific problems encountered in numerical combustion modelling. Furthermore, the algorithm will be used to study effects of approximations in transport and chemical models on lean methane-air flames. These flames are the main subject of the thesis.

In combustion modelling with complex chemistry, the inherent stiffness of the governing equations generally leads to large data-structures. Therefore, from a computational point of view it is preferable to choose a testcase for which the equations become as simple as possible. However, the availability of an experimentally well-defined analogon for testing purposes is indispensable. There exist roughly two types of experimental burner concepts that meet this prerequisite: the counter flow jet flame and the flat-flame geometry. In our group flat-flame burners are used for experimental verification of the developed reaction models and numerical codes. The construction of these burners is such that both the velocity- and the temperature profiles are uniform [Maa92]. This is achieved by using a perforated metal plate with a cooling rim at the outlet of the burner (see Fig. 2.1). Near the center of the burner the flow can be considered one-dimensional. In a numerical model this greatly reduces the amount of memory and CPU-time needed, which makes this experimental configuration a very suitable testcase. Here, it is used to test the numerical algorithms, developed to deal with the intrinsic stiffness present in the governing equations.

In mathematical terms the burners are constructed in such a way that the flame becomes almost one-dimensional, or equivalently all variables obey

\[
\left| \frac{\partial C}{\partial z} \right| \ll \left| \frac{\partial C}{\partial x} \right|, \quad \left| \frac{\partial C}{\partial y} \right| \ll \left| \frac{\partial C}{\partial x} \right| \quad \forall (x, y, z)
\]

where \( C \) is any observable and \((y, z)\) are the coordinates along the burner surface and \( z \) the coordinate (distance) perpendicular to the burner surface. From a numerical point of view the advantages of this flat-flame burner type are apparent.
The equations governing the flow are simplified considerably, at least in a region far enough from the burner edges where the flow still behaves essentially three-dimensional. Near the center of the burner the system can be considered to be one-dimensional. Equations (1.1, 1.2, 1.21, 1.26) governing a laminar flat flame then reduce to,
\[
\frac{\partial \rho}{\partial t} + \frac{\partial \rho u}{\partial x} = 0
\]  
(2.1)

where \( u \) is the velocity along the \( x \)-axis, the center-line of the burner. The Navier-Stokes equations now become,
\[
\rho \frac{\partial u}{\partial t} + \rho u \frac{\partial u}{\partial x} = -\frac{\partial p}{\partial x} + \frac{\partial}{\partial x} \left( \frac{\mu}{\rho} \frac{\partial u}{\partial x} \right) + \rho g_x
\]  
(2.2)

which is the only equation involving the pressure gradient in the earlier introduced 'Combustion Approximation'. Gravity is considered to be the only external force field indicated by the term \( \rho g_x \). The enthalpy-balance and mass-balance of the species are given by,
\[
\frac{\rho c_p}{\partial t} + \rho u_c \frac{\partial T}{\partial x} - \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) = -\sum_{i=1}^{N} h_i \hat{\beta}_i - \sum_{i=1}^{N} \rho Y_i c_{pi} U_i \frac{\partial Y_i}{\partial x}
\]  
(2.3)

\[
\frac{\rho}{\partial t} + \rho u \frac{\partial Y_i}{\partial x} - \frac{\partial}{\partial x} \left( \rho D_{mi} \frac{\partial Y_i}{\partial x} \right) = \hat{\beta}_i, \quad i = 1(1)N,
\]  
(2.4)

respectively where \( \hat{U}_i \) denotes the diffusion velocity along the \( x \)-axis. The set of equations is closed with the ideal gas-law,
\[
\rho = nRT
\]  
(2.5)
2.1. Introduction

It can be shown that the pressure in the approximation used for laminar flames, can be written as,

$$\rho(x, t) = P_0 + \delta p(x, t) \quad \text{with} \quad \delta p(x, t) / P_0 = O(Ma^2) \ll 1$$

The Mach number is defined as $Ma = u/c$ where $c$ is the speed of sound. Here $P_0$ is a constant pressure and $\delta p(x, t)$ the small spatial pressure variation determined by the momentum equation (2.2) only [Buc82]. For an atmospherical methane-air flame typical flow speeds do not exceed $3m/s$. Corrections to the molar density $\rho$ stemming from $\delta p(x, t)$ are then of the order $\left(3.0/300.0\right)^2 \approx 10^{-4}$. It is therefore often sufficient to consider the equations (2.1), (2.3) and (2.4) only. The molar density $\rho$ is then determined from,

$$P_0 = \rho RT \quad (2.6)$$

instead and the momentum equation can therefore be omitted\(^1\).

Experimentally, the flat flames are stabilized near the cold burner surface at a fixed position in space. In the laboratory frame of reference this flame is in a steady-state, meaning that all terms involving $\partial J/\partial t$ are zero. For these stabilized flames the governing equations are even simpler since the continuity equation (2.1) now reduces to,

$$\rho u = \dot{m}$$

with $\dot{m}$ the given constant mass-flux. For such burner-stabilized premixed flat flames the problem is then described by the following set of equations,

$$\begin{align*}
\dot{m} \frac{\partial T}{\partial x} - \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) &= - \sum_{i=1}^{N} k_i \rho_i \sum_{i=1}^{N} \rho Y_i c_p U_i \frac{\partial T}{\partial x}, \\
\dot{m} \frac{\partial Y_i}{\partial x} - \frac{\partial}{\partial x} \left( \rho D_{ij} \frac{\partial Y_i}{\partial x} \right) &= \dot{h}_i \quad i = 1(1)N, 
\end{align*} \quad (2.7)$$

and the ideal gas law (2.6). The number of differential equations to be solved is equal to $N + 1$.

In Fig. (2.2) the contributions of all four terms in Eq. (2.7) are compared for a selected premixed $CH_4$-air flame. The enthalpy flux induced by the diffusive fluxes, the sum $\sum_{i=1}^{N} \rho Y_i c_p U_i \frac{\partial T}{\partial x}$ in Eq. (2.7), is small compared to the other parts of the differential equation [Smo91]. As can be verified easily, it is even exactly zero if all heat capacities are equal. For that case the mixture enthalpy equation is completely equivalent with that of a single species fluid.

In the remainder of the thesis this term will not be taken into account unless mentioned otherwise.

The description of the system of equations is not complete yet since the boundary conditions for the flat-flame geometry have not been specified. Since for the present geometry the set of governing equations is reduced to a set of second-order differential equations, two boundary conditions for every unknown have to be introduced. To illustrate these we consider a typical solution as given in Fig. 2.3. The computational domain extends from the burner inlet ($x = -L_i$) to some distance

\(^1\)This is not true in $N$-dimensional systems with $N \geq 1$. It is impossible to replace the $N$ momentum equations by (2.6) since only one variable ($\delta p(x, t)$) is eliminated.
fig. 2.2: Convective heat transport, conduction, mass-flux accompanied heat-flux and heat generation by chemical reactions as a function of the distance from the burner in an adiabatic methane-air flame ($\varphi = 0.8$).

fig. 2.3: Typical flame structure. The $R$ is a typical reactant profile, $I$ an intermediate and $P$ a product. The temperature $T$ is continuous, $dT/dx$ is discontinuous at the burner surface.
downstream of the flame \((x = L_0)\). The origin \(x = 0\) is positioned at the burner surface. The first set of boundary conditions is specified at \(x = L_0\); for species and temperature zero gradients are imposed which implies that the computational domain has to be extended to a point where the system is in equilibrium. However, for the second set of boundary conditions different types of boundary conditions have to be taken for species and temperature. On one hand, for all species the concentrations are given at the burner inlet \((x = -L_i)\), while on the other hand the temperature is taken fixed at the burner surface \((x = 0)\) due to the forced cooling of the burner. The latter implies that the burner is a perfect conductor and the cooling system is able to keep the burner at a fixed temperature, equal to temperature of the mixture at the inlet. The boundary conditions for the species at the burner inlet can be transferred to the burner surface as well but only under the assumption of zero chemical source terms within the burner \((\rho_i = 0 \forall x \in [-L_i, 0])\). In practice, this is a good approximation since the temperature is normally so low\(^2\) that the mixture is chemically inert. For that case the differential equations for the species reduce to a pure convection-diffusion equation and can be integrated from \(x = -L_i\) to \(x = 0\), yielding,

\[
\int_{-L_i}^{0} \left( \frac{m}{\partial x} \frac{\partial Y_i}{\partial x} - \frac{\partial}{\partial x} \left( \rho \frac{D_{im}}{\partial x} \frac{\partial Y_i}{\partial x} \right) \right) dx = 0
\]

or

\[
\epsilon_i(0) - \epsilon_i(-L_i) = 0
\]

where we introduced the total flux \(\epsilon_i(x)\) according to,

\[
\epsilon_i(x) = \bar{m} Y_i(x) - \rho D_{im} \frac{\partial Y_i}{\partial x}(x)
\]

At \(x = -L_i\) the first derivatives vanish and we obtain the so-called flux-condition for the species at the burner surface yielding,

\[
\epsilon_i(0) = \bar{m} Y_i(-L_i).
\]

Note that the quantity \(\rho \frac{D_{im}}{\partial x}\) is not necessarily constant.

With (2.11) the domain has been reduced to \(x \in [0, L]\) where we dropped the subscript \(_o\). \(L\) will be referred to as the length of the computational domain. We now have as boundary conditions,

\[
\begin{align*}
x = 0: & \quad \frac{\partial T}{\partial x} = \frac{\partial Y_i}{\partial x} = 0, \\
x = L: & \quad \epsilon_i = \bar{m} Y_i(-L_i), \\
& \quad \bar{m} Y_i(-L_i) = 0. \quad (2.12)
\end{align*}
\]

\(^2\) However, it is not exactly true since the Arrhenius-terms, proportional to \(\exp(-\frac{E_a}{RT})\), only approach zero. This problem has come to be known as the so-called 'cold boundary difficulty' merely indicating that from a mathematical point of view the source terms have to be exactly zero for the problem to be well posed[Bus82].
Together with the differential equations (2.7) and (2.8) and the ideal gas-law (2.6), the boundary conditions (2.12) complete the mathematical description of the stabilized premixed flame. It should be noted that for the detailed modelling of dynamic phenomena, like blow-off, flash-back and flame oscillations the time dependent equations must be used. Even more, in that case the introduction of the so-called flux boundary condition is not possible, since the integration (2.9) cannot be carried out to yield (2.10).

The relative simplicity of the governing flow equations for this practical burner geometry led to a wide interest for the premixed flat flame burner as a testcase in the previous decade. Especially in the development and testing of chemical schemes it played a major role which has led to a general availability of a vast variety of chemical schemes for many hydrocarbons. The main goal of this chapter is the development and testing of an algorithm that can be used to solve the equations describing the premixed laminar flat-flame problem. It will be used to perform studies on the effects of certain approximations on the structure of methane-air flames in this chapter as well as in the following chapter. Furthermore, the know-how and techniques developed for the flat-flame geometry will be applied to the modelling of multi-dimensional flame problems with complex chemistry presented in the fourth chapter of this thesis.

In the following section the main chemical scheme used in the present thesis, will be presented and discussed. In section 2.3 the specific numerical aspects and techniques for complex chemical systems will be treated. In section 2.4 the algorithm is tested and results are compared with results from the SANDIA premix-code. The reference calculations for comparison with reduced chemical models used in chapter 3 will be presented. Furthermore, a study on the effects of some transport model approximations is presented and the performance of the skeletal mechanism in rich flames is discussed. Finally, the conclusions are presented and discussed in the last section of this chapter.
2.2 Detailed Chemistry: A Skeletal Mechanism for $CH_4$-air

Generally, natural gas can be considered as a mixture of mainly methane ($CH_4$), ethane ($C_2H_6$) and traces of some higher hydrocarbons like propane ($C_3H_8$) diluted with nitrogen ($N_2$). The actual composition depends on the exploitation well$^3$. Even more, significant differences in composition occur between process-industry sources (steam cracking of crude oil and naphtha) and geo-physical sources of natural gas(-like) mixtures. Typically the former mixtures contain levels of hydrogen- ($H_2$) and ethane of approximately 20% and may therefore be expected to show different burning behavior. A more detailed review of these data is given by Jessen and Melvin$^{[jes76]}$.

However, most hydrocarbons, in spite of the fact that the reaction paths are very different, show remarkable similarity in their combustion characteristics (with respect to major species profiles and burning velocity). The main reason for this is the claimed ([War81]) dominance of the reactions,

$$H + O_2 \rightarrow HO + O$$
$$CO + OH \rightarrow CO_2 + H$$

which occur in the combustion of any hydrocarbon$^4$. For the computation of the detailed structure of a hydrocarbon flame a reaction mechanism covering the details of the reaction path of the alkane to carbon-monoxide is inevitable. Also for the prediction of soot-formation and $NO_x$, accurate profiles of the intermediates are indispensable. For the case of natural gas combustion the reaction data of at least methane and to a lesser extent of ethane would have to be used.

In this thesis we will not treat natural gas flames, though these form the subject of the research project. Since most sources produce methane mainly, we will focus on pure methane-air flames for which the reaction data are relatively well known. In this section a set of reactions is presented that will be used throughout the thesis. The main aspects of this specific mechanism are treated.

For cases where the initial concentration of the fuel is not too high the path given in Fig. (2.4) describes the essential chain of reactions of the methane oxidation.

Only under very fuel rich conditions the path to the $C_3\cdot$ and $C_4\cdot$ hydrocarbons becomes more and more important$^6$. A good compilation of all the reaction rate data available to date is given in [Gar84a] and more recently in [Ego90]. The latter authors claim to find good agreement for the burning velocities of most $C_1\cdot$ and $C_2\cdot$-fuels with a reaction scheme consisting of 36 species and 210 reversible reactions.

Fortunately, in fuel-lean to stoichiometric conditions good agreement with experimental data can be found if one considers the $C_1\cdot$-path only$^{[Smo91]}$. This leads to

---

$^3$Natural gas composition denoted as $(X_{CH4}, X_{C2H6}, X_{XH})$ for several sources are:
- North Sea (0.94,0.03,0.03), Slochteren (The Netherlands) and most Northern-American gasfields (0.82,0.03,0.15), Algerian (LNG) (0.87,0.09,0.04)

$^4$Warnatz claims that the global combustion phenomena (burning velocity, quench rate etc...) of any alkane can be modelled within a factor of two, by using only the $H_2 - O_2 - CO$ mechanism, a realistic reaction set covering Alkane $+$ $O, H, OH$ $\rightarrow$ Alkyl $+$ $OH, H_2, H_2O$ conversion followed by an infinitely fast Alkyl to CO reaction.

$^6$A complication in higher hydrocarbon fuels ($> C_5$), is the existence of different isomers of the alkyl, formed after decomposition. Each of these isomers (e.g. $n - C_5H_{12}$ versus $\delta - C_5H_{12}$ in the case of propane decomposition) has its own formation rate.
fig. 2.4: Main reaction path in methane combustion [War83] for not too fuel-rich initial conditions. The dashed box describes what is usually referred to as the $C_2$-chain. The $C_1$ chain is shown in the box on the left.
a large reduction in the number of species and reactions involved which is the main reason that we consider lean methane-air flames first. In table (2.1) this mechanism is presented. It is sometimes referred to as a skeletal mechanism since it represents only a minimal subset of the complete mechanism. However, it is claimed in literature that it predicts the most important flame-features well, e.g. burning velocities, species profiles, flame temperatures [Smo91]. There are 25 reactions and 15 species present in this scheme, which provides a considerable reduction of the problem size.

The reaction set \( r_1 - r_3 \) in table (2.1) is in fact the main reaction chain in the \( H_2-O_2 \) sub-system which is embedded in any hydrocarbon reaction mechanism. These reaction rates are very well known because of extensive studies in the early eighties on hydrogen flames. The reaction parameters of the chain \( CH_4 \rightarrow CO \) and \( (CH_4) \rightarrow CO_2 \) became well known in the late eighties when more computing power and sophisticated algorithms were developed and the research focussed on more complex fuels than hydrogen.

In the following the role of several reactions in the hydrocarbon combustion process is discussed. The terminology used can be found in most literature on combustion [Gar84a, Smo91]. First of the so-called initiation reactions are treated. These are the reactions that account for the ignition of the reaction chain. The only initiation reaction\(^6\) in the skeletal mechanism is a thermal-decomposition reaction \( (r_{10}) \) which is considered to be the most important,

\[
CH_4(M) \rightarrow CH_3 + H + (M). \tag{r_{10}}
\]

Sensitivity analysis shows that this initiation reaction is of minor importance for concentration profiles, burning velocity and flame temperature in a steady flame. For studies where ignition is important (e.g. engines, engine knock, shock-tubes) it is essential and other initiation reactions have to be provided as well [Gar84a, Smo91].

Once initiated the fuel breakup to carbon-monoxide proceeds via a chain of reactions \( (r_{11} \text{ to } r_{20}) \).

\[
\begin{align*}
CH_4 + H & \rightarrow CH_3 + H_2 \\
CH_4 + OH & \rightarrow CH_3 + H_2O \\
CH_3 + O_2 & \rightarrow CH_2O + O \\
CH_2O + H & \rightarrow CH_2O + H_2 \\
CH_2O + M & \rightarrow CH_2O + H + M \\
CH_3 + O & \rightarrow CH_2O + H \\
CH_2O + H & \rightarrow HCO + H_2 \\
HCO + H & \rightarrow CO + H_2 \\
HCO + M & \rightarrow CO + H + M
\end{align*}
\]

This cascade of reactions is claimed to be very fast, which means that every intermediate product (i.e. \( C = CH_3, CH_2O, CH_2O \) and \( HCO \)) is rapidly consumed even at very low concentrations. The relatively slower oxidation step of \( CO \) to \( CO_2 \) proceeds via reaction \( r_9 \).

---

\(^6\) Another initiation reaction in CH\(_4\)-air flames, but not tabulated here, is the \( CH_4 + O_2 \rightarrow CH_3 + NO_2 \) reaction.
The total fuel-breakup chain in $CH_4$ flames consumes radicals. To keep the oxidation going, the so-called chain-branching reactions are important. These account for a fast increase of the concentration of the radicals $O$, $OH$ and $H$, often referred to as the 'radical pool'. The most important chain-branching reaction in methane-air combustion is $r_1$,

$$H + O_2 \rightarrow OH + O \quad (r_1)$$

which is essential in the analysis of methane-air combustion. It is called branching because out of an initially present stable species (e.g. $O_2$) and a $H$-radical it produces two new radicals and thereby gives rise to an increase of the radical pool.

A third type of reactions are the shuffle- or chain-propagating reactions, reactions $r_2$ - $r_4$ in table (2,1),

$$O + H_2 \rightleftharpoons OH + H \quad (r_2)$$

$$OH + H_2 \rightarrow H_2O + H \quad (r_3)$$

$$OH + OH \rightarrow H_2O + O \quad (r_4)$$

The overall effect of these latter three reactions does not lead to an increase in the radical pool but is merely a conversion of radicals into another. Thereby stable products (e.g. $H_2O$) are created.

Finally, the reaction chain terminates because of the so-called chain breaking reactions. In the skeletal mechanism these are given by,

$$H + O_2 + M \rightarrow HO_2 + M \quad (r_5)$$

$$OH + H + M \rightarrow H_2O + M \quad (r_{24})$$

$$H + H + M \rightarrow H_2 + M \quad (r_{25})$$

The net effect of this reaction set reduces the radical pool because it converts the radicals into stable products and is responsible for the formation of the final products. Note that although reaction $(r_5)$ in principle is radical conserving it still is considered as chain-breaking since the created peroxide-radical is less reactive than $H$ and the rapid chain $(r_{67}r_8)$,

$$H + HO_2 \rightarrow OH + OH \quad (r_6)$$

$$H + HO_2 \rightarrow H_2 + O_2 \quad (r_7)$$

$$OH + HO_2 \rightarrow H_2O + O_2 \quad (r_8)$$

has an overall effect of a conversion of $HO_2$ into stable products.

The latter 6 reactions $(r_5, r_6, r_7, r_8, r_{24}$ and $r_{25}$) convert radicals into stable species either directly $(r_7, r_8, r_{24}$ and $r_{25}$) or indirectly $(r_5, r_6)$ by creating radicals that open a fast chain towards stable species.
### Table 2.1: Skeletal Mechanism for \( \text{CH}_4 \)-air combustion

The coefficients of the Arrhenius term \( k = A \exp(-E_a/R T) \) are given in the three columns on the right (see Chapter 1). All units are cm·s·K and calories according to conventions used in standard literature on combustion.

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
<th>( A )</th>
<th>( n )</th>
<th>( E_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{H} + \text{O}_2 \rightleftharpoons \text{OH} + \text{O} )</td>
<td>( 2.000 \cdot 10^{14} )</td>
<td>0.0</td>
<td>16800.0</td>
</tr>
<tr>
<td>2</td>
<td>( \text{O} + \text{H}_2 \rightleftharpoons \text{OH} + \text{H} )</td>
<td>( 1.575 \cdot 10^{13} )</td>
<td>0.0</td>
<td>690.0</td>
</tr>
<tr>
<td>3</td>
<td>( \text{H}_2 + \text{O}_2 \rightleftharpoons \text{H}_2\text{O} + \text{H} )</td>
<td>( 1.800 \cdot 10^{10} )</td>
<td>1.0</td>
<td>8826.0</td>
</tr>
<tr>
<td>4</td>
<td>( \text{OH} + \text{OH} \rightleftharpoons \text{O} + \text{H}_2\text{O} )</td>
<td>( 8.00 \cdot 10^{9} )</td>
<td>1.0</td>
<td>6760.0</td>
</tr>
<tr>
<td>5</td>
<td>( \text{H} + \text{O}_2 + \text{M} \rightleftharpoons \text{H}_2\text{O}_2 + \text{M} )</td>
<td>( 1.170 \cdot 10^{6} )</td>
<td>1.3</td>
<td>3626.0</td>
</tr>
<tr>
<td>6</td>
<td>( \text{H} + \text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{OH} )</td>
<td>( 5.090 \cdot 10^{9} )</td>
<td>1.3</td>
<td>18588.0</td>
</tr>
<tr>
<td>7</td>
<td>( \text{H} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{H}_2\text{O} )</td>
<td>( 1.510 \cdot 10^{6} )</td>
<td>1.3</td>
<td>-758.0</td>
</tr>
<tr>
<td>8</td>
<td>( \text{CO} + \text{O} \rightleftharpoons \text{CO}_2 + \text{H} )</td>
<td>( 1.570 \cdot 10^{7} )</td>
<td>1.3</td>
<td>22337.0</td>
</tr>
<tr>
<td>9</td>
<td>( \text{CH}_4 + \text{O} \rightleftharpoons \text{CH}_3 + \text{H} + \text{O} )</td>
<td>( 6.300 \cdot 10^{14} )</td>
<td>0.0</td>
<td>104000.0</td>
</tr>
<tr>
<td>10</td>
<td>( \text{CH}_3 + \text{O} \rightleftharpoons \text{CH}_2\text{O} + \text{H} )</td>
<td>( 5.200 \cdot 10^{12} )</td>
<td>0.0</td>
<td>-1310.0</td>
</tr>
<tr>
<td>11</td>
<td>( \text{CH}_4 + \text{H} \rightleftharpoons \text{CH}_3 + \text{H}_2 )</td>
<td>( 2.200 \cdot 10^{4} )</td>
<td>3.0</td>
<td>8750.0</td>
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<td>12</td>
<td>( \text{CH}_4 + \text{OH} \rightleftharpoons \text{CH}_3 + \text{H}_2\text{O} )</td>
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<td>3.0</td>
<td>8750.0</td>
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<td>14</td>
<td>( \text{CH}_2\text{O} + \text{H} \rightleftharpoons \text{HCO} + \text{H}_2 )</td>
<td>( 3.020 \cdot 10^{5} )</td>
<td>2.1</td>
<td>17422.0</td>
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<tr>
<td>15</td>
<td>( \text{CH}_2\text{O} + \text{OH} \rightleftharpoons \text{HCO} + \text{H}_2\text{O} )</td>
<td>( 6.800 \cdot 10^{13} )</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>16</td>
<td>( \text{HCO} + \text{H} \rightleftharpoons \text{CO} + \text{H}_2 )</td>
<td>( 2.500 \cdot 10^{6} )</td>
<td>0.0</td>
<td>3991.0</td>
</tr>
<tr>
<td>17</td>
<td>( \text{HCO} + \text{M} \rightleftharpoons \text{CO} + \text{H} + \text{M} )</td>
<td>( 3.000 \cdot 10^{9} )</td>
<td>0.0</td>
<td>1195.0</td>
</tr>
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<td>18</td>
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<td>0.0</td>
<td>25652.0</td>
</tr>
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<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>20</td>
<td>( \text{CH}_2\text{O} + \text{M} \rightleftharpoons \text{CH}_2\text{O} + \text{H} + \text{M} )</td>
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<td>0.0</td>
<td>28812.0</td>
</tr>
<tr>
<td>21</td>
<td>( \text{H}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{H}_2\text{O} )</td>
<td>( 2.000 \cdot 10^{12} )</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>22</td>
<td>( \text{H}_2\text{O}_2 + \text{M} \rightleftharpoons \text{H}_2 + \text{OH} + \text{M} )</td>
<td>( 1.300 \cdot 10^{17} )</td>
<td>0.0</td>
<td>45500.0</td>
</tr>
<tr>
<td>23</td>
<td>( \text{H}_2\text{O}_2 + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{H}_2\text{O} )</td>
<td>( 9.860 \cdot 10^{11} )</td>
<td>0.0</td>
<td>-5070.0</td>
</tr>
<tr>
<td>24</td>
<td>( \text{OH} + \text{H} + \text{M} \rightleftharpoons \text{H}_2\text{O} + \text{M} )</td>
<td>( 2.200 \cdot 10^{22} )</td>
<td>-2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>25</td>
<td>( \text{H} + \text{H} + \text{M} \rightleftharpoons \text{H}_2 + \text{M} )</td>
<td>( 1.800 \cdot 10^{18} )</td>
<td>-1.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\( ^a \) High-pressure limit: switching function \( \Gamma ([M]) = (\text{M}/[\text{M}])^{0.0063} \) with \( [\text{M}] = 1000 \text{ cm/RT} \).

\( ^b \) Enhanced third body efficiencies \( \tau \): \( \text{CH}_4 = 6.5, \text{H}_2\text{O} = 6.5, \text{CO}_2 = 1.5, \text{CO} = 0.75, \text{O}_2 = 0.4, \text{N}_2 = 0.4 \). Others = 1.0.
The skeletal mechanism is used throughout this thesis for comparison with the several even more simple mechanisms. However, it should be kept in mind that because of the absence of the \( C_2 \)-chain, the skeletal mechanism is not considered to be adequate for rich flames. In rich flames a path to the \( C_2 \)-chain through reactions like \( CH_3 + CH_3 \rightarrow C_2H_6 \) becomes more and more important, primarily due to the relatively high \( CH_3 \) concentration. Effects of incorporating the \( C_2 \)-chain are dealt with in section 2.4.4. In the next section the numerical techniques, used to solve the reacting flow equations with complex chemical schemes, are described.
2.3 Numerical Method

In general terms we are interested in solving a set of N+1 strongly non-linear coupled partial differential equations (PDE's). Any implementation of a numerical procedure to solve this set can roughly be subdivided in three distinctive tasks.

- Discretization of the differential equations
- A mesh generation technique
- Solution procedure for the discrete set of equations

First, we have to set up the spatial and time discretization. Appropriate representations of the differential operators have to be introduced. The spatial discretization is dealt with in the next subsection 2.3.1 and is not specific for modelling laminar combustion phenomena. However, some specific problems have to be accounted for.

Due to the nature of flames, there exist very steep gradients in the field variables, or equivalently the chemically active layer is very thin (O(1mm)) compared to the length of the computational domain (O(10cm)). In order to resolve these gradients properly and yet keep the number of grid points within reasonable bounds, a non-uniform grid is used. Since the location of the high gradients is not known a priori, an adaptive gridding technique is inevitable. The strategy to generate the grid is dealt with in subsection 2.3.2. Finally, a suitable solution strategy of the (non-linear) discrete set of equations has to be developed and implemented. The methodology used in this thesis is presented in the last subsection 2.3.3.

2.3.1 Discretization

The discretization technique will be presented in this part. Before this is treated in more detail, the energy equation is put in a form closely related to the mass fraction equations. There exist many ways to introduce a non-dimensional temperature and it is more or less a matter of taste. In this thesis we will use the following dimensionless quantity[1an92],

\[ \hat{T} = \frac{\hat{c}_p T}{\Delta h} \] (2.13)

where \( \hat{c}_p \) is a reference value of the specific heat capacity and \( \Delta h \) a reference enthalpy difference. This then leads to,

\[ \dot{m} c_p \frac{\partial \hat{T}}{\partial x} - \frac{\partial}{\partial x} \left( \lambda \frac{\partial \hat{T}}{\partial x} \right) = - \frac{\hat{c}_p}{\Delta h} \sum_{i=1}^{N} h_i \hat{q}_i, \] (2.14)

It is worth mentioning that in the assumption of constant \( c_p \), Eq. (2.8) and Eq. (2.14) can be put in a form which is very popular in theoretical treatments. Introducing the (dimensionless) Peclet number,

\[ Pe = \frac{\dot{m} c_p L}{\lambda} \]
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with \( L \), a reference length scale, here equal to the length of the calculational domain, and the species dependent Lewis number,

\[
Le_i = \frac{\lambda}{\mu D_{i\text{m}} c_p}
\]

leads to an analogous form for both equations,

\[
\begin{align*}
\frac{\partial Y_i}{\partial \tilde{x}} & = \frac{\partial}{\partial \tilde{x}} \left( Pe^{-1} \frac{\partial Y_i}{\partial \tilde{x}} \right) - \frac{L}{\bar{m} \Delta \tilde{x}} \sum_{i=1}^{N} \tilde{h}_i \tilde{\rho}_i, \\
\frac{\partial Y_i}{\partial \tilde{x}} & = \frac{\partial}{\partial \tilde{x}} \left( PeLe_i \right)^{-1} \frac{\partial Y_i}{\partial \tilde{x}} \equiv \frac{L}{\bar{m} \tilde{\rho}_i}
\end{align*}
\]

where we have taken \( \tilde{c}_p = c_p \) and used \( \tilde{x} = x/L \) for the non-dimensional \( x \)-coordinate. The Lewis number, \( Le_i \), can be regarded as a measure of the ratio of conductive and diffusive transport and is for many species of the order of one.

In our case, where the effect of variations in transport models and between various choices for the conductivity will be studied, the advantages of the non-dimensional formulation are not so obvious. Instead, Eqs. (2.8, 2.14) are used in the implementation of the differential equations. However, in section 2.4.3 the Lewis numbers are used, to test the effect of certain transport model approximations.

Since the gridding strategy will be treated thoroughly in the next section the grid will be assumed as given for the time being. For matters of convenience the tildes are dropped and all (dependent) variables are non-dimensional unless mentioned otherwise. The grid points are assumed,

\[
x_j \in [0, L], \quad j = 1(1) K \quad \text{and} \quad x_{j-1} < x_j.
\]

Since the discretization will be similar for all variables due to the analogous form of the conservation equations a variable, \( Y \) can be used for which we may substitute \( Y_i \) and \( \tilde{Y} \). The variable \( Y \) obeys a generalized convection-diffusion equation,

\[
\mu \frac{\partial Y}{\partial \tilde{x}} - \tilde{\alpha} \frac{\partial}{\partial \tilde{x}} \left( \Lambda \frac{\partial Y}{\partial \tilde{x}} \right) - \bar{S} = 0
\]

with appropriate values for \( \mu, \Lambda \) and \( \bar{S} \), depending on the variable used.

Here a finite-volume approach is used to discretize the differential operators. The PDE's are integrated over a control volume as given in Fig. (2.5) in a way proposed by Thirk[Thir90A] and all variables are given at the grid points. Consider a specific location in the grid denoted by its center point \( P \) and its eastern- (E) and western (W) neighbor. The control volume is then defined by the interval \( \epsilon \in x_P - \delta_w, x_P + \delta_e \) and for constant\(^7 \mu \) within this interval, (2.17) can be integrated, formally yielding,

\[
\epsilon (x_P + \delta_e) - \epsilon (x_P - \delta_w) = \int_{x_P-\delta_w}^{x_P+\delta_e} \bar{S} dx.
\]

\(^7\)For the mass fraction equation this is exactly true, for the enthalpy equation this can only be met in the case of constant \( c_p \).
fig. 2.5: Finite volume discretization. The interfaces e and w of the control volume are at the midpoints of the eastern \( <x_P, x_E> \) and western \( <x_W, x_P> \) interval, respectively.

where the definition for the flux \( \epsilon = \mu Y - \Lambda \frac{\partial Y}{\partial x} \) is introduced, analogous to the flux introduced in the derivation of the boundary conditions at the burner surface (2.10). The points \( x_P - \delta_w \) and \( x_P + \delta_e \) are the midpoints of the western and eastern interval, respectively. It should be noted that the western and eastern intervals do not need to be equally large, anticipating the adaptive gridding strategy described further on.

In order to calculate the flux at the interfaces, \( Y \) and \( \partial Y / \partial x \) have to be expressed in terms of the values at the grid points. The approach Thiart uses to evaluate (2.18) is based on the exact solution of the convection-diffusion equation (2.17), with constant \( \Lambda \) and source term \( S \), on an interval \( x \in [x_1, x_e] \), yielding,

\[
Y(x) = Y_l + \frac{S}{\mu} (x - x_l) + \frac{Y_r - Y_l - (S \Delta / \mu)}{\epsilon (\mu \Delta / \Lambda) - 1} \left[ \epsilon (x - x_l) / \Lambda - 1 \right] \quad (2.19)
\]

where \( \Delta = x_e - x_l \) is the length of the interval and the left and right boundary values of \( Y \) are denoted as \( Y_l = Y(x_l) \) and \( Y_r = Y(x_e) \), respectively. An extension of this approach for the 2D convection-diffusion equation is available [Thi90B] and will be used in chapter 4.

Now Eq. (2.19) is used on the intervals \( <x_P, x_E> \) and \( <x_W, x_P> \) to evaluate the expression for the flux at the western and eastern midpoint. The flux \( \epsilon (x_P + \delta_e) \) at the eastern interface \( e \), can be expressed in values of \( Y \) at the grid points according to,

\[
\epsilon (x_P + \delta_e) = \mu_e \left[ Y_P + \frac{Y_l - Y_r}{\epsilon P_e} \right] + \frac{S}{\epsilon P_e} \left[ \delta_e - \frac{\Delta E}{P_e} + \frac{\Delta E}{P_e} \right] \quad (2.20)
\]

where the local Peclet number \( P_e = \frac{\mu_e \delta_e}{\Lambda_e} \) is introduced. It should be noted that there is a certain freedom of choice in the definition of the 'constant' \( \mu_e, \Lambda_e \) and \( S \) in an implementation of the discretization scheme. Currently for \( \mu_e = \mu = \text{constant} \),

---

8 It is equal to \( P_e = P_e \cdot L / (\Delta \phi_{Le} \Delta e) \) as can be seen by substituting the equality \( \epsilon \phi / \Lambda = (\rho D_m Le) \) into the definition for the Peclet number introduced earlier. The factor \( L / (\Delta \phi_{Le} \Delta e) \) is dimensionless.

9 For the species balance equation this is no approximation since \( \mu = m = \text{constant} \).
\[ \mu_w = \mu(x_P) \] and \[ S_r = S_w = S(x_P) \] the values at the gridpoint \( x_P \) are taken. The diffusivity/conductivity on the other hand are evaluated at the interfaces \( \Lambda_r = \Lambda(x_{P_r} + \delta_r) \) and \( \Lambda_m = \Lambda(x_{P_m} - \delta_m) \). Note that no choice has been made for these quantities yet.

Using an analogous expression for the western flux \( \epsilon_w \) and substitute both in (2.18),

\[ \epsilon(x_{P_r} + \delta_r) - \epsilon(x_{P_r} - \delta_m) = S_r \delta_r + S_w \delta_w \]

leads to a discretized version of the differential equation,

\[
\mu_r \left[ \frac{Y_P + Y_F}{e^{P_r} - 1} \right] - \mu_w \left[ \frac{Y_W + Y_P}{e^{P_m} - 1} \right] - S_r \Delta_k \left[ \frac{1}{P_E - e^{P_r} - 1} \right] + S_w \Delta_k \left[ 1 - \frac{1}{P_W - e^{P_m} - 1} \right].
\]

(2.21)

Gathering all terms per gridpoint and introducing the functions

\[ A(P) = \frac{P}{e^P - 1} \quad \text{and} \quad W(P) = \frac{1}{P} \left( \frac{1}{e^P - 1} \right) \]

where the latter can be expressed as,

\[ W'(P) = \frac{1 - A'(P)}{P} \]

gives a discretization similar to the exponential fitting scheme of Patankar [Pat89],

\[ a_P Y_W + b_P Y_P - c_P Y_E = s \]

with \[ a_P = \Lambda_w A(P_W)/\Delta_k, \quad b_P = \Lambda_r A(P_r)/\Delta_k \quad \text{and} \quad b_P = a_P + c_P. \] Only the source-term weighing,

\[ s = S_w \Delta_k \left[ 1 - W(P_W) \right] + S_r \Delta_k W(P_r), \]

is typical for the Thiart-approach and is not present in the Spalding-approach\(^{11}\).

Reformulation of the discretization to the grid index \( j \) and using the notation

\[ Y_j = Y(x_j) \]

leads to the following definition of the discretized convection-diffusion equations,

\[ -a_j Y_{j-1} + b_j Y_j - c_j Y_{j+1} = s_j \]

(2.23)

on the mesh \( x_j \). The coefficients are equal to,

\[ a_j = \frac{\Lambda_{j-1}}{\Delta_j} A(-P_{j-1}) \]

\[ b_j = \frac{\Lambda_j}{\Delta_j} A(P_j) \]

\[ c_j = a_j + c_j \]

\[ s_j = S_{j-1} \Delta_j \left[ 1 - W(P_{j-1}) \right] + S_j \Delta_j W(P_j) \]

\(^{11}\)Or the method presented by Gintali, [Gin91], which can be shown to yield identical discretization as presented in Appendix A.1.
2.3. Numerical Method

where $\Delta_j = x_{j+1} - x_j$. It is worth mentioning that the earlier mentioned choice
for $S_e, S_w, \Lambda_e$ and $\Lambda_w$ for equidistant meshes leads to a source term disretization,

$$ s_j = S(x_j)(\Delta_{j-1} + \Delta_j)/2 $$

identical to the ones obtained by Chilani [Ghi91], see Appendix A.1.

In our case we can distinguish between two different realizations of the presented scheme. The discretization of the mass fraction equations leads to the definitions,

$$ p_{j}^V = \frac{\rho c \Delta_j}{\Lambda_j} \quad \text{with} \quad \Lambda_j = (\rho D_m)_j $$

and similarly for the energy equation we get,

$$ p_{j}^R = \frac{\rho c \Delta_j}{\Lambda_j} \quad \text{with} \quad \Lambda_j = \lambda_j $$

which completes the discretization of the differential equations.

Like Spalding’s scheme, the Thiart-scheme is in fact a discretization which switches smoothly from central-differencing to upwinding for the first derivative wherever the local Peclet number (or Reynolds number) becomes too large (> 2) to give stable integration with a central-difference formula. Since a non-uniform grid will be used, large variations in local interval lengths may be encountered and therefore local Peclet numbers can vary significantly.

2.3.2 Adaptive Gridding

In combustion modelling very large gradients ($10^4$-$10^8$ K/cm temperature increase may occur) in the variables can be expected. An equidistant grid will not be employed because the number of points would become excessive and render the calculation inefficient. Furthermore, since the magnitude and position of the gradients are not known a priori the positions have to be chosen adaptively. These problems are not specific for the numerical simulation of flames with detailed chemistry but are also present in simple (one-step) chemical treatments.

If the number of grid points during the computation is kept constant, fundamentally, one can choose one of two approaches, dynamic and static rezoning. In a dynamic rezoning strategy, the positions of the grid points are evaluated dynamically. Actually, the grid positions are allowed to have a velocity and are an integral part of the computation\textsuperscript{11}. In a static rezoning technique the position of the grid points is reevaluated and adapted only at certain (pseudo-) time levels during the calculation process. In an ideal situation the advantage of the dynamic strategy over static rezoning is that no interpolations on a new grid have to be performed and therefore reduction in the rate of convergence does not occur. However, in practice dynamic rezoning is mostly accompanied with a static rezoning at some time levels to redistribute the grid points.

\textsuperscript{11}A specific variant, the adaptive travelling grid, where all grid points travel with the same velocity was developed by Larrouaru et al. [Lar92]. It is well suited for computing freely propagating flames, which in its 'steady-state' are structures traveling with constant velocity.
In this thesis static rezoning will be used which is also simpler to implement. However, the main reason for using the static technique is that in the computational methods for multi-dimensional\footnote{In multi-dimensional systems dynamic rezoning is extremely difficult, and in most combustion modelling problems only static rezoning is used.} reactive flow developed in our group, also static rezoning is used\cite{Lan92}. Since we will implement complex chemical models in the method for 2D-reactive flow (see Chapter 4), we want to use similar methods.

There exist various ways to apply a static rezoning. Many of these methods are based on equidistributing some positive mesh-function, $M > 0$, to compute a new mesh by requiring,

$$\int_{x_j}^{x_{j+1}} M dx' = \text{Constant} \quad (2.27)$$

illustrated in Fig. (2.6). The new positions can then be evaluated by an 'inverse' interpolation method\cite{Hym83}.

Many choices for the mesh functions are possible, but mostly an estimate of the local truncation error (e.g. \cite{Lar92}), or of the first and/or second derivative of the variables (e.g. \cite{Smo83}) are used. We choose a mesh function which depends on
both the gradient and curvature of all variables, according to,

\[
\mathcal{M} = \sum_{i=1}^{N+1} w_i \left( \frac{\partial^2 Y_i}{\partial x^2} \right)_{\text{max}} \leq \left( \frac{\partial^2 Y_i}{\partial x^2} \right)_{\text{max}} + C \quad (2.28)
\]

where \( w_i \) gives control over the weight of each variable in the determination of the new grid. The maxima, \( |\partial^2 Y_i/\partial x^2|_{\text{max}} \) and \( |\partial^2 Y_i/\partial x^2|_{\text{max}} \) of the absolute values of the gradient and curvature of \( Y_i \) on the mesh, are used for scaling purposes only. The constant parameter \( C \) affects the uniformity of the resulting grid. For instance, when \( C \) equals the sum given in Eq. (2.28), 50% of the points is concentrated in the region where the solution exhibits large gradients and curvature. A typical grid development is given in Fig. (2.7) where \( C \) was chosen equal to one-fifth of the sum in (2.28).

![Grid Illustration](image)

**Fig. 2.7**: Illustration of the adaptive gridding technique. The movement of the grid points for which \( x \in [0.0\text{cm}, 0.1\text{cm}] \) is given as a function of an iteration count. The computation has not reached a converged state yet after the presented number of iterations.

In the next section we will give the solution strategy we use for solving the set of non-linear PDE's.

### 2.3.3 Calculation Strategy

Due to the non-linear form of the discretized PDE's (2.23) some kind of linearization has to be performed. Due to the inherent stiffness of the set of equations an implicit method will have to be used. First we define the residual \( r_j \) at each grid point
Chapter 2. Complex Chemistry

\[ r_j = s_j + a_jY_{j-1} - b_jY_j + c_jY_{j+1} \]  
(2.29)

according to (2.23) which obviously is a vector of dimension \( K \) for every variable \( Y_i \). Labeling the residual vector of each variable with its index the following compact representation evolves,

\[ r_i = s_i \quad a_iY_{hi-1} \quad b_iY_i \quad c_iY_{h(i+1)} \]  
(2.30)

where \( i \in [1, N + 1] \) and \( Y_{N+1} \) denotes the temperature \( T \). We now introduce an index \( k = i + (j-1) \cdot (N + 1) \) and define a state-vector \( \mathbf{Y} \) according to this numbering scheme. This is in fact a grouping of all variables per gridpoint,

\[ \mathbf{Y} = [(Y_1 \ldots Y_{N+1})_1, (Y_1 \ldots Y_{N+1})_2, \ldots, (Y_1 \ldots Y_{N+1})_K]^T \]

where we denoted \( \mathbf{Y} \) in the original numbering in the order defined by the new index \( k \). Using these definitions, (2.30) can be written in a matrix representation,

\[ r(\mathbf{Y}) = \mathbf{Y} - \mathbf{D}(\mathbf{Y})\mathbf{Y} \]  
(2.31)

where the matrix \( \mathbf{D} \) has a block tri-diagonal structure containing the coefficients \( a_i, b_k \) and \( c_k \) arising from the spatial discretization on the diagonal of the blocks.

It is obvious that both \( \mathbf{Y} \) and \( \mathbf{D} \) are as such \( r \) and \( r' \) are non-linear functions of \( \mathbf{Y} \) and that this matrix equation can not be solved unless some linearization is introduced. We will use a Newton technique very similar to the one described by Smooke et al.[Smo83]. The Newton technique can be illustrated by introducing a first-order Taylor expansion of the residual in (2.31) around the state vector \( \mathbf{Y}^n \) found after \( n \) iterations,

\[ r^{n+1} = r^n + \frac{\partial r^n}{\partial \mathbf{Y}^n} \Delta \mathbf{Y}^{n+1}. \]

Here we employ the shorter notations, to be used from now on, for \( r^n = r(\mathbf{Y}^n) \) and \( \Delta \mathbf{Y}^{n+1} = \mathbf{Y}^{n+1} - \mathbf{Y}^n \).

Now introduce the Jacobian \( J^n \) according to

\[ J^n = \frac{\partial r^n}{\partial \mathbf{Y}^n} \]  
(2.32)

and Newton’s method evolves if one requires the solution of the \((n + 1)^{th}\) iteration to be a solution of the discretized PDE, i.e.

\[ r^{n+1} = 0 \]

this leads to the matrix equation,

\[ J^n \Delta \mathbf{Y}^{n+1} = -r^n, \]  
(2.33)

which has to be solved to obtain the new estimate \( \mathbf{Y}^{n+1} = \mathbf{Y}^n + \Delta \mathbf{Y}^{n+1} \).

The structure of the Jacobian is completely determined by the discretization on one hand and the numbering of the variables introduced earlier on the other.
2.3. Numerical Method

Hand in our case this leads to a block tri-diagonal structure of the matrix equation as sketched in Fig. (2.8), which can be solved easily using a block tri-diagonal solver [Fle88]. In fact, this is the reason for the specific ordering of the variables.

In contrast to the sub-matrices in \( \mathbf{D} \), which are all diagonal, the \( (N+1) \times (N+1) \)-submatrices \( \mathbf{J}_j^p \), \( \mathbf{J}_j^f \) and \( \mathbf{J}_j^c \) given in Fig. (2.8) are in principle dense matrices due to the composition and temperature dependency of \( a_k \), \( b_k \) and \( c_k \) in \( \mathbf{D} \), through the coefficients \( c_p \), \( \lambda \), \( \mu \) and \( \bar{D}_{im} \). More important is the coupling contained in the chemical source terms \( \mathbf{s} \), due to the exponential temperature dependency of the Arrhenius coefficients, the composition dependency of the elementary reactions and the specific enthalpy \( h_c \). The actual values of the entries in \( \mathbf{J}_j^p \), \( \mathbf{J}_j^f \) and \( \mathbf{J}_j^c \) are determined by the 'level of implicitness'. If we choose, for instance, the following form for the residual,

\[
\mathbf{r}^n(\mathbf{J}_j^p, \mathbf{J}_j^f, \mathbf{J}_j^c) = \mathbf{s}(\mathbf{J}_j^{n-1}) - \mathbf{D}(\mathbf{J}_j^{n-1})\mathbf{J}_j^n,
\]

It is completely equivalent with an ordinary tri-diagonal solver with all multiplications and divisions replaced with their matrix-counterparts. LU-decomposition of the submatrices is used in practice.

Fig. 2.8: Block tri-diagonal structure evolving in 1D laminar flame problems.
where the residual at iteration level \( n \) is fully determined by the solution properties of a previous level, this leads to \( J = -D \). Then equation (2.33) can be solved very fast since the equations of one variable become uncoupled from the rest and an ordinary tri-diagonal matrix equation for each variable evolves.

For stiff equations, as they occur in detailed chemistry treatments, this approach would lead to impractically small steps\(^{14}\) to give convergent behavior [Ora81]. Instead of (2.34) we choose a fully implicit approach according to

\[
\bar{r}^n(\bar{\mathbf{Y}}^n) = \bar{r}(\bar{\mathbf{Y}}^n) - D(\bar{\mathbf{Y}}^n)\bar{\mathbf{J}}^n, \tag{2.35}
\]

which in general leads to full submatrices \( J_{ij}^{n,n} \) in the Jacobian-matrix.

Still, it cannot be guaranteed that the Newton technique always gives a converging iteration sequence. In practice it depends on the initial guess which is used to start the iterative process. Therefore, the robustness of the solver is increased by implementing a pseudo-transient\(^{15}\) formulation of the problem. The residual for the time dependent equations as we use it becomes,

\[
\bar{r}_i(\bar{\mathbf{Y}}^n, \bar{\mathbf{Y}}^{n-1}) = \bar{r}(\bar{\mathbf{Y}}^n) - d\frac{\bar{\mathbf{Y}}^n - \bar{\mathbf{Y}}^{n-1}}{\Delta t} . \tag{2.36}
\]

A backward Euler discretization of the time derivative in equations (2.3) and (2.4) is used. The coefficients \( d \) are equal to \( \rho(\delta_s + \delta_u) \) for all species \((i < N)\) and to \( c_p \rho(\delta_s + \delta_u) \) for the enthalpy equation, respectively. In the next subsection the actual strategy used to solve the differential equations in laminar flame problems is presented.

Our implementation

Formally, one could derive an analytical expression for all elements of the Jacobian. However, this is an error-prone and cumbersome task. Furthermore, since we anticipate to vary many parameters and study their effect on the flame, this would have to be done for every new formulation of the problem. Therefore, the Jacobian is evaluated numerically, which is very flexible when changes are made in the residual formulation.

An artificial (small) disturbance \((\delta\bar{\mathbf{Y}})\) is imposed on one variable field and the residual is re-evaluated. The Jacobian is then calculated with the one-sided difference scheme,

\[
J = \bar{r}(\bar{\mathbf{Y}} + \delta\bar{\mathbf{Y}}) - \bar{r}(\bar{\mathbf{Y}}) \tag{2.37}
\]

where \(\bar{\mathbf{Y}}\) is a unit-vector and \(\delta\) a small parameter. Details of the procedure to evaluate the Jacobian are described in Appendix (A.2).

The Jacobian evaluation obviously is a CPU-intensive task. For this reason the full Newton methodology is not used, since then the Jacobian is calculated at every iteration step. Instead a modified Newton technique is applied. First, the Jacobian is

\(\text{Proportional to the smallest timescale in the physical system which is not treated implicitly.}\)

\(\text{It will not give the correct time dependent behavior of the flame structure since we still use } \frac{\partial f}{\partial x} = 0 \text{ which need not be true. For a realistic time dependent formulation we would have to solve the one dimensional continuity equation [Ghi91].}\)
not calculated at every iteration step but only at selected iteration levels, say \( n = 0 \), during the calculation. Secondly, the solution is not corrected by the computed increment, but a damping parameter \( \lambda^n \leq 1.0 \) is introduced. The modified Newton methodology thus can be denoted formally by,

\[
\Delta \tilde{Y}^{n+1} = -\lambda^n (J^0)^{-1} r^n
\]

where the Jacobian is evaluated at iteration level 0 and the \( n + 1 \)-th adaption is damped with a factor \( \lambda^n \). The magnitude of the damping parameter is determined as the largest value smaller than one which reduces the norm of the residual vector defined by,

\[
||r^{n+1}||_2 = \max(|r_k^{n+1}|) \quad \forall \; k \in [1, (N+1) \cdot K^c].
\]

leading to the following criterion for \( \lambda^n \),

\[
\lambda^n \rightarrow ||\tilde{r}(\tilde{Y}^n + \Delta \tilde{Y}^{n+1})||_2 < ||\tilde{r}(\tilde{Y}^n)||_2 \quad (2.38)
\]

In practice a trial and error method is applied to determine this optimal \( \lambda^n \). Starting with a full Newton-step \( (\lambda^n = 1.0) \), the damping factor is multiplied by \( \frac{1}{2} \) until Eq. (2.38) is satisfied. The Jacobian is re-evaluated if either the damping factor at a certain iteration \( (n + 1) \) becomes too small \( (\lambda^n \leq \frac{1}{10}) \) or the number of successful iteration steps reaches a preset value (e.g. 20). Then the procedure starts again until the convergence criterion, \( ||r^{n+1}|| < \epsilon \), is reached. In Fig. (2.9) a pseudo flow diagram of the implementation of the modified Newton iteration procedure is shown.

However, if the modified Newton method fails to find any successful step, meaning for \( n = 0 \) no damping factor is found so that (2.38) is satisfied, the procedure switches to the pseudo time dependent formulation (2.36). As before the Jacobian matrix is kept fixed for a number of time levels to reduce the amount of work. A predictor-corrector procedure is applied to calculate the time step where the initial guess at every time level is given by the solution of the previous level. A first estimate \( (\Delta \tilde{Y}^{n+1}_0) \) for the time step is then obtained when \( \tilde{Y}^{n+1}_0 = \tilde{Y}^n \) is substituted in (2.36) and the predictor step

\[
\Delta \tilde{Y}^{n+1}_0 = - (J^0)^{-1} \tilde{r}_i(\tilde{Y}^{n+1}_0)
\]

is evaluated. Note that for the predictor step the time dependent residual \( \tilde{r}_i \) is exactly equal to the steady state residual\(^\text{16} \) (2.31) since \( \tilde{Y}^{n+1} - \tilde{Y}^n = 0.0 \). Subsequently the corrector procedure,

\[
\tilde{Y}^{n+1} = \tilde{Y}^{n+1}_{n-1} + \Delta \tilde{Y}^{n+1}_l
\]

\[
\Delta \tilde{Y}^{n+1}_l = -(J^0)^{-1} \tilde{r}_i(\tilde{Y}^{n+1}_l)
\]

is applied for \( l = 1 \) to a certain preset maximum number until a sufficiently converged time step is obtained. The time step convergence criterion currently applied is,

\[
||\tilde{r}_i(\tilde{Y}^{n+1}_l)||_2 < \epsilon ||\tilde{r}_i(\tilde{Y}^{n+1}_0)||_2 \quad (2.39)
\]

\(^\text{16} \)In fact the norm of the time residual vector for the predictor is monitored to check whether the time iteration approaches a steady-state.
with \( c < 0.005 \). Smaller values of \( c \) are possible but would only require more corrector steps. Since time iteration is used only when Newton's method fails, an accurate description of the time dependent behavior is not needed. If time iteration fails to find a converged time step for \( n > 0 \) or a preset maximum of time steps is taken, the Jacobian is reevaluated. For the case that the time iteration fails to find a converged time step for the solution used to start the time iteration, e.g. \( n = 0 \), the magnitude of the time step \( \Delta t \) is decreased\(^{17} \). Then the Jacobian is re-evaluated and the time iteration procedure is started again. In Fig. (2.10) the predictor-corrector procedure used in the time step iteration method is shown.

It is worth mentioning that although the Newton method and time step method have very similar flow diagrams there is a subtle difference. For a successful time step the Jacobian matrix equation \( J_i \Delta Y_i^{n+1} = -r_i \) is solved \( t \) times whereas in the Newton method the adaption vector \( \Delta Y_i^{n+1} \) is calculated only once per iteration step \( n \). From that point of view the modified Newton method is more economic.

In the algorithm, the time step method is used only whenever the Newton method fails to find any suitable damping factor obeying (2.38) for \( n = 0 \). For that case the algorithm switches to the time step procedure with a step size \( \Delta t \), usually taken in the order of \( 10^{-6} \). A new Jacobian is calculated a preset number of successful time step iterations are performed. Then the Newton method is tried again until the global convergence criterion is met and a solution to the flame problem is found. However, if no successful time step is obtained for a preset minimum size of \( \Delta t \) (e.g. \( \Delta t_{\text{min}} = 10^{-6} \)), the algorithm fails. For that case no strategy is found to obtain a solution for the burner stabilized flame problem with the fields supplied at initialization. Normally this means a better starting estimate has to be provided by the user. In Fig. (2.11) a diagram of the complete algorithm is given.

All results presented in the next section are obtained with this algorithm. In the first subsection some of these are compared with results obtained with the SANDIA premix-code to test the correctness of our implementation.

\(^{17}\) The smaller the time step, the better the initial guess for the predictor becomes.
2.3. **Numerical Method**

Newton iteration algorithm

*fig. 2.9: A flow diagram of the modified Newton iteration technique. Typical values for $l_{\text{max}} = 10$ and $n_{\text{max}} = 20.$*
fig. 2.10: A flow diagram of the predictor-corrector time iteration technique. Typical values for $l_{\text{max}}$ and $n_{\text{max}}$ are $l_{\text{max}} = 10$ and $n_{\text{max}} = 20$. 

**Time step algorithm**
fig. 2.11: Flow diagram of the algorithm. The Newton- and the time-iteration algorithm are shown in figures (2.9) and (2.10) respectively.
2.4 Results

We consider flames with mixtures varying between fuel-lean and stoichiometric conditions. The results will be used as reference results for comparison with results obtained after the introduction of various approximations later in this section and in Chapter 3. Some results will be compared with results of the SANDIA premixed code and experiments. In section 2.4.3 the effects of variations in the transport- and thermodynamical model will be studied. Finally, in section 2.4.4 rich flames are considered and computed results are compared with the results obtained with a more complex chemical model which contains the O2-chain. Before these studies are performed, in the following section the type of properties that will be presented are discussed.

2.4.1 Definition of the observable properties

Generally, the observable properties in premixed laminar flat flame studies are associated with two different flame-types. Most theoretical and numerical investigations are concerned with adiabatic (or freely-propagating) flames. The observables that can be identified for this flame-type are the so-called adiabatic burning velocity $S$, and the adiabatic flame temperature $T_{ad}$. The other flame-type is the non-adiabatic (or burner-stabilized) flame which has been treated in section 2.1. The properties identified with this flame are the flame temperature $T_f$ and the stand-off distance $\delta$.

For comparison of the detailed flame structure obtained with different models, concentration and temperature profiles are presented as well. These type of results are referred to as detailed flame properties in contrast to the global (or bulk) properties $S_{ls}, T_{adi}, T_f$, and $\delta$ which have an overall character.

The observables can be presented as a function of pressure, mass flow rate (iii) and initial mixture-composition and -temperature. We consider atmospheric combustion at room temperature. Therefore, only the mass flow rate (for burner-stabilized flames) and the initial mixture composition remain as free parameters. Since fuel-air mixtures are considered, the initial mixture composition can be specified with one parameter \(^\text{16}\), the equivalence ratio $\varphi$. In fact $\varphi$ is nothing more than the ratio of the initial fuel and oxidizer concentration, scaled with the ratio giving complete combustion theoretically. An equivalence ratio equal to one now indicates that there is precisely enough oxygen present to convert the methane completely into water and carbon dioxide, i.e. two moles $O_2$ per mole $CH_4 (CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O)$. Furthermore, it is common practice to refer to fuel lean mixtures as having equivalence ratios less than one thus leading to the following definition,

$$\varphi = \frac{2X_{CH_4}}{X_{O_2}} \quad (2.41)$$

where $X$ indicates the mole fraction of either species. Thus having specified the parameters we will treat the global properties in the next paragraphs.

\(^{16}\text{Assuming the concentration ratio of } N_2 \text{ and } O_2 \text{ in air as fixed.}\)
2.4. Results

Adiabatic Flames: $S_L$ and $T_{ad}$

Consider an infinitely long tube with a fresh combustible mixture (see Fig. (2.12)). Some time after the mixture is ignited at $x = -\infty$ the flame will propagate toward $x = +\infty$ with a constant velocity. The mass consumption rate $\dot{m}_L$ is then an eigenvalue of the set of equations governing this system. Alternatively, if a mass flow rate with precisely the value $-\dot{m}_L$ would be generated in the tube the flame would be at rest (see Fig. (2.12)). The adiabatic burning velocity $S_L$ is defined as the velocity of the gas flow at the cold unburnt side of the system. The adiabatic flame temperature $T_{ad}$ on the other hand is referred to as the temperature at the burnt side of the mixture.

Since the equations are formulated in a fixed frame of reference, the algorithm we use is not particularly suited for the calculation of these freely propagating flames. Formally one can proceed via two ways, either by reformulating the equations in a moving (Lagrangian) frame of reference (e.g. [Das83]) or by removing the translational degree of freedom and considering the mass flow rate as a variable\(^\text{19}\). The latter is used by Smooke et al. [Smo83]. He introduces a dummy variable for the mass flow rate $\dot{m}_L = \rho$ such that\(^\text{20}\)

$$\frac{\partial \dot{m}_L}{\partial x} = 0$$

and removes the translational degree of freedom by fixing the temperature at a certain value at one specific point in space. The advantage of this approach is that

---

\(^{19}\)For the burner-stabilized flame the mass flow rate is a given parameter.

\(^{20}\)In fact this is the stationary continuity equation.
the structure of the Jacobian is maintained and the same matrix solving technique can be used. Furthermore, the extra equation can be implemented easily and the discretization of the species- and enthalpy balance equations remains unchanged. In fact, for both flame-types the discretization introduced in section (2.3) can be used. If the Lagrangian formulation would have been used, we would have to develop two different discretization methods.

**Non-Adiabatic Flames: \( T'_f \) and \( \delta \)**

The second set of results will deal with burner-stabilized flames, our prime interest. The flame temperature \( T'_f \) is simply the temperature of the mixture at the end of the calculational domain, which is always lower than \( T_{ad} \) due to heat loss to the burner edge. The stand-off distance \( \delta \) is a measure\(^{21}\) for the distance between the flame-front and the burner, which we choose equal to the distance of the point where the maximum heat release occurs to the burner (see fig. (2.13)). A definition which would rely on the position of the maximum of some intermediate would possibly not be applicable to other (overall) chemical models which we plan to investigate in Chapter 3.

\(^{21}\) It is not possible to define one unique distance of the flame-front from the burner, since then a definition of the flame front would have to be given, which is quite arbitrary.

---

**Fig. 2.13:** The definition of the stand-off distance. The bell-shaped curve is the source term \( \sum h_i \rho \) (or heat release) in the enthalpy equation. The burner is located at \( x=0 \).
The detailed structure will be investigated by comparison of the concentration profiles for the species and temperature. Such a comparison for all parameters would be impractical, therefore a specific mass flow rate and equivalence ratio will be selected.

In section 2.4.2 the reference calculations, which will be used throughout this section and Chapter 3, are presented and discussed. The comparison with experiments and calculations with the SANDIA premixed flame code is performed there. In section 2.4.3 the effects of transport- and thermodynamical-models on the structure and properties of flames are studied. The mixture-averaged approach (section 1.2.3) and the often used \( Le_2 = 1 \) approximation are tested and compared with the reference results. Finally, in subsection 2.4.4 the treatment is extended to richer flames (with \( 1.0 < \varphi \leq 1.6 \)). The results of the skeletal mechanism are compared with a more complex chemical model including the \( C_2 \)-chain.

### 2.4.2 Lean to stoichiometric flames with simplified transport: The Benchmarks.

In this subsection the results obtained with the skeletal chemical model given in section 2.2 are presented. This model is believed to perform well under fuel-lean and stoichiometric conditions which implies that equivalence ratios \( \varphi \leq 1.0 \) are considered only. Furthermore, a simplified transport formulation of the problem is used yielding constant Lewis numbers (see Table (2.2)) and a model for the conductivity of the mixture [Smo91],

\[
\frac{\lambda}{c_p} = 2.58 \times 10^{-4} \left( \frac{T}{298.0} \right)^{0.7} \text{ (gcm}^{-1} \text{s}^{-1}),
\]

instead of the mixture averaged formulation (1.33, 1.34). The effects of these approximations are discussed in the next subsection.

<table>
<thead>
<tr>
<th>( CH_4 )</th>
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<th>( CH_2O )</th>
<th>( CH_2O )</th>
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<td>( CO_2 )</td>
<td>( CO )</td>
<td>( H_2 )</td>
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</tr>
<tr>
<td>1.27</td>
<td>1.39</td>
<td>1.10</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>( H )</td>
<td>( O_2 )</td>
<td>( O )</td>
<td>( OH )</td>
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</tr>
<tr>
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<td>( H_2O )</td>
<td>( H_2O_2 )</td>
<td>( N_2 )</td>
<td>( 1.00 )</td>
</tr>
<tr>
<td>1.10</td>
<td>0.83</td>
<td>1.12</td>
<td>1.00</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2.2:** Lewis numbers for calculations with the skeletal mechanism.
The values are obtained from a least-squares fit on the mixture averaged properties[Smo91].

This simple transport model will be used as default and is applied also in the reduced chemistry method presented in Chapter 3. Therefore, the results are discussed in somewhat more detail.
Adiabatic Properties

The adiabatic global properties $S_L$ (fig. (2.14)) and $T_{ad}$ (fig. (2.15)) are presented here.

![Diagram](image)

**Fig. 2.14: Adiabatic burning velocity vs equivalence ratio.** The cross-marks (+) and the open dots (o) are obtained from experiments [Maa92] and [Law93], respectively. The solid dots (*) are calculated values obtained by Smooke et al. [Smo91]. The solid line represents calculations with the Warnatz rate for the thermal decomposition (Eq. 2.42). The calculations with the original rate for the thermal decomposition of $C\text{H}_4$ are indicated with the dashed line.

Deviations between the dashed and the solid line in Fig. (2.14) show that the original reaction rate parameters for $C\text{H}_4(1\;M) \rightarrow C\text{H}_3 + H + (M)$ as given in Table (2.1), referred to as the Smooke rate from now on, yield high burning velocities. As argued by Smooke et al. [Smo91] better agreement with experimental values is obtained, if these rates are replaced by a corrected value according to Warnatz\textsuperscript{22} [War83],

$$k_{10}^{f} = 2.3 \times 10^{38} \ T^{-7} \ e^{-11430/T}$$
$$k_{20}^{f} = 1.9 \times 10^{36} \ T^{-7} \ e^{-9050/T}$$

(2.42)

as was argued already by Smooke et al.

We used a 65 point adapted mesh and total domain length equal to 10 cm in all adiabatic calculations. The algorithm we developed, predicts both adiabatic properties well. The burning velocity and the flame temperature are very close to the

\textsuperscript{22}Units are cm, s, calorie/(r.H thus calorie/mole).
results of Smooke et al. [Smo91], indicated with the solid dots in Figs. (2.14, 2.15). At higher equivalence ratios the burning velocity deviates more from Smooke's results, which might be attributed to a difference in the oxygen concentration fraction in air (here taken equal to 0.21). Effects of this difference will not show up at low equivalence ratios since then an excess of $O_2$ is present. It should be noted that the adiabatic temperature is completely determined by the equilibrium composition. This composition is a function of the chemical scheme and initial composition only and could in fact be calculated independently using a 0D time-dependent code\textsuperscript{23.}

It should be noted that the computations with the skeletal mechanism and the original decomposition rates of Smooke are very close to the measured data of Law. This is due to the fact that the skeletal mechanism is fitted to reproduce this data set. Since the measurements of van Maaren show a different dependency on $\varphi$, the skeletal mechanism does not predict these experiments.

Non-Adiabatic Properties

The non-adiabatic global properties are presented in Figs. (2.16) and (2.17). As before the continuous lines indicate the results with the revised rate for the thermal decomposition of $C_3H_8$. Furthermore, experimental data obtained from experiments

\textsuperscript{23}A homogeneous reactive system.
in our group and from W.E. Kaskan ([Kas67]) are included in Fig. (2.17) as well. The specific representation of the reciprocal of the flame temperature vs. the logarithm of the mass flow rate will be referred to as a Kaskan plot throughout this thesis.

The curved shape of the stand-off distance is typical for all premixed hydrocarbon-air flames. It shows that the flame is in fact stabilizing closer to the burner when the mass flow rate is increased. Still, the heat loss to the burner must decrease since the flame temperature increases as well, as can be seen in the Kaskan-plot. This behavior can only occur if the curvature of temperature profile increases yielding smaller conductive heat loss to the burner, as shown in Fig. (2.18). However, at a certain point the heat loss to the burner becomes zero and the flame approaches the adiabatic state. For mass flow rates larger than the adiabatic mass-burning rate the flame will move away from the burner with a specific fixed velocity. In Fig. (2.19) we plotted the profiles of temperature and the species methane and methyl at three equidistantly spaced time levels. In this case it indeed shows that the distance traveled is constant, thus implying a fixed propagation velocity of the flame-structure also present in the numerical burner-stabilized flame method.

To study the detailed structure we will choose the following values for the initial parameters,

\[
\begin{align*}
\dot{m}_0 &= 0.0250 \text{ g cm}^{-2} \text{s}^{-1} \\
\varphi &= 1.0 \text{.} 
\end{align*}
\]  

\[24\text{Originally, Kaskan plotted } 1/T^2 \text{ on the x-axis and the } 4\pi m \text{ on the y-axis. However, the temperature is the dependent variable and the mass flow rate the free parameter. Therefore we choose to present it the other way around.}\]
2.4. Results

fig. 2.17: Flame temperature vs mass flow rate for $\varphi = 0.8$ and $\varphi = 1.0$. Solid line: Warrant rate for decomposition of C114 ($t_{10}$). Open- (o) and solid dots (•) are calculations with the original decomposition rate. The dotted line --- are interpolated values from experiments performed by Kaskan et al. ([Kas67]). Crosses (x) and (+) are experimental data obtained by van Maaren et al. [Maa92] for $\varphi = 1.0$ with two different experimental techniques.

All figures on the detailed structure are obtained from a burner-stabilized calculation with these values unless mentioned otherwise. We will present the species in three groups. The first group is referred to as the major species, with typical peak mole fractions exceeding 0.01: $CCH_4$, $O_2$, $N_2$, $H_2O$, $H_2$, $CO$ and $CO_2$. It should be noted that this is not a sharp definition, since it is not true for all species under all conditions. The second group will be referred to as the radical pool, which, according to the definitions in section (2.2), can be identified with species $H$, $O$, $O$. The hydroperoxyl, $H_2O$, and hydroperoxide, $H_2O_2$, are included in this group as well. The final group of species that will be plotted are the so-called intermediates of the $C1$-chain, being $CH_3$, $CH_2O$, $CH_3O$ and $HCO$. Again, all calculations of the burner-stabilized flames are performed on a 10 cm, 65 point adapted mesh. However, due to the extreme small width of the fuel consumption layer, only a small part of the total computational domain is presented in the figures.

In Fig. (2.20) the profiles of the major species are given, in the first five millimeters downstream of the burner at $x = 0.0$ cm.

Already, it can be seen that the conversion from $CO$ to $CO_2$ is much slower than the consumption of methane: the concentration of the carbon-monoxide decreases much slower than the initial decrease of the alkane $C1H_4$.

The intermediates are presented in Fig. (2.21).
Chapter 2. Complex Chemistry

fig. 2.18: The development of the temperature profile for \( \varphi = 1 \). Only the first 2 mm of the domain are plotted. The arrow indicates increasing mass flow rates.

Since these occur only in a small region where the fuel is consumed, the plot domain is taken as \([0.0, 0.02]\) (cm) instead. The sequence of the positions of the maxima is exactly as might be expected from the schematical picture of the \( C_1 \)-chain (see Fig. (2.4)) and occur in the immediate vicinity of the position where the concentration \( CH_4 \) becomes almost zero and \( CO \) reaches its peak value.

The profiles of the radical pool are presented in Fig. (2.22). The radicals, \( H \), \( OH \) and \( O \) are of extreme importance for the attack on the fuel as was mentioned in section 2.2.

In the conversion of the hydrocarbon they are rapidly consumed as indicated by their steep gradient at the reaction layer. The concentrations of \( H \), \( OH \) and \( O \) only increase when the intermediates are consumed and converted into \( CO \). Since the hydroxyl molecule (\( OH \)) plays an important role in the \( CO \rightarrow CO_2 \) conversion through reaction^{25} \( r_9 \), the carbon-dioxide starts to form when all \( CH_4 \), \( O_2 \) molecules are broken up. The gradual decrease of the radicals \( H \), \( OH \) and \( O \) after \( x = 0.1 \) cm indicates that recombination of the radicals and the oxidation of the carbon-monoxide proceeds much slower than the hydrocarbon break up from \( CH_4 \) to \( CO \). In fact these slower processes force the computational domain to be extended so far beyond the fuel-consumption layer, to a point where the zero-gradient boundary condition at the outlet has a negligible effect on the structure of the flame.

The presented global properties \( S_L \), \( y'_{ad} \) for the adiabatic flame and \( \delta \) and \( T_f' \) for the burner-stabilized flame together with detailed structure of the specified burner-

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^{25} The only \( CO \rightarrow CO_2 \) reaction in our model.
2.4. Results

fig. 2.19: Flame with numerical blow-off. Mass flow rate $\dot{m} = 0.0340$ for $\varphi = 0.8$ (Adiabatic mass burning rate $\dot{m}_a = 0.0269$).

fig. 2.20: A reference set of the major species, $\text{CH}_4$, $\text{O}_2$, $\text{H}_2\text{O}$, $\text{H}_2$, $\text{CO}$ and (')$\text{O}_2$. On the left a logarithmic plot is shown and on the right a linear plot where the mole fraction of $\text{H}_2$ is multiplied by 10.
fig. 2.21: A reference set of the intermediate species, CH₃, CH₂O, CH₅O and HCO. On the left a logarithmic plot is shown and on the right a linear plot where the mole fraction of CH₂O and HCO are multiplied by 50.

fig. 2.22: A reference set of the radical pool, H, OH, O, HO₂ and H₂O₂. On the left a logarithmic plot is shown and on the right a linear plot where the mole fraction of HO₂ and H₂O₂ are multiplied with 50.
stabilized flame with $\dot{m} = 0.0250$ and $\varphi = 1.0$ will be used for comparison and for studies on the performance of different approximations. In the next section we will investigate the effects on burner-stabilized flames of the changes in transport and thermodynamic models.

### 2.4.3 Effects of changes in the transport and thermodynamic model on burner-stabilized flames.

In the previous section we used constant Lewis numbers and a simplified relation for the thermal diffusivity to evaluate the diffusion coefficients and the conductivity of the mixture. The difference between this approximation and the mixture averaged approach as sketched in section 1.2.3 will be investigated here. Furthermore, calculations are performed with a $Le = 1$ assumption, which is used in many theoretical treatments.

#### Mixture averaged transport model.

In Fig. (2.23) the stand-off distance and the flame temperature are presented. To rule out effects of differences in discretization, the adapted mesh, obtained from the reference calculations, is used for the mixture averaged transport model as well. Fixing of the grid-position is viable, because the expected changes in profiles are very small. The transport models give almost identical results and differences become only visible at low mass flow rates. At high mass flow rates the global properties overlap. For this reason results for adiabatic flames are not presented.

![Fig. 2.23: Stand-off distance and Kaskan plot of the skeletal mechanism with constant Lewis numbers (continuous line) compared to mixture averaged transport model (open dots $\varphi = 0.8$, solid dots $\varphi = 1.0$).](image)

To compare the detailed structure we plotted the profiles of four of the major species in Fig. (2.24) where the complex transport calculations are indicated with marked lines. The radical pool shows similar results as can be seen in Fig. (2.25) where we also used markers to indicate the complex transport calculations.
fig. 2.24: The effects of complex transport modelling on the profiles of CH₄, O₂, CO and CO₂. The markers indicate the calculations with the mixture averaged transport properties.

fig. 2.25: The effects of complex transport modelling on the profiles of H, OH, O and HO₂ (mole fraction of HO₂ is multiplied by a factor 50). The complex transport calculation is indicated with markers.
Again no significant differences can be observed. The largest deviation can be found for the methyl radical $CH_3$ (Fig. (2.26)), with an approximately 2% - 3% larger peak value.

![Graph showing mole fraction vs distance for $CH_3$ and other species](image)

fig. 2.26: Effect of complex transport on intermediate species, $CH_3$, $CH_2O$, $CH_2O$ and $HCO$ (mole fractions of $CH_3O$ and $HCO$ are multiplied by a factor 50).

The resemblance between both transport models is remarkable, which agrees with the conclusions of Smooke et al. on adiabatic flames [Sm91]. Only at low mass flow rates the Kaskan lines seem to deviate more from the ones for the simple transport case\(^\text{26}\). This can be expected for these calculations as the relative importance of the cooling effect of the burner (through $\lambda$) becomes more important for small flow velocities.

For the solution of these complex transport equations, always a starting estimate from the simple transport calculation is used. Mostly it took only one Jacobian evaluation to compute the new flame. In table (2.3) typical evaluation times for the Jacobian-matrix\(^\text{27}\) are given for both transport models. Values for a larger chemical model which involves 24 species are included as well (see section 2.4.4). Obviously, it is always preferable to start a calculation with a simplified transport model until convergence is reached and then perform the complex transport calculation as a kind of post-processing. Furthermore, the observed dependency of the CPU-times

\(^{26}\)E.g., for $\varphi = 1.0$ the absolute temperature difference between simple and complex transport model is for the lowest mass flow rates of the order of 10$K$ and at the highest mass flow rate of the order of 1$K$. The overall tendency is that the complex transport model yields higher flame temperatures, which indicates that the simple transport model over-estimates the cooling of the burner.

\(^{27}\)The Jacobian evaluation takes about 90% of the total calculation time.
### Table 2.3

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The table above compares the CPU times in seconds of one evaluation of the Jacobian for the simple and complex transport models. Superscript 16 is a 16 species model (skeletal) and 24 a 24 species (C_1 - C_7) model. In all tests a 65 point adapted grid is used to ensure that differences in computing time are caused by the transport model only.

On the number of species suggest that this strategy will become more efficient if the chemical model becomes larger\textsuperscript{24}.

\textsuperscript{24} This would therefore be efficient in studies on extremely large reaction sets, e.g. for heavy-fuel combustion.
2.4. Results

$Le_i = 1$ approximation.

In this part all the species-specific Lewis numbers of table (2.2) are replaced by $Le_i = 1$. The effects of this approximation are very pronounced. In both Figs. (2.27) and (2.28) the results of these calculations are indicated with open dots ($\circ$). The adiabatic burning velocity shows a different trend, giving lower values for stoichiometric flames and higher values at lean conditions.

The non-adiabatic calculations are consistent with these results. At stoichiometric conditions the stand-off distance in Fig. (2.28) approaches blow-off at lower mass flow rates than the reference calculations indicating lower burning velocities. Equivalently, the Kaskan line reaches the adiabatic flame temperature for smaller $\varphi$. For $\varphi = 0.8$ the flame temperatures for burner-stabilized flames merge at high mass flow rates whereas the stand-off distance at high mass flow rates is shifted with respect to the reference calculations. This trend is consistent with the fact that at $\varphi = 0.8$ the adiabatic burning velocity $S_L$ is equal to the one found in the reference calculation (Fig. (2.28)).

![Graph](image)

fig. 2.27: Adiabatic burning velocity (left) and flame temperature (right). The continuous lines indicate the reference calculations. Open symbols ($\circ$) indicate the $Le_i = 1.0$ approximation and solid symbols ($\bullet$) calculations with the same approximation except for the H-radical which has been set back at its original value ($Le_H = 0.18$).

The effect of the $Le_i = 1.0$ approximation on the detailed structure is presented in Figs. (2.29) and (2.30). Because we expect the largest effects to occur in the $H_2$ and $H$ profiles, $H_2$ is presented in Fig. (2.29) instead of $CO$ which is given in the previous sections. Indeed, the curvature and peak values of the $H$ and $H_2$ differ considerably from the reference calculation.

Since the hydrogen radical plays an important role in the initial $CH_4$-attack and has the largest deviation from $Le_i = 1.0$ we expect that this effect of the $Le_i = 1.0$-approximation can be attributed mainly to the decreased ability of the $H$ radical to diffuse upstream. This presumption is tested by repeating the same calculations with the Lewis number of atomic hydrogen set back at its original value, $Le_H = 0.18$ (see table (2.2)).
fig. 2.28: Stand-off distance (left) and flame temperature (right). Symbols according to Fig. (2.27).

fig. 2.29: Calculations with \( L_{o_1} = 1 \) (symbols). Profiles of \( CH_4, O_2, H_2 \) and \( CO_2 \) are shown. The lines are the reference results.
2.4. Results

![Figure 2.30: Effects of $Le_i = 1.0$ on $H$, $OH$, $O$ and $HO_2$. The mole fraction of $HO_2$ is multiplied with 50.](image)

Now the global properties show excellent agreement for lean flames as can be seen in the Figs. (2.27) and (2.28) (indicated with ●). For stoichiometric conditions the agreement between the results decreases, but is still reasonable as is supported by the detailed structure in Figs. (2.31) and (2.32). Only the $H_2$-mole fraction exhibits the same behavior as in the $Le_i = 1.0$ calculation, which is clearly a transport effect (see Fig. (2.31)). The diffusivity of the hydrogen molecule is decreased by a factor of 3, approximately, while for the other species a factor of 1.3 or less is introduced by the $Le_i = 1.0$ assumption. However, as shown by the last calculation, the significant difference in the $H_2$ profile has no large effect on the burning velocity ($S_L$), flame temperature ($T_f$) and stand-off distance ($\delta$). This is in contrast with the large effects that the decreased diffusivity of the $H$-radical has on these global properties.
fig. 2.31: All Lewis numbers are taken equal to 1.0 except \( l.e_{HH} = 0.18 \) (symbols). The profiles of \( C_3H_4, O_2, H_2 \) and \( CO_2 \) are given.

fig. 2.32: \( l.e_1 = 1.0 \) calculation with \( l.e_{HH} = .18 \). The radical pool \( H, OH, O \) and \( H O_2 \). The mole fraction of \( H O_2 \) is multiplied with 50.
2.4.4 Chemical effects: comparison with a $C_1 - C_2$ chemical scheme.

In this section the effect of a different, more complex chemical model on the laminar premixed methane-air flames, will be studied. All previous calculations are performed on lean and stoichiometric flames for which the skeletal mechanism is assumed to be a suitable chemical model. To test this assumption, simulations are performed with a $C_1 - C_2$-mechanism [War83]. This scheme consists of 62 reactions among 24 species, including all species in the $C_1$ chain$^{29}$ and $C_2$-chain presented earlier (see Fig. (2.4)). The reactions and their rate parameters are presented in Appendix (A.3).

In this section the calculations are extended to (fuel-)rich conditions $\varphi > 1.0$. To determine the conditions for which the skeletal mechanism is valid, its results are compared with the results of the 24 species model. In order to rule out effects of differences in the transport model, the Lewis numbers are taken constant in all calculations. For the species in the $C_2$-chain these were evaluated by performing some complex transport calculations and applying a least-square fit to the non-constant values found. These are tabulated in table (2.4).

<table>
<thead>
<tr>
<th>Species</th>
<th>Lewis Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH</td>
<td>0.64</td>
</tr>
<tr>
<td>$C_2H_2$</td>
<td>1.28</td>
</tr>
<tr>
<td>$C_2H_3$</td>
<td>1.41</td>
</tr>
<tr>
<td>$C_2H_4$</td>
<td>0.95</td>
</tr>
<tr>
<td>$C_2H_5$</td>
<td>1.29</td>
</tr>
<tr>
<td>$C_2H_6$</td>
<td>1.42</td>
</tr>
<tr>
<td>$HCO$</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Table 2.4: Lewis numbers for all species in the $C_2$-chain.

Following the same presentation as in the previous sections, first the global phenomena are given. The adiabatic properties are determined for a range of equivalence ratios $0.5 \leq \varphi \leq 1.5$ and presented in Fig. (2.33). For the burner-stabilized flames we selected equivalence ratios on the fuel rich side and presented the stand-off distance and Kaskan-lines for $\varphi = 1.0, 1.2$ and 1.4 in Fig. (2.34). The adiabatic flame temperature compares extremely well for both mechanisms.

Only for very rich conditions the skeletal mechanism predicts slightly higher values, indicating that the equilibrium composition of the major species in this mechanism is becoming significantly different. The other global properties agree well for lean and stoichiometric conditions. The burning velocity of the $C_1 - C_2$ mechanism is even in excellent agreement with the ones calculated with the reference skeletal mechanism (see Fig. (2.33)). For rich conditions the differences increase. The burning velocity is systematically underestimated by the skeletal mechanism which will therefore predict hotter burner-stabilized flames which is observed in the Kaskan-plot. For $\varphi = 1.4$ these differences become even more pronounced, and the flame temperature differences range from 80 K for high mass flow rates to 150 K for low flow rates.

As in the previous section the detailed structure of the earlier introduced stoichiometric flame is presented. For most species the agreement is reasonable (Figs. (2.35) and (2.36)). However, the intermediates of the $C_1$-chain given in Fig. (2.37) and the

$^{29}$Only $C_1H_3O$ is not present in this model.
fig. 2.33: Adiabatic properties for lean and rich (0.5 ≤ φ ≤ 1.5) conditions. The continuous line indicates the reference calculations with the skeletal mechanism. The solid dots (●) indicate the C1 - C2 results.

fig. 2.34: Comparison of stand-off distance and Kaskan-plot with a C1-C2 mechanism. Equivalence ratios φ = 1.0, 1.2, 1.4 are given. The continuous lines indicate the reference calculations with the skeletal mechanism. The C1 - C2 calculations are plotted with marked lines.
2.4. Results

fig. 2.35: Comparison of major species profiles $CH_4$, $O_2$, $CO$ and $CO_2$ with $C_1 - C_2$ mechanism (markers) for $\varphi = 1.0$ and $n = 0.0250$. Results of reference simulation with the skeletal mechanism are given by the solid lines.

fig. 2.36: Comparison of radical profiles $H$, $OH$, $O$ and $HO_2$ ($HO_2$ mole fraction is multiplied with a factor 20). Markers indicate the $C_1 - C_2$ model.
fig. 2.37: Comparison of C'1-intermediates for skeletal and C'1-C2 mechanism, only CH3O is not present (HCO mole fraction is multiplied with a factor 50).

HO2 mole fraction in Fig. (2.36), show significant differences. Peak values deviate by a factor of two to three and are systematically over-estimated by the C'1-scheme.

The relative importance of the C2-chain is investigated by calculating the fraction $f_2$ of the consumption of CH3 that proceeds via the C2-chain (see fig. (2.38)). The reactions that can be identified with the fraction $f_2$ are given by:

$$
\begin{align*}
\text{CH}_3 + \text{CH}_3 & \rightarrow \text{C}_2\text{H}_6 \\
\text{C}_2\text{H}_4 + \text{O} & \rightarrow \text{CH}_3 + \text{CO} + \text{H} \\
\text{C}_2\text{H}_3 + \text{H} & \rightarrow \text{CH}_3 + \text{CH}_3
\end{align*}
$$

The value for fraction $f_2$ is defined by the integral,

$$
f_2 = \int_0^t \left(-2k_{37}(x') + k_{34}(x') + 2k_{37}(x')\right)dx'. \tag{2.44}
$$

where $k$ indicates the net reaction rate of reaction $r$ according to the numbering given in Appendix (A.3). For $f_1$ a similar expression can be derived which comprises all consumption reactions of CH3 down the C1-chain.

$$
\begin{align*}
\text{CH}_3 + \text{H} & \rightarrow \text{CH}_2 + \text{H}_2 \\
\text{CH}_3 + \text{O} & \rightarrow \text{CH}_2\text{O} + \text{H} \\
\text{CH}_3 + \text{O}_2 & \rightarrow \text{CH}_2\text{O} + \text{OH}
\end{align*}
$$

\[r\]
It should be noted that all reactions describing the methane to methyl conversion are not to be considered (reactions \( r_{34}, r_{35}, r_{39}, r_{40} \) and \( r_{41} \) in (Appendix A.3)). The reaction fraction into the \( C_2 \)-chain will now be given by the relation

\[
f_{C_2} = \frac{f_2}{f_1 + f_2}.
\]

For the burner-stabilized flames \( f_{C_2} \) is determined for four different equivalence ratios, being \( \varphi = 1.0, 1.2, 1.4 \) and 1.5 as a function of the mass flow rate (see Fig. (2.39)). To investigate the contribution of each reaction in Eq. (2.44), the individual contributions are presented as well.

Overall, the importance of the \( C_2 \)-chain increases with decreasing mass flow rates. This implies that in general the \( C_1 \)-chain becomes more important with increasing temperature. As a result of this, conclusions on the importance of the \( C_2 \)-chain obtained by considering adiabatic calculations, i.e. burning velocity \( S_L \) and adiabatic temperature \( T_{ad} \) only, might not be true for burner-stabilized flame modelling. Even for a stoichiometric flame the fraction is of the order 0.4 for low mass flow rates to 0.2 for high mass flow rates. For \( \varphi = 1.2 \) the net fraction decreases from approximately 0.6 to 0.3. For even richer conditions (\( \varphi = 1.4, 1.5 \)) it is obvious that the \( C_2 \)-chain cannot be neglected since at least 60\% of the \( CH_3 \) consumption is accounted for by the \( C_2 \)-reactions. It is interesting to observe that the reaction,

\[
C_2H_5 + H \rightleftharpoons C_2H_3 + CH_3
\]

changes from \( CH_3 \) forming to \( CH_3 \) consuming when the initial composition changes from stoichiometric to rich (solid symbols in top figure of (2.39)).

Some aspects of the detailed structure are investigated for high equivalence ratios as well. In Fig. (2.40) a subset of the major species is plotted for \( \varphi = 1.2 \) and \( \varphi = 1.4 \). As might be expected from the previous observations the deviations between both...
Chapter 2. Complex Chemistry

\[ r_{54} = C_2H_4 + O \rightarrow CH_3 + CO + H \]
\[ r_{57} = C_2H_6 + H \leftrightarrow CH_3 + CH_3 \]

**Figure 2.39:** The top figure gives the contribution to \( f_{C_2} \) of the less important reactions \( r_{54} \) (open symbols) and \( r_{57} \) (solid symbols). In the lower figure the total reaction fraction \( f_{C_2} \) (solid symbols) and the major contributor \( r_{37} \) (open symbols) are given for several equivalence ratios.
2.4. Results

![Profiles of the major species for burner-stabilized flames.](image)

Fig. 2.40: Profiles of the major species for burner-stabilized flames with \( \phi = 1.2 \) and 1.4. The mass flow rates are equal to \( n = 0.0250 \text{ gcm}^{-2}\text{s}^{-1} \) and \( \dot{m} = 0.0130 \text{ gcm}^{-2}\text{s}^{-1} \) respectively. The solid lines indicate the results for the \( C_1 \) chain and the marked lines the results for the \( C_1-C_2 \) chain. In both figures the mole fraction of the carbon-oxides are multiplied by a factor of 2.

The prediction of the carbon-oxides show the same trend, though the skeletal mechanism over-estimates the \( CO-CO_2 \) conversion. For \( \phi = 1.2 \) the qualitative behavior of the detailed structure is similar. The over-estimation of the \( CO \) - \( CO_2 \) conversion of the skeletal mechanism is the cause of the higher temperatures found with the \( C_1 \)-chain at the right tail of the adiabatic temperature in Fig. (2.33).

---

30 Maximum temperature deviation is 30 K for \( \dot{m} = 0.050 \text{gcm}^{-2}\text{s}^{-1} \) and 6 K for \( \dot{m} = 0.043 \text{gcm}^{-2}\text{s}^{-1} \), burning velocity difference \( St \) approximately 1cm/s.
Chapter 3

One-Dimensional Flames: systematically reduced chemical models

3.1 Introduction

In the previous chapter the modelling of laminar premixed flat flames is discussed employing detailed chemical models. The chemical model used has in principle the virtue to be independent of the type of flame which is studied as long as the same fuel is used. Formally, the same chemical model can be used for any type of reacting flow, e.g. diffusion and premixed flames either in pseudo one-dimensional configurations (flat flame, counter-flowing jets) or multi-dimensional flows. However, carrying out calculations is hampered by an important drawback. Due to the stiffness present in the governing equations, implicit techniques have to be used. This leads to large sparse matrix equations to be solved, with the leading dimension proportional to $N \times K$, where $N$ is the number of species and $K$ the number of gridpoints. It can readily be seen that for modelling of multi-dimensional reacting flows the memory requirements are large. The Newton-type iteration which is applied invokes a Jacobian matrix which, mostly, is evaluated numerically. This is a very CPU-intensive process and is in fact the most important drawback of the detailed chemical models. Only due to the fast increase in computing power, the simulation of multi-dimensional reactive flows with detailed chemical models comes within our grasp. However, for the development of engineering tools for designing realistic (domestic) burner concepts as well as for computations of large scale reacting flow configurations, the application of detailed models is still (and will remain in the near future) impractical. Reduction of the problem size and removing the stiffness in the equations is the best way to proceed.

In the early years of computational combustion when even complex calculations on the simplest geometries were impossible due to low computer capability, so-called global reaction models were used frequently. These models replace the

\textsuperscript{1}On a contemporary supercomputer the computing time is of the order of two hours for a co-flowing axis-symmetrical laminar diffusion flame (computational domain 2.5cm x 30cm, 15 species reaction model)\cite{Smo92}.
complex chain reactions with an overall reaction of the type,

\[ \text{Fuel} + \text{Oxygen} \rightarrow \text{Products}. \]

Generally the parameters \( A, b, E_a' \) in the Arrhenius-like reaction rate relation

\[ \dot{\rho} f_0 = -A \left( \frac{P}{\rho_0} \right)^a [O_2]^{b} |v|^{1/2} \exp \left( -\frac{E_a}{RT} \right) \]

were fitted to reproduce data, like the adiabatic burning velocity \((S_d)\) and temperature \(T_{ad}\) and occasionally the non-adiabatic flame temperature\(^2\) obtained by either experiments, e.g. [Lan92, Maa94], or detailed chemistry computations, e.g. [Wes81]. The main advantage of this simplified chemical model is the reduced stiffness of the flow equations. Explicit techniques can now be used which do not require much storage [Lan92]. The (expensive) evaluation of the Jacobian is not necessary and techniques similar to the ones used in non-reactive flow computations may be used. For this reason most numerical studies on multi-dimensional reacting flows have been performed employing a global reaction model e.g. [Lar92, Lan92]. However, these global reaction models do have important drawbacks. The fitting parameters in the above Arrhenius reaction-rate relation are specific for the composition of the fuel for which they are obtained and have to be reevaluated for every change in the composition. It cannot even be guaranteed that the same parameters can be applied safely for different types of flames (e.g. diffusion versus premixed, flat-flames versus counterflow). The parameters have to be adapted to the configuration and the type of flame considered. Another fundamental problem with these global models is that for a specific burner concept information can not be obtained of species like \( NO_x \) (and to a lesser extent \( CO_x \)), which is very unfortunate since exhaust limitations due to governmental regulations become more and more important. For this reason, in recent years new approaches have been developed to reduce the computational problem size (and stiffness) of the reactive flow equations, but to preserve the detailed information of the complex chemical model. Recent proposed techniques like Computational Singular Perturbation [Gou92, Lam88] and mathematically reduction of complex chemical models look very promising [Maa92, Egg94]. However, in the present thesis we will report calculations with another approach, introduced some years ago by Peters et al. [Pet91], referred to as 'systematically reduced chemical models'. It is used in many applications nowadays, see e.g. [Smo91, Pet93, Pac86, Boe93].

The strategy of this approach is to use the detailed chemical model as basis and to apply steady-state and partial equilibrium assumptions to eliminate a number of the species in the model and to replace the corresponding (partial, ordinary) differential equations by algebraic relations. This leads to a reduction of the dimension of the matrix equations, which is desirable from a computational point of view. In general a systematically reduced chemical scheme is not very specific for the type of flame considered, e.g. for the one-dimensional premixed and diffusion flames the same model can be used [Smo91, Pet93]. However, as for the global mechanism, each reduced scheme is to a certain extent deduced for the mixture which is to be considered and the properties which have to be predicted accurately.

\(^2\) Burner-stabilized flames.
For example, although the same basic detailed chemical model can be used for the combustion of most simple hydrocarbons\(^3\), they all yield different systematically reduced schemes\(\text{[Pet93]}\).

In this chapter we will compare the results of systematically reduced chemical models with results of detailed chemistry computations. The comparison will deal with the global properties introduced earlier (i.e. \(S_L, T_{ad}, T'\)) and where possible with detailed properties. Because deduction of a reduced chemical model is not straightforward, we will first discuss the general strategy in section 3.2, followed by the deduction of a systematically reduced chemical model for lean methane-air combustion. A new approach will be introduced which uses a specific kind of sensitivity analysis. A major part of this section is published in [Som94]. In section 3.3 attention is paid to the numerical treatment of the resulting set of equations. The results of the various chemical models are presented and discussed in section 3.4.

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\(^3\)E.g. one basic detailed kinetic scheme for combustion of several small hydrocarbon molecules is presented, but all fuels yield different reduced models.
3.2 Systematically Reduced Chemical mechanism for lean Methane-Air Flames

Systematically reduced chemical mechanisms are, contrary to earlier mentioned global mechanisms, obtained by a careful analysis of a detailed reaction model describing oxidation of a specific fuel. Effectively, the objective of such an analysis will be to replace the (partial) differential equations for some species by algebraic expressions which, in principle, reduces the computational effort. The reduction strategy is based on two distinctive tasks. First, there is the actual reduction of the number of differential equations which have to be solved, i.e. the identification of the species that to adequate accuracy can be assumed to be in steady-state. Secondly, there is the so-called truncation of the expressions for the species which are to be considered in steady-state. Both the reduction of the problem size as well as the truncation of the resulting expressions will be treated in this section. Before these steps are treated in detail, first some general concepts will be introduced which can be applied to any detailed reaction mechanism. These principles will be applied to the skeletal mechanism used for lean methane-air flames, in the previous chapter.

3.2.1 General Principles in Systematic Reduction

Two important features in the systematical reduction of the detailed chemical models are the so-called steady-state approximation and the partial-equilibrium approximation. The most important assumption is the steady-state approximation. It simply states that for a species the chemical source term is zero, i.e. for the \( i \)-th species

\[
\dot{\rho}_i = M_i \sum_{j=1}^{M} u_{ij} q_j = 0, \tag{3.1}
\]

with \( M_i \) the molar mass. Eq. (3.1) gives an algebraic equation for each species considered to be in steady-state (involving many reactions in general). Obviously, the nomenclature stems from the description of homogeneous reacting systems, where this equation implies that the time-derivative of the concentration is zero. Physically in a flame, the assumption implies that the time scales of the reactions consuming and producing a 'steady-state' species are much shorter than the time scales associated with diffusion and convection. Generally, if no further simplifications are made, the assumption (3.1) for each of the species taken in steady-state form a set of non-linear coupled algebraic equations. To reduce the complexity of this set and even more to obtain an explicit expression, often the partial-equilibrium assumption is applied. In contrast to the steady-state assumption this is an approximation applied to a specific reaction. If applied to a certain reaction \( j \) symbolically denoted by \( A_1 + A_2 \Leftrightarrow B_1 + B_2 \) the partial-equilibrium assumption yields,

\[
\eta_j = 0 \tag{3.2}
\]

\(^4\)By explicit is meant; the equation that determines a variable is expressed in known quantities only, e.g. \( X_1 = f(X_c) \) with all \( X_c \) known at the point where \( X_1 \) is evaluated.
and the species involved in such a reaction relate to each other through,

\[
\frac{[B_1][B_2]}{[A_1][A_2]} = K = \frac{k_f}{k_r}.
\]

(3.3)

It is worth mentioning that in the special case that the reaction rate of a steady-state species involves only one reaction, it effectively is a partial equilibrium approximation for the specific reaction.

The next subsection discusses which species can be considered in a steady-state. The first part will deal with the arguments leading to the decisions as they are applied by most authors. In the second part a new method is presented, which uses a sensitivity analysis on which the decisions will be based. The partial-equilibrium assumption will be used in the last subsection 3.2.4 where the derivation of an explicit expression from the set of algebraic equations is derived.

3.2.2 Applying the Steady-State Assumption

The success of reducing a detailed chemical model is strongly related to the ability of applying the steady-state assumptions to the proper set of species. Classically, this is done by simply comparing the contributions of the different parts (convection-, diffusion- and reaction- part) in the balance equation for a specific species and a detailed investigation of the chemical source term. In order to make a direct comparison between the magnitude of the different components in these balance equations and the reaction rates of the individual reactions \( q_j \) in the chemical source terms, the balance equations are often expressed in terms of the 'specific molenumber'\(^6\) of species \( i \),

\[
\Gamma_i = Y_i/M_i = X_i/\bar{M}.
\]

The reason for this is best illustrated if we consider the conservation equation, e.g. Eq. (1.26). For convenience we define the operator \( L \) as

\[
L\{Y_i\} = \rho \bar{u} \cdot \bar{\nabla} Y_i - \bar{\nabla} \cdot (\rho D_i Y_i \bar{v} Y_i).
\]

(3.4)

Whenever the flame is stationary, the time derivative vanishes and the conservation equation (1.26) reduces to,

\[
L\{Y_i\} = M_i \sum_{j=1}^{M} \nu_{ij} \dot{q}_j
\]

(3.5)

where the expression for \( \dot{\rho} \) is written explicitly in terms of the elementary reactions. It is clear that the equation for \( \Gamma_i \) yields,

\[
L\{\Gamma_i\} = \sum_{j=1}^{M} \nu_{ij} \dot{q}_j
\]

(3.6)

where \( M_i \) cancels in the right-hand side. This cancelation is the reason for the introduction of \( \Gamma_i \). It is now possible to compare the magnitude of diffusive and convective fluxes expressed in \( \Gamma_i \) with the reaction rates \( q_j \) directly.

\(^6\)Some authors refer to it as the 'specific abundance' of a species \( i \).
The idea behind the steady-state assumption is best illustrated by comparing the magnitude of the different contributions to the balance equation. These terms are evaluated from results of a complete reaction model (using methods as described in Chapter 2) specifically for two species e.g. \( \text{H}_2\text{O} \) (Fig. 3.1), generally a non-steady state species, and \( \text{HCO} \) (Fig. 3.2) an intermediate species that will be considered to be in a steady-state later on. To compare the importance of each term in the convection-diffusion equation (3.6) the different fluxes and the net chemical reaction source term are shown in the figure on the left as a function of \( x \). On the right the contributions to the chemical source term in terms of the elementary reactions of the skeletal mechanism are given.

![Graphs showing diffusion and convection fluxes and net reaction rate](#)

**Fig. 3.1:** The diffusion and convection fluxes in terms of \( V \) and the net reaction rate for \( \text{H}_2\text{O} \) (left). The different parts of the source term (right), solid lines indicate the elementary reactions and the dotted line the net reaction rate. The listed numbers correspond to the ones in Table (2.1).

From Figs. (3.1) and (3.2) it is clear that for \( \text{H}_2\text{O} \) the contribution of the elementary reactions is comparable to the magnitude of the net reaction rate as well as that of the convective and diffusive parts. For \( \text{HCO} \), on the other hand, the magnitude of the reaction term is almost negligible compared to that of the elementary reactions of which it is composed. Since the diffusive and convective fluxes are comparable in magnitude to the net reaction rate in the flame zone their magnitude is thus negligible compared to that of the elementary rates. One could say that the concentration of \( \text{HCO} \) is determined mainly by the balance of formation and consumption reactions, thus implying the steady-state assumption, Eq. (3.1). The time scales associated with the consumption and production of \( \text{HCO} \) are much smaller than the ones associated with diffusive and convective processes.

We will now derive a 4-step mechanism for lean premixed methane-air flames. The number of steady-state assumptions that has to be employed can be obtained by a simple count of the free parameters in the flame problem. The skeletal mechanism can be considered as a 15 parameter (species) model, since there are 15 independent variables, i.e. the species. In order to obtain a 4 parameter model out of a set of 15, one has to pose 11 relations. Since conservation of elements is valid as long as
nuclear reactions do not take place, there are 3 conservation equations, one for each of the elements $C, H$ and $O$. This means that 8 relations have to be introduced artificially (the steady state assumptions). For which species these assumptions apply best will be discussed in the following two subsections. First the classical approach is treated, which is applied by most authors. Then a new method is introduced to determine the species for which the steady-state assumption is made. This new approach is based on a specific kind of sensitivity analysis developed in our group.

**Steady-State species selection based on the Classical Approach**

Which species are most suitable for the steady-state assumption can be obtained either by plotting figures like Fig. (3.2) or looking at the maximum mole-fraction of each species in the flame for which the reduced mechanism is to be used. In our case we consider a lean adiabatic premixed flame and compute the maximum mole numbers of the intermediate species in table (3.1). The set of intermediates can now be subdivided in two groups, one with a maximum mole fraction well below 1% and one well above. It is then common practice to consider the first group to be in steady-state since, due to fast reactions involving these species, every reaction creating a particle in this group is effectively balanced with a reaction consuming it. Therefore, the maximum mole fraction remains small and the net reaction rate can considered to be zero. In table (3.1) weighted mole fractions are given as well. These are equal to the original mole fraction weighted by the quantity $\sqrt{M_{N_1}/M_i}$, where

$$M_{i,N_1} = \frac{2M_iM_{N_1}}{M_i + M_{N_1}}$$  (3.7)

Without $N_2$ chemistry the $N$ conservation can be left out since $N_2$ itself acts as a conserved scalar.
which is roughly proportional to the binary diffusion coefficients of each species with respect to Nitrogen (which is abundant). It is known from asymptotic analysis that in the reactive layer, diffusive transport is dominant over convective transport (\[耐\]). Therefore, the weighted mole fractions are considered to be more significant and it is better to use the weighted maximum mole numbers. This is illustrated by the observation that in most treatments \([II]\) is not taken in steady state whilst \([O]\) and \([OII]\) are. This would not have been concluded if the original maximum mole numbers would have been considered. In the next subsection we will describe a more fundamental approach for the selection of the steady-state species.

### Steady-State species selection based on Sensitivity Analysis

Although most authors rely on the method described above, the decisions which species are to be taken in steady-state are mostly based on the 'chemical' experience of the researcher. This is most unsatisfactory and for this reason an alternative, more rational method is introduced. It is based on a first-order sensitivity analysis which can be performed as a kind of post-processing following a detailed flame simulation. Before we will explain how the method works, the concept of sensitivity analysis is briefly described.

Suppose we want to study the effect of the variation of a certain parameter on the dependent variables. A straightforward approach would be to alter the value of the parameter and recompute the solution. This would be a viable approach only if the effect of a variation of a few parameters is to be studied and/or the considered problem is not too computational intensive. Generally, in the field of combustion modelling, where both the number of parameters is large and obtaining the solution is very costly this is not a practical way to proceed.

First-order sensitivity analysis is a tool to predict the effect of parameter variations without recomputing the problem. Most applications of sensitivity analysis in combustion literature deal with predicting the effect of certain reaction rates on observable properties like the burning-velocity \(S_l\) and quantities like the temperature \(T\). Writing down the flame equations in terms of the residual vector, see Eq. (2.31),

\[
\mathbf{r}(\mathbf{J}|k) = 0
\]  

(3.8)
where \( \mathbf{\hat{Y}} \) contains all the dependent variables\(^7\), the species \( Y_1 \ldots Y_N \), the temperature \( T = Y_{N+1} \) as well as the mass flow rate \( \dot{m}_L = Y_{N+2} \) for the special case of an adiabatic flame. The vector \( \mathbf{k} \) is a short notation for the set of parameters \( k_i \), with \( l = 1, P \) with \( P \) the number of parameters. Thus the quantity we are interested in is the sensitivity matrix consisting of the partial derivative \( \partial \mathbf{\hat{Y}} / \partial \mathbf{k} \). To determine this matrix we differentiate Eq. (3.8) with respect to the vector of parameters \( \mathbf{k} \) leading to,

\[
\frac{d}{dk} (\mathbf{r}(\mathbf{\hat{Y}}|\mathbf{k})) = \frac{\partial \mathbf{r}}{\partial \mathbf{\hat{Y}}} \frac{\partial \mathbf{\hat{Y}}}{\partial \mathbf{k}} + \frac{\partial \mathbf{r}}{\partial \mathbf{k}}.
\]

If it is assumed that \( d(\mathbf{r}(\mathbf{\hat{Y}}|\mathbf{k}))/dk = 0 \), this gives the following set of equations for the sensitivity matrix \( \partial \mathbf{\hat{Y}} / \partial \mathbf{k} \),

\[
J \frac{\partial \mathbf{\hat{Y}}}{\partial \mathbf{k}} = - \frac{\partial \mathbf{r}}{\partial \mathbf{k}},
\]

thus implying that \( \mathbf{r}(\mathbf{\hat{Y}}|\mathbf{k} + d\mathbf{k}) = 0 \) as well. The Jacobian \( J \) is introduced here according to its definition in section 2.3. The advantages of the sensitivity analysis now becomes clear. It can be performed as a post-processing routine after the actual flame simulation. The only decision which has to be made a priori is the set of parameters whose effect will be studied. Since the Jacobian is already available in the computational procedure for the numerical simulation of the flame, the extra costs are small. Furthermore, each column \( (\partial \mathbf{\hat{Y}} / \partial k_i) \) of the sensitivity matrix can be calculated with the same techniques as used in the flame computation itself. The extra programming effort is restricted to the evaluation of the matrix \( \frac{\partial \mathbf{r}}{\partial \mathbf{k}} \). However, this can be done numerically, with similar routines used for the evaluation of the columns in the Jacobian.

Usually one uses the relative- or logarithmic sensitivity matrix \( \mathbf{S} \) rather than the sensitivity matrix \( \partial \mathbf{\hat{Y}} / \partial \mathbf{k} \). The elements of \( \mathbf{S} \) are related to \( \partial Y_{ij}/\partial k_i \) by,

\[
S_{ij}^{k_i} = \frac{k_i \partial Y_{ij}}{Y_{ij}} \frac{\partial \ln(Y_{ij})}{\partial \ln(k_i)},
\]

and will be used here unless mentioned otherwise. In Eq. (3.10) \( i \) is the species index and \( j \) the position index. It should be clear that the sensitivity coefficients are functions of space itself and generally can not be expected to be constant throughout the domain. Only for specific variables, like the adiabatic mass-flow rate, it is constant.

If, for instance, the sensitivity of certain reaction parameters \( k \) on the burning velocity is studied, we have to consider the \( S_{ij}^{k_i} \) since \( Y_{N+2} \) corresponds to the mass-flow rate and the burning velocity is defined as the flow velocity at the inflow boundary, mesh point \( j = 1 \), of the calculation interval\(^8\).

Introduction of a set of dummy parameters \( \mathbf{\hat{J}} \) in the residual formulation of the discretized equations (see Eq. (2.30)) according to,

\[
r_{ij} = J_i a_{ij} + a_{ij} Y_{i(j-1)} - b_{ij} Y_{ij} + c_{ij} Y_{i(j+1)}
\]

\(^7\)Recall that the dimension of this vector is equal to \((N + 1) \times K\) (or \((N + 2) \times K\) in case of an adiabatic flame).

\(^8\)In our case \( \frac{\partial \mathbf{\hat{J}}}{\partial \mathbf{k}} \) and \( \frac{\partial \mathbf{\hat{J}}}{\partial \mathbf{\hat{J}}} \) are computed. To obtain \( S_{ij}^{k_i} \), basic differentiation rules have to be applied.
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yields the set \( \mathcal{I}_i \), \( i = [1, N + 2] \) each corresponding to a dependent variable \( \mathcal{Y}_i \). In the course of the flame calculation these parameters are set equal to one and do not affect the solution. However, following the flame simulation, the sensitivity matrix \( S^Y \) is evaluated. For the observables in the vector \( \mathcal{Y} \) which need to be predicted accurately, those \( \mathcal{Y}_i \)'s can be considered in steady-state which show the smallest sensitivity, \( S^Y_{i,j} \). Specifically, if the main objective of the reduced mechanism to be derived is to predict the burning velocity and temperature profile accurately, the sensitivity coefficients \( S^Y_{i,j} = S^Y_{i,j|a} \) and \( S^Y_{i,j} = S^Y_{i,j|a+b} \) are to be considered. Note that the latter is a function of position. The choice of the species \( \mathcal{Y}_i \) to be considered in steady-state will then be the ones which yield the smallest sensitivity \( S^Y_{i,j} \) and \( S^Y_{i,j} \).

The basic idea behind this method is the following observation. A scaling of the residual according to,

\[
 r_{ij} = \mathcal{J}_i \left[ s_{ij} + a_{ij} \mathcal{Y}_{i,-1} \cdots b_{ij} \mathcal{Y}_{i} + c_{ij} \mathcal{Y}_{i,1} \right]
\]

has no effect on the solution (found when \( r_{ij} = 0 \)) because it is a global scaling. A low sensitivity for the scaling applied in Eq. (3.11), therefore, indicates that the residual in good approximation is equal to,

\[
 r_{ij} = s_{ij}
\]

for species \( i \), which is precisely the implementation of the residual for a steady-state species. Physically this means that the concentration of a steady-state species is determined by the balance of chemical production (\( s_{ij}^+ \)) and chemical consumption (\( s_{ij}^- \)) rather than a balance of diffusive- , convective fluxes and the net chemical source term (\( s_{ij} = s_{ij}^+ - s_{ij}^- \)), e.g. see Figs. (3.1) and (3.2). We will refer to this type of sensitivity as the steady-state sensitivity. Note that inerts will yield steady-state sensitivities which are small as well, although the physical reasoning sketched above is not valid in that case. However, like for reactants, steady-state assumptions never apply to species which are present in the fresh mixture and the sensitivity for these species does not have to be considered. In fact, this steady-state sensitivity analysis should only be applied to species which are possible candidates, i.e. intermediates and product species.

The method is tested for the deduction of the earlier mentioned 4-step model based on the skeletal mechanism for lean methane-air oxidation. We performed the sensitivity analysis for the adiabatic burning velocity and the temperature profile. In figure (3.3) the sensitivity of the burning velocity for equivalence ratios between \( \varphi = 0.6 \) and \( \varphi = 1.1 \) is plotted. Because the results show a large variation in magnitude, two groups are distinguished. One group involving the species which are taken in steady-state later on (bottom), and one involving the others (top).

Indeed the species that were chosen to be in steady-state earlier (table 3.1), show the smallest steady-state sensitivity with respect to the burning velocity. The steady-state sensitivity with respect to the temperature profile for a \( \varphi = 0.9 \) flame gives for \( S_{i,j}^T \) the same conclusion. In figures (3.4) and (3.5) the non-steady-state species and the steady-state species are plotted separately.

\[\text{If for instance the objective is to predict accurate NO profiles, of course } S_{i,j}^T, \text{ should be}\]
fig. 3.3: The steady-state sensitivity of the burning velocity for selected values of $\phi$, for the major species (top) and the steady-state species (bottom). For reference purpose the steady-state sensitivity of the atomic Hydrogen is plotted in both figures with a solid bar.
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fig. 3.4: The steady-state sensitivity of the temperature distribution for $\varphi = 0.9$. The species for which a steady-state assumption is not made in the 4-step model are presented.

fig. 3.5: The steady-state sensitivity of the temperature for $\varphi = 0.9$. The species for which a steady-state assumption is applied in the 4-step model are presented. The profile of $II$ is included as a reference. The species indicated in the box are not given because the magnitude of their sensitivities is too small to be resolved on the scale of this plot.
Both the steady-state sensitivity analysis of the burning velocity and that of the temperature profile confirm the assumptions made in the previous subsection. However, this method gives a more rational basis\textsuperscript{10} to the selection of the steady-state species. Moreover, if the reduced model is derived to predict another flame property adequately, the sensitivity analysis presented here can be applied directly to that specific observable. Furthermore, the implementation is as easy as any conventional sensitivity analysis at no extra costs.

In the next sections, the procedure to derive a 4-step model will be described, using the steady-state approximations for the species indicated here and in the previous section.

3.2.3 Reduction of the chemical set

In Eq. (3.13) the differential equations are given and each individual reaction is specified explicitly. For all species present in the skeletal mechanism this yields,

\begin{align*}
L\{\Gamma_{\text{CH}_4}\} &= -q_{10} - q_{11} - q_{12} \\
0 &= L\{\Gamma_{\text{CH}_3}\} = q_{10} + q_{11} + q_{12} + q_{13} - q_{18} \\
0 &= L\{\Gamma_{\text{CH}_2O}\} = q_{18} - q_{19} - q_{20} \\
0 &= L\{\Gamma_{\text{CH}_2O}_2\} = q_{13} - q_{14} - q_{15} + q_{19} + q_{20} \\
0 &= L\{\Gamma_{\text{CO}}\} = q_{14} + q_{15} - q_{16} - q_{17} \\
L\{\Gamma_{\text{CO}}\} &= -q_9 + q_{16} + q_{17} \\
L\{\Gamma_{\text{CO}_2}\} &= q_9 \\
L\{\Gamma_{\text{H}_2}\} &= -q_2 - q_3 + q_7 + q_{11} + q_{14} + q_{16} + q_{19} + q_{25} \\
L\{\Gamma_{\text{H}}\} &= -q_1 + q_2 + q_3 - q_5 - q_6 - q_7 + q_9 + q_{10} - q_{11} + q_{13} - q_{14} - q_{16} + q_{17} + q_{19} + q_{20} - q_{24} - 2q_{25} \\
L\{\Gamma_{\text{O}_2}\} &= -q_1 + q_5 + q_7 + q_8 - q_{13} + q_{21} \\
0 &= L\{\Gamma_{\text{O}}\} = q_1 - q_2 + q_4 - q_{13} + q_{18} \\
0 - L\{\Gamma_{\text{OH}}\} &= q_1 + q_2 + q_3 - 2q_4 + 2q_6 - q_8 - q_9 - q_{12} - q_{15} + 2q_{22} - q_{23} - q_{24} \\
0 &= L\{\Gamma_{\text{HO}_2}\} = q_8 - q_6 - q_7 - q_8 - 2q_{21} + q_{23} \\
L\{\Gamma_{\text{H}_2O}\} &= q_3 + q_4 + q_8 + q_{12} + q_{15} + q_{23} + q_{24} \\
0 &= L\{\Gamma_{\text{H}_2O}_2\} = q_{21} - q_{22} - q_{23} \\
L\{\Gamma_{\text{N}_2}\} &= 0
\end{align*}

For the steady-state species the net reaction rate is taken equal to zero. The set is now reduced by eliminating precisely as much reaction rates as there are steady-state species. For instance if reaction 21 is to be eliminated, the steady-state assumption

\textsuperscript{10}In contrast to the more heuristic argumentation based on the weighted maximum mole number as is applied by most authors.
for $H_2O_2$ can be used to perform this task. Using $q_{21} - q_{22} - q_{23} = 0$, each occurrence of $q_{21}$ can consequently be replaced by $q_{22} + q_{23}$, thereby eliminating $q_{21}$ from all equations. Which reactions are to be eliminated is arbitrary\footnote{See for instance [Pet91, Bil90] for typical differences in choices as applied by different authors.} and does not affect the results of a computation as long as the expressions for the steady-state species are not truncated. The main idea is to eliminate the fastest reactions that destroy the steady-state species since the slowest are rate-determining. A kind of main chain by which the complete combustion takes place is then derived. Here, we choose to follow the approach of Peters and Seshadri or Peters and Williams [Ses90, Pet87, Pet91]. From the $H_2O_2$ subsystem they eliminate reactions $q_{22}, q_{31}, q_{7}$ and $q_{22}$ being the fastest consumption rates for $O, OH, H_2O_2$ and $H_2O_2$, respectively. For the intermediates in the $C_1$-chain, $CH_3, C_2H_5O, C_2H_5O$ and $HCO$, these 'fastest' reactions are $q_{13}$, $q_{p1}, q_{14}$ and $q_{17}$. The last four complete the minimum set of reactions that can be removed from the main reaction chain. Other reactions, which are linear combinations of the previously selected reactions, disappear as well from the main chain. For instance, reaction $r_8$ can be written as a linear combination of $r_3$ and $r_7$ i.e.,

$$
\begin{align*}
H_2 + OH & \rightarrow H_2O + H & r_3 \\
H + H_2O & \rightarrow H_2 + O_2 & r_7 \\
OH + H_2O & \rightarrow H_2O + O_2 & r_8.
\end{align*}
$$

Similar arguments apply for reactions $r_4 (- r_3 - r_2)$ and $r_{15} (= r_{14} + r_3)$, leading to the elimination of reaction rates $q_4$ and $q_{15}$.

The resulting work is to carry out the linear algebra with the set of balance equations. This is a rather tedious job, which can be automated as is done by Göttgens et al. (REDMECH [Göt93]) or the algorithm presented in appendix B.1. Both the package developed by Göttgens et al. and the algorithm developed here, only need the basic detailed mechanism, the chosen steady-state species and for each of the latter a corresponding reaction to be removed from the main chain. The program then gives the global mechanism and the corresponding overall reaction rates. Here we will present the results only, yielding the following conservation equations for the non steady-state species,

$$
\begin{align*}
L\{O\} & = -q_{11} \quad (3.14) \\
L\{O_2\} & = -q_{111} + q_{11} \quad (3.15) \\
L\{H_2\} & = q_{11} \quad (3.16) \\
L\{H\} & = 4q_{11} + q_{111} + q_{1111} - q_{11V} \quad (3.17) \\
L\{H_2O\} & = 2q_{11} + 2q_{111} + 2q_{11V} \quad (3.18) \\
L\{O_2\} & = -q_{11V} \quad (3.19) \\
L\{H_2O_2\} & = -q_1 - q_{11} + 2q_{11V} \quad (3.20)
\end{align*}
$$

Here, the global reaction rates of the 4-step model are introduced,

$$
\begin{align*}
q_{11} & = q_{111} + q_{10} + q_{12} \quad (3.21) \\
q_{11V} & = q_4 \quad (3.22)
\end{align*}
$$
3.2. Systematical Reduced Mechanism

\[ q_{III} = q_5 - q_{10} + q_{16} - q_{18} + q_{19} - q_{21} + q_{23} + q_{24} + q_{25} \]  
(3.23)

\[ q_{IV} = q_1 + q_6 + q_{18} + q_{21} - q_{23} \]  
(3.24)

The so-called principal rate of each overall reaction is the one appearing first after the equal-sign. The magnitudes of the overall reactions are determined by these reactions mainly. The global reactions are obtained from the stoichiometry in the set (3.14-3.20). The rate of reaction \( II \), associated with \( q_{11} \), for instance, appears \(-1\) in the \( CO \)-balance Eq. (3.15), \(+1\) in the \( CO_2 \)-balance Eq. (3.16), \(-1\) in the \( H_2 \)-balance Eq. (3.17), \(+1\) in the \( H_2O \)-balance Eq. (3.20) and is not present in all the others. When we gather all species with negative numbers on the left hand side and all those with positive numbers on the right hand side, we find global reaction \( II \),

\[ CO + H_2O \rightleftharpoons CO_2 + H_2 \]  
(3.25)

In a similar fashion all other overall reaction may be obtained and are presented below

\[ CH_4 + 2H + H_2O \rightleftharpoons CO + 4H_2 \]  
\( r_I \)

\[ CO + H_2O \rightleftharpoons CO_2 + H_2 \]  
\( r_{II} \)

\[ H + H + M \rightleftharpoons H_2 + M \]  
\( r_{III} \)

\[ O_2 + 3H_2 \rightleftharpoons 2H + 2H_2O \]  
\( r_{IV} \)

where we included reaction \( r_{II} \) again. It should be noted that these overall reactions can be obtained by the same algorithm which performs the linear algebra mentioned earlier (App. B.1).

Some aspects of the overall reactions are worth mentioning. First, we see that fuel-breakup \( r_I \) itself is chain-breaking since it consumes radicals. It is for this reason that the \( H \)-radicals are not able to diffuse upstream, as can be seen in several figures in the previous section. Furthermore, it is interesting to see that not \( O_2 \) but \( H_2O \) acts as the oxidizer in the fuel breakup. Overall reaction \( r_{II} \) is the water-gas shift-reaction, which accounts for the \( CO - CO_2 \) conversion in the postflame zone. The recombination reaction \( r_{III} \) accounts for the chain-breaking in the post-flame zone. Its principal rate is given by reaction \( r_5 \) \((H + O_2 + M \rightarrow PO_2 + M)\) and apparently not \( r_{28} \) \((H + H + M \rightarrow H_2 + M)\) as one might expect. Chain-branching is accounted for by the oxygen breakup reaction, \( r_{IV} \), which effectively produces two radicals.

However, the set of equations is not complete yet. We may not expect that all steady-state species have disappeared from the rates \( q_1 \ldots q_{IV} \) of the overall reactions. This would have been pure coincidence and indeed is not the case as one can see easily. Even if one would truncate the overall rates to the principal rates \((q_{11}, q_9, q_5 \text{ and } q_1)\) respectively which is the minimum set, we still need expressions for the concentration of \( HO_2, O \) and \( OH \) since these occur in reactions \( r_5, r_1 \) and \( r_9 \). The set \((3.14 - 3.20)\) is not closed and we need expressions for most steady state species. These have to be solved from the steady-state subset of equations in \((3.13)\) leading to a set of nonlinear algebraic equations, which is complicated to solve as it stands. In simulations this has to be done for each mesh point, which is in general very CPU time consuming in 1D and specifically in 2D and 3D. Therefore, one often tries to truncate the expression for the steady-state species in such a way
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that an easy-to-evaluate explicit set of equations evolves. The truncation procedure is again a sort of post-processing procedure since the strategy for the truncation procedure can be obtained only after carefully examining the separate parts in the expressions for the steady state species which follow from a simulation with the detailed chemical model. The procedure for lean methane-air flames ([Pet93]) will be presented in the next subsection.

3.2.4 Truncation of the steady-state relations

Formally for the evaluation of the truncation of the steady-state species we should solve the set:

\[
\begin{align*}
q_{10} + q_{11} + q_{12} + q_{13} - q_{18} &= 0 \quad \{CH_3\} \\
q_{14} - q_{19} - q_{20} &= 0 \quad \{H_2O\} \\
q_{13} - q_{14} - q_{15} + q_{19} + q_{20} &= 0 \quad \{CH_3O\} \\
q_{14} + q_{15} - q_{16} - q_{17} &= 0 \quad \{HCO\} \\
q_{1} - q_{2} + q_{4} - q_{13} + q_{18} &= 0 \quad \{O\} \\
q_{1} + q_{2} + q_{3} + q_{4} - q_{8} - q_{9} - q_{12} + q_{15} + 2q_{22} - q_{23} - q_{24} &= 0 \quad \{OH\} \\
q_{5} - q_{6} - q_{8} - 2q_{11} + q_{23} &= 0 \quad \{H_2O\} \\
q_{21} - q_{22} - q_{23} &= 0 \quad \{H_2O_2\}
\end{align*}
\]

for fixed non steady-state species and temperature, which is non-linear and coupled in the steady-state species concentrations. To reduce the amount of work, which is one of the main objectives of the reduction strategy, the complexity is to be reduced. Therefore truncation of this set has been given much attention in the last years and can be considered to be the most important step in reducing the detailed chemical model from a numerical point of view. First the approach which is used by Peters et al. to truncate the steady-state expressions is presented. This will be referred to as the classical approach. Next another new implementation [Som94] of a sensitivity analysis is introduced, which can be used to simplify the task of truncation considerably.

The classical approach towards truncation.

First we determine the minimum set of expressions we have to deduce in order to perform a flame calculation with the reduced mechanism. Simple bookkeeping leads to the observation that in order to calculate the set \( q_{1} - q_{14} \) as presented earlier, we need expressions for all steady-state species. If the overall rates would be restricted to the principal rates alone, this minimum set would be reduced to the species \( CH_3, O, OH \) and \( H_2O_2 \). Note that, since the steady-state relations for these species involve many reactions, there is no guarantee that the evaluation of the obtained expressions does not involve the other steady-state species as well.

We now continue with the deduction of expressions as proposed by Peters [Pet91]. The way in which these expressions are obtained is by analyzing the source term of the different species. At first, a truncated expression for the concentration
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of OH is derived. For an estimate of the magnitudes of the contributions of the different elementary reactions consider Fig. (3.6). In the reaction zone the main contribution stems from reaction r3 which leads to a leading order approximation\(^2\) for OH:

\[
[OH]_* \approx \frac{k_3[H_2O][H]}{k_2[H_2]}
\]

(3.27)

The next extension can be obtained if the forward rate, \(q_1^f\), of reaction r1 is included, since this rate has a non-negligible contribution in the reaction layer. However, if only \(q_1^f\) would be added this leads to an expression for \([OH]\) which does not satisfy the correct equilibrium value downstream. Therefore, the backward rate of \(r_1\) has to be added as well. The contribution of this backward rate is very small and can be viewed upon as a second-order correction to the expression for the OH concentration.

The expression for the OH concentration now follows from balancing \(q_1\) and \(q_3\):

\[
[H_2][OH]k_3^f - [H_2O][H]k_2^f - [H][O_2]k_1^f + [O][OH]k_1^f = 0.
\]

(3.28)

Since an explicit relation for \([OH]\) is the principal goal, the yet unknown \([O]\) in Eq. (3.28) should be replaced by an expression in terms of known quantities. Once more, it should be kept in mind that at this point the concentrations of the non steady-state species are assumed to be known and the only other unknown is the O-concentration. The elimination is performed by introducing an ad hoc approximation for the O-radical satisfying the partial equilibrium of reaction 4 leading

\(^2\)In fact this leads to a partial equilibrium assumption of reaction 3.
to:

\[
[O] = \frac{[OIII] k_4^f}{[H_2O] k_4^r} = \frac{[H_2O][H] k_4^f}{[H_2]^2 k_4^r} \left( \frac{k_3^r}{k_3^f} \right)^2.
\]  

(3.29)

Note that the leading-order approximation (3.27) for \([OIII]\) is substituted in the partial equilibrium expression. Substituting this downstream value\(^1\) in the balance equation (3.28) leads to an explicit expression for \([OIII]\):

\[
[OIII] = \frac{[H_2O][H] k_3^r + [H][OII] k_4^f}{[H_2] k_3^r + [H]^2[H_2O] k_4^r} \frac{[OII] k_3^f}{k_3^f} \left( \frac{k_3^r}{k_3^f} \right)^2.
\]  

(3.30)

This manipulation is expected not to be seriously in error, since the term involving the \(O\) radical \((q_1)\) was only added to yield the correct equilibrium value for \([OIII]\) in the region downstream of the flame. It should be stressed that the ad hoc expression (3.29) does not necessarily lead to a correct value for \([O]\) itself. In fact it is not correct as we can see when proceeding with a more systematic approach to estimate the \(O\)-radical concentration. Following the same procedure for \(O\) as for \(OIII\) the main contributions are determined. This leads to the balance equation:

\[
[OIII][OII] k_4^r + [OIII][H] k_3^r + [OIII]^2 k_4^f = [O][k_3^f[OIII] + k_3^r[H_2] + k_3^f[H_2O] + k_{13}[C:HI_3])
\]  

(3.31)

Now a problem arises because a non-negligible contribution (i.e. \(r_{13}\)) necessitates the evaluation of an expression for \([C:HI_3]\) which is not available yet. However, from the balance equation for \(C:HI_3\),

\[
([H] k_1^f + [OIII] k_1^f k_{12}) [C:HI_4] = k_1^f[H_2] + k_{13}[H_2O] + k_{13}[O] \quad (3.32)
\]

it can be observed that reaction 13 links both equations. But, except \(OIII\), which is known at this point, no other steady-state variables are involved. Therefore and due to the simple coupling between Eq. (3.31) and Eq. (3.32), this set can be solved in closed form leading to a quadratic expression for \([O]\) yielding,

\[
[O] = \frac{-b + \sqrt{b^2 - 4ac}}{2a}.
\]  

(3.33)

where

\[
a = k_{13}B, \quad b = BD + k_{13}(C - A), \quad c = -AD
\]  

(3.34)

\(^1\)Note that this expression may only be expected to be a correct estimate for \([O]\) downstream, where the mixture approaches equilibrium.
and,

\[
\begin{align*}
\Lambda &= [HI][O_2]k_1^f + [OH][H]k_2^f + [OH]^2_k^f \\
B &= [OH]k_1^f + [H_2]k_4^f + [H_2O]k_5^f \\
C &= \left( [H]k_{11}^f + [OH]k_{12}^f \right) [CH_4] \\
D &= [H][M]k_{10}^f + [H_2]k_{11}^f + [H_2O]k_{12}^f.
\end{align*}
\]

(3.35)

Using the expression for the \(O\)-radical gives,

\[
[C,II_3] = \frac{C}{D + k_{13}[O]}
\]

(3.36)

which is the last species needed for the principal rates. Note that already an evaluation order for the steady-state relations appears, first \(OH\) and then \(O\) and \(C,II_3\) have to be calculated.

For the studies we want to perform, expressions for the other species are necessary as well. Once the expressions for \(OH\), \(O\), and \(C,II_3\) are known, the truncated values for the other steady state species are easy to obtain. Below the results for the remaining intermediates \(CH_2O\), \(CH_2O\) and \(HCO\) in the main chain are listed,

\[
\begin{align*}
[CH_3O] &= \frac{[C,II_3][O_2]k_{18}}{[H]k_{19} + [M]k_{20}} \\
[CH_2O] &= \frac{[C,II_3][O]k_{13} + [CH_2O]([H]k_{19} + [M]k_{20})}{[H]k_{14} + [OH]k_{15}} \\
[HCO] &= \frac{([H]k_{14} + [OH]k_{15})[CH_3O]}{[H]k_{16} + [M]k_{17}}
\end{align*}
\]

(3.37) (3.38) (3.39)

The expressions for ([\(HO_2\)]) and hydrogen-peroxide ([\(H_2O_2\)]) can be obtained from their main rates in the \(H_2O_2\) subsystem \((r_5 - r_8)\). This leads to the following expressions,

\[
\begin{align*}
[HO_2] &= \frac{[H][O_2][M]k_5}{[H](k_6 + k_7) + [OH]k_8} \\
[H_2O_2] &= \frac{[HO_2]^2k_{21} + [OH]^2[M]k_{22} + [H_2O][HO_2]k_{23}}{[M]k_{22} + [OH]k_{24}}
\end{align*}
\]

(3.40) (3.41)

It should be stressed that the above set of equations form explicit expressions if they are evaluated in the order (3.30...3.41). The steady-state expressions together with the differential equations for the non steady-state species and the chemical source terms given in section (3.2.3) define the complete system.

**Truncation based on sensitivity analysis.**

Although most authors use the approach presented above to truncate the steady-state expressions, the success and amount of work depends on the expertise of the researcher. In the following an implementation of a sensitivity analysis is treated, which helps to perform this task more easily. Before this analysis is introduced, the truncation process has to be put in a more mathematical context.
Basically, each steady-state species $i$ is determined by an equation of the form,

$$ \sum_{m=1}^{M} \nu_{im} q_m = 0 \quad (3.42) $$

where the stoichiometric coefficients $\nu_{im}$ determine which reactions are involved. Effectively, truncation of these equations is no more than discarding some of the reactions $m$ which have no or little influence on the solution of the equation (3.42). Classically, this influence is determined by investigating the contributions of each reaction with the help of figures like Fig. 3.6. However, this process can also be performed with a sensitivity analysis. In principle what has to be estimated is the effect of variations in each reaction $(q_m)$ on the solution of Eq. (3.42), i.e. the concentration of $i$ itself. In terms of sensitivity coefficients this could be determined by evaluating either

$$ S_{ij}^{q_m} \quad (3.43) $$

or

$$ S_{ij}^{m} \quad (3.44) $$

where $j$ is the position index. However, the sensitivity $S_{ij}^{q_m}$, if evaluated by the procedure described earlier in this chapter affects other steady-state equations and the source terms of the non steady-state species as well as the temperature. It thus gives an estimate for the effect of discarding a certain reaction in all source terms, which is not necessarily intended by the truncation procedure. A reaction can be left out of the truncated expression of a specific steady-state species, but it still remains in the source terms of the non steady-state species or in the truncated expressions of other steady-state species. Therefore, the sensitivity with respect to the stoichiometric coefficients $S_{ij}^{m}$ has to be used instead. These will predict the effect of discarding a specific reaction from the steady-state relation of one specific species.

Apart from the more mathematical and controllable approach, another advantage of the sensitivity analysis is that we do not necessarily have to consider the effect of truncation of a certain steady-state relation on the steady-state species $i$ itself. It is as simple to compute the sensitivities of the truncation of a specific steady-state species $i$ with respect to other observables $j$ as well, yielding the coefficients,

$$ S_{ij}^{q_m} \quad (3.45) $$

instead. It is of course more important that the truncation procedure predicts the observables you are interested as accurate as possible, which in our case would be the burning velocity and flame temperature for the case of an adiabatic flame. For this reason only the sensitivities with respect to the burning velocity are determined. So, instead of evaluating the $S_{ij}^{q_m}$ for every steady-state species $i$, we evaluate $S_{ij}^{m}$ ($= S_{ij}^{q_m}$) only. We will refer to this analysis, as the truncation sensitivity.

For three equivalence ratios, $\varphi = 0.6, 0.8$ and $1.0$, these sensitivities for the steady-state species in the 4-step model are given in Fig. 3.7. Since only $O_{2}H$, $CO$, $CO_2$ and $HO_2$ are truncated in the model of Peters et al., the other steady-state species are not presented. The reactions that are involved in the truncated model are indicated with arrows.
3.2. Systematical Reduced Mechanism

From the plots it can be seen that for the species O, CH₃ and H₂O₂ most reactions are included in the truncated expressions of Peters et al. The ones that are not, show sensitivities which are negligible compared to the others. However, for O₁H only two reactions, r₁ and r₃, are included in the truncated expression of the previous section. Indeed, for the equivalence ratios ϕ = 0.8 and 1.0, these two show the largest sensitivities, and again validate the choices made by Peters and coworkers. However, for ϕ = 0.6, r₃ is not the reaction with largest sensitivity next to reaction r₁, which indicates that the truncation procedure might be improved by taking another reaction instead. This is tested and investigated in the last section of this chapter.

It should be noted that the procedure presented here will not automatically give an easy-to-evaluate explicit set of expressions. However, the sensitivity analysis gives a more tractable and rational approach to the truncation process.

Before the results with the systematically reduced chemical model are presented, some numerical techniques often employed in modelling flames with systematically
reduced chemical models are discussed.
3.3 Numerical Aspects of Reduced Chemistry Modelling

In the previous section a set of algebraic equations for the steady-state species has been deduced. Under some assumptions these equations could be 'truncated' to yield an explicit formulation. Most of the relations for the concentration, $n_i$, of the steady-state species are (or can) be expressed in the form,

$$n_i = \frac{N}{D},$$

(3.46)

which requires special attention to avoid the so-called Zero-Denominator problem. In general, if $D$ and $N$ approach zero, the fractional expression $N/D$ will have a well-defined finite value. But, during a calculation it might occur that due to numerical round-off errors $D$ is much closer to zero than $N$ and $n_i$ becomes infinite. Rogg et al. [Wan93] now argue that this problem can be avoided, by replacing Eq. (3.46) by a modified expression, using,

$$n_i D + \epsilon n_i = N + \epsilon n_i,$$

to obtain,

$$n_i = \frac{N + \epsilon n_i}{D + \epsilon},$$

(3.47)

where $\epsilon$ is a small parameter. For appropriate values of $\epsilon$, Rogg claims that this expression is to be preferable to ad hoc approaches like

$$n_i = \frac{N}{\max(D, \epsilon)},$$

since Eq. (3.47) avoids the zero-denominator problem but still is adequately accurate. He takes $\epsilon$ so that

$$\epsilon_{\text{min}} < \epsilon < \epsilon_{\text{max}},$$

where $\epsilon_{\text{min}}$ is 10 to 100 times the smallest positive real number that can be represented on the computer. For $\epsilon_{\text{max}}$ a value of 10 to 100 times the smallest value for $n_i$ in the flame is suggested. We employed the same strategy in our computational method and no problems were encountered during the simulations.

Another problem, often encountered when dealing with reduced chemical schemes is associated with the unrealistically high values for concentrations of certain steady-state intermediates in the pre-flame zone defined in figure 3.8.

In the flame zone the profiles of the species are determined by a balance of the diffusion-, convection- and source term. In the post-flame zone the values for the intermediates are determined by a balance of consumption and formation rates and the steady-state assumption will perform well. However, in the pre-flame zone chemical source terms of most species, both formation and consumption, are negligible because of the low temperatures. Then, for most species, the profile is determined by a balance of convection- and diffusion fluxes and the steady-state approximation is not valid. For some species, in the skeletal mechanism these are $HCO_2$ and $H_2O_2$, the main contributions to the chemical source term do not decrease as the temperature decreases. For example the source term for $HCO_2$ is given by,

$$\dot{s}_{HCO_2} = [H][O_2][M]k_5 - [HCO_2][H]k_6 - [HCO_2][H]k_7 - [OH][HCO_2]k_8$$
thus yielding the steady-state expression,

\[
[H_2O] = \frac{[H][O_2][M]k_5}{[H]([k_6 + k_7] + [OH]k_8)}.
\] (3.48)

This equation involves the specific reaction rate \(k_5\) given by,

\[k_5 = 2.3 \cdot 10^{18} T^{-0.8} \]

which contains a negative power of the temperature. The other rates (\(k_6, k_7\) and \(k_8\)) behave 'well' and decrease exponentially as the temperature decreases as is shown in figure 3.9. In a detailed chemistry simulation this chemical source term is balanced by large diffusion and convection fluxes\(^\text{14}\) in order to satisfy the boundary conditions. However, in a steady-state approximation the profiles of steady-state species are determined completely by the chemical source term and in the pre-flame zone yield unrealistically high values for \([H_2O]\) and \([H_2O_2]\) if no special measures are taken. It should be noted that this occurs also when the steady-state species are not truncated. To illustrate this phenomenon, the mole-fraction obtained by the steady-state expression\(^\text{15}\) for \(H_2O_2\) are presented in figure 3.10.

To handle this difficulty most authors replace the expression for these species at temperatures lower than a given temperature, sometimes referred to as the cut-off.

\(^\text{14}\)Generally, \(H_2O_2\) profiles show high derivatives and curvature in the pre-flame zone.

\(^\text{15}\)For \(H_2O_2\) the situation is even worse since \(H_2O_2\) enters the numerator quadratically.
3.3. Numerical Aspects of Reduced Chemistry Modelling

**fig. 3.9:** The Arrhenius terms of $HO_2$ - reactions $r_5$, $r_6$, $r_7$ and $r_8$ as a function of the temperature on the left. On the right we present the Arrhenius terms of the reactions $r_{22}$, $r_{23}$, and $r_{24}$ involved in the $H_2O_2$ steady-state relation as a function of the temperature. The rates that determine the nominator are indicated with solid symbols in both figures.

**fig. 3.10:** Illustration of the $HO_2$ profile obtained by the steady-state expression. Cut-off is applied where the convection diffusion profile intersects the steady-state profiles. The dotted line is a result of computation without steady-state assumptions.
temperature \( T_c \). We employ this cut-off strategy also and in the present calculations a value of \( T_c = 1100 K \) is taken. At the low temperature side the steady-state expression is replaced by the solution of the convection-diffusion equation with constant Peclet \( Pe \) and Lewis numbers \( Le \), thus yielding for \( T < T_c \):

\[
n_i(x) = (n_i)_u + ((n_i)_e - (n_i)_u) \frac{1.0 - \exp(-PeLe_i(x - x_u))}{1.0 - \exp(-PeLe_i(x_e - x_u))},
\]

(3.49)

where \( x_e \) is the last position where the steady-state expression is still assumed to be valid with \((n_i)_u\), the value at that position. Furthermore, \( x_u \) indicates the position of the unburnt boundary and \((n_i)_u\) the boundary value for the species under consideration. The discontinuity in the first derivative, introduced by this cut-off procedure, did not affect the solution of the flame problem, nor the convergence behavior of the algorithm.

In reduced chemical modelling another difficulty occurs when the steady-state relations are not arranged or manipulated in such a way that the equations are explicit in the unknown quantities, the concentrations of the steady-state species. This would be the case when truncation is not employed. Then the resulting set of equations is a nonlinear set of coupled algebraic equations which we choose to solve by a simple successive substitution procedure. The steady-state expressions are all manipulated such that the concentration of each species \( i \) is formulated as,

\[
n_i = \frac{N_i}{D_i}.
\]

(3.50)

For example, the untruncated steady-state relation for \([HC\text{O}]\) then yields,

\[
\begin{align*}
N &= [H][C\text{O}]/k_{14} + [OH][C\text{O}]/k_{15} \\
D &= [H]k_{16} + [M]k_{17} \\
[HC\text{O}] &= \frac{N}{D}.
\end{align*}
\]

(3.51)

This expression for \([HC\text{O}]\) is identical with the one mentioned in section 3.2.4. It is possible to derive a formulation analogous to Eq. (3.51) for all steady-state species. An algorithm has been developed to generate the complete (untruncated) set of equations governing the steady-state species.

To solve all the steady-state concentrations from this set of equations we use the iteration cycle presented in Fig. (3.11). At the 'input' section the temperature, concentration of non steady-state species and specific rates \( k_i \) are given. Then an initial estimate for the concentration of steady-state species is provided at the second stage of the flow-chart ('initialize'). In practice we take the values of a previously converged iteration step as initial guess. Finally, the iteration loop over \( l \) is entered until convergence is reached. The solution is converged when the quantity \( e \), at the iteration step \( l \),

\[
e_{l} = \frac{||N_i^l - D_i^l * n_i^{l-1}||}{||N_i||}
\]

is smaller than a previously set value, taken to be \( 10^{-3} \), for every species \( i \). \( n_i^l \) is the concentration of species \( i \) at iteration level \( l \).

This iteration procedure is often referred to as 'inner iteration' in the field of combustion modelling [Wan93]. The adjective 'inner' is clearly related to the fact that
3.3. Numerical Aspects of Reduced Chemistry Modelling

this procedure is used inside the iteration loop performed to solve the conservation equations of the non steady-state species, temperature, mass and momentum. We will conform ourselves to this nomenclature and refer to this approach as inner iteration whenever it is used. Clearly, the truncated set of equations for the steady-state species derived in section 3.2.4 is explicit and does not need an inner iteration loop to be evaluated. Inner iteration will be used to compare results of the truncated set, with approaches that do not lead to a set of explicit expressions. In the next section we will report results of calculations with the 4-step mechanism introduced here. Several assumptions introduced will be tested and compared with results of the detailed chemistry simulations presented in chapter 2, section 2.4.2.
fig. 3.11: The inner iteration loop to calculate the steady-state species. At the input section all known quantities are provided. At INITIALIZE, initial estimates for the steady-state species are calculated and the iteration loop over $t$ is started until convergence is reached. Here $C'$ is a previously set convergence ratio and $t_{\text{max}}$ a maximum number of cycles.
3.4 Systematic analysis of a 4 step reduced chemical model.

A systematic analysis of the 4-step methane-air chemical model presented earlier, will be performed in this section. The deduction of this model consists of two distinct parts: the application of steady-state assumptions and the truncation of the steady-state relations. In the first section the effect of the steady-state assumptions on the behavior of the observables is investigated without truncation of the steady-state relations. Then, in the subsequent subsection the effect of the truncations as applied by Peters et al. is studied.

3.4.1 Effect of the steady-state assumption.

To disregard any effect, other than related to the steady-state assumptions, the original algorithm of the study presented in chapter 2 is modified by altering the definition of the residual. For all steady-state species the residual is replaced by,

\[ r_{ij} = s_{ij} \]

which is a straightforward implementation of the steady-state assumption; the diffusion- and convection fluxes are simply discarded. However, as might be expected from the discussion in the previous section, this leads to unrealistically high values for \( H_2O_2 \) and \( H_2O \) concentrations in the pre-flame zone. It is found that this straightforward application does not lead to a convergent calculation strategy. For this reason a cut-off similar to the one mentioned in section 3.3 has been implemented. A switching function \( F_c = F(T, T_c, \delta T_c) \) is introduced in the residual of \( H_2O_2 \) and \( H_2O \) according to

\[ r_{ij} = F_c s_{ij} + (1.0 - F_c) (a_{ij} \gamma_{i(j-1)} - b_{ij} \gamma_{i} + c_{ij} \gamma_{i(j+1)}) \]  

(3.52)

which switches gradually from zero to one in a region around \( T_c \), schematically presented in Fig. (3.12). Furthermore, during the computational study it occurred that the formulation \( r_{ij} = s_{ij} \) for the other steady-state species leads to a poorly conditioned \( J \) Jacobian matrix in the pre-flame zone. The reason is that in the pre-flame zone the concentrations are determined by a balance of the convective- and diffusive fluxes. The chemical source terms approach zero exponentially, due to the Arrhenius terms. Then for the steady-state species the entries in the Jacobian matrices become extremely small compared to those of the major species for which the convective- and diffusive fluxes are not discarded, which leads to a poorly conditioned Jacobian. To circumvent this numerical problem the residual of the other steady-state species is modified according to,

\[ r_{ij} = F_c s_{ij} + (1.0 - F_c) (a_{ij} \gamma_{i(j-1)} - b_{ij} \gamma_{i} + c_{ij} \gamma_{i(j+1)}) \]  

(3.53)

\[ F(T, T_c, \delta T_c) = \begin{cases} 
1.0 - \frac{1}{2} e^{-\frac{T_c}{\delta T_c}} & \text{for } T > T_c \\
\frac{1}{2} e^{-\frac{T_c}{\delta T_c}} & \text{for } T < T_c 
\end{cases} \]

\[ \text{We used} \]

\[ F(T, T_c, \delta T_c) = \begin{cases} 
1.0 - \frac{1}{2} e^{-\frac{T_c}{\delta T_c}} & \text{for } T > T_c \\
\frac{1}{2} e^{-\frac{T_c}{\delta T_c}} & \text{for } T < T_c 
\end{cases} \]

\[ \text{Singular to working precision.} \]
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Fig. 3.12: Cut-off function $F$. Function switches smoothly from 0.0 to 1.0. The value for $\delta T_k$ is a measure for the 'width' of the cut-off.

where the functional form of $F_k = F(T, T_k, \delta T_k)$ is identical to the earlier introduced $F_k$. The only difference between this definition and Eq. (3.52) is the value of $T_k$ which, in contrast to $T_{nc}$, is taken well inside the pre-flame zone where chemical reactions are of no importance. A value of $T_k \approx 400K$ works fine for all computations performed with this model. For both 'widths' $\delta T_n$ and $\delta T_k$ typically 10K is taken.

In order to make sure that possible differences between the steady-state studies and the original detailed chemistry calculations of chapter 2 are not induced by the introduction of $F_k$ the residuals of all species are replaced by

$$r_{ij} = F_k s_{ij} + a_{ij} Y_{i(j-1)} - b_{ij} Y_{j} + c_{ij} Y_{i(j+1)}.$$  \hspace{1cm} (3.54)

Flame calculations with this definition (Eq. 3.54) of the residual, but without steady-state assumptions applied, show that the introduction of $F_k$ alone has no noticeable effects on the results (see App. B.2). In fact all detailed computations reported in this chapter have been performed with a residual definition according to Eq. (3.54) rather than with the original implementation Eq. (3.12) unless mentioned otherwise.

To illustrate that the implementation of equation (3.53) is equivalent with a steady-state assumption, the reaction term of $C/H_3$ is given in figure 3.13. Indeed, chemical production- and consumption terms cancel and the net reaction rate is exactly equal to zero throughout the complete computational domain. In Fig. (3.14) the resulting burning velocity as a function of the equivalence ratio $\phi$ is compared with the results of a detailed chemistry simulation. On the lean side the 4-step model predicts the burning velocity well. Near the stoichiometric point the difference increases to approximately 3 cm/s (about 10%). The calculations with the 5-step model (for $\phi = 0.6, 0.8,$ and 1.0) show that this difference can be reduced
3.4. Systematic analysis.

fig. 3.13: Source term ($s_{ij}$) of $CH_3$ in a full steady-state computation ($\bullet$). The total consumption ($s_{ij}^-$) and formation ($s_{ij}^+$) rates are included as well (continuous lines).

by taking $CH_3$ not in steady-state. This finding can be found from the sensitivity analysis. In Fig. (3.3) it can be seen that the steady-state sensitivities at stoichiometric conditions for $CH_3$ and $OH$ are comparable with that of $H$. However, the sensitivity of the methyl radical, with respect to the burning velocity, has a negative value. This indicates that applying the steady-state assumption to $CH_3$ will lower $S_f$. Consequently, taking $CH_3$ not in steady-state will increase the burning velocity, which is confirmed by the results of the 5-step calculation. Similarly, the sensitivity of the hydroxyl radical has a positive sign. Leaving $OH$ out of the set of steady-state species will lead to a further decrease of the burning velocity as is observed in the results (Fig. (3.14)). For the sake of completeness a 5-step model with the $O$-radical not in steady-state is included as well. Since the steady-state sensitivity has the same sign as the one of $CH_3$ but is smaller in magnitude, we expect that taking $O$ not in steady-state increases the burning velocity as well, but has a smaller effect. This is confirmed by the results of the simulations (Fig. (3.14)).

For the burner-stabilized flame, calculations have been performed with the 4-step and one 5-step model ($CH_3$ not in a steady-state). Results of the stand-off distance and flame temperature are presented in Fig. (3.15). These confirm the conclusion of the adiabatic flame simulations. Again the 5-step model with no steady-state assumption applied to $CH_3$ performs better than the 4-step model for both equivalence ratios.

For the same two reduced models (4- and 5-step) differences in the detailed structure of the flame have been investigated. The profiles of both reduced models are
fig. 3.14: Burning velocity $S_1$, as function of $\varphi$. The solid line is the full scheme calculation with constant Lewis numbers. The line with the open circles indicates the results of the computations with 8 steady-state approximations and without any truncation (4-step scheme). Computations are included at $\varphi = 0.6, 0.8,$ and 1.0, for which each time one steady-state assumption has been dropped. These are for $CH_3$ (solid circle), $O$ (open square) and $OH$ (solid triangle), respectively (5-step model).

Compared with the results of a detailed chemistry simulation of a burner-stabilized flame for the same conditions as used in Chapter 2 ($\varphi = 1.0$, $u_i = 0.0250 \text{ cm}^{-2} \text{s}^{-1}$). The results of the reduced models are presented in different plots (Figs. (3.16)-(3.18)). For the intermediates of the $C_1$-chain different linetypes and symbols are used to distinguish the different species (Fig. (3.18)).

It is clear that the profiles for most major species are predicted accurately. Only the maximum mole fraction of $H_2$ is overpredicted in both reduced models. The 5-step model performs better: the profiles of the species practically coincide. With respect to the radicals, there does not exist a significant difference between both models. Both predict higher peak concentrations for $H$, $O$, and $OH$ as can be seen in Fig. (3.17). The difference between the 5-step model and the detailed chemistry simulation is smaller in the pre-flame and flame zone ($x < 0.05 \text{ cm}$). However, this is again due to the larger stand-off distance predicted by the 4-step model\textsuperscript{15}. The cut-off procedure, described in section 3.3, is clearly visible in both figures.

\textsuperscript{15} As mentioned in the previous chapter, the $H$, $O$ and $OH$ radicals cannot diffuse past the flame zone, since they are rapidly consumed in the $CH_4$ breakup.
3.4. Systematic analysis.

fig. 3.15: Stand-off distance and flame temperature as a function of the mass-flow rate with untruncated steady-state expressions. The solid line is the full scheme calculation with constant Lewis numbers. The (o) indicates the results of the computations with 8 steady-state approximations (4-step scheme). For the computation indicated with (•) the steady-state expression for CH₃ has been dropped (5-step model).

Ma(s) flow rate (g cm⁻² s⁻¹)

`φ=0.8`

`φ=1.0`

Temperature (Tₑ = 1100K). For the C₁-intermediates the differences between the 4- and 5-step model are much larger. The 4-step model overpredicts the CH₃ peak value by approximately 100%. Consequently, the profiles of the other intermediates in the C₁-chain are different from the detailed chemistry simulation as well. Furthermore, due to the steady-state assumption, the concentration of all intermediates in the pre-flame zone is lower than that of the reference results, indicating that the higher concentrations found there in the detailed computation must be attributed to diffusion. This conclusion is supported by the results of the 5-step computation, where the CH₃-radical is not taken in steady-state. For this radical the profiles for the detailed- and reduced calculation practically coincide. The concentrations of the other intermediates are now reproduced better as well. Only the gradual increase from \(x = 0.00\) cm to \(x = 0.05\) cm is not present in the 5-step model, since for these species diffusion has been switched off.

Generally, it can be concluded that the untruncated 5-step model given by the global reactions,

\[
\begin{align*}
    & \text{CH}_4 + \text{H} \quad \Rightarrow \quad \text{CH}_3 + \text{H}_2 \\
    & \text{CH}_3 + \text{H} + \text{H}_2\text{O} \quad \Rightarrow \quad \text{O} + 3\text{H}_2 \\
    & \text{CO} + \text{H}_2\text{O} \quad \Rightarrow \quad \text{CO}_2 + \text{H}_2 \\
    & \text{H} + \text{H} + \text{M} \quad \Rightarrow \quad \text{H}_2 + \text{M} \\
    & 3\text{H}_2 + \text{O}_2 \quad \Rightarrow \quad 2\text{H} + 2\text{H}_2\text{O}
\end{align*}
\]

performs better for the prediction of the global adiabatic- and burner-stabilized flame properties. Consequently, the detailed structure is predicted better as well.
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Note the difference with the 4-step model. In this 5-step model the $CH_4$ to $CO$ conversion is covered by two reactions $r_7$ and $r_{14}$ instead of one (section 3.2.3). The rest of the reactions ($r_{11}$, $r_{111}$ and $r_{114}$) is identical to the last three global reactions in the 4-step model.

It should be stressed that the implementation of a reduced model as is described in this section does not lead to a reduction of the ‘numerical’ effort to simulate a flame. Here the application of the steady-state assumption only changes the definition of the residual of some species and will therefore not lead to shorter computing times. Therefore, for simulating flames there is no reason to employ this strategy. However, it is easy to implement in an existing flame code and gives an ideal tool to predict the performance of systematically reduced models, without truncation applied to the steady-state species. Furthermore, the results obtained with this implementation will indicate the theoretical limit of the reduced model since there are no other approximations applied. In fact, it would be fortuitous if any observable is predicted better when truncation, i.e. further approximations, of the steady-state relations is applied. For this reason the results of the 4-step model presented in the present section, will be used as the reference computations in the next subsection.
3.4. Systematic analysis.

![Mole fraction vs. distance for 4-step and 5-step models](image1)

**fig. 3.17:** The results of the major species profiles of the 4-step model (o, left figure) and the 5-step model (●, right figure). $H_2O_2$ and $HO_2$ are multiplied by a factor 50. The solid lines are the original calculations in both figures. ($\phi = 1.0, \dot{m} = 0.0250 \text{ gcm}^{-2}\text{s}^{-1}$.)

![Mole fraction vs. distance for 4-step and 5-step models](image2)

**fig. 3.18:** The results of the $C_1$ intermediate species profiles of the 4-step model (o, left figures) and the 5-step model (●, right figures). The solid lines are the original calculations in all figures. ($\phi = 1.0, \dot{m} = 0.0250 \text{ gcm}^{-2}\text{s}^{-1}$.)
3.4.2 A systematic analysis of truncation.

To take advantage of the reduced models, we have to modify the algorithm described in the previous chapter. For the non steady-state species the combined modified-Newton / time iteration approach, symbolically,

$$J_{(i)} \Delta \tilde{y} = -\tilde{r}_{(i)}$$

will still be used. It should be noted that the dimension of the block matrices $J_i^{\rho,\varphi,\sigma}$ in the Jacobian matrix $J_{(i)}$, now equals $(N_n + 2)$ with $N_n$ the number of non steady-state species. This reduces the problem size drastically and in principle leads to the claimed reduction in CPU-time necessary to compute the Jacobian matrices and thus to tackle flame problems. The source terms $s_i$ in the residual, are now composed of the overall reactions $q_1 \ldots q_{1v}$ introduced in Eq. (3.24) according to the stoichiometry defined in equations (3.14-3.20). For the evaluation of the overall reaction rates the elementary reactions rates, for which the same routines are used as in the detailed chemical model implementation, need to be computed. These routines need values for the concentrations of all species, including the steady-state species. To obtain a flexible implementation, a new routine is introduced which produces the concentrations of the steady-state species at all grid-points, for fixed values of the other variables (temperature, non steady-state species and mass-flow rate). The only algorithmic difference between the studies presented in this subsection, is the contents of this new routine. The routine depends on the approximations that are applied to the steady-state relations. Four different models will be studied and compared with the 4-step untruncated calculation (denoted symbolically with F4) presented in the preceding section. The first model will be the one with the truncated expressions for the steady-state species as given by Peters et al. in section 3.2.4 (symbolically denoted with EP). The second model uses the same truncated expressions but another choice (Bilger et al. [Bil91, Che91]) for the overall reactions (symbolically denoted with EB). In the third model the original 4-step global reactions are used, but some approximations, introduced to obtain the explicit set of expressions for the steady-state species, will be dropped. This model will be denoted symbolically as IP. The final model to study the effects of truncation will be an improvement to the IP model. This fourth model uses an extension to the steady-state expressions, induced by the sensitivity analysis, which will be shown to perform better than the three other models. It will be indicated with IS.

Before we present the results we will describe the first three models into more detail. The first two (EP and EB) are inspired by the truncation procedure for the steady-state relations. Due to the truncation the reaction rates which are eliminated from the overall reactions are no longer arbitrary. Formally the relations between sets of reaction rates presented in section 3.2.4, imposed by the steady-state assumptions, are no longer valid. Therefore, different choices for the overall reactions do not necessarily lead to identical results after the truncation process. To test this observation, calculations have been performed with another 4-step mechanism. It is based on the same detailed chemical model and is presented by Bilger and Dibble.

---

15 Recall that most of the computing time is involved with the evaluation of the Jacobian elements (section 2.3).
3.4. Systematic analysis.

[Bil91, Che91],
\[
\begin{align*}
\text{C} + \text{H}_4 + 2\text{H} + \text{H}_2\text{O} & \Rightarrow \text{C} \text{O} + 4\text{H}_2 & r_1 \\
\text{CO} + \text{H}_2\text{O} & \Rightarrow \text{CO}_2 + \text{H}_2 & r_{11} \\
2\text{H}_2 + \text{O}_2 & \Rightarrow 2\text{H}_2\text{O} & r_{111} \\
\text{O}_2 + 3\text{H}_2 & \Rightarrow 2\text{H}_2 + 2\text{H}_2\text{O} & r_{1 IV}
\end{align*}
\]

with overall reaction rates given by,
\[
\begin{align*}
q_1 &= q_{13} + q_{18} \\
q_{11} &= q_9 \\
qu &= q_{25} - q_{11} + q_{16} - q_{20} - q_{22} + q_{24} + q_{25} \\
q_{1 IV} &= q_1 - q_7 + q_{10} - q_{16} + q_{18} + q_{20} - q_{24} - q_{25}
\end{align*}
\]

which differ from earlier presented overall rates (3.24). Computations with this 4-step model are performed only for the expressions for the steady-state species presented in section 3.2.4. Since these form an explicit set, the calculations with the 4-step model presented above will be referred to as Explicit-Bilger (EB). The original set of overall reactions together with the explicit expressions is therefore referred to as the Explicit-Peters model (EP).

The third model, earlier denoted as IP, is introduced to attain insight in the effect of the application of the partial-equilibrium assumptions in Eq. (3.29) (introduction of [O], section 3.2.4). These assumptions are only made to render the set of steady-state relations explicit. To study the effect calculations have been performed without these assumptions as well. A consequence of this modification is that the equations can no longer be manipulated such that they form an explicit set. The expression for [O], [\text{OH}], and [\text{H}_3] are now coupled and the resulting relation for [\text{OH}] is given by,
\[
\begin{align*}
N &= k_7'[\text{OH}][\text{H}]k_5[\text{H}_2\text{O}][\text{H}] \\
D &= k_2[\text{O}] + k_3[\text{H}_2] \\
[\text{OH}] &= N/D.
\end{align*}
\]

which is coupled to the expression for [\text{OH}] through the term \( k_1'[\text{O}] \) in the denominator. The expressions for the other steady-state species remain unaltered. However, due to the coupling the relations for the concentration of the steady-state species cannot be manipulated such that they form a set of explicit expressions and thus remain implicit. Therefore, the results of this approach will be indicated as Implicit-Peters (IP). To solve the set of equations for the steady-state species, the inner-iteration approach mentioned in section 3.3 will be used. Before we introduce the fourth model, results for the burning velocity are shown of the computations with these three models in Fig. (3.19).

The calculations with the EP and EB model show that the different choice for overall reaction does not lead to large differences in predicted burning velocities. For this reason, computations with the Bilger 4-step model are restricted to the standard explicit set of equations for the steady-state species only. The calculations with the IP model yield better results for the complete domain. Apparently, the application of the partial equilibria has a negative effect on the burning velocity. For lean flames all three reduced models perform equally well. However, the
difference between the reference calculation and the reduced models approaches 5cm/s an error which is almost as large as the value of \( S_i \) itself. Since it occurs in all three models (EP, EB and IP), this is an effect of the truncation procedure which, as mentioned earlier, might not be correct for lean flames. To investigate this further, the \( S_i^{\text{red}} \) for \( OH \) (see Fig. (3.7)), are presented again in Fig. (3.20), but now grouped per equivalence ratio. Although reactions 1 and 3 show the largest sensitivities for \( \varphi = 0.8 \) and \( \varphi = 1.0 \), this is clearly not the case for \( \varphi = 0.6 \). To gain insight on the meaning of the sensitivity coefficients, a short numerical study has been performed. For \( \varphi = 0.8 \) the burning velocity is recomputed, where the truncated expression Eq. (3.56) for \( OH \), is extended with one of the reactions \( r_2, r_4, r_9, r_{12} \) or \( r_{15} \). The results of these calculations are shown in the insert of Fig. (3.19). It shows that whenever \( S_i^{\text{red}} \) has a positive sign, the burning velocity decreases compared to the IP model if the particular reaction \( j \) is included in the truncated expression for the \( OH \)-radical (reactions 2 and 4). Therefore, to increase the burning velocity, reactions have to be added which show negative sensitivities, as is confirmed by the other computations (reactions 9, 12 and 15 in Fig. (3.19)).

The fourth (final) model, is based on the observations made with the sensitivity study. Since reaction 15 shows the largest negative sensitivity for all three equiva-
3.4. Systematic analysis.

fig. 3.20: The $S_{ij}^{0.6}$ coefficients for $i = OH$ and reactions $j$, grouped per equivalence ratio. The solid bars indicate the reactions that are included by the truncation procedure of Peters et al.

For both equivalence ratios, this reaction is included in Eq. (3.56). Explicitly, the resulting truncated expression for $OH$ now reads,

$$N = k_1^f[H][O_2] + k_2^j[H_2O][H]$$
$$D = k_1^f[O]+ k_2^j[H_2] + k_{15}([C]H_2O)$$
$$[OH] = N/D.$$ 

It may be expected that this model, indicated by Implicit-Somers (IS), increases the burning velocity over the complete range. The burning velocities with this model are presented in Fig. 3.19 by the solid markers ($\bullet$). Indeed the burning velocity increases over the whole range of equivalence ratios. Compared to the (untruncated) reference calculations, the extended expression gives almost identical velocities, which is a definite improvement of the Peters model for lean methane-air flames.

The performance of the four models, EP, EB, IP and IS for burner stabilized flames is studied as well. As for the adiabatic case results are compared with those for the untruncated 4-step model presented in the previous subsection. Again the burner stabilized data confirm the earlier mentioned conclusions (see Fig. (3.21)). For both equivalence ratios both the stand-off distance and the flame temperature is predicted better by the extended expression for $OH$ (IS). As for the adiabatic properties the differences between the results of the other 4-step models and the reference calculation become more pronounced for leaner flames. This might be expected since the relative difference in the burning velocity increases with decreasing stoichiometry. However, for burner-stabilized flames it may be argued that the explicit Peters (EP) performs better than the Bilger model; although for both
equivalence ratios the flame temperature is approximately the same, the stand-off distance is predicted better by the Peters model. This was not so clear from the adiabatic results.

The detailed structure is not studied for all truncated models. Since differences in stand-off distance are significant between the several models, differences in detailed structure will be large as well. To illustrate this the temperature profiles for all reduced models are plotted in Fig. (3.22). Indeed as might be expected from the results for the stand-off distances in Fig. 3.21 both implicit models IP and IS resemble the reference calculation (F4) the most. The Bilger model yields a larger stand-off distance, which is reproduced by the temperature profile as well. Temperature differences up to 100 K occur through the flame for this case, as can be seen in the insert in Fig. (3.22). Therefore, only the detailed structure for the extended OII model (IS) is presented (Figs. (3.23),(3.25)).
3.4. Systematic analysis.

fig. 3.22: The temperature profiles of the four truncated 4-step models. Only the first millimeter is plotted. The symbols are explained in the figure. A small region around \( x = 0.05 \, \text{cm} \) is enlarged in the insert in the right bottom corner. The solid line is the reference calculation (F4).

As was already suggested by the results for the global phenomena, the detailed structure of the flame is generally reproduced well. The major species profiles for the truncated model almost coincide with the untruncated 4-step model. Even the \( \text{H}_2-\text{O}_2 \) radicals are predicted well. Peak values for the \( \text{H}, \text{OH} \) and \( \text{O} \) profiles differ 2% at most. For \( \text{H}_2\text{O}_2 \) and \( \text{H}_2\text{O}_2 \) these differences are much larger, but that is clearly related to the cut-off procedure which is different in the untruncated 4-step model. In the IS model cut-off is applied differently. There, at temperatures below the cut-off temperature \( T_c \), the steady-state relations for \( \text{H}_2\text{O}_2 \) and \( \text{H}_2\text{O}_2 \) are simply replaced by the constant Peclet-Lewis solution of the convection-diffusion equation (Eq. (3.49)), whereas in the reference calculation at \( T_c \) the chemical source term is switched off gradually. The equation which determines both radicals becomes effectively a convection-diffusion equation (Eq. (3.52)). For the profiles of the \( \text{C}_1 \)-intermediates, larger discrepancies are found. Differences up to approximately 10% may occur. Apparently these do not have a large effect on the global flame characteristics.
fig. 3.23: Mole fraction profiles of the major species of burner stabilized methane-air flame ($\varphi = 1.0, \dot{m} = 0.0250\text{gcm}^{-2}\text{s}^{-1}$). The symbols (o) represent the calculations with the truncated 4-step model (18). $\text{H}_2$ is multiplied by 5. The solid lines indicate the 4-step reference results (F4).

fig. 3.24: Mole fraction profiles of the $\text{H}_2$-$\text{O}_2$ radicals of burner stabilized methane-air flame ($\varphi = 1.0, \dot{m} = 0.0250\text{gcm}^{-2}\text{s}^{-1}$). The symbols (o) represent the calculations with the truncated 4-step model (18). $\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}$ are multiplied by a factor 50. The solid lines indicate the 4-step reference results.
3.4. Systematic analysis.

fig. 3.25: Mole fraction profiles of the C_1 intermediates of burner stabilized methane-air flame ($\phi = 1.0, m = 0.0250 \text{g cm}^{-2} \text{s}^{-1}$). The symbols, explained in the figure, represent the results with the truncated 4-step model (1S). HCO and CH_3O are multiplied by 100. The solid lines indicate the 4-step reference results (F4).
3.5 Conclusions and Discussion

Two implementations of a first-order sensitivity analysis are presented, that can be used to deduce and analyze systematically reduced reaction schemes. The steady-state sensitivity is applied to the 4-step methane-air model of Peters et al. (Peters91) and confirms their choices for the steady-state species. Using the sensitivity analysis, a 5-step mechanism for lean methane air flames could be deduced which performs better for both adiabatic- and burner-stabilized flames. Furthermore, the sensitivities \( S_i^N \) can be used to simplify and rationalize the truncation procedure of the steady-state relations significantly. For instance the choices made by Peters et al. for the truncation of the different steady-state relations were identified by this analysis. Even more, the sensitivity analysis suggests a simple extension of the truncated expression for the reaction rates which improves the performance of the truncated 4-step model. Therefore, it may be concluded that sensitivity analysis can be used as a flexible tool to deduce and improve systematically reduced reaction mechanisms. Both aspects, the identification of the steady-state species and the truncation of the resulting algebraic expressions has been analyzed successfully.

From a numerical point of view, the use of reduced chemical models is justified only by the decrease of the computational effort. Since in most flame applications most of the CPU-time is needed to evaluate the Jacobian, this process is considered in more detail here. In an implementation of a reduced chemistry model, the dimension of the matrix equations (2.8) is reduced considerably. For an adiabatic flame problem, the 4-step model yields subblocks of dimension 10 in the Jacobian rather than 18 for the detailed chemistry model based on the skeletal mechanism\(^\text{20}\). Values for the ratio

\[
\frac{t_r}{t_d}
\]

of 0.46, 0.52 and 0.53 for testcases EP, IP and IS are found, respectively. Here \( t_r \) and \( t_d \) are the times to evaluate the Jacobian in the 4-step reduced and the detailed model simulations. Although there is a decrease in the evaluation times, the reduction is clearly not quadratic in the number of variables. This is related to the implementation of the reduced model. Still the rates of all the elementary reactions present in the basic detailed chemical scheme are calculated and the transport- and thermodynamical properties are formulated in terms of all species. Furthermore, since the steady-state species are evaluated prior to any calculation of the residual vector, the evaluation time \( t_f \) for one vector \( \tilde{\mathbf{r}} \) will only be marginally shorter than that for the detailed chemistry implementation. Therefore the amount of work to evaluate the Jacobian is proportional to \( (N^n + 2) \times t_f \), where \( N^n \) equals the number of non steady-state species. Since in the detailed computation the effort is proportional to \( (N + 2) \times t_f \), an implementation of a reduced model will lead only to a linear decrease in computation time, approximately equal to \( ((N^n + 2)/(N + 2)) \). 10/18 \( \approx \) 0.56, which indeed agrees with the above observation. The difference between the results of testcases EP and (IP,IS) originates from the application of the 'inner iteration' procedure applied in testcases IP and IS. Since EP uses explicit expressions, only one 'sweep' in the inner iteration loop is necessary to evaluate the

\(^{20}\)For a burner stabilized flame this becomes 9 and 17, respectively.
steady-state species accurately. For both IP and IS, the steady-state equations are processed several times to obtain a sufficiently accurate solution for the steady-state expressions. It is worth mentioning that the so-called 'Partial Explicit' approach proposed by Wang et al. [Wan93] will lead to a slightly larger decrease in CPU-time necessary to evaluate the Jacobian ($t_r/t_f$ was found to be 0.43).

From a computational point of view this reduction of work remains the main advantage of the reduced model. The reduction in CPU-time might be increased slightly if the evaluation of the elementary chemical reaction terms is tuned to the reduced chemical model. However, it should be noted that the relative increase of performance of the 4-step mechanism in the presented case, is the least one may expect, because the skeletal mechanism is approximately the smallest methane-air detailed mechanism which performs well. Therefore, for reduced models based on more extensive detailed mechanisms the relative reduction will increase, since the denominator $N$ in $(N^n + 2)/(N + 2)$ increases whilst $N^n$ remains the same, e.g. for the '1'-model presented in chapter 2, a theoretical reduction of $10/27 \approx 0.37$ will be obtained.
Chapter 4

Two-Dimensional Flat Flames with detailed chemistry

4.1 Introduction

The previous two chapters dealt with the simulation of perfectly one-dimensional flames, for which the differential equations can be simplified considerably. In this chapter the computational method introduced and discussed in section 2.3 will be extended to deal with two-dimensional flames. The study presented here deals with a relatively simple flow configuration, but is essentially two-dimensional. Therefore, it offers a convenient testcase for the development of a multi-dimensional extension to the numerical method developed in chapter 2.

The one-dimensional flame computations presented in chapters 2 and 3 describe an idealized experimental situation. A realization of this pseudo one-dimensional flame burner is used in our group (Fig. 2.1, p. 22) to determine the one-dimensional flame characteristics. The construction of this burner is such that it may be assumed that all variables are constant in each plane parallel to the burner (at least in a region near the burner axis). Variations in the unknowns only occur perpendicular to the burner surface and the reactive flow equations become one-dimensional (see section 2.1).

In this chapter, it will be investigated whether flames on such an experimental burner are flat on a small scale. According to a previous computational study [Bos93], performed with the two-dimensional flame method developed by de Lange [Lan92] which uses a one-step global reaction model, two different multi-dimensional effects may be observed:

- 'Global' effects and
- 'Local' effects.

These two possible multi-dimensional effects in the flat-flame burner are discussed first.

(*) The global effects are associated with the deviation from true one-dimensionality which occurs at the edges of the burner rim. Due to differences between the (hot) reacting gas and the (cold) environment, the gas-flow will expand. The streamlines
Fig. 4.1: Top view of the burner head (left). The so-called 30° elementary structure is presented in the right figure, the diameter d of the drilled holes, the pitch p of the holes and the thickness h of the burner plate are indicated in the figures.

diverge and the flow, temperature and concentration will not be perfectly constant in planes parallel to the burner plate.

(*) The local effects occur due to the construction of the burner plate. The perforation of the burner plate forms a regular pattern of small drilled holes, see Fig. (4.1). Formally, this perforated plate may be viewed upon as an ensemble of tiny premixed Bunsen-like burners of diameter d ordered in a regular honeycomb structure with pitch p. Obviously, when the diameter and/or pitch of these elementary Bunsen burners increases, the importance of the local multi-dimensional behavior on the flat-flame will increase as well.

The two-dimensional method will be tested on the effect of the local disturbances on the one-dimensional profiles. Due to symmetry considerations, the local effects may be studied with a computational domain describing only a small part of the burner. For the simulation of the global effects a representative piece of the complete burner head and the surroundings would have to be modelled. Compared to a representative domain necessary for a study of the local effects, a much larger computational area would have to be taken. Therefore, a study of the local effects appears to be a good test case for the new method.

In principle, the local effect can be neglected only when both the diameter and pitch are chosen infinitely small, which is a theoretical limit. For the perforated-plate burners used in our group the diameter of the burner head is approximately 5 cm, and values $d = 0.5\, \text{mm}$, $p = 0.7\, \text{mm}$ and $d = 0.4\, \text{mm}$, $p = 0.6\, \text{mm}$ for the perforations are used. The study presented by Bosch et al. [Bos93], is performed with a one-step global reaction model. In this chapter this study will be extended to a detailed chemical model and results will be compared with the results of the one-step model. In section 4.2 the two-dimensional model used to study the local effects will be presented and the appropriate equations and boundary conditions are introduced. In section 4.3 the discretization of the differential equations and boundary conditions are given and the method employed to solve the resulting
set of non-linear equations is discussed. Finally, in section 4.4, the results of the simulations will be presented and discussed.
4.2 Definition of the two-dimensional model.

The computation of the local effects would involve a three-dimensional simulation which is not yet feasible. Therefore a two-dimensional model will be introduced which is believed to give a good indication of the local effects which are supposed to play a role in the experimental burner setup.

The definition of the two-dimensional model consists of three parts:

- the two-dimensional burner model
- the governing equations
- the boundary conditions.

These will be treated in that order in the following three sub-sections.

4.2.1 A Two-dimensional Burner Model.

Formally, the burner may be represented schematically as in Fig. (4.1). If the burner would have an infinite radius (so that global effects are unimportant), the 30°-element presented in Fig. (4.1) with symmetry boundary conditions on all sides would be an appropriate representation. Because this elementary structure is three-dimensional, it cannot be simulated with the methods developed by de Lange [Lan92]. Furthermore, it would be too CPU-intensive to incorporate detailed chemical models in multi-dimensional flame simulations. Therefore, a two-dimensional approximation is introduced which is believed to give a good indication of the effect of the local disturbances on the pseudo one-dimensional behavior of the experimental burner at relatively small computational cost. The model used is composed of an array of parallel micro-slits, presented schematically in Fig. (4.2). Note that the parameters \( d \) and \( p \) for the two-dimensional model are different from the diameter \( d \) and pitch \( p \) introduced in Fig. (4.1). The ratio \( d/p \), however, gives the porosity of the burner plate for both cases and the average mass flow rate in every micro-slit is therefore equal to the mass flow rate in the corresponding three dimensional micro burner. It may be expected that the qualitative results obtained with the two-dimensional model are valid for the experimental burners. However, quantitatively, small differences are to be expected.

4.2.2 Equations for Two-dimensional Flow.

In one-dimensional flame simulations the equations for conservation of enthalpy and species together with the equation of state, are sufficient to determine the flame structure completely. This is related to the combustion approximation, implying iso-baric circumstances (see section 2.1), which for one-dimensional flow systems leads to a constant pressure field \( p(x) = p_0 \). For multi-dimensional flows the Navier-Stokes equations have to be considered as well. De Lange has shown that for the simulation of stationary two-dimensional reactive flows on unstructured grids, it is preferable to cast the flow equations in a stream function \( (\psi) \)/vorticity \( (\Omega) \) formulation [Lan92]. This method avoids the use of staggered grid structures, since
4.2. Definition of the two-dimensional model.

![Diagram of two-dimensional burner model]

fig. 4.2: Schematic view of the two-dimensional burner model. A cross-section is presented in the right figure. The elementary micro-slit burner (see also Fig. 4.3), for which the reactive flow will be computed, is given in the small box.

The pressure is eliminated from the equations. The vorticity vector is introduced as the curl of the velocity vector

$$\mathbf{\omega} = \nabla \times \mathbf{u}, \quad (4.1)$$

which in two-dimensional flows reduces to a scalar property since only the $z$-component of $\omega = (\omega_x, \omega_y, \omega_z)$ is different from zero. Therefore, from now on the $z$-subscript will be dropped and with $\omega$ we refer to $\omega_z$. The stationary equation for $\omega$ takes the form of a convection-diffusion equation

$$\rho \mathbf{u} \cdot \nabla \omega - \nabla \cdot \eta \nabla \omega = S_\omega \quad (4.2)$$

as shown in [Smo89, Lan92]. The source term $S_\omega$ is given by

$$S_\omega = \frac{\partial \rho}{\partial y} \frac{\partial \zeta}{\partial x} + \frac{\partial \rho}{\partial x} \frac{\partial \zeta}{\partial y}$$

$$- \left[ \frac{\partial^2 \eta}{\partial x \partial y} \left( \frac{\partial \psi}{\partial y} + \frac{\partial \psi}{\partial x} \right) + \frac{\partial \eta}{\partial y} \left( \frac{\partial \omega}{\partial y} + 2 \nabla^2 \eta \right) \right]$$

$$+ \frac{\partial \eta}{\partial x} \left( \frac{\partial \omega}{\partial x} - 2 \nabla^2 \eta \right) - \left[ \frac{\partial^2 \eta}{\partial x^2} + \frac{\partial^2 \eta}{\partial y^2} \right] \left( \frac{\partial \omega}{\partial y} + \frac{\partial \omega}{\partial x} \right), \quad (4.3)$$

where $\nabla^2 = \nabla \cdot \nabla$ is used and $\zeta$ is introduced according to

$$\zeta = \frac{u^2 + v^2}{2}.$$

It should be noted that the terms on the second- and third line of Eq. (4.3) do not appear for the case that the viscosity $\eta$ is constant.

The stream function ($\psi$) is defined in such a way,

$$\frac{\partial \psi}{\partial y} \equiv \rho u \quad \text{and} \quad -\frac{\partial \psi}{\partial x} \equiv \rho v, \quad (4.4)$$
that the stationary continuity equation is satisfied automatically

$$\frac{\partial \rho u}{\partial x} + \frac{\partial \rho v}{\partial y} = 0.$$  \hspace{1cm} (4.1)

The stream function may be calculated from a Poisson-like equation if the definition of \( \omega = \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} \) (Eq. (4.1)) is used to give

$$\frac{\partial}{\partial x} \left( \frac{\partial \psi}{\partial x} \right) + \frac{\partial}{\partial y} \left( \frac{\partial \psi}{\partial y} \right) = -\omega.$$  \hspace{1cm} (4.5)

which reduces to a true Poisson equation in case of incompressible flows. It should be stressed that the \( (\psi, \omega) \) formulation introduced here only applies for the simulation of stationary two-dimensional phenomena. The stream function is defined such that \( \vec{V} \cdot \vec{\rho} = 0 \) is valid locally, which is not true in unsteady flows.

For stationary reactive flows the set of differential equations is completed by the conservation of enthalpy and species which read

$$\rho c_p \vec{V} \cdot \vec{\nabla} T - \vec{V} \cdot \lambda \vec{\nabla} T = \sum_{i=1}^{N} h_i \dot{\rho}_i - \sum_{i=1}^{N} \rho Y_i c_{pi} \dot{V}_i \cdot \vec{\nabla} T$$  \hspace{1cm} (4.6)

and

$$\rho \vec{V} \cdot \vec{\nabla} Y_i - \vec{V} \cdot (\rho D_{i0} \vec{\nabla} Y_i) = \dot{\rho}_i,$$  \hspace{1cm} (4.7)

respectively. The equation of state

$$\rho = nRT,$$  \hspace{1cm} (4.8)

together with the definitions (see section 1.2) of the transport \( (\lambda', D_{i0}, \text{and } \eta) \) and thermodynamic properties \( (c_p \text{ and } h_i) \) close the set of equations. As in chapter 2 and 3, the second term on the right-hand side of the enthalpy equation (Eq. (4.6)), which involves the species diffusive fluxes \( \dot{V}_i \), will not be included here. As mentioned in chapter 2, effects of this term may be expected to be small due the cancellation of the diffusive fluxes.

### 4.2.3 The Boundary Conditions

The mathematical description of the model is completed with the appropriate boundary conditions. For a straightforward implementation of model for the elementary micro-slit burner (see Fig. (4.2)) a uniform flow field at some distance below the burner plate would represent the experimental situation. However, Bosch has shown that for all simulations to be presented here, the computational domain can be reduced further. For the flow velocities and the Reynolds numbers of interest for the present configuration, a Poiseuille-flow develops in the micro-slit before the flow leaves the burner. Consequently, the uniform flow below the burner plate may be transferred to a parabolic velocity profile imposed at a position in the slit \( y = L_0 \).
4.2. Definition of the two-dimensional model.

In Fig. (4.3)). Effectively, the experimental situation is mapped to the area specified by

\[(x, y) \in [(0, 0), (\frac{1}{2}l, l)]\]

where \( \mu \) is the specified width (pitch) and \( L \) the specified length of the computational domain.

Boundary conditions have to be specified on all four boundaries present in the computational set-up, being, (see Fig. (4.3)):

- Inlet: (I)
- Symmetry: (II) and (II')
- Walls: (III) and (III')
- Outlet: (IV)

The boundary conditions are specified for all primitive variables \( (u, v, T, Y_i) \), in the following. The implementation of the boundary conditions for \( (w, \psi) \) will be treated in section 4.3 where the discretization method is presented (section 4.3.1).

The boundary condition at the inlet (I) is given by a homogeneous isothermal stoichiometric mixture of methane and air with a parabolic velocity profile. The velocity at \( (x, y) = (0, 0) \), from now on referred to as the center velocity \( v_c \), is determined completely by the specified uniform velocity \( v_{\infty} \) at \( y = -\infty \), and the overall conservation of mass. This leads to the boundary conditions

\[
Y_i(x, 0) = Y_i^{\infty}
\]
\[
T(x, 0) = T^{\infty}
\]
\[
u(x, 0) = 0.0 \text{, } v(x, 0) = v_c(1 - \left(\frac{2x}{d}\right)^2)
\]

for \( x \in [0, \frac{1}{2}d] \) and where \( v_c = \frac{3}{2}p_{\infty}v_{\infty}/d \). Note that in the definition of \( v(x, 0) \) it is assumed implicitly that a no-slip boundary condition applies for the burner-wall (III).

For the planes of symmetry (II and II') it is specified that the normal velocity (here \( u \)) and the normal derivative of the tangential velocity (here \( \partial v/\partial x \)) is zero. For all scalar variables \( (Y_i, T \text{ and } \rho) \) the derivative normal to the plane of symmetry is zero. For the specified geometry this gives for \( y \in [0, L] \) (II):

\[
\frac{\partial Y_i}{\partial x}(0, y) = 0
\]
\[
\frac{\partial T}{\partial x}(0, y) = 0
\]
\[
u(0, y) = 0 \text{, } \frac{\partial v}{\partial x}(0, y) = 0.
\]

(4.10)

Similar for \( y \in [L, 0, L] \) (II'):

\[
\frac{\partial Y_i}{\partial x}(\frac{1}{2}l, y) = 0
\]
Chapter 4. Two-Dimensional Flat Flames

fig. 4.3: Definition of the computational setup. The solid area is the brass-plate. The computational domain is bounded by the inlet at \( y = 0 \) (I), two symmetry planes (II) at \( x = 0 \) and (II') at \( x = \frac{1}{2}d \) (dash-dotted lines), two walls (III),(III') at \( x = \frac{1}{2}d \) and \( y = L_0 \) respectively, and an outflow boundary (IV) at \( x = L_0 \). The effective computational domain is illustrated by the hatched area.
4.2. Definition of the two-dimensional model.

\[
\frac{\partial T}{\partial x} \left( \frac{1}{2} p, y \right) = 0
\]

\[
u\left( \frac{1}{2} p, y \right) = 0.0; \quad \frac{\partial v}{\partial x} \left( \frac{1}{2} p, y \right) = 0
\]

(4.11)

The walls (III and III') are assumed to be impermeable and chemically inert\(^1\). Furthermore a no-slip velocity boundary condition is assumed. A consequence of the impermeability boundary condition is that the total flux of a species perpendicular to the wall \((\mathbf{r}_i \cdot \mathbf{\hat{n}})\) is equal to zero. Within the Fickian approximation of the diffusive fluxes this yields for (III) (for a wall along the \(y\)-axis)

\[
\epsilon_x = \rho u Y_i - \rho D_{im} \frac{\partial Y_i}{\partial x} = 0
\]

which together with \(u = 0\) leads to the observation that of all species the derivative perpendicular to a wall equals zero. With respect to the enthalpy boundary condition, it is assumed that the brass-plate is a perfect conductor at temperature \(T_w = T_{\infty得起} and the capacity of the cooling system of the burner head is large enough to carry off all the heat conducted to the burner. Effectively, this implies that the temperature at the burner can be taken constant. Summarizing the boundary conditions for (III) \(x = \frac{1}{2} d, y \in [0, L_0]\) yields:

\[
\frac{\partial Y_i}{\partial x} \left( \frac{1}{2} d, y \right) = 0
\]

\[
T \left( \frac{1}{2} d, y \right) = T_w
\]

\[
v \left( \frac{1}{2} d, y \right) = 0; \quad v \left( \frac{1}{2} d, y \right) = 0
\]

(4.12)

and for (III') \(y = L_0, x \in \left[ \frac{1}{2} d, \frac{1}{2} p \right]\) similarly:

\[
\frac{\partial Y_i}{\partial y} \left( x, L_0 \right) = 0
\]

\[
T \left( x, L_0 \right) = T_w
\]

\[
u \left( x, L_0 \right) = 0; \quad v \left( x, L_0 \right) = 0
\]

(4.13)

may be found.

Finally, the outflow has to specified. It is presumed that the outflow boundary is placed far enough downstream (values for \(L\) should be large enough) so that the flow has become uniform, meaning that the tangential velocity is zero and the normal derivatives of all scalar variables and normal velocity component with respect to \(x\)- and \(y\)-direction of the outflow vanish:

\[
\frac{\partial Y_i}{\partial y} \left( x, L \right) = 0
\]

\[
\frac{\partial T}{\partial y} \left( x, L \right) = 0
\]

\[
\frac{\partial v}{\partial y} \left( x, L \right) = 0; \quad v \left( x, L \right) = 0
\]

(4.14)

\(^1\)This means that it is assumed that the burner material does not have any chemical activity.
for $y = l$, $x \in [0, \frac{1}{2}p]$ (IV). Note that it should be checked afterwards whether variations in the presumed value for $l$ do not affect the solution.

It is worth mentioning that the number of equations $N$ to be solved is determined mainly by the chemical model which is used. Here the skeletal mechanism (section 2.2, p. 31) is used, which consists of 15 species. This implies that the number of differential equations $N = 15 + 2 + 1 (Y_i, \psi, \omega$ and $T$ respectively) to be solved is only marginally larger than for the one-dimensional case, where $N = 15 + 1 (Y_i$ and $T$). However, due to the two-dimensionality, the structure of the Jacobian equations are altered and the algorithm presented in section 2.3 should be adapted to handle the multi-dimensional effects. Together with the discretization method this is presented in the following section.
4.3 Numerical method

Like for the simulation of the one-dimensional flame in chapter 2, a set of basic steps has to be made before computations of the two-dimensional flame characteristics are possible. Although not completely independent, they are thought of as the following three steps:

- Discretization of the differential equations
- A mesh generation technique
- Solution procedure for the discrete set of equations.

In this section all three aspects are treated. First, the discretization of the differential equations is introduced and the implementation of the boundary conditions is presented in section 4.3.1. Then, in section 4.3.2, the gridding strategy is given. Like in one-dimensional simulations, the expected large gradients and curvature of at least some of the variables require an adaptive grid strategy in order to keep the total number of mesh-points within reasonable bounds. The special features of the local grid refinement technique [Lan92] employed here, are presented and discussed. Finally, in section 4.3.3 the approach used to solve the resulting coupled set of discretized differential equations is given.

4.3.1 Discretization

The computational mesh, considered given for the time being, consists of a number of non-overlapping control volumes. Principally, the conversion of the mathematical model to a discrete set of equations consists of two tasks, viz.

- the discretization of the differential equations
- the discretization of the boundary conditions.

Discretization of the differential equations

Let \( P \) be a point of the mesh and let \( W, E, N \) and \( S \) be its western, eastern, northern and southern neighbors, respectively according to the definition in Fig. (4.4). The control volume interfaces, denoted with \( w, e, n \) and \( s \) in the figure, are located midway between the grid points according to the proposition of Thiart[Thi90A]. Furthermore, all variables are specified at the mesh-points.

In section 4.2, two different types of differential equations were introduced, i.e. a convection-diffusion equation for most variables \( (\omega, T, Y_i) \) and a Poisson-like equation for the stream function \( (\psi) \). First, the discretization of the convection-diffusion equations is presented. The equation for \( \psi \) is treated subsequently.

In a generalized form a convection-diffusion equation reads

\[
\mu \cdot \nabla Y - \nabla \cdot (\Lambda \nabla Y) = S
\]

(4.15)

where representations of the coefficients \( \mu = (\mu_T, \mu_Y) \), \( \Lambda \) and \( S \) depend on the variable considered.
Chapter 4. Two-Dimensional Flat Flames

![Diagram of a two-dimensional flow configuration](image)

Fig. 4.4: The control volume (shaded) in a two-dimensional flow configuration. P is the center point and W, E, N and S its nearest neighbors in the mesh. The boundaries (interfaces) of the shaded volume (w, e, n and s) are located exactly midway between the grid points. The surface of the shaded area equals $\Delta x \Delta y$ where $\Delta x = x_w - x_p$ and $\Delta y = y_n - y_p$.

A derivation of the discretization, as was done for the one-dimensional convection-diffusion equation ([Thi90A], see section 2.3), is for the multi-dimensional case not possible. A general analytical solution for Eq. (4.15) with constant $\bar{\mu}$, $A$ and $S$ does not exist for the two-dimensional control volume. The extension of the Thiagarajan scheme to two dimensions without source weighing is not straightforward [Thi90A, Thi90B]. Therefore, the one-dimensional scheme is applied to both directions separately and the contributions are added thus yielding

$$-a_P \chi_W + b_P \chi_P - c_P \chi_N - d_P \chi_S - e_P \chi_S = S_P \Delta x \Delta y$$

(4.16)

where $\Delta x = (x_s - x_w)/2$ and $\Delta y = (y_N - y_S)/2$ and $\Delta x \Delta y$ equals the area of the control volume. The coefficients are equal to [Thi90A]

$$a_P = \frac{A_w \Delta y}{\Delta w} \Lambda(-P_W), \quad b_P = \frac{\mu_s \Delta w}{A_w}$$

$$c_P = \frac{A_s \Delta y}{\Delta s} \Lambda(P_N), \quad d_P = \frac{\mu_s \Delta s}{A_s}$$

$$e_P = \frac{A_s \Delta y}{\Delta s} \Lambda(P_S), \quad e_P = \frac{\mu_s \Delta s}{A_s}$$
4.3. Numerical Method

\[ d_P = \frac{A_x \Delta x}{\Delta S} \Lambda (-P_S), \quad P_S = \frac{\mu_x \Delta S}{A_x} \]
\[ e_P = \frac{A_n \Delta x}{\Delta N} \Lambda (P_N), \quad P_N = \frac{\mu_n \Delta N}{A_n} \]
\[ b_P = a_P + c_P + d_P + e_P \quad (4.17) \]

and \( S_P \) is the source term evaluated at \( P \). Definitions of \( \Delta_w, \delta_{w,e,n,s} \) and \( \delta_{w,e,n,s} \) are presented in Fig. (4.4). The function \( \Lambda (P) \) is defined by Eq. (2.22). Properties like \( \mu \) and \( \Lambda \) are evaluated at the appropriate interface, where similar to the one-dimensional case some freedom of choice is present. Unless mentioned otherwise, for all variables obeying a convection-diffusion equation, \( \mu_{e,w} \) is taken equal to \( \mu_e(X_e, Y_e) \) and \( \mu_{n,s} \) is taken equal to \( \mu_n(X_n, Y_n) \). The composition dependent transport properties \( \Lambda_{e,w,n,s} \) are evaluated using linearly interpolated values of \( X \) and \( T \) at the interfaces.

The stream function obeys a Poisson-like equation, for which a second-order accurate (if \( \Delta x \) and \( \Delta y \) are constant) finite-difference expression may be used yielding [Lan92]

\[ \frac{1}{\Delta x^2}(\psi_E - \psi_P) - \frac{1}{\Delta y^2}(\psi_P - \psi_W) + \frac{1}{\Delta x^2}(\psi_S - \psi_P) - \frac{1}{\Delta y^2}(\psi_P - \psi_N) = -\omega_P. \]

If represented in the formulation adopted for the convection-diffusion equation (Eq. (4.16)), the coefficients \( a_P, \ldots, e_P \) would read

\[ a_P = \frac{\Delta y}{\Delta x \rho_N} \]
\[ c_P = \frac{\Delta y}{\Delta y \rho_N} \]
\[ d_P = \frac{\Delta x}{\Delta y \rho_N} \]
\[ e_P = \frac{\Delta x}{\Delta y \rho_N} \]
\[ b_P = a_P + c_P + d_P + e_P \quad (4.18) \]

and the source term is equal to

\[ S_P = \omega_P \Delta x \Delta y. \quad (4.19) \]

Note that, in the limit for \( \mu_{x,y} \to 0 \) and thus \( P_{e,w,n,s} \to 0 \), the coefficients in Eq. (4.18) and Eq. (4.19) are precisely equal to the presented discretization of the convection-diffusion equation\(^2\) on meshes with constant \( \Delta x \) and \( \Delta y \). This is of course true in exact arithmetic only, since in the implementation of the function \( \Lambda (P) \), due to numerical round-off, a division by zero occurs. However, this can be avoided if the power-law scheme

\[ A^* (P) = \max(0, 1 - \frac{1}{10} P^5) + \max(0, \cdots P) \]

\(^2\)Note that \( A(P \to 0) = 1 \)
[Pat89] is used to approximate \( A(P) \). Then the limit \( A(0) \) is numerically well-defined and gives the right value. Furthermore, it can be shown that the first-order accurate finite-difference approximation for \( \Delta x \) and \( \Delta y \) not constant should give the expression obtained with Eq. (4.17) for \( P - 0 \). For this reason the discretization presented by Eq. (4.17) is used for all differential equations in the method developed to simulate two-dimensional reactive flows.

**Discretization of the boundary conditions**

Here, the discretization of the \( \psi \) and \( \omega \) boundary conditions according to de Lange [Lan92] are stated explicitly for the four types of boundaries involved. The other (primitive) variables \( Y \) and \( T \) only involve Dirichlet or Neumann boundary conditions for which the discretization is straightforward. In section 4.2 the boundary conditions are presented in terms of primitive variables. These need to be converted to the \( \omega \) and \( \psi \) variables, using their definitions. For the determination of the stream function, an analytical approach is used

\[
\psi(x, y) = -\int_{y_1}^{y} \rho v dy' + \psi(x_1, y)
\]

and similarly

\[
\psi(x, y) = \int_{x_1}^{x} \rho w dx' + \psi(x, y_1)
\]

for all boundaries in \( x \)-direction with \( y = y_c \) and \( y \)-direction with \( x = x_c \), respectively.

- **Walls**

On the walls (III) and (III') both velocity components are zero (no-slip). According to its definition, the stream function may be obtained by the integration of the normal velocity distribution along the boundary. Since both velocities are zero on the walls, the boundary conditions for the stream function become effectively Dirichlet boundary conditions.

For the vorticity de Lange uses the approach of Dennis et al. [Den79], which is based on the second-order finite-difference discretization of Eq. (4.2) in a so-called half-way point \( X \) between \( P \) at the wall and \( P' \) perpendicular to the wall \( P - W \) (III) and \( P' = N \) (III'), see Fig. (4.5). Using \( \omega_X = (\omega_P + \omega_{P'})/2 \) on an equidistant grid, the boundary condition for a wall point \( P \) on (III) now yields

\[
\omega_P = -\omega_{P'} + 2 \frac{\nu_P - \nu_{P'}}{x_P - x_{P'}} - \frac{u_N - u_S}{y_N - y_S} - \frac{u_{N'} - u_{S'}}{y_{N'} - y_{S'}}
\]

\[
\psi_P = \psi_{111}
\]

where \( N' \) and \( S' \) are the northern and southern neighbors of \( P' \). Similarly for (III') the boundary conditions may be found to yield

\[
\omega_P = -\omega_{P'} + \frac{\nu_P - \nu_W}{x_P - x_W} + \frac{\nu_{P'} - \nu_{W'}}{x_{P'} - x_{W'}} - 2 \frac{\nu_P - \nu_{P'}}{y_{P'} - y_{P'}}
\]

\[
\psi_P = \psi_{111'}
\]
1.3. Numerical Method

![Diagram showing discretization points for vorticity on a wall.]

**fig. 4.5: The discretization points for the vorticity on a wall.**

Note that the constant $C_{II}$ is not specified and may be chosen freely, since only derivatives of $\psi$ are involved in the formulation.

- **Symmetry**
  The vorticity boundary condition along a symmetry line is trivial. For both symmetry boundaries the $u$-velocity and $\partial v/\partial z$ are zero by definition. Substituting this in the definition of the vorticity leads to the observation that $\omega = 0$ for (II) and (II').

The discretization of symmetry boundary conditions for the stream function is obtained from the analytical integration of the normal velocity distribution along the plane of symmetry. Since, the normal velocity is zero, again a constant Dirichlet boundary condition can be imposed on both symmetry lines. However, now the value for this constant may no longer be taken arbitrarily since this degree of freedom is already used to define $C_{III}$ on the walls (Eqs. (4.20, 4.21)). To obtain $C_{II}$, the mass-flow in $y$-direction $\rho v$ must be integrated along the inlet. In the reduced computational domain this would lead to the integration of the parabolic profile. However, according to mass conservation we already know what the outcome of this integration must be, namely $-p/2 \rho \infty v'\infty + \psi(1/2, 0)$. Since $\psi(1/2, 0) = C_{III}$, for $C_{II} = -p/2 \rho \infty 0'\infty + C_{III}$ is found. The freedom of choice is now used to take $C_{III} = C_{III}' = p/2 \rho \infty 0'\infty$ thus leading to $C_{II} = 0$ which is implemented in the two-dimensional simulations. At the other symmetry boundary, $C_{II}' = C_{III} = p/2 \rho \infty 0'\infty$ can be found.

Summarized the discretization for the boundary conditions along the symmetry
lines are given by,

\[ \omega = 0 \]
\[ \psi = C_{II} \]

and

\[ \omega = 0 \]
\[ \psi = C_{II'} \]

for (II) and (II'), respectively.

- **Outflow**
  At the outflow boundary it is presumed that the flow variables have attained a value independent of \( y \) and are one-dimensional, which implies that the derivatives of the \( u \)- and \( v \)-velocity in both directions are zero, thus leading to a zero vorticity as well. For the stream function again two choices are possible. The analytical integration of \( \rho u(-c) \) along the outflow boundary, will lead to a linearly increasing function\(^3\) of \( z \). However, currently we employ for the stream function \( \partial^2 \psi/\partial y^2 = 0 \), which may be derived using \( \partial \rho u/\partial y = 0 \). The second-order derivative is discretized using a second-order one-sided finite difference scheme.

- **Inflow**
  To complete the definition of the computational set-up, the boundary conditions at the inflow have to be discretized. For the vorticity the definition of the vorticity at the point halfway between point \( P \) and its nearest perpendicular neighbor, here \( N \), is used once more.

The stream function is again specified with the analytical integration of \( \rho u \) along the \( x \)-axis, from \( x = 0 \) to \( x = \frac{1}{2} d \). Using the specified parabolic velocity profile at the inlet this yields a third order polynomial dependence on \( x \),

\[ \psi(x, L) = C_{III} + \rho^{-\infty} u x \left( 1 - \frac{1}{3} \left( \frac{x}{\frac{1}{2}d} \right)^2 \right) \]

which gives the proper values for \( \psi(0, L) \) and \( \psi(\frac{1}{2}d, L) \) as can be verified easily. All boundary conditions have been specified now.

### 4.3.2 Mesh generation technique in two-dimensional reactive flows.

The adaptive gridding strategy developed by de Lange is presented here. As for the one-dimensional flame, it may be expected that large variations exist in first and second derivatives of the variables in the computational domain. A simple but costly measure would be to reduce the grid spacing uniformly over the complete domain. Clearly, for realistic burner geometries (\( O(1cm) \)) this is not a feasible way to proceed. Especially when detailed chemical models are used, phenomena occur which need

\(^3\) Equal to \( C_{II} + (C_{II'} - C_{III})(\frac{y}{y_2}) \), with \( C_{II} \) and \( C_{II'} \) introduced earlier.
grid spacings of the order $O(0.1 mm)$. If equidistantly distributed, this leads to a number of grid points equal to $100 \times 100$. Anticipating the Newton strategy used to solve the stiff differential equations, the memory requirements become large since per grid point at least $N \times N$ reals have to be stored (see section 2.3). Furthermore, the evaluation of all the elements in the Jacobian matrix, which often is performed by numerical differentiation, will become a very time consuming process.

Therefore, some kind of adaptive gridding has to be used to keep the number of grid points and therewith the CPU time and computer storage requirements within reasonable bounds. In the two-dimensional method developed by de Lange a static local refinement method is implemented [Lan92], which is used in the simulations presented here as well. This method starts with a fixed coarse mesh and a converged (or initially guessed) solution on this mesh. Additional points are added where some controlling function, depending on the solution, exhibits large values. This procedure is performed in such a way that always a five-point discretization molecule is added to the current level of the mesh, see Fig. (4.6). Or equivalently, any rectangular region between four points for which a refinement would be necessary is subdivided in four equally large rectangles. This added level of refinement to the coarse mesh will be referred to as the first refinement layer. The procedure may be repeated for the first layer to give a second layer, etc. and a kind of hierarchy arises. On this multi-layered mesh the solution procedure is restarted until some convergence is reached. If possible, grid points, which have become superfluous during the computation process, are removed. If the controlling function indicates no further refinement is necessary, apparently the solution is sufficiently resolved.

As might be clear from Fig. (4.6), three kinds of mesh points can be identified in this local grid refinement strategy. Following the nomenclature introduced by de Lange [Lan92] these will be referred to as 'boundary'-, 'live'- and 'interpolation'- points. Boundary points are such points of the mesh where the boundary conditions are imposed. The relation for each variable at these points is treated in the previous subsection. Live points are those points for which a control volume defined in Fig. (4.4) can be assigned. The discretization of the differential equations for these points is already given. However, due to the special refinement technique, such a control volume cannot be found for some points. One of the neighbors of these points is not available on the same level. To determine a relation for each variable on these points some kind of interpolation has to be introduced. Therefore, these are referred to as 'interpolation' points ($\star$).

The treatment of these interpolation points as given by the Lange for variables $\mathcal{Y} = (\mathcal{Y}_s, \mathcal{T}, \omega)$ has appeared to give good results. The interpolation depends on the orientation, which for points where either the western or eastern neighbor is 'missing' is given by

$$\mathcal{Y}_p = -\frac{1}{2} \mathcal{Y}_{\phi} + \mathcal{Y}_{p'} - \frac{1}{2} \mathcal{Y}_{\omega} + \frac{1}{2} \mathcal{Y}_{\omega} + \frac{1}{2} \mathcal{Y}_S$$

(4.24)

where $\mathcal{Y}_{\phi}$ is the eastern or western neighbor, respectively. $\mathcal{Y}_{\phi}$ and $\mathcal{Y}_{\omega}$ is a short notation for the southern and northern neighbor of $p'$ (see Fig. (4.6)). As can be

---

4 Recall that concentration profiles of $C_1$ intermediates have typical widths of the order of $0.2$ mm. If this is resolved properly, with say 10 grid points to capture the first and second derivatives, this in fact leads to grid spacings which are even an order of magnitude smaller.
verified, this relation states that the second-order discretized second derivative of \( y \) with respect to \( y \) in \( P \) is equal to the one in \( P'' \). For the case where a southern or northern neighbor is not available, a similar expression is used.

The stream function is treated somewhat differently. Effectively the differential equation (4.5) is used still. However, for the case where the western (or eastern) neighbor is not available, variations in the \( x \) (i.e. East - West) direction are not taken into account, yielding

\[
\frac{1}{\rho u}(\psi_N - \psi_P) - \frac{1}{\rho u}(\psi_P - \psi_S) = -\omega_P. \tag{4.25}
\]

Similarly in the opposite direction

\[
\frac{1}{\rho w}(\psi_W - \psi_P) - \frac{1}{\rho w}(\psi_P - \psi_N) = -\omega_P. \tag{4.26}
\]

is used. Crucial in this definition is that \( \omega_P \), in both previous expressions, depends on the orientation as well. Analogously, variations in the perpendicular direction
are not taken into account. Therefore, for the West-East orientation this leads to
\[ \omega_{i} = -\frac{u_N - u_S}{2\Delta y} \]
and for the North-South orientation
\[ \omega_{i} = \frac{v_E - v_W}{2\Delta x} \]
respectively, with \( \Delta x \) and \( \Delta y \) introduced in the previous subsection. It should be noted that the expressions, presented here, are identical to the ones used by de Lange.

This kind of local grid refinement strategy has important consequences for the data organization. In structured (tensor-product) meshes a numbering method can be used which implicitly localizes the \((E,W,N,S)\) neighbors. Here, due to the unstructured grids, special measures have to be taken to keep track of all neighbors. Therefore, for all points, pointers to the nearest \((E,W,N,S)\) neighbors are stored. Furthermore, for structured grids only two types of points are found, here referred to as 'boundary' and 'live' points. In the meshes used here, for points at boundaries of refinement layers it is not always possible to define a control volume according to the one defined in Fig. (4.4). As mentioned in the treatment of these 'interpolation' points, these must be distinguished explicitly since other coupling relations are used. Therefore, the type of mesh point has to be stored as well. Furthermore, the orientation (perpendicular to \( x \) or \( y \)) of the interpolation points and boundary points determines which coupling relation should be used and has to be known as well.

Summarizing, this leads to a data management structure where four (integer) arrays are needed to store the pointers to all four neighbors, one array to determine the type of point and one array to determine the orientation of a boundary or interpolation point. However, this extra storage requirement is marginal compared to storage required by the Newton method.

4.3.3 Solution Procedure

Like in the one-dimensional flame simulations a Newton strategy is applied to deal with the intrinsic stiffness of the discretized equations. For structured grids the extension to multi-dimensional flows is straightforward. Using a mesh numbering scheme according to \((x, y) \leftrightarrow (k, l)\), the residual of all variables may be introduced yielding
\[
\begin{align*}
    r_{ikl} &= \varepsilon_{ikl} + a_{ikl}Y_{i(k-1)l} - b_{ikl}Y_{i(k-1)l} + c_{ikl}Y_{i(k+1)l} \\
    &\quad + d_{ikl}Y_{i(k-1)l} + e_{ikl}Y_{i(k+1)l} \\
    &\quad + \Delta x \frac{1}{2}\sum_{p}F_p \Delta y (k) \Delta x (l) \Delta y (k), \quad k = 1(1)K_x, \quad l = 1(1)K_y.
\end{align*}
\]  

Here \( i \) corresponds to a variable and \( K_x \) and \( K_y \) are the number of grid points in \( x \)- and \( y \)-direction, respectively. Note that \( \Delta x \) and \( \Delta y \) do not need to be constant\(^\text{a}\)

\(^{a}\)Non-rectangular boundaries are not considered.
or equally large. Eq. (4.28) may be rewritten if an appropriate (slab by slab) grid numbering scheme is introduced, e.g.,

\[ j = 1(1)K_xK_y = [(1 \ldots K_y), (K_y + 1 \ldots 2K_y), \ldots, ((K_x - 1)K_y \ldots K_xK_y)] \]

which is a column oriented ordering of the variables. A row oriented approach may be introduced as well. The residual can be reformulated according to this column oriented numbering yielding

\[
\begin{align*}
    r_{ij} &= s_{ij} - (a_{ij}Y_{(j-1)} - b_{ij}Y_{ij} + c_{ij}Y_{(j+1)} - d_{ij}Y_{(j-K_y)} + e_{ij}Y_{(j+K_y)}) \\
    i &= 1(1)N; j = 1(1)K
\end{align*}
\]

where \( N \) are the number of variables and \( K = K_xK_y \) the total number of grid points. This formulation is very similar to the one appearing in the one-dimensional flame problem. Using the same organization of the variables per grid point (section 2.3) the extension to multi-dimensional case is now obvious.

In vector notation the residual is given by

\[ r(\vec{Y}) = s(\vec{Y}) - D(\vec{Y})\vec{Y} \]

where the structure of \( D \), determined by the grouping of all variables per grid point, is illustrated in Fig. (4.7). The linearization performed by the Newton strategy leads to a the set of equations to be solved, symbolically written as

\[ J_{(t)} \Delta \vec{Y} = -r_{(t)} \]

where 't' denotes the pseudo-transient reformulation of the discretized equations, which is not treated here but is rather straightforward.

It is obvious that the structured grid approach leads to a regular Jacobian structure as given in Fig. (4.7). Note that according to this structure, it is implied that a 5-point discretization molecule is considered sufficient to discretize all differential equations. Formally, this is only true if no mixed partial derivatives (like \( \partial^2/\partial x \partial y \)) appear. Strictly this is only the case if the corresponding terms in \( S_y \) (Eq. (4.3)) are taken equal to zero. Otherwise a 9-point pencil should be used to include cross-derivatives like \( \partial^2/\partial x \partial y \) which leads to a Jacobian with 8 off-diagonals containing micro-blocks.

For grid structures as presented in section 4.3.2, the extension to multi-dimensional systems (Eq. (4.28)) is not straightforward. A numbering like \((k, l)\) is not possible as can be seen in the schematic picture of an unstructured grid on the left in Fig. (4.8). Depending on the choice for \( \Delta x_i \) and \( \Delta y_j \), either some pairs \((k, l)\) do not correspond with an existing grid point or some grid points a pair \((k, l)\) cannot be assigned. Here a numbering scheme is employed which is a column oriented count of all points encountered, processing each column from bottom to top as illustrated in the left part of Fig. (4.8).

The residual now becomes

\[
\begin{align*}
    r_{ij} &= s_{ij} + a_{ij}Y_{(j-1)} - b_{ij}Y_{ij} + c_{ij}Y_{(j+1)} + d_{ij}Y_{(j-K_y)} + e_{ij}Y_{(j+K_y)} \\
    i &= 1(1)N; j = 1(1)K
\end{align*}
\]
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with $jw$ and $je$ the pointers to the western and eastern neighbors of point $j$, respectively. $K$ still equals the total number of points. Due to the different data organization implied by the local grid refinement strategy the structure of the vector of unknowns now becomes

$$\vec{y} = \begin{bmatrix} \vec{y}_1^T, \ldots, \vec{y}_{K_1}^T, \vec{y}_{K_1+1}^T, \ldots, \vec{y}_{K_1+K_2}^T, \ldots, \vec{y}_{K_1-K_1}^T, \ldots, \vec{y}_{K_1}^T \end{bmatrix}^T$$

where $K_1$ are the number of grid points of column $l$ and $L$ equal to the number of columns that is present in the grid. The 'micro-vectors' $\vec{r} = (\vec{y}_1^T, \ldots, \vec{y}_N^T)^T$ are introduced for typographical reasons.

Although the residual is given by Eq. (4.30) as well, the structure of the discretization matrix $D$ becomes more irregular. This has immediate consequences for the structure of the Jacobian as well, since in principle, the only differences between the Jacobian $J$ and the discretization matrix $D$ are the values of the entries in the micro-blocks. In the $D$-matrix all micro-blocks are diagonal matrices, whereas due to the non-linear nature of the differential equations the micro-blocks of the Jacobian become (partially) filled. For the example (unstructured) grid given in the left picture of Fig. (4.8), the structure of the Jacobian (and the discretization matrix) is given explicitly.

The method presented here is a first attempt to solve the two-dimensional flame problem. The resulting equations are to be solved with the method developed for
the block-tridiagonal Jacobian arising in pure one-dimensional flame problems (see chapter 2). Therefore, the matrix equations have to be adapted. This is achieved by treating the coupling which is not associated with the three center block diagonals in the Jacobian in an 'explicit' way. Since the evaluation of the Jacobian will be performed numerically, this approximated Jacobian matrix can be calculated quite easily as will be shown.

The residual at iteration level \( n \) is split up into 'explicit' and 'implicit' contributions:

\[
\tilde{r}_y (\tilde{y}^n, \tilde{y}^{n-1}) = \tilde{r}_y (\tilde{y}^n) \cdot D^I (\tilde{y}^n) \tilde{y}^n - D^a (\tilde{y}^{n-1}) \tilde{y}^{n-1} \tag{4.33}
\]

where \( D^I \) contains the coefficients \( a_{ij}, b_{ij} \) and \( c_{ij} \) while \( D^a \) contains \( d_{ij} \) and \( e_{ij} \). The east-west coupling are treated in an 'explicit' manner in this way. The numerical evaluation of the approximated Jacobian is still performed by the method developed for the one-dimensional flames:

\[
\tilde{J}_y = \frac{\tilde{r}_y (\tilde{y}^n + \delta e_i, \tilde{y}^{n-1}) - \tilde{r}_y (\tilde{y}^n, \tilde{y}^{n-1})}{\delta}
\]

with \( e_i \) a unit-vector and \( \delta \) a small disturbance. \( J_y \) is now a block-tridiagonal matrix again. It should be noted that if the numbering of the grid points is altered from column to row oriented the coupling associated with the \( a_{ij} \) and \( e_{ij} \) become the 'far' micro-block entries in the Jacobian matrix equations. The resulting equation for \( \tilde{r}_y \) is very similar to Eq. (4.33), but now \( D^I \) contains \( d_{ij}, b_{ij} \) and \( e_{ij} \) and \( D^a \) contains...
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... 

$\alpha_{ij}$ and $c_{ij}$. The approximated Jacobian associated with this 'sweep' direction is indicated with $J_y$.

In fact the introduction of the residual vectors $\tilde{r}_x, \tilde{r}_y$ only ensures that the Jacobian contains the three center diagonals only and these micro-blocks contain the correct entries for the implicit coupling only. Therefore, to solve the corresponding set of equations, only a small adaption has to be made to the algorithmic set-up described in chapter 2. In fact the method to evaluate the Jacobian numerically and the technique to solve the resulting set of equations are identical to the corresponding ones developed for the one-dimensional flame. The modified Newton technique may now be applied to the approximated Jacobian equations associated with the two possible 'implicit' directions separately. Currently $J_y$ is held constant for a preset number of iterations and the approximated Jacobian equations

$$J_y^0 \Delta \tilde{y}^{n+1} = -\tilde{r}_y$$

(see section 2.3) are solved. If the preset number of iterations is reached the 'implicit' direction is switched and the approximated Jacobian $J_x$ is evaluated. Subsequently

$$J_x^0 \Delta \tilde{y}^{n+1} = -\tilde{r}_x$$

is solved for the same preset number of iterations. This procedure is repeated until convergence is reached. Convergence is checked by monitoring the norm of $\tilde{r}(\tilde{y}^n)$, to ensure that the solution obeys the correct set of discretized differential equations.

Since the Jacobian still contains the important coupling between all species through the chemical source terms, it may be expected that this partially explicit approach is able to deal with the stiffness induced by the chemistry. If the numbering method is switched from a column-by-column ordering to a row-by-row ordering of the grid points, the 'implicit' direction switches from $y$ to $x$. In fact, if both approximated Jacobians $J_y$ and $J_x$ were evaluated and stored at the same starting level and Newton steps were computed consecutively, a method similar to the Alternating Direction Implicit method evolves. However, it is not exactly an ADI method since then the $b_{ij}$ would have to be taken either $b_{ij} = a_{ij} + c_{ij}$ or $b_{ij} = d_{ij} + e_{ij}$ for the $x$- and $y$-implicit direction respectively, which is not the case in the sketched approach. In numerical experiments it was found that the introduced method gives better convergence behavior than the ADI method.

"Typically 5 is used now, which has been determined heuristically."
4.4 Results and Discussion

The method described in section 4.3 will be applied to for some selected values of the width \( d \) and pitch \( p \) of the drilled holes (see section 4.4.1). It is expected that for small values of \( d \) and \( p \) the flame approximates a flat flame as studied in the previous chapters. This gives a unique opportunity to compare the 1D and 2D results. Before we present the results of the multiple-slit burner with several values for \( d \), the calculation strategy will be introduced (section 4.4.2). Finally, the results will be presented and compared with those of the one-step global model (section 4.4.3). A discussion of the method and the obtained results is given in the final subsection of this chapter (section 4.4.4).

4.4.1 Studies

In order to have a well-defined reference frame, cases will be considered which have already been simulated using the one-step global chemical model used in our group [Bos93]. Although in general not preferable, densities and velocities will be specified using \( \text{cm} \) and \( \text{g} \) units instead of the SI-units, according to conventions used in previous chapters and in combustion literature.

For the simulation of the reactive flow field in the elementary geometry presented earlier, the values for the width \( d \), pitch \( p \), length of the domain \( L \) and the length of the inflow \( L_0 \) are specified to determine the geometry. In the one-step chemical model study, simulations are presented with a constant thickness \( L_0 = 0.08 \text{cm} \) and various choices for \( d \) and \( p \). However, as argued by Bosch et al. [Bos93] a constant ratio for the porosity \( d/p \) will give a clear picture of the influence of the geometry on flame characteristics such as the flatness. For, if this ratio is constant, the average mass flow \( \dot{m} \) per unit area through the slits is constant

\[
\dot{m} = \dot{m}^{\infty} \frac{p}{d}
\]

with \( \dot{m}^{\infty} \) the mass flow rate specified by the experimentator at the burner entry (conservation of mass is used). For the study presented here, the ratio is fixed and given by

\[
\frac{d}{p} = \frac{2}{3}.
\]

(4.34)

Larger values of this ratio are not recommendable as was experienced in experimental studies. It was found that \( d/p = 0.8 \) can be considered as an upper limit to avoid too large burner loads\(^7\). Too small values for \( d/p \) will lead to early blow-off due to the high velocity in the slits. This was observed numerically using the one-step model [Bos93]. Furthermore, the latter studies showed that the domain length \( L = 0.4 \text{ cm} \) is sufficiently large to obtain solutions, which are not distorted by the outflow boundary conditions, while at the same time keeping the computational domain as small as possible. Given the constant length of the inflow and the constant length of the computational domain, the geometry is now completely specified if the value for \( d \) is given.

---

\(^7\)Corrosion of the burner plate material.
4.4. Results and Discussion

The computational set-up is completed by specifying the inlet conditions, which are given by the concentration fractions, the temperature and the mass flow rate. The latter will be specified through \( \dot{m}^{\infty} \). However, instead of presenting the mass flow rate, all studies will be 'labeled' by a specified uniform velocity

\[
v^{\infty} = 35.0 \frac{cm}{s}
\]

at the burner entry (located at \( y = -\infty \)), since this concurs with the experimental situation. The corresponding mass flow rate may then be determined by the temperature and composition of the gas at the burner entry, which are also user-specified. As in the one-dimensional simulations, for methane-air combustion the initially present mole- (or mass-) fractions are determined completely by the equivalence ratio \( \varphi \), which for all simulations will be taken equal to 1.0.

Thus, assuming the oxygen mole-fraction in air to be equal to 0.21, this gives for the initial mole-fractions

\[
\begin{align*}
X_{CH_4}^{\infty} & = 0.095 \\
X_{O_2}^{\infty} & = 0.190 \\
X_{N_2}^{\infty} & = 0.715 \\
X_i^{\infty} & = 0.0 \quad \forall i \neq (CH_4, O_2, N_2)
\end{align*}
\]

Using this initial composition\(^9\), the density may be calculated with \( \rho^{\infty} = \frac{nM}{\dot{m}^{\infty}} \) to obtain the mass-flow rate \( \dot{m}^{\infty} \). The molar density \( n \) can be calculated with the ideal gas law (Eq. (4.8)), given the pressure \( p = 1 \text{ atm} \) and the initial temperature \( T = 298.2 \text{ K} \).

Below the range of all parameters are summarized:

\[
\begin{align*}
\varphi & = 1.0 \\
p & = 1(\text{atm}) \\
T^{\infty} & = 298.2\text{K} (25^\circ\text{C}) \\
v^{\infty} & = 35.0 \frac{cm}{s} \quad (\dot{m}^{\infty} = 0.0395 \frac{g}{cm^2s}) \\
\frac{d}{p} & = \frac{2}{3}
\end{align*}
\]

For the values of the width \( d \) we select a subset of the studies presented in [Bos93] being

\[
d = 0.030, 0.050, 0.080 \text{ and } 0.1 \text{ (cm)}.
\]

An outline of the computational domain of the smallest and the largest case is shown in Fig. (4.9).

---

\(^9\)Since the composition of air is assumed to be known.

\(^{9}\)Specifying the average molar mass \( M \).
Fig. 4.9: The computational domain of the smallest $d = 0.03\text{cm}$ (left) and largest $d = 0.1\text{cm}$ (right) elementary micro-slits ($L = 0.4\text{cm}$, $L_0 = 0.08\text{cm}$).
4.4.2 Calculation strategy

In all results presented a coarse-to-fine grid strategy is used. Using an initially prescribed starting estimate for the solution, a converged solution is calculated on the coarsest grid, with grid spacing taken equal to $\Delta x = 0.0025\text{cm}$ and $\Delta y = 0.01\text{cm}$ in all cases (see Fig. (4.10)). Subsequently, one refinement layer is added and the solution is interpolated onto this new grid level. The simulation is restarted with this 'initial' guess on the finer mesh until a solution is found. Finally, the second refinement layer is added, interpolation of the solution found on the previous grid is performed and using this initial guess, the simulation is restarted once more. The procedure may be repeated on even finer meshes, but here the refinement strategy is stopped after two layers of refinement. The three meshes are illustrated for a simulation with $d = 0.08\text{cm}$ in Fig. (4.10).

It should be mentioned that the regions which are refined are determined by using the one-step calculations. In fact, the grid generation is performed separately and uses data of the one-step global chemical model calculations. Therefore, the grid might not be optimal for the detailed calculations. This did not appear to be a problem for the simulations presented here. However, it is recommended that, the grid strategy is coupled directly to the solution incorporating the detailed chemistry.

In the coarse-to-fine calculation strategy described above, it has been assumed implicitly that some kind of initial guess for all variables is available on the coarse mesh. The procedure employed here, to obtain this initial guess is presented now.

For the flow field and the temperature distribution, the results of the computations with a one-step global mechanism on a coarse regular grid are used. However, these simulations do not provide values for the chemical species. Since it may be expected that the simulations of the two-dimensional flame structure will resemble a one-dimensional flame (especially for small $d$-values), the result of a comparable ($\varphi = 1$, $\dot{m} = 0.0395\text{ g}/(\text{cm}^2\text{s})$) one-dimensional detailed chemistry simulation, as presented in chapter 2, is used. The one-dimensional flame results of the species are interpolated on the two-dimensional mesh using the temperature field of the one-step two-dimensional calculation and the temperature field of the one-dimensional simulation. This interpolation approach in fact presumes that the temperature field of the two-dimensional one-step simulation gives a good initial guess for the temperature field of the detailed chemical model computation.

To perform the interpolation the solution for the mole fractions of the one-dimensional calculation is described as a function the temperature $T^{1D}$ values found in the one-dimensional calculation, $X_i^{1D}(T^{1D})$. The temperature profile $T(x, y)$ found in the one-step two-dimensional simulation is used subsequently to obtain the interpolated values according to

$$X_i(x, y) = X_i^{1D}(T(x, y))$$

which completes the initial values for all variables in the two-dimensional domain.

Note that this kind of interpolation only gives unique values for the interpolated variables if $T^{1D}$ is a monotone function of $x$ for the one-dimensional simulation. However, this is the case for all one-dimensional flame computations in this thesis. Furthermore, it should be realized that the initial guess obtained by this procedure gives only reasonable results for this specific geometry and is generally not
fig. 4.10: Three levels of refinement for $d = 0.8$. Only small part of the complete domain is presented in the figures on the right.
4.4. Results and Discussion

extendable to other geometries

4.4.3 Results

In the study, presented by Bosch [Bos93], an indicator of the stand-off distance is introduced. The so-called $\delta T_{iso}$ parameter, is defined as being the distance of a certain isotherm with value $T_{iso}$ above the burner at the left symmetry boundary ($II$ in Fig. (4.3)), from now on referred to as the center boundary. Obviously, this height is equal to the height of the same isotherm above the burner at the right symmetry axis ($II'$) if the flame is flat. For matters of convenience the $II'$-boundary will be referred to as the side boundary.

If the flame becomes more curved, the height found at the center boundary will differ more and more from the one found at the side boundary. Schematically, this concept is represented in Fig. (4.11), where four isotherms are shown for the four introduced detailed chemical computations.

![Fig. 4.11: The definition of $\delta T_{iso}$. From left to right, parts of the $d = 0.03$, 0.05, 0.08 and $d = 0.1$ cm geometries are shown. Temperature contours with the values $T' = 900, 1200, 1500$ and 1800 K are presented.](image)

The $\delta T_{iso}$ values are calculated for temperatures equal to 900K, 1200K, 1500K, 1800K respectively, see Fig. (4.13). Bosch et al. presented results for $T = 1500K$, 1800K and 2000K instead (Fig. (4.12)). The reason for not presenting the 2000K isotherm here, is that a detailed chemical model gives a different temperature distribution. The $T' = 2000K$ isotherm is located far downstream, in a region where the flow has become uniform already. Small differences in computed temperatures will therefore lead to quite large differences in the parameter $\delta T_{iso}$ between the four cases. For that matter the 2000K isotherm is not a good indicator of the flame flatness in our simulations.
Global properties of the flat flame: $\delta T_{iso}$-criterion.

In Fig. (4.13) the $\delta T_{iso}$-parameters are presented for the four cases of $d$ that are studied. Compared to the one-step global chemical model results (see Fig. (4.12)),
the trend observed is confirmed by the detailed model simulations. Both smaller geometries \( d = 0.03 \text{ cm} \) and \( d = 0.05 \text{ cm} \) produce 'flat' flames in the sense defined by the \( \delta T_{iso} \) criterion. The distance of the three lowest isotherms above the burner is equal within 0.01 \( \text{mm} \), whereas both larger slits show an increasing difference for all three isotherms, e.g. for the 900 \( K \) isotherm this difference increases to 0.05 \( \text{mm} \) and 0.1 \( \text{mm} \) for \( d = 0.08 \text{ cm} \) and \( d = 0.1 \text{ cm} \), respectively.

![Graph showing \( \delta T_{iso} \) vs \( d \)](image)

\[ \text{Fig. 4.13: Values for } \delta T_{iso}(o) \text{ found for the studies with } d = 0.03, d = 0.05, d = 0.08 \text{ and } d = 0.1 \text{ (cm). } T_{iso} = 900, 1200, 1500, \text{ and } 1800 \text{ K are shown.} \]

It can be observed that as the width of the slit becomes smaller and the two-dimensional flame approaches the one-dimensional limit, the isotherms become less curved (see also Fig. (4.11)). Furthermore, in the 'flat' flame zone (i.e. \( d = 0.03, 0.05 \text{ cm} \)), the plots suggest that the height of the isotherm is given by the value at the center boundary and not the height of the isotherm at \( x = \frac{1}{2}l \), as one might expect.

**Detailed properties of the flat flame.**

The comparison of the profiles of the temperature and mole fractions of the major species along the center boundary and the profiles along the side boundary are
presented now. Since the one-step global chemical model simulations are used to provide an initial estimate of the temperature for detailed model calculations, the results of the one-step simulation are presented as well.

To illustrate the differences between a flat and a curved flame, the detailed properties are shown for the two extreme values of $d$ that have been used, i.e. $d = 0.03 \text{ cm}$ and $d = 0.1 \text{ cm}$. In Fig. (4.14) the temperature profiles along both boundaries are presented for the two elementary burners. The one-step global model temperature profile that is included (dash-dotted line), is the one found at the center boundary.

Compared to the one-step calculation the final temperatures at $y = L$ for the detailed chemical model are lower by approximately $100 K$. This difference cannot be attributed to differences due to the chemical model since both chemical models give flame temperatures in a one-dimensional calculation which differ only a few degrees. This difference is induced by the too small calculational domain, which causes the slower (\text{C}_O - \text{C}_O^2) conversion to stop too early in the detailed chemistry simulations.$^{10}$

The temperature along both boundaries give very similar profiles for the $d = 0.03 \text{ cm}$ case. Although poorly resolved, at the side boundary the temperature derivative shows a discontinuity at $x = \frac{1}{2} L$ (as it should be above the cold wall) whereas at the center boundary the temperature derivative is smoother (insert in top figure of Fig. (4.14)). Obviously, a discontinuity should occur at the burner edge otherwise no cooling mechanism would be present and the flame would propagate upstream. In the $d = 0.1 \text{ cm}$ case, both boundaries can be distinguished from each other more clearly. The temperature profile at the side edge is clearly shifted upstream with respect to the profile found at the center boundary, showing the larger curvature of the temperature contour which was already observed in Figs. (4.11)-(4.13).

With respect to the species, no information is available from the one-step model calculations. In Figs. (4.15) and (4.16) the major species profiles are presented at the center- and side boundaries of both cases. As was found for the temperature profile already, the $d = 0.1 \text{ mm}$ geometry yields the largest two-dimensional effects. This is confirmed by the profiles of the major species along both boundaries (Fig. (4.16)). For $x = \frac{1}{2} L$ the species profiles are shifted upstream with respect to those at the center line and coincide with the center boundary results where the flow has become nearly uniform and the mixture has approached chemical equilibrium.

For the smallest geometry, the profiles of the major species along both lines coincide before the reaction layer is reached. Differences occur in a small region in the pre-flame zone only, where the temperature is low and the mixture is chemically frozen. These differences in the pre-flame zone are induced by the different boundary conditions at both boundaries.

Concluding, the calculations clearly show that the results for the smaller slit widths approach a one-dimensional limit. Only in a small layer above the burner plate, variations in the direction parallel to the burner plate occur and the flame shows multi-dimensional effects. However, these multi-dimensional variations only affect the region with relatively low temperatures and the reaction layer may

$^{10}$In chapters 2 and 3 the domain lengths were taken equal to $10 \text{ cm}$ here they are typically $0.4 \text{ cm}$.
4.4. Results and Discussion

fig. 4.14: Temperature profiles along the $x = 0.0$ (solid line) and $x = \frac{1}{2}p$ (dashed line) boundaries. The profile along the center boundary of the one-step global chemical model is shown as well (dash-dotted line). Top figure: case with $d = 0.03$ cm; bottom: case with $d = 0.1$ cm.
fig. 4.15: Mole fractions for $x = 0$ and $x = \frac{1}{2}p$ for the calculations with $d = 0.03cm$. The solid lines indicate the center boundary values, the side boundary results are presented by dotted lines.
fig. 4.16: Mole fractions for $x = 0$ and $x = \frac{1}{2}p$ for the calculations with $d = 0.1cm$. The solid lines indicate the center boundary values, the side boundary results are presented by dotted lines.
therefore be considered to be truly one-dimensional\textsuperscript{11}. For the two largest widths this is not the case and the reactive flow becomes uniform in a region where the mixture reaches chemical equilibrium, thus behind the reaction layer.

\footnotesize\textsuperscript{11}Optically, the flames is flat since the luminous zone in a CH\textsubscript{4}-flame is related to the concentration of excited CH, OH and OH radicals, which reach their maximum in the reaction layer.
Comparison with the one-dimensional limit

In the limit of \( d \to 0 \) the results should approach those of the one-dimensional model. The profiles of the major species along the center line are compared to results of a simulation of a one-dimensional model in this subsection. Only four of the major species are treated to get a clear picture, i.e. the reactants \( CH_4, O_2 \) and the major products \( CO_2 \) and \( H_2O \) (see Fig. (4.17)).

For the largest slit the profiles are clearly shifted downstream. Furthermore, the equilibrium composition is different for the one-dimensional and the two-dimensional simulation (2.5% difference in maximum mole fraction for \( H_2O \), see Fig. (4.17)). However, for the smallest slit \( (d = 0.03 \text{ cm}) \) all profiles are shifted downstream also, which contradicts the assumption that the model approaches the one-dimensional limit for small \( d \)-values. Furthermore, the difference in the equilibrium composition is here even more pronounced than for \( d = 0.1 \text{ cm} \). Here, the \( H_2O \) mole fraction at the outflow, is increased by 6% compared with the one-dimensional calculation. Although it is clear from the previous section that the smallest slit width behaves one-dimensional, the results shown here indicate that the difference in equilibrium composition between the one-dimensional and the two-dimensional simulation increases with decreasing \( d \) values.

To investigate this contradiction, the equilibrium composition of all cases is studied more closely. Since all elementary reactions conserve the elements it may be shown that the so-called 'specific element mole number' \( \Gamma_e = X_e/M \), obeys a convection-diffusion like equation without chemical source term

\[
\rho \vec{V} \cdot \nabla \Gamma_e - \nabla \cdot (\rho \Gamma_e \vec{V}_e) = 0
\]  
(4.36)

where \( \Gamma_e \vec{V}_e \) is a linear combination of the diffusive fluxes \( \Gamma_i \vec{V}_i \) of the species (see Appendix C.1). The element mole fraction \( X_e \) is defined as being

\[
X_e = \sum_{i=1}^{N} \chi_{ei} \cdot \vec{x}_i \quad e = 1(1)N_e
\]  
(4.37)

where \( N_e \) is the number of elements present in the mixture, here \( N_e = 4 \) (C,H,O,N). The coefficient \( \chi_{ei} \) denotes the elemental composition of a species \( i \) formally indicated with

\[
\chi_i = \chi_{C1}, \chi_{H2}, \chi_{O2}, \chi_{N4}
\]

for an arbitrary species\(^{12}\).

Since at the burner entry \( y = -\infty \) and the outflow \( y = L \), the flow is considered as being uniform in \( y \)-direction the diffusive velocities vanish at both sides of the computational domain. By integration of Eq. (4.36) over the complete computational domain, it can be derived for the present geometry that \( \Gamma_e(x, -\infty) = \Gamma_e(x, L) \), which is obvious since at both sides \( \rho \vec{V} \) is equal and uniform. Similarly, for \( y = 0 \) and \( y = L \) (i.e. where the inlet and outlet is specified in the computational domain), it may be shown that

\[
\Gamma_e(0, 0) = \Gamma_e(0, L)
\]

\(^{12}\)E.g. the coefficients for \( C1H4 \) are equal to the sequence \((x_{c1}, x_{c2}, x_{c3}, x_{c4}) = (1, 4, 0, 0)\).
fig. 4.17: The major species along the center boundary (solid line) versus the results of a one-dimensional simulation (dotted line). Results are presented for the the $d = 0.03\text{cm}$ (top) and $d = 0.1\text{cm}$ (bottom) cases.
should be valid for all elements (see Appendix C.1). To illustrate this phenomenon the quantities, $\Gamma_C$, $\Gamma_H$, $\Gamma_O$ and $\Gamma_N$, are plotted for a one-dimensional calculation (solid lines) together with the results at the center boundary of all the four two-dimensional simulations (marked lines) considered in the present study, see Fig. (4.18).

![Graphs of C, H, O, N mole fractions vs. y(cm)]

Fig. 4.18: The properties $\Gamma_e$ along the center boundary (markers are indicated in the figure) compared to the one-dimensional simulation (solid lines). Four elements are shown, C (top-left), H (top-right), O (bottom-left) and N (bottom-right).

The solid lines indicate that discretization in the one-dimensional calculation is such that the specific element mole-fraction is conserved perfectly (error within 0.2%). However, the marked lines in Fig. (4.18) show that elemental conservation is violated in all two-dimensional simulations. Furthermore, the smaller $d$ the larger the difference with the one-dimensional calculation and thus elemental conservation becomes increasingly violated. This observation correlates with the increasing differences observed between one- and two-dimensional cases for the major species
Table 4.1: The relative error in elemental conservation defined according to
\( \Delta_x = (\Gamma_x(x_0, L) - \Gamma_x(0, 0))/\Gamma_x(0, 0) \). In the bottom part of the table the values for \( \Gamma_x(0, L) \) are given. The values presented for \( d = 0.00 \) are obtained with the one-dimensional method.

Mole fractions as well (in Fig. (4.17)).

In Table 4.1, the relative error for the four 2D cases and the one 1D \((d = 0.00)\) is presented. The dependence of the elemental deficit on the width of the slit \((d)\) suggests that this effect may be attributed to the discretization of the boundary conditions. If this is assumed, the effect of the error would scale like

\[
\frac{L_b}{A^1}
\]

where \( L_b \) is the total length of the boundaries and \( A \) the area of the computational domain. For all geometries considered \( A \approx \frac{1}{2} p \cdot L \) while the total length of the boundaries equals \( p + 2L \). Therefore, if the error would be induced by the boundary conditions only, the deficit could possibly depend on \( d \) like

\[
\Delta_v(d) \propto \frac{p + 2L}{\frac{1}{2}p \cdot L} = \frac{\frac{3}{2}d + 2L}{(\frac{3}{4}d) \cdot L}
\]

Investigating this fraction for the cases \( d \to 0 \) gives \( \Delta_v(d) \propto \frac{1}{d} \) which correlates with the increase found in Table 4.1 with decreasing \( d \).

For this reason, the boundary conditions are investigated in more detail. Currently, for all species the boundary conditions along the walls and symmetry axes are the same, viz. \( \frac{\partial \Gamma_x}{\partial x} = 0 \) or \( \frac{\partial \Gamma_x}{\partial y} = 0 \) (see section 4.3.1). In the numerical implementation these conditions are represented by a one-sided difference scheme. The effect of this implementation on elemental conservation will be studied for a wall along the \( y \)-axis. The argumentation, however, holds for the symmetry-axes and walls along the \( x \)-axis as well.

In Fig. (4.19) a diagram is presented of the two-dimensional finite-volume areas used to discretize the convection-diffusion equation for the species in a "conservative way". Effectively, the discretization of the corresponding differential equation for
4.4. Results and Discussion

![Diagram](image)

**Fig. 4.19:** Illustration of a conservative Thiel-like implementation of the zero-flux boundary condition.

The finite-volume around point A may be represented by the formal expression

$$
\epsilon^A - \epsilon^B + \epsilon^A - \epsilon^A = S
$$

where $\epsilon$ is the flux perpendicular to the eastern, western, northern, and southern interfaces $e$, $w$, $n$, $s$. The total flux $\epsilon$ across an interface (e.g. the dotted lines in Fig. (4.19)) is conserved exactly if the flux on that interface is calculated in the same way for both points (i.e. for the control volumes belonging to $B$ and $A$, respectively, in Fig. (4.19)) that share that interface. For example, the flux across the east interface of $A$ is conserved exactly if in the implementation of the discretization scheme

$$
\epsilon^B = \epsilon^A
$$

holds. Overall conservation is guaranteed if this is true for all interfaces. However, if the zero normal flux boundary condition is discretized with a one-sided difference scheme (as is used in the present calculations),

$$
\frac{\partial \Gamma_i}{\partial x} = \frac{\Gamma^B_i - \Gamma^A_i}{x^B - x^A}
$$

conservation along interfaces near walls is no longer guaranteed. In fact, it can be shown that this implementation of the boundary conditions does not conserve species mole-fractions and thus acts as a source or sink term.

A correct way to ensure conservation and yet to avoid a flux of species through the wall is to introduce a fictitious mirror-point ($A'$ in Fig. (4.19)) with all scalars equal to the values at $A$ but the velocity vector$^{13}$ equal to $\vec{v}' = (-u, v)$, where

$^{13}$More generally, the velocity vector $\vec{v}'$ at a point mirror-imaged in an arbitrary boundary with $\vec{n}$ the outward unit normal vector (see Fig. (4.19)), can be defined according to $\vec{v}' = \vec{v} - 2(\vec{v} \cdot \vec{n})\vec{n}$. 

$\vec{n}$
\( \mathbf{v} = (u, v) \) is the velocity vector of point A. Furthermore, if a flux along the wall, through the control volume is allowed, the discretization of the impermeable wall will yield

\[
\mathbf{t}^c - \mathbf{t}_w^B + \mathbf{t}_u^B - \mathbf{t}_s^B = -S^B
\]

which gives with the use of the approach of Thiart (see section 4.3.1)

\[
a_p \mathbf{Y}_w + b_p \mathbf{Y}_p - c_p \mathbf{Y}_E - d_p \mathbf{Y}_N - e_p \mathbf{Y}_S - S_p \Delta x \Delta y.
\]

(4.38)

Here, all coefficients are determined according to their definitions\(^{14}\) Eq. (4.17). Recalling the definitions of \(a_p\) and \(c_p\)

\[
a_p = \frac{\Delta_w \Delta y}{\Delta W} A(-P_W), \quad P_W = \frac{\mu_w \Delta W}{\Lambda_w}
\]

\[
c_p = \frac{\Delta_e \Delta y}{\Delta E} A(P_E), \quad P_E = \frac{\mu_e \Delta E}{\Lambda_e}
\]

it can be shown that since \(P_W = -P_E\) for \(B\), \(a_p = c_p\) and that the introduction of the fictitious mirror-point effectively yields a second-order accurate discretization of the diffusion flux which formally assures conservation of species in the control volume for walls.

With respect to the overall conservation of elements the conservative discretization of the boundary condition is investigated by implementing these in the algorithm. Since it may be expected that the local refinement method introduces new 'boundary' points, (viz. the interpolation points, see Fig. (4.6)) simulations have been performed using a regular unrefined mesh only. Furthermore, since the largest element deficit \(\Delta_e\) is found for \(H\) in the \(d = 0.03\ cm\) geometry, \(\Delta_H\) for the smallest geometry is considered only. The implementation of the 'new' boundary conditions is performed in several stages, all shown in Fig. (4.20) together with the original results (dash-dotted line). In the first stage only the symmetry boundaries \(II\) and \(II'\) are treated in this conservative way. Results of this implementation are shown with a dotted line. In the second stage, the walls are treated as well (marked line). It was found that the intersections of boundaries need special attention as well (e.g. the edge of the burner at \((x, y) = (\frac{1}{2}d, L_0)\)). The discretization of these special points has to be considered with care, since they have a relative large effect on the elemental conservation as is illustrated in Fig (4.20). The results show that using conservative discretization for all points in the computational domain (solid lines in Fig. (4.20)) yields best results, i.e. \(\Delta_H \approx 0.7\%\).

Finally, the species profiles along the center boundary are compared to the onedimensional simulation (see Fig. (4.21)) for the case where all boundaries and intersection are treated conservatively. Now, the agreement between the one- and two-dimensional simulation is excellent. The difference in \(H_2O\) mole fraction at \(y = L\) has now decreased to 0.4\% which is a clear improvement over the original 2D simulation (6\%). Furthermore, all profiles coincide except in a small zone near \(y = 0\ cm\). There, due to the much higher velocity in the two-dimensional simulation \((v \approx 75\ cm/s\) in the slit compared to \(v \approx 35\ cm/s\) in the 1D simulation) the profiles show a different curvature.

\(^{14}\) Note that using this formalism, surface reactions at walls can be incorporated simply.
4.4. Results and Discussion

4.4.4 Discussion

The simulations have shown that the results obtained with the global one-step model [Bos93] are confirmed by the detailed chemistry simulations. Furthermore, the comparison with the one-dimensional detailed simulation (Fig. (4.21)) clearly shows that if the width $d$ of the slits is taken small enough the detailed structure is almost identical to the one found in the one-dimensional case.

For all cases presented the method developed here to model the two-dimensional flat flames obtains a converged solution. For the smallest value for $d$ typically 600 Jacobian evaluations\(^{15}\) were needed to reduce a measure for the error to $5 \times 10^{-4}$ on the 2-layer refined mesh. However, the larger the slit width becomes, the more curved the flame structure becomes, convergence behavior becomes worse. For those cases, the couplings that are treated explicitly become more important. It may, therefore, be expected that the convergence behavior will be improved if all spatial couplings are treated implicitly. However, for that case the method developed for one-dimensional flames cannot be used. Currently, a method (Bi-CGSTAB) is implemented to deal with the full set of Newton equations arising if all couplings are treated implicitly.

\(^{15}\)The CPU-time needed to evaluate one Jacobian is of the order $O(500\mu s)$, on a MIPS 4400 processor.
Chapter 4. Two-Dimensional Flat Flames

![Diagram of mole fraction of major species in the final 2D simulation compared with 1D results. Solid lines are the results from center boundary from \( d = 0.03 \) cm, dotted lines results from the corresponding one-dimensional simulation.]

fig. 4.21: Mole fraction of major species in the final 2D simulation compared with 1D results. Solid lines are the results from center boundary from \( d = 0.03 \) cm, dotted lines results from the corresponding one-dimensional simulation.
Appendices Chapter 2

A.1 On the equivalence between Thiart- and Larroutourou discretization.

In [Ghi91] Ghilani and Larroutourou present an analysis for an upwind scheme for the discretization of the convection-diffusion equation with a realistic transport model. This type of equations appears frequently in the simulation of one-dimensional premixed laminar flames. They prove that this scheme preserves the positivity of the mass-fraction of all species and does not induce oscillatory behavior of the solution for any value of the local cell Peclet number and/or magnitude of the timestep. The latter is the main drawback of central discretizations of the convective flux. However, opposed to upwind methods, the method of Ghilani is second-order accurate (depending on the value of the Peclet numbers). Therefore, this difference method leads to a more robust yet accurate algorithm. These results are very useful in the simulation of one-dimensional flames with detailed chemistry, since large variations in local cell Peclet numbers may be expected.

For the generalized convection-diffusion equation mentioned on page 34,

\[ \frac{\partial \phi}{\partial t} = \frac{\partial}{\partial x}(\Lambda \frac{\partial \phi}{\partial x}) - S \]  

with variable diffusivity \( \Lambda \), given in the nomenclature adopted in chapter 2 (section 2.3), the discretization presented by Ghilani yields,

\[ -a_j \phi_{j-1} + b_j \phi_j - c_j \phi_{j+1} = s_j \]  

with

\[ a_j = 2 \frac{\Lambda_j}{\Delta_j} - \mu(\alpha(P_j-1) + 1) \]  

\[ b_j = 2 \frac{\Lambda_j}{\Delta_j} + 2 \frac{\Lambda_j}{\Delta_j} + \mu(\alpha(P_j-1) + \alpha(P_j)) \]  

\[ c_j = 2 \frac{\Lambda_j}{\Delta_j} - \mu(1 - \alpha(P_j)) \]  

\[ s_j = s_j(\Delta_j + \Delta_{j-1}) \]
where $\Delta_j = x_{j+1} - x_j$ and the local Peclet numbers (or Reynolds number for that matter) $P_j = \mu \Delta_j / \Lambda_j$ are introduced. $S_j$ is the (chemical) source term at gridpoint $x_j$.

It should be mentioned that the expressions (A.3 ... A.5) are equivalent with the original relations of Ghilani [Ghi91] p. 85, multiplied with $(\Delta_j + \Delta_{j-1})$ and without the typing error in expression (84) for $c_j$ on the same page. The function $\alpha$ is given by,

$$\alpha(P) = \coth \left( \frac{P}{2} \right) - 2 / P$$

which involves some exponential behavior in $P$ as does the function $A$ on page 36,

$$A(P) = \frac{P}{e^P - 1}$$

appearing in the method proposed by Thiart\(^1\).

Now it can be shown that the discretization of the same convection-diffusion equation proposed by Thiart,

$$a_j' = \frac{\Lambda_{j-1}}{\Delta_{j-1}} A(-P_{j-1})$$
$$c_j' = \frac{\Lambda_j}{\Delta_j} A(P_j)$$
$$b_j' = a_j' + c_j'$$
$$s_j' = S_{j-1} \Delta_{j-1} (1 - W(P_{j-1})) + S_j \Delta_j W(P_j)$$

is equal to the Ghilani discretization if $S_{j-1}$ is replaced with $S_j$ and the source term weighing is not applied. The source term $s_j$ then yields,

$$s_j = S_j (\Delta_{j-1} + \Delta_j) / 2$$

which in fact is the implementation chosen in our algorithm. To prove this statement $a_j$ will be reformulated such that the $a_j'$ arises.

First realize that $a_j$ is equivalent with,

$$a_j = \mu \left[ \frac{2}{P_{j-1}} + \left( \coth \left( \frac{P_{j-1}}{2} \right) - 2 / P_{j-1} + 1 \right) \right]$$

where the identity $2 / P_{j-1} = 2 \Lambda_{j-1} / (\mu \Delta_{j-1})$ is used to get $\mu$ outside the square brackets. Now, the $2 / P_{j-1}$ terms cancel and

$$a_j = \mu \left( \coth \left( \frac{P_{j-1}}{2} \right) + 1 \right)$$

arises which is rewritten according to,

$$a_j = \mu \begin{bmatrix} e^{P_{j-1}/2} + e^{-P_{j-1}/2} \\ e^{P_{j-1}/2} + e^{-P_{j-1}/2} \end{bmatrix} \begin{bmatrix} e^{P_{j-1}/2} + e^{-P_{j-1}/2} \\ e^{P_{j-1}/2} + e^{-P_{j-1}/2} \end{bmatrix} - \mu \begin{bmatrix} 2e^{P_{j-1}/2} \\ 2e^{P_{j-1}/2} \end{bmatrix}$$

\(^1\)Note that $\coth(x) = \frac{e^x + e^{-x}}{e^x - e^{-x}}$.
A.1. On discretization schemes

Multiplying the nominator and the denominator in Eq. A.11 with $e^{-I_j - 1/2}$ gives,

$$a_j = \frac{\Lambda_{j-1}}{\Delta_{j-1}} \left( \frac{2I_{j-1}}{1 - e^{-I_{j-1}}} \right)$$

$$= 2 \frac{\Lambda_{j-1}}{\Delta_{j-1}} \left( \frac{-I_{j-1}}{e^{-I_{j-1}} - 1} \right)$$

(Eq. A.12)

which is thus equal to

$$2\Lambda_{j-1}/\Delta_{j-1} \Lambda(-I_{j-1}) = 2a_j.$$ 

The factor 2 originates from the fact that $s_j = S_j(\Delta_{j-1} + \Delta_j)/2$ appears in the Thiart formulation (Eq. (A.9)), instead of $s_j = S_j(\Delta_{j-1} + \Delta_j)$ which is introduced above (Eq. (A.6)). An analogous reasoning can be applied to show that $c_j = 2c_j$. Like for the Thiart method, $a_j + c_j = b_j$ is valid. Indeed, this can easily be shown from the original relations (A.3 + A.5).
A.2 The numerical evaluation of the Jacobian matrix.

Here the numerical evaluation of the Jacobian matrix mentioned in section 2.3 is treated in more detail. The one-sided difference scheme

$$J \approx \frac{r(Y + \delta \varepsilon_i) - r(Y)}{\delta}$$

is the starting point of this treatment. To evaluate the complete Jacobian matrix with the least computational effort, of course an analytical approach would have to be chosen. However, this is a very cumbersome task and the analytical expressions have to be reconsidered for every change in the description of the residual vector. Furthermore, if certain iteration schemes are used to obtain specific quantities, an analytical approach might not be available\(^2\) at all.

The main goal will be to determine the Jacobian numerically with the least possible evaluations of the residual vector. To meet this pre-requisite some knowledge about the dependence of the residual of species \(i\) at position \(j\)

$$r_{ij} = s_{ij} + a_{ij} Y_{i(j-1)} + b_{ij} Y_{i(j)} + c_{ij} Y_{i(j+1)}$$

on species \(i'\) at position \(j'\) is needed. Obviously, this is closely related to the discretization star (molecule, pencil), for which here a three-point molecule is chosen. On one hand the residual \(r_{ij}\) is explicitly dependent on \(Y_{i(j-1)}, Y_{i(j)},\) and \(Y_{i(j+1)}\) as would occur for the case of a convection-diffusion equation with constant diffusivity and mass-flow rate.

On the other hand, implicit dependencies are present as well. In flames, the most important coupling is induced by the (complex) chemical source term \(s_{ij}\), which depends on the concentrations of many species and the temperature due to the elementary reactions. Depending on the transport- (\(\lambda, D_{im}\)) and thermodynamical (\(c_p, h_i\)) models that are used,\(^3\) the coefficients \(a_{ij}, b_{ij}\) and \(c_{ij}\) also introduce a coupling between \(r_{ij}\) and the other species \(i'\) at positions \(j - 1, j\) and \(j + 1\).

From this consideration it might be clear that in order to obtain proper values for the Jacobian elements

$$J_{ij}^{i'j'} = \frac{\partial r_{ij}}{\partial Y_{i'j'}} i', i' = 1(1) N, j' = j - 1, j, j + 1$$

the disturbance vector \(\delta\) has to be chosen carefully. Obviously, through the implicit coupling of \(r_{ij}\) with all species \(i'\) only one species may be disturbed at a time. Furthermore, through (explicit and implicit) dependence of \(r_{ij}\) on \(Y_{i(j-1)}, Y_{ij}\) and \(Y_{i(j+1)}\) only these entries in the disturbance vector \(\delta\) may be different from zero which share the same value \(i'\) and a constant \(j\) value, with

$$j = \text{mod}(j', 3)$$

\(^2\)Like the 'inner' iteration procedure applied in simulations with reduced chemical models to evaluate certain species concentrations (Chapter 3).

\(^3\)Be aware that the diffusivity of species \(i\) for instance depends on all species:

$$D_{im} = (1-Y_i) \left( \sum_{j=1}^{N} X_j / D_{ij} \right)^{-1}.$$
The calculated 'disturbed' residual vector $\tilde{r}(\hat{Y} + \delta)$ may then be used to evaluate all elements

$$J_{i(i'-1)}^{j''}, J_{i(i'+1)}^{j''} \text{ and } J_{i(i'+1)}^{i(j')}$$

simultaneously! In Fig. (A.1) this procedure is elucidated.

![Diagram showing numerical evaluation of the Jacobian matrix](image)

**fig. A.1:** Numerical evaluation of the Jacobian matrix. Here a theoretical model with four coupled differential equations ($N = 4$) is used as an illustration. A value for $j = \text{mod}(j', 3) = 1$ is indicated with the solid symbols in the disturbance vector (right). These correspond to the only entries which differ from zero. The corresponding elements of the Jacobian to be evaluated simultaneously with this $\delta$ are indicated with solid symbols in the micro-blocks.

From this it may be concluded that the evaluation of the complete Jacobian requires $3N$ residual vector evaluations, where $N$ equals the total number of differential equations to be solved.
A.3 A $C_1 - C_2$ Chemical scheme for methane combustion.

The $C_1$-$C_2$ chemical scheme by Warnatz [War83]. The reaction rate data for the thermal decomposition of $CH_4$, reactions 34 and 35, are different from the original reference. Here the rate data, mentioned in Eq. (2.42), page 52 are substituted.

<table>
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<tr>
<th>Number</th>
<th>Reaction</th>
<th>$A$</th>
<th>$n$</th>
<th>$k_{\text{nu}}$</th>
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### A.3. A C₁-C₂ mechanism

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<tr>
<td>30</td>
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### Chapter 2

#### A. Appendices

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### Notes

1. High-pressure limit: switching function $F([M]) = [M]^{0.0063}e^{0.000002/M}$ with $[M] = 0.000002/RT$.

2. Enhanced third body efficiencies $\sigma$: 

<table>
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<tr>
<th>$CH_4$</th>
<th>$H_2O$</th>
<th>$CH_2$</th>
<th>$CO$</th>
<th>$CO_2$</th>
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Table A.1. $C_4-C_5$ mechanism for $CH_4$-air combustion. The coefficients of the Arrhenius term $k = AT^n \exp(-E_a/RT)$ are given in the three columns on the right (see Chapter 1). All units are $cm$, $s$, $K$ and $\text{Kjoules}$ according to conventions used in standard literature on combustion.
Appendices Chapter 3

B.1 On the automatic generation of systematically reduced mechanisms.

Much of the reduction process is based on basic linear algebra. At least to the point where the truncation of the resulting steady-state expressions everything can be automated. Below the algorithm which is developed here, is described.

To derive a reduced model of order $O$ out of a reaction mechanism which consists of $N$ species and $E$ elements, a fixed number $S$ of steady-state assumptions has to be applied. A count of the free parameters in the chemical scheme leads to the observation that

$$S = N - E - O$$

which means that for the skeletal mechanism $(N = 16, E = 4)$, to obtain a four step model $(O = 4)$, eight steady-state assumptions have to be applied $S = 8$ (see chapter 3). For every species which is considered in a steady-state, the assumption

$$L(T_i) = 0 = \sum_{j=1}^{N_i} \nu_{ij} q_j$$

can be used to eliminate one, say $q_k$, of the reactions $q_j$ $(j = 1, \ldots, N_r)$ present in the source term $(L$ represents the convection-diffusion operator). This process is automated simply with the following pseudo fortran algorithm which eliminates $\nu_{ik}$ for all $i$ using the coefficient $\nu_{ik}$ of the selected steady-state species $i$:
It zeros out the column $k$ in the stoichiometry matrix $\nu_{ij}$ of the chemical scheme.

The approach is illustrated with the derivation of the 4-step model of Peters et al. [Pet91] which is based on the skeletal mechanism. The program needs an input file 'chemistr' which provides the species and the chemical mechanism and a file 'reduct' which specifies the steady-state species.

**File: chemistr**

**Elements**

H O C N

**End**

**Species**

CH4 CH3 CH3O CH2O HCO CO2 CO N2

H O2 OH HO2 H2O H2O2 N2

**End**

**Reactions**

H + O2 = OH + O
O + H2 = OH + H
H2 + OH = H2O + H
OH + OH = H2O
H + O2 = HO2 + M
H + HO2 = OH + HO2
HO2 + H = HO2 + M
CO + OH = CO2 + H
CH4 = CH3 + H
CH4 + H = CH3 + H2
CH3 + O = CH2O + H
CH2O + H = HCO + H2
HCO + OH = H2O + CO
HCO + M = CO + H + M
CH3 + O2 = CH3O + O
CH3O + H = CH2O + H2
CH3O + M = CH2O + H + M
HO2 + HO2 = H2O2 + O2
H2O2 + M = OH + OH + M
HO2 + OH = H2O + HO2
OH + M = H2O + M
H + H + M = H2 + M

**File: reduct**

**Steady**

CH3 CH3O CH2O HCO OH O HO2 H2O2

**End**

**Eliminate**

CH3 = K13
CH3O = K29
CH2O = K14
HCO = K17
O = K02
OH = K03
HO2 = K07
H2O2 = K22

**End**
Both files are read and processed to fill the stoichiometric matrix \( \nu_{ij} \) corresponding with this chemical model. The users choice for the reactions to be eliminated should correspond to the order in which the reaction scheme is read.

Below the stoichiometry matrix \( \nu_{ij} \) is presented and the reactions which are eliminated are indicated with an \( x \).

Original Stoichiometry
\( x \) indicates eliminated reactions

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<td>x</td>
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Table B.1: Stoichiometry matrix. The \( \nu_{ij} \) corresponding to the reactions that are going to be eliminated are indicated with an \( x \).

The algorithm then presents the result of the zeroing process for the non steady-state species afterwards, which for the specific choice gives:

Non Steady-State species
Reduced Stoichiometry

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</tbody>
</table>

Eliminated reactions: \( K_{02}, K_{03}, K_{07}, K_{13}, K_{14}, K_{17}, K_{20}, K_{22} \)
Additional (accidental, linear dependent) eliminated reactions: \( K_{04}, K_{08}, K_{15} \)

Table B.2: Stoichiometry matrix of the non steady-state species after the elimination process. The \( x \) correspond to the chosen reaction rates that are eliminated. The empty columns are reaction rates that have disappeared from the reduced mechanism also.
Now the user is prompted to choose a number of overall reactions from the possible set. Since in the file 'reduct' eight species are specified, the total number of global reactions is equal to \(4(= 16 - 4 - 8)\). All possible global reactions based on the input are presented by the algorithm, here being:

01: \(3H_2 + O_2 \rightarrow 2H + 2H_2O\)
05: \(2H \rightarrow H_2\)
06: \(3H_2 + O_2 \rightarrow 2H + 2H_2O\)
09: \(CO + H_2O \rightarrow CO_2 + H_2\)
10: \(CH_4 + H_2O \rightarrow CO + 3H_2\)
11: \(CH_4 + 2H + H_2O \rightarrow CO + 4H_2\)
12: \(CH_4 + 2H + H_2O \rightarrow CO + 4H_2\)
16: \(2H \rightarrow H_2\)
18: \(4H_2 + O_2 \rightarrow 4H + 2H_2O\)
19: \(2H \rightarrow H_2\)
21: \(4H_2 + O_2 \rightarrow 4H + 2H_2O\)
23: \(4H + 2H_2O \rightarrow 4H_2 + O_2\)
24: \(2H \rightarrow H_2\)
25: \(2H \rightarrow H_2\)

The number preceding the global reactions correspond to the column number of the stoichiometry matrix and are in fact derived from the columns of Table B.2 by reversing the approach which is used to extract the stoichiometry matrix from the input.

The choice of the global reactions is tested for linear dependence using Singular Value Decomposition (from [Pre93]), if not the user is prompted for another choice. Here, as an example we take the choice of Peters et al. being

\[
\begin{align*}
CH_4 + 2H + H_2O & \rightarrow CO + 4H_2 & r_1 \\
CO + H_2O & \rightarrow CO_2 + H_2 & r_{11} \\
H + H + M & \rightarrow H_2 + M & r_{111} \\
O_2 + 3H_2 & \rightarrow 2H + 2H_2O & r_{1111}
\end{align*}
\]

which corresponds to numbers 11, 9, 5 and 6 in the list presented above. Since all global reactions must be a linear combination of the chosen set, this fact can be used to determine the global reactions rates (again using SVD since the set of relations is overdetermined). For instance, it can be seen that \(r_{21} = r_6 - r_5\), thus leading to the observation that reaction 21 is present in both global reactions. Finally, the algorithm presents the global reactions with their global reaction rates:

11: \(CH_4 + 2H + H_2O \rightarrow CO + 4H_2 : K_{10} + K_{11} + K_{12}\)
09: \(CO + H_2O \rightarrow CO_2 + H_2 : K_{09}\)
05: \(2H \rightarrow H_2 : K_{05} - K_{10} + K_{16} - K_{18} + K_{19} - K_{21} + K_{23} + K_{24} + K_{25}\)
06: \(3H_2 + O_2 \rightarrow 2H + 2H_2O : K_{01} + K_{06} + K_{18} + K_{21} - K_{23}\)

which concludes the derivation of the Peters model. It should be mentioned that the Dibble model [Che91] can be derived if instead of the previously given file 'reduct', the one below is used:
This shows the dependency of the global reactions on the choices of the reactions that are eliminated. In fact, this is the reason that for different types of flames, different global models exist.

The presented approach is very flexible and the 5 step model mentioned in chapter 3 has in fact been derived using this algorithm. Furthermore, it should be noted that by far the largest effort is necessary to implement the string manipulations to extract the stoichiometry matrix from the reaction mechanism. All the linear algebra can be performed with standard software ([Pre93]) or is trivial.

B.2 Effect of cut-off on the burning properties.

In chapter 3 (section 3.4), cut-off (Fig. (3.12), p.104) is applied to deal with the numerical singularity appearing in the Jacobian. Here, a short numerical study is presented to determine at which value of $T_c$ the cut-off of the chemical source terms alters the observables. As mentioned in chapter 3 the cut-off strategy is applied to all variables, thus not only to the steady-state species. We will only study the effect on the adiabatic burning velocity $S_L$ since this is the most important parameter in premixed flames.

To get a clear picture of the effect of $T_c$ alone, no steady-state assumptions are employed in the calculations presented below. In Fig. (B.1), several values for $T_c$ are taken and the values for $S_L$ are indicated with different symbols. The computation with $T_c = 500$ $K$ is the lowest value for $T_c$ presented here, since for lower values for $T_c$ the results coincided with this computation. It may, therefore, be concluded that the value $T_c = 450$ $K$ which is used in the studies presented in chapter 3, has no noticeable effect on $S_L$ for the whole plotted range of $\varphi$.

Note that only at fairly high values (e.g. $T_c = 1100$) the $S_L$ deviates considerably from the computations with $T_c = 500$ $K$ (dashed line). In fact this value correlates with the so-called cross-over temperature $T_{cross} = 1300$ $K$. Often it is argued in reaction models where $H$ radicals play a significant role, chemical activity becomes important at temperatures higher than $T_{cross}$. Below the cross-over temperature it is believed that the recombination reaction

$$H + H + M \rightarrow H_2 + M$$
fig. B.1: The effect of different values for $T_C$ on the computed burning velocity. In all computations the width of the switching function ($\delta T_C$, p. (103)) is taken equal to $20K$. The symbols are explained in the figure. The cases with $T_C = 1100, 1300 K$ are connected by lines.

...is always larger than its reverse, the dissociation reaction and therefore at low temperatures the recombination of $H$ causes the chain reactions to stop, through the lack of $H$-radicals.
Appendices Chapter 4

C.1 On the convection-diffusion equation for elements

The conservation of elements will be illustrated with a fictitious, small reaction mechanism

\[
\begin{align*}
H_2 + M & \rightarrow H + H + M \quad r_1 \\
H_2 + O & \rightarrow H_2O \quad r_2 \\
O + OH & \rightarrow O_2 + H \quad r_3
\end{align*}
\]

consisting of only three reactions and six species. Furthermore, only two elements \( H \) and \( O \) are present in this scheme, which are conserved in every elementary reaction, as can be observed easily.

Let's consider the sum

\[
X_e = \sum_{i=1}^{N} \chi_{ie} X_i
\]

for the case of \( e = H \) (\( N \) is the number of species) and write the result explicitly:

\[
X_e = 2X_{H2} + 2X_{H2O} + X_H + X_{OH}
\]  

(C.1)

where a subscript \( h \) is used to distinguish \( X_h \) from mole fraction \( X_H \) of the \( H \)-radical. If we now consider the source term associated with \( X_h \) and write it explicitly:

\[
s_h = 2(-q_1 - q_2) + 2(q_2) + (2q_1 + q_3) - q_3 = 0
\]

it is zero as it should be, since elementary reactions do not create elements. It may be derived that \( s_e = \sum_{i}^{N} X_{ie} s_i = 0 \) for every element \( e \), where \( s_i \) equals the total chemical source term of species \( i \). Using this and the fact that Eq. (C.1) may be divided by \( M \), it may be derived that the specific element number \( \Gamma_e = X_e/M \) obeys a convection-diffusion equation with zero-source term,

\[
\rho \vec{\nabla} \cdot \vec{\nabla} \Gamma_e - \nabla \cdot (\rho l_e \vec{V}_e) = 0
\]

since all operators are linear and therefore, the summation \( \sum \chi_{ie} \) can be substituted in the derivatives. Obviously the elemental diffusion velocity is given by,

\[
\Gamma_e \vec{V}_e = \sum_{i=1}^{N} \Gamma_i \vec{V}_i
\]  

(C.2)
where \( \Gamma'_s = X_s/M \) and \( \vec{V}_s \), the species diffusion velocity. The convection-diffusion equations may be reformulated (using the continuity equation) to yield

\[
\nabla \cdot \vec{Q}_s - 0, \quad \text{with } \vec{Q}_s = \rho \nabla \Gamma'_s - \rho \Gamma'_s \vec{V}_s. \tag{C.3}
\]

Now we use the divergence theorem: \( \int_A \nabla \cdot \vec{Q}_s dA = \int_S \vec{Q}_s \cdot \vec{n} \) where \( A \) is two-dimensional area, \( S \) a closed surface bounding \( A \) and \( \vec{n} \) the unit outward normal vector at surface element \( dA \). Applied to the elementary micro-slit (Fig. (4.3)) and Eq.(C.3) the integration over \( S \) may be shown to give:

\[
\int_{(0,0)}^{(1/2,0)} Q_s^x dx + \int_{(0,0)}^{(1/2,1)} Q_s^y dx = 0 \tag{C.5}
\]

where the \( x \) and \( y \) component \( Q_s^x \) and \( Q_s^y \) of the element flux vector \( \vec{Q}_s \) are introduced. The quantities \( \frac{1}{2}p, L \) and \( \frac{1}{2}d \) are defined in Fig. (4.3). Due to the boundary conditions, the contributions of the other parts (walls II and II', symmetry III and III') vanish. At the inlet \( (x, y) \in [(0, 0), (1/2, 0)] \) the diffusional velocities are zero and the first part of the contour integral gives:

\[
\frac{1}{2}d, 0 \quad \Gamma'_s(0, 0) \int_{0,0}^{1/2,0} \rho(x, 0) v(x, 0) dx.
\]

with \( v \) the \( y \)-component of \( \vec{v} \). Using mass conservation this expression yields

\[
\Gamma'_s(0, 0) \int_{0,0}^{1/2,0} \rho(x, 0) v(x, 0) dx.
\]

The integration along the outlet, where it is assumed that the flow is uniform in \( y \)-direction the integral reduces to:

\[
\Gamma'_s(0, L) \int_{0,0}^{1/2,1} \rho(0, y) v(0, y) dx.
\]

which yields

\[
- \Gamma'_s(0, L) \int_{0,0}^{1/2,1} \rho(0, y) v(0, y) dx.
\]

which thus gives that for this particular geometry and set of boundary conditions elemental conservation can be checked by considering \( \Gamma'_s(0, 0) \) and \( \Gamma'_s(0, L) \) only.

\[\text{Remind that the mole fractions are constant along the inlet.}\]
Summary

The premixed flat flame burner enjoys a wide interest. The concept offers a well-defined experimental set-up which, due to the specific flow conditions, can be simulated using a simplified flow model. The main subject of this thesis is the simulation of (premixed) laminar flames stabilized on this type of burner with complex chemical models (detailed and reduced).

In chapter 1, a general introduction to combustion modelling is presented. The basic concepts, the reactive flow equations and elementary reaction kinetics, are discussed. Furthermore, the evaluation of transport and thermodynamic quantities in multi-component mixtures is addressed.

In chapter 2 a method is developed which enables the simulation of strictly one-dimensional premixed flames with detailed chemical models. Most important aspects involving the specific problems of modelling flames with detailed models are dealt with (discretization, adaptive gridding, modified Newton method). Using this method and a skeletal mechanism for lean methane/air combustion [Sm091], several approximations to the transport- and thermodynamical model are tested. It is found that the constant Lewis number approximation combined with a simplified model for the conductivity performs extremely well compared to the mixture-averaged approach. Global properties (burning velocity, stand-off distance and flame temperature) as well as the detailed structure (species profiles) are in close agreement for adiabatic as well as for burner-stabilized flames. In fact, simulations show that only the Lewis number of the $H$-radical has a significant effect on the global and detailed properties. All other Lewis numbers may be taken equal to one, still giving quantitatively good agreement with mixture-averaged transport results.

Compared to experiments and a larger chemical model ($C_1-C_2$ [War83]), the skeletal model has been shown to give good results for lean methane/air flames. As expected, for rich flames results tend to deviate from the ones obtained with the $C_1-C_2$ mechanism for both adiabatic and burner-stabilized flames. However, the burner-stabilized flame simulations show also that the importance of the $C_2$-chain increases with decreasing mass flow rate. This fact indicates that the region of validity of $C_1$ chemistry for adiabatic simulations, cannot be simply transferred to burner-stabilized flames.

In chapter 3 the 'systematic reduction' of detailed chemical mechanisms is studied. A method, using sensitivity analysis, is introduced to rationalize the reduction process. Both aspects, the selection of steady-state species as well as the truncation
of the resulting steady-state relations are covered by the sensitivity analysis. On the basis of the derivation of the 4-step model of Peters et al. [Pet87, Ses90], the method proves to give a relatively simple tool to derive a systematically reduced model.

A more important feature of the method is its ability of predicting the qualitative effects of the assumptions in reduced models. Therefore, it can be used to improve the performance of these models. Using the sensitivity analysis a 5-step model is derived which performs better than the 4-step model. These observations are confirmed by simulations of adiabatic and burner-stabilized flames. Furthermore, based on the sensitivity analysis, a simple extension was postulated to the expression of the \( OH \) radical in the 4-step model. Again, simulations show that this extended model performs better for adiabatic and stabilized lean methane/air flames than the original 4-step model.

In chapter 4, a method is developed to simulate two-dimensional premixed flames with detailed chemical models. The method is used to study the effect of the local structure of the ‘perforated plate’ burner [Maa94] on the flatness of the flame. A two-dimensional ‘multiple-slit’ model is introduced to simulate the effect of the plate perforation on the small scale disturbance of the flat flame. The detailed flame structure is computed for one value of the burner-plate porosity and some different values of the slit width. The results for the maximum stand-off distance confirm the conclusion already obtained by the simulations with a one-step global reaction model. Below a critical value for the slit width, the flame on the ‘perforated-plate’ burner behaves essentially as a one-dimensional flame. Even more, for the smallest modelled value of the slit width, the detailed structure along the center of the slit is almost indistinguishable from the results of a one-dimensional simulation.
Samenvatting

De voorgemengde vlakke vlam brander is een veelgebruikt instrument binnen het verbrandingsonderzoek. Het biedt een goed gedefinieerde experimentele situatie terwijl door zijn specifieke constructie, simulaties met een simpel stromingsmodel kunnen volstaan. Het hoofd onderwerp van dit proefschrift is nu de berekening van (voorgemengde) vlakke vlammen op dit soort branders, met complexe chemische modellen (gedetailleerd en gereduceerd).

In hoofdstuk 1 wordt een algemene inleiding gegeven over het modelleren van verbranding. De basis ingredienten, de stromingsvergelijkingen in reagerende media en elementaire reactie kinetiek, worden geïntroduceerd. Bovendien wordt de bepaling van transport- en thermodynamische grootten in mengsels besproken.

In hoofdstuk 2 wordt een methode ontwikkeld voor de berekening van zuiver een-dimensionale voorgemengde vlammen met gedetailleerde chemie. De belangrijkste aspecten van het modelleren van vlammen met dit soort chemische modellen worden behandeld (discretisatie, adaptief verroosteren, Newton methode). Met de ontwikkelde methode en een chemisch model[Smo91] specifiek voor arme methaan/lucht mengsels (skelet model), zijn verschillende aannamen in de transport- en thermodynamische modellen getest. Uit berekeningen volgt dat de constante Lewis getal aannemer is een zeer goede benadering is. Zowel de globale grootten (verbrandingssnelheid, stand-off distance, vlamtemperatuur) als de gedetailleerde structuur (temperatuur en stof profielen) stemmen uitstekend overeen met de resultaten van het complexere 'mixture-averaged' transport model. Het blijkt dat alleen het Lewis getal van het waterstof radicaal (H) een realistische waarde dient te hebben om de resultaten in goede mate te laten overeenstemmen met het complexe transport model.

Vergeleken met de experimenten en een uitgebreider mechanisme (C1-C2,[War83]), geven de berekeningen met het chemische skelet model goede resultaten voor arme mengsels. Als verwacht, wijken met name de resultaten voor rijke mengsels af van die van het C1-C2-model. Berekeningen aan brander gestabiliseerde vlammen laten zien dat het belang van de C2 keten toeneemt naarmate de massa stroom dichtheid afneemt. Hieruit, blijkt dat het geldigheidsgebied van de C1-chemie voor adiabatische vlammen niet zonder meer vertaald mag worden naar brander gestabiliseerde vlammen.

In hoofdstuk 3 wordt de systematische reductie van gedetailleerde reactie modellen bestudeerd. Er wordt een methode geïntroduceerd, gebaseerd op een 'sen-
sitivity' analyse, die het reductie proces rationaliseert. Beide aspecten, de keuze van de 'steady-state' componenten en het afbreken van de resulterende algebraische vergelijkingen, kunnen met de analyse geanalyseerd worden. De afleiding van het 4-staps model van Peters et al. [Pet87, Ses90], laat zien dat de methode een rationalisatie biedt van de afleiding van gereduceerde chemische modellen.

Bovendien kan met de geïntroduceerde 'sensitivity' analyse, de kwalitatieve effecten van verscheidene aannamen in de gereduceerde modellen voorspeld worden. De analyse kan daarom gebruikt worden om gericht verbeteringen aan te brengen. Gebruikmakend van deze techniek is een 5-staps model afgeleid. Dit model presteert beter dan het 4-staps model, wat bevestigd wordt door de berekeningen aan adiabatische en gestabiliseerde vlammen. Met behulp van de sensitivity analyse, is het mogelijk gebleken het 4-staps model belangrijk te verbeteren door de uitdrukking van

In hoofdstuk 4, wordt een methode ontwikkeld waarmee twee-dimensionale voorge- mengde vlammen gesimuleerd kunnen worden met gedetailleerde reactie mechanismen. De methode is toegepast op de berekening van het effect van de 'lokale' structuur van de 'geperforeerde plaat' brander [Maa94] op de vlahheid van de vlam. Een twee-dimensionaal meerdere spleten model is geïntroduceerd om het effect van de perforaties te modelleren. De gedetailleerde structuur is berekend voor een vaste waarde van de porositeit en een aantal waarden van de spleet breedte. De resultaten voor de maximum stand-off afstand stemmen overeen met die van een-staps reactie model. Beneden een kritische waarde van de spleet breedte gedraagt de vlam zich een-dimensionaal en blijkt de gedetailleerde structuur langs symmetrie als nagenoeg ononderscheidbaar van een zuivere een-dimensionale berekening.
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Stellingen

behorende bij het proefschrift van

L.M.T. Somers

The Simulation of Flat Flames
with
Detailed and Reduced
Chemical Models
1. De stabiliteit van een vlakke vlam, wordt veelvuldig gerelateerd aan het Lewis nummer van de brandstof. In methaan-lucht verbranding blijkt de structuur van de vlam in grote mate onafhankelijk hiervan. Om de stabiliteit van dit soort vlammen te beschrijven zou een complexer verbrandingsmodel genomen moeten worden. *Hoofdstuk 2, dit proefschrift.*

2. Het op 'fysische intuition' gebaseerde differentie schema van Thiart en het op mathematische analyse gebaseerde schema van Ghilani voor één-dimensionale convectie diffusie vergelijking zijn, mits er geen bronterm aanwezig is, identiek. *Hoofdstuk 2, Appendix A dit proefschrift.*

3. De slechtere convergentie eigenschappen van simulaties van vlakke vlammen met gereduceerde chemische modellen zijn niet te wijten aan de beperking van het aantal vrijheidsgraden in de toestandsruimte, maar aan slechte convergentie van de expliciet behandelde steady-state relaties.

4. Gezien het feit dat het relatief eenvoudig is om het effect van de meeste aannamen in klassiek gereduceerde chemische modellen te kwantificeren, zou dit bij de eerste publicatie van het betreffende model geëist moeten worden van de betreffende auteur. *Hoofdstuk 3, dit proefschrift.*

5. Mits de diameter-steek verhouding van de zogenaamde 'geperforeerde plaat' brander aan bepaalde voorwaarden voldoet, zijn de gemeten concentratie- en temperatuur profielen niet te onderscheiden van de resultaten van een zuiver één-dimensionale simulatie. *Hoofdstuk 4, dit proefschrift.*

6. Juist bij de simulatie van meer-dimensionale brander geometrieën met gedetailleerde chemische modellen, is de correcte discretisatie van de randvoorwaarden van uiterst belang. *Hoofdstuk 4, dit proefschrift.*

8. Het overdragen van de verantwoordelijkheid voor de wachtgelden aan de universiteiten, getuigt van een groot inzicht van de minister in het lange termijn effect van de AIO regeling en de economische ontwikkelingen.

9. Het appèl aan de zogenaamde 'kleine man' bij de beursgang van de KPN is niet bedoeld om het volk een leuke kans op winst de bieden, maar is juist een veilige manier om het bedrijfkapitaal te vergroten.

10. Als de neiging om fundamenteel onderzoek af te rekenen op de op korte termijn commercieel exploiteerbaarheid ervan in het verleden al had bestaan, was dit proefschrift om vele redenen nooit tot stand gekomen.

11. De weg van eerste concept naar uiteindelijke versie, wordt vaak als een iteratief proces beschreven. Het enige wat aan deze beschrijving ontbreekt is een goed gedefinieerd convergentie criterium.

12. Bij de fascistische uitingen in Duitsland in het afgelopen jaar reageert het Nederlandse volk 'spontaan' met een briefkaarten actie. In Italië worden vier fascistische ministers geïnstalleerd en Nederland zwijgt. Dit is een duidelijk gebrek aan relativeringsvermogen.