STELLINGEN

behoorende bij het proefschrift

Numerical modeling of turbulent natural-gas diffusion flames

van

Tim Peeters

1. Het kunstmatig triggeren van de omslag van laminaire naar turbulente stroming bij de numerieke simulatie van grenslaagstromingen verhindert een eerlijke vergelijking van de geldigheid van lage-Reynolds-turbulentiemodellen voor algemene toepassingen.

2. De kandschheitsverdeling van een reagerende scalar in een turbulente diffusievlam kan in algemene zin niet goed beschreven worden met behulp van een aangenomen verdelingsfunctie die slechts gebaseerd is op gemiddelde en variantie van die scalar.

3. Preferentiële diffusie van waterstof uit de reactiezone van voorgemengde laminaire koolwaterstofvlammen uit vlakke-vlam branders vergroot de stabiliteit van deze vlammen.

4. Bij het toepassen van de Discrete Transfer Methode voor de berekening van warmteoverdracht door straling van vlammen in een axisymmetrische geometrie, is de nauwkeurigheid erg gevoelig voor de verdeling van de discrete stralen over de hemisfeer.

Dit proefschrift

5. Het gebruik van zogenaamde pilot-vlammen voor de stabilisatie van turbulente diffusievlammen bemoeilijkt een nauwkeurige validatie van numerieke modellen voor deze vlammen. Dit proefschrift

6. Het feit dat de stromingsleer zich veelal bezig houdt met verschijnselen die beschreven worden door niet-lineaire partiële differentiaalvergelijkingen, leidt er toe dat de ontwikkelingen in dit wetenschapsgebied trager verlopen dan in wetenschapsgebieden waar vooral lineaire vergelijkingen van toepassing zijn.

7. De verbreding van de Westerse beschaving en de democratie leidt niet tot minder oorlogen.

8. Schoonheid is geen objectieve eigenschap van dingen, maar wordt bepaald door de gemoedsstoestand en culturele achtergrond van de waarnemer, en het tijdsgewricht waarin hij leeft.

9. Het zou de kwaliteit van de voetbaljournalistiek ten goede komen, indien jaarlijks een voetbalwedstrijd gespeeld zou worden tussen het Nederlands elftal en een elftal bestaande uit voetbalverslaggevers.

10. Coffeeshops kunnen beter drugstores genoemd worden.
Numerical modeling of
turbulent natural-gas diffusion flames
Numerical modeling of turbulent natural-gas diffusion flames

Numerieke modellering van turbulente aardgas diffusievlammen

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
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CHAPTER 1

Introduction

1.1 Natural gas combustion

The economic success of Western civilization is based upon its high energy consumption for industrial and household purposes. Important energy carriers are fossil fuels, viz. oil, coal and natural gas. In the Netherlands, natural gas combustion is one of the primary energy sources used in the production of electric power and for direct heating purposes in industry and households, simply because one of the world’s largest natural gas reserves is exploited there. The ongoing exploration efforts by oil and gas companies show that the estimated natural gas reserve still increases every year, in spite of the growing natural gas consumption. Therefore it is expected that natural gas will remain an important fuel for the next 50 years.

At present, governments in Europe and in the Netherlands in particular, are applying stricter regulations concerning the efficient use of fuel and the reduction of environmental pollution. Fossil fuel combustion inevitably produces large amounts of carbon dioxide (CO₂), which is believed to be an important contributor to the greenhouse effect and global climate change. Hence, efficient use of natural gas will automatically lead to lower CO₂ emission, and the common goals of higher efficiency and lower pollutant emission coincide. Besides, natural gas (consisting mainly of methane) has a relatively low carbon content and in this respect is a cleaner fuel than other fossil fuels, such as oil or coal. One would say that natural gas is a favourable fuel to use, if compared with other hydrocarbon fuels.

However, other important by-products of natural gas combustion are nitrogen oxides (NOₓ), which contribute to acid rain. The chemistry of NOₓ formation is complex and is still the subject of fundamental scientific study on chemical kinetics. Thus far, scientific studies have clearly shown that the two objectives of higher efficiency and cleaner combustion cannot be reconciled easily as far as NOₓ is concerned. A deeper insight into the chemistry of natural gas combustion and pollutant formation is warranted to be able to minimize environmental pollution without loss of efficiency.

1.2 Turbulent diffusion flames

The principal way of controlling a high-temperature large-scale flame is by feeding the fuel and oxidizer (air) through separate channels. Such a flame is called a non-premixed or diffusion flame: combustion can only occur upon mixing of the reactant streams induced by the (turbulent) flow beyond the inlet channels. The use of diffusion flames is widespread in industry and therefore has great economical and environmental significance.
In this respect it is easily understood that the interaction between turbulent mixing and chemical reactions is a key subject of investigation, both for the scientist and the engineer. One of the fundamental questions is how to optimize the efficiency and reduce the pollutant emissions by controlling the turbulent mixing processes and chemical reactions in flames. Despite many efforts over the last decades, this fundamental question is still unanswered, which is mainly due to the complex nature of turbulent mixing processes on the one hand, and to the complexity of natural-gas combustion and pollutant formation on the other hand.

The wide range of length scales and time scales of turbulent flames make a direct numerical solution of the governing equations intractable even for the fastest computers available. In practice, one has to resort to simplified models for the turbulent mixing as well as the flame chemistry, in order to have a computationally feasible tool for predictions (Libby and Williams, 1994). The challenge for the modeler who wishes to simulate turbulent diffusion flames is to combine the different physical and chemical submodels into a computer code which has reasonable computational costs, but still captures the most important features of the flames under investigation. The models need to be valid for a wide range of applications: high-temperature or low-temperature flames, high turbulent mixing intensity or low turbulent mixing intensity, including radiation effects, pollutant formation, soot formation, etc. This can only be accomplished by introducing several simplifications and assumptions based on physical or chemical reasoning, to be checked by comparison with experimental data. The experiments are to be performed under well-defined circumstances, in order to control the boundary conditions and to minimize experimental uncertainties. A crucial aspect of the experimental method is not to disturb the flame. Therefore, mostly laser-diagnostic methods are used (Bilger, 1994).

1.3 The importance of turbulent fluctuations

Because of the chaotic movement of the fluid, a turbulent diffusion flame exhibits strong temporal and spatial fluctuations of all of the relevant physical quantities, like velocity, pressure, temperature and species concentrations. As stated before, this chaotic behavior cannot be predicted by present-day theory and numerical models. Fortunately, in many applications one is mainly interested in the time-averaged behavior of the flame, and this can be modeled fairly well. An important feature to be included into the mathematical model, however, is the role of turbulent fluctuations. This can best be illustrated by the fact that the rates of chemical reactions occurring in a natural-gas flame usually have a strongly exponential dependence on the temperature. In order to evaluate the mean reaction rates, the exact nature of the temperature fluctuations, as contained in their local probability density function (PDF) is important (Williams, 1985).

Much theoretical research on combustion is aimed at the reduction of the number of independent thermochemical variables required to describe the flame accurately. In turbulent diffusion flames, the assumption of very fast reactions leads to a theoretical description with only a single independent scalar quantity: the mixture fraction (repre-
senting the mixedness of fuel and oxidizer) (Bilger, 1976b). If the statistics of the mixture fraction are known, the dependent quantities (temperature, species concentrations) are automatically known as well. A more sophisticated physical model treats the turbulent diffusion flame as an ensemble of many laminar flames with a one-dimensional structure. Again, the mixture fraction emerges as the key quantity in this model. The prediction of local PDF shapes of mixture fraction (in the simplified models) or temperature (in chemical kinetic models) is viewed as a major challenge for the modeler who wishes to obtain reliable numerical predictions.

1.4 Aims of this study

In the present investigation several aims are pursued. The first principal subject of this thesis is the exploration of the validity of relatively simple chemistry models for natural gas combustion in the specific application to large-scale furnace flows. Our interest in furnace flows stems from earlier work in the Section Heat Transfer in Delft by Post (1988), Koster (1993) and Wieringa (1992), and from work that is still in progress. Important phenomena like radiative heat transfer, turbulent flow and mixing of species, chemical reactions and the formation of NOx are incorporated in the FURNACE code, a 3D Navier-Stokes solver for furnace flow simulation.

Thus far, the treatment of chemistry and turbulent fluctuations of scalar quantities in the FURNACE code was carried out by crude approximations. In order to study the sensitivity of simulation results to the modeling assumptions of the mixture-fraction chemistry model, we implemented more elaborate chemistry models, using chemical equilibrium assumptions and more sophisticated PDF types. Emphasis is on the prediction of the thermal behavior of the furnace flow and the formation of NOx. As a side effect, much effort is devoted to the numerical efficiency of the implemented models, in order to keep computational costs within reasonable bounds.

The second principal subject is the study of axisymmetric turbulent jet diffusion flames. These flames are geometrically simple, allowing us to apply advanced models for turbulent combustion. Furthermore, laboratory experiments can be carried out in order to validate the numerical results, in contrast to the large-scale furnaces where experiments are very difficult. The experiments used for validation in this thesis were carried out in a parallel project and were performed mainly by laser-diagnostic methods (Laser-Doppler Anemometry, Laser-Induced Fluorescence), which produced high-quality data. The experiments of that project (and this simulation study) were conducted at the Section Heat Transfer, at the Department of Applied Physics of the Delft University of Technology. Thus, large amounts of local and spatial information on velocities, species concentrations and temperature were obtained, to be compared with calculated values. Consequently, these data are compared with the numerical results of two different chemistry models.

The first chemistry model is the simplified chemistry model used for the furnace flow simulations, in order to test its general validity and applicability. Usually, furnace simulations are very time consuming and a significant improvement of algorithms is
Chapter 1. Introduction

sought in order to enhance the speed of the calculations to such an extent that more elaborate models come within reach. The second model is a chemical kinetics model, first developed by Bockhorn (1989), which allows a detailed insight into the relevant chemical reactions and species present in natural-gas flames. This chemical kinetics model uses assumed-shape joint-PDFs for temperature and mass fractions in order to close the mean chemical reaction rates. This chemistry model is a challenge to the modeler, since a large number of coupled transport equations are to be solved on sufficiently fine grids, which can only be performed by large and fast computers, like Cray or Convex supercomputer.

As a side step, the detailed structure of one-dimensional laminar flames has been studied. The geometrical simplicity of one-dimensional laminar flames allows a detailed numerical investigation, without the modeling assumptions so common in turbulent flame calculations. The results of the laminar flame simulations are used for the detailed kinetics model, in order to determine the relative influence of reaction rate constants and the types of reaction mechanisms used. Hence, a suitable reaction mechanism may be selected from literature without too much numerical effort. Furthermore, the simplified chemistry models for the furnace simulations are compared with laminar flame data.

1.5 Outline of this thesis

The thesis consists of eight chapters. Chapter 2 gives the basic physical and chemical theory required for the description of transport phenomena, turbulent flow, chemical reactions and radiative heat transfer. Chapter 3 describes in more detail various techniques to reduce the number of independent variables for a chemically reacting and radiating system, the modeling of laminar flames, models for turbulence-chemistry interactions by assumed-shape PDFs, and the modeling of pollutant species formation such as NO and soot. Subsequently, Chapter 4 deals with the numerical tools used to solve the model equations.

Results of the numerical simulations are presented in Chapters 5 to 7. Chapter 5 shows results for laminar flame simulations, in Chapter 6 results are shown for the piloted laboratory-scale diffusion flames, and Chapter 7 discusses the simulation of large-scale industrial furnaces. At the end of each chapter, a separate section is devoted to conclusions. In the last chapter, the most important conclusions are reconsidered and held against the aims put forward in the Introduction.
CHAPTER 2

Basic theory

2.1 Introduction

The theory of turbulent diffusion flames involves the description and modeling of turbulent flow, chemical reactions and radiative heat transfer. In this chapter the most important basic descriptions of these phenomena relevant to combustion problems will be presented. A restriction is made to steady-state combustion, thereby excluding typical non-stationary effects such as explosions or reciprocating engine combustion. We will only deal with gaseous flow, without droplets or solid particles.

The chapter first deals with the general conservation equations for the independent variables in reacting flows. The fundamentals of the theory and the application to combustion phenomena is given by Williams (1985). The major transport properties for mass, momentum and energy are discussed in separate subsections, as are the fundamentals of chemical reaction kinetics.

The conservation equations, although considered to be valid at every point in space and time, are intractable for numerical solution in the case of turbulent reacting flow. The common way out of this dilemma is the use of ensemble or time averaged equations and quantities. Unfortunately several unknown correlations and quantities enter these averaged equations. This well-known closure problem of turbulence is how to close the set of equations by suitable models to allow a physically realistic solution. Most turbulence closure models are based on the so-called moment closure, which will be discussed in a subsequent section.

The moment closure of turbulence fails in the case of the highly non-linear chemical reaction rates in flames. For the closure of these terms the probability density function (PDF) of the independent quantities is employed. Therefore some general stochastic theory is presented, which is a useful tool in the formulation and application of PDFs in turbulent reacting flow.

The last section focusses on the modeling of radiative heat transfer in flames.

2.2 Deterministic description of reacting flow

2.2.1 Conservation equations

The conservation laws of physics can be used to derive transport equations for mass, momentum, energy, chemical species in a reacting gaseous flow. We will simply state the equations to be used for atmospheric gaseous flames.

The continuity equation or conservation of mass reads:

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

(2.1)
where $\rho$ is the density of the mixture and $v$ the velocity. Momentum conservation is described by the Navier-Stokes equations:

$$\rho \frac{\partial v}{\partial t} + \rho v \cdot \nabla v = -\nabla p - \nabla \cdot T + \rho g \quad (2.2)$$

In this equation, $p$ is the pressure, $T$ is the viscous stress tensor and $g$ is the gravitational acceleration. Energy conservation is expressed by:

$$\rho \frac{\partial E}{\partial t} + \rho v \cdot \nabla E = -\nabla \cdot q - (p I + T) : (\nabla v) + \rho S_{\text{rad}} \quad (2.3)$$

where $E$ is the total energy per unit mass, i.e. the sum of the internal energy $U$ and the kinetic energy $\frac{1}{2}v_i v_i$. The energy flux vector $q$ remains to be specified, just like the radiation source/sink term $\rho S_{\text{rad}}$. One can also include the radiation term in the energy flux vector by defining $\rho S_{\text{rad}} \equiv -\nabla \cdot q_{\text{rad}}$.

Conservation of a chemical species $\mathcal{M}_i$ is expressed by the equation for the mass fraction $Y_i$:

$$\rho \frac{\partial Y_i}{\partial t} + \rho v \cdot \nabla Y_i = -\nabla \cdot (\rho Y_i V_i) + \dot{w}_i \quad (2.4)$$

where $V_i$ is the molecular diffusion velocity for species $\mathcal{M}_i$, and $\dot{w}_i$ is the net chemical formation rate of the species in kg$\cdot$m$^{-3}$$\cdot$s$^{-1}$. The set of $N + 5$ transport equations involves $N + 7$ independent quantities, namely $\rho, v, p, E, T$ and $Y_i, i = 1, \ldots, N$. The set is closed by the hydrodynamic equation of state, which relates the pressure to the density, and the caloric equation of state, which relates the enthalpy $h \equiv E + p/\rho$ to the temperature $T$:

$$p = \rho R^0 T \sum_{i=1}^{N} \frac{Y_i}{M_i} \quad (2.5)$$

$$h = \sum_{i=1}^{N} h_i Y_i \quad (2.6)$$

$$h_i = \int_0^T c_{p,i}(\theta) d\theta \quad (2.7)$$

where $M_i$ are the molar masses of the species and $c_{p,i}$ are the specific heats. This closes the set of equations. Quantities which still have to be specified in terms of the basic variables are the properties such as dynamic viscosity $\mu$, specific heat $c_{p,i}$, the heat flux vector $q$, the radiation term $\rho S_{\text{rad}}$, the species diffusion velocities $V_i$ and the chemical reaction rates $\dot{w}_i$. These will be discussed in the next subsections.

The definition of the mass fraction provides an additional equation:

$$\sum_{i=1}^{N} Y_i = 1, \quad (2.8)$$
2.2. Deterministic description of reacting flow

which means that only \( N - 1 \) transport equations for the \( N \) different species in the flow are required. The mole fractions are related to the mass fractions by:

\[
X_i = \frac{M_m Y_i}{M_i}
\]  

(2.9)

where \( M_m \equiv (\sum_{i=1}^{N} Y_i/M_i)^{-1} \) is the average molar mass of the mixture.

2.2.2 Transport properties

In evaluating the multicomponent transport properties for a given mixture, it is convenient to start with the pure-species properties (viscosity, conductivity) and the binary diffusion coefficients. Next, the mixture averaged or multicomponent properties can be determined from these pure-species properties and the mixture composition. In general, the species properties in the mixture are found by solving a set of equations commonly referred to as the \( L \) matrix (Hirschfelder et al., 1954). In the sequel, however, we will assume that this solution can be obtained by numerical methods (Kee et al., 1986).

Viscosity

For a Newtonian fluid, the momentum flux is given by the viscous stress tensor:

\[
T = -\mu \left( (\nabla v) + (\nabla v)^T \right) + \frac{2}{3}\mu (\nabla \cdot v) I
\]  

(2.10)

where \( \mu \) is the dynamic viscosity of the mixture, \( (\nabla v) \) is the dyadic product and \( I \) is the identity tensor. The bulk viscosity has been neglected.

The semi-empirical formula of Wilke (1950) relates the mixture averaged dynamic viscosity \( \mu \) to the pure-species viscosities \( \mu_i \) by:

\[
\mu = \sum_{i=1}^{N} \frac{X_i \mu_i}{\sum_{j=1}^{N} X_j \Phi_{ij}}
\]  

(2.11)

where

\[
\Phi_{ij} = \frac{1}{\sqrt{8}} \left( 1 + \frac{M_i}{M_j} \right)^{-1/2} \left[ 1 + \left( \frac{\mu_i}{\mu_j} \right)^{1/2} \left( \frac{M_j}{M_i} \right)^{1/4} \right]^2
\]  

(2.12)

This formula may be used for laminar flames. For turbulent flames simplified forms can be used, such as Sutherland's law with species weighting:

\[
\mu = \sum_{i=1}^{N} \frac{A_i T^{3/2} Y_i}{B_i + T}
\]  

(2.13)

or even the averaged form of Sutherland's law for air:

\[
\mu = \frac{A_m T^{3/2}}{B_m + T}
\]  

(2.14)
These approximate expressions usually will capture the major temperature dependence of the mixture averaged dynamic viscosity. The kinematic viscosity is then defined by $\nu = \mu / \rho$.

**Specific heat**

The specific heat of each individual pure species generally strongly depends on the temperature. We can represent this by means of a polynomial in $T$:

$$c_{p,i} = \sum_{n=1}^{P} n a_{n,i} T^{n-1}$$  \hfill (2.15)

In this thesis we have adopted the CHEMKIN polynomial tables (Kee et al., 1987; Kee et al., 1989). The number of coefficients $P = 5$, and different polynomials are used for low and high temperatures, continuously matched at the common temperature of 1000 K.

The enthalpy $h_i$ as a function of temperature reads (see eq. 2.7):

$$h_i = \sum_{n=0}^{P} a_{n,i} T^n$$  \hfill (2.16)

Here $a_{0,i}$ denotes the enthalpy of formation at $T = 0$ K, which is a constant for each species.

**Species diffusion**

The multicomponent species diffusion flux is given by:

$$J_i = \rho Y_i V_i$$  \hfill (2.17)

The diffusion velocities $V_i$ of the species are implicitly given by:

$$\nabla X_i = \sum_{j=1}^{N} \left( \frac{X_i X_j}{D_{ij}} \right) (V_j - V_i) + (Y_i - X_i) \left( \frac{\nabla p}{p} \right), \ i = 1, \ldots, N$$  \hfill (2.18)

with $D_{ij}$ the multicomponent diffusion coefficients of the species. In the above equation we have assumed that gravity is the only external force acting on the gas, and thermal diffusion (Soret effect) has been neglected.

The diffusion velocities $V_i$ depend on mole fraction gradients and pressure gradient. Due to the complex nature of (2.18) simplifications are sought. In atmospheric flames at moderate velocities the influence of the pressure gradient can usually be neglected. Hence, the equation for the diffusion velocity can be rewritten as:

$$\nabla X_i = \sum_{j=1}^{N} \left( \frac{X_i X_j}{D_{ij}} \right) (V_j - V_i)$$  \hfill (2.19)
This equation is referred to as the Stefan-Maxwell equation. The multicomponent diffusion coefficients $\bar{D}_{ij}$ can be obtained from equations which are provided by kinetic gas theory (Hirschfelder et al., 1954; Williams, 1985). Numerical codes exist which solve the Stefan-Maxwell equations for a given number of species (Kee et al., 1986). The $\bar{D}_{ij}$ depend on pressure and temperature by $T^{\alpha}/p$, with $\frac{3}{2} \leq \alpha \leq 2$. The multicomponent diffusion coefficients depend on the mixture as well as the pure species properties; in general $\bar{D}_{ij} \neq \bar{D}_{ji}$. This is in contrast with the pure binary diffusion coefficients $D_{ij}$ which do not depend on the composition of the mixture, and which can be computed from the kinetic gas theory.

The evaluation of multicomponent diffusion coefficients is computationally expensive. In many cases, e.g. turbulent flames, these coefficients do not matter much and one may often want to use mixture averaged diffusion coefficients or even one and the same diffusion coefficient for all species. In laminar flame calculations the same approximations may also yield sufficient accuracy. In accordance with Fick’s diffusion law one may write:

$$V_i = -\bar{D}_i \frac{\nabla X_i}{X_i}$$  \hspace{1cm} (2.20)

where $\bar{D}_i$ is the mixture averaged diffusion coefficient of $i$:

$$\bar{D}_i = \frac{1 - Y_i}{\sum_{j \neq i} X_j / \bar{D}_{ij}}$$ \hspace{1cm} (2.21)

This formula should be used for $N - 1$ species only, since the $N$th species is used to satisfy $\sum_{i=1}^{N} Y_i V_i = 0$. The error thus introduced is minimized if the $N$th species is a dominant species ($X_i$ not too small).

**Heat diffusion**

The energy flux vector $\mathbf{q}$ appearing in (2.3) reads:

$$\mathbf{q} = -\lambda \nabla T + \rho \sum_{i=1}^{N} h_i Y_i V_i + R^0 T \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \frac{X_j \bar{D}_{T,i}}{M_i \bar{D}_{ij}} \right) (V_i - V_j)$$ \hspace{1cm} (2.22)

where $\lambda$ is the thermal conductivity of the mixture. The energy flux vector consists of several contributions: thermal conductivity (described by Fick’s law), multicomponent heat diffusion and Dufour effects (heat flux due to concentration gradients). In turbulent flames, the Dufour effect and the multicomponent diffusion term are often negligible. For laminar flames, however, multicomponent diffusion and Dufour effects may become important.

The mixture averaged thermal conductivity is computed from:

$$\lambda = \frac{1}{2} \left( \sum_{i=1}^{N} X_i \lambda_i + \left( \sum_{i=1}^{N} X_i / \lambda_i \right)^{-1} \right)$$ \hspace{1cm} (2.23)
2.2.3 Chemical reaction kinetics

The chemical reactions in hydrocarbon flames are of various nature and complexity. The complete set of possible elementary reactions and species involved can be very large. Natural gas combustion, for example, may be described by over 100 reversible elementary reactions, involving over 40 different species (Warnatz, 1984). The kinetics of chemical reactions are of great importance when calculating the structure of flames. In the sequel some fundamental notions will be discussed. Detailed information on reaction kinetics in flames can be found in numerous review papers (Basevich, 1987; Gardiner and Troe, 1984; Warnatz, 1984; Westbrook and Dryer, 1984).

If we consider a set of $K$ elementary reactions, which may be reversible or irreversible, these reactions can be formalized as:

$$\sum_{i=1}^{N} \nu_{ik}^\prime M_i = \sum_{i=1}^{N} \nu_{ik}^\prime M_i$$  \hspace{1cm} (2.24)

Here the numbers $\nu_{ik}^\prime$ and $\nu_{ik}''$ are the stoichiometric coefficients of the species $i$ in reaction $k$, and $M_i$ is the chemical symbol for species $i$. Generally, the stoichiometric coefficients are integers for elementary reactions, and not more than three different species will act as reactants (or products) in each elementary reaction. We can define generalized coefficients $\nu_{ik} = \nu_{ik}'' - \nu_{ik}^\prime$. These coefficients are zero if the species $i$ is not changed, positive if it is formed, and negative if it is consumed by reaction $k$.

If the chemical reaction rate of reaction $k$ is denoted as $\omega_k$, then the net formation/destuction rate of $i$ (in kg·m$^{-3}$·s$^{-1}$) due to all reactions reads:

$$\dot{\omega}_i = \sum_{k=1}^{K} M_i \nu_{ik} \omega_k$$  \hspace{1cm} (2.25)

where

$$\omega_k = k_{f,k} \prod_{j=1}^{N} C_j^{\nu_{j}^f} - k_{r,k} \prod_{j=1}^{N} C_j^{\nu_{j}^r}$$  \hspace{1cm} (2.26)

In this expression $C_i$ denotes the molar concentration of species $i$, which is equal to $\rho Y_i / M_i$, and $k_{f,k}$, $k_{r,k}$ represent the forward and reverse reaction rate constants. The reaction rate constants depend on temperature according to the Arrhenius rate expression:

$$k_{f,k} = A_k T^{\beta_k} \exp \left( \frac{-E_{A,k}}{R^o T} \right)$$  \hspace{1cm} (2.27)

In this equation $A_k$ is the pre-exponential factor, $\beta_k$ the temperature exponent and $E_{A,k}$ the activation energy of the forwards reaction $k$. The activation energy $E_{A,k}$ is sometimes expressed as an activation temperature $T_{A,k} \equiv E_{A,k} / R^o$.

Although it is possible to specify the forward and reverse rate constants separately for each elementary reaction, it is customary to derive the reverse rates from the forward
2.2. Deterministic description of reacting flow

rates and the equilibrium constants. The equilibrium constant of an elementary reaction is defined as:

$$K_k^{eq} = \frac{k_{f,k}}{k_{r,k}}$$  \hfill (2.28)

The advantage of this approach lies in the fact that the equilibrium constants can be determined from thermodynamic properties, which are often known with better accuracy than the individual forward or reverse rate constants. Hence, although the forward rate may be suffering from possible experimental uncertainties in its constants, the reverse rate will be defined in such a way as to preserve the correct chemical equilibrium properties.

The equilibrium constant reads:

$$K_k^{eq} = \left( \frac{p^0}{R^0 T} \right) \sum_{i=1}^{N} \nu_{ik} \exp \left( \frac{\Delta S_k^0}{R^0} - \frac{\Delta H_k^0}{R^0 T} \right)$$  \hfill (2.29)

where the quantities $\Delta S_k^0$ and $\Delta H_k^0$ denote the change in entropy and enthalpy respectively, if reaction $k$ passes completely from reactants to products:

$$\Delta S_k^0 = \sum_{i=1}^{N} \nu_{ik} S_i^0$$  \hfill (2.30)

$$\Delta H_k^0 = \sum_{i=1}^{N} \nu_{ik} H_i^0$$  \hfill (2.31)

Here $S_i^0$ and $H_i^0$ are species properties in molar units, which are often known with sufficient accuracy.

Three-body recombination reactions

Elementary reactions describing the dissociation of a single molecule into two radicals require the presence of a third molecule in order to preserve the momentum and energy of the collision. The same holds for a recombination of two radicals forming a larger molecule. Formally this is expressed by writing:

$$M_1 + M_2 + M \rightleftharpoons M_3 + M$$  \hfill (2.32)

The reaction rate then reads:

$$\omega_k = \left( \sum_{i=1}^{N} \alpha_{ik} C_i \right) \left( k_{r,k} \prod_{j=1}^{N} C_{j}^{\nu_{jk}} - k_{r,k} \prod_{j=1}^{N} C_{j}^{\nu_{jk}} \right)$$  \hfill (2.33)

Here, the $\alpha_{ik}$ are efficiency factors for the species acting as a third body. If all species have equal efficiency for participating as a third body, then $\alpha_{ik} = \alpha_k$ and one may write:

$$\sum_{i=1}^{N} \alpha_{ik} C_i = \alpha_k \frac{p}{R^0 T}$$  \hfill (2.34)
Generally, however, the efficiency factors will differ among the species.

Some three-body recombination reactions will behave in a regime falling between the asymptotic low-pressure and high-pressure limits. For high pressures the role of the third body becomes negligible and one may write $\mathcal{M}_1 + \mathcal{M}_2 \rightleftharpoons \mathcal{M}_3$, whereas for low pressures $\mathcal{M}_1 + \mathcal{M}_2 + \mathcal{M} \rightleftharpoons \mathcal{M}_3 + \mathcal{M}$ should be written. The intermediate region is called the fall-off region, and is denoted by $\mathcal{M}_1 + \mathcal{M}_2(+\mathcal{M}) \rightleftharpoons \mathcal{M}_3(+\mathcal{M})$. The fall-off reactions have special rate constants, according to the formulations called the Lindemann form, Troe form or SRI form (Gardiner and Troe, 1984).

2.3 Probability theory

The deterministic time-dependent transport equations for the major variables in a turbulent reacting flow are unsolvable from the theoretical as well as the computational point of view. Theoretically, the time-dependent partial differential equations are only solvable if the boundary conditions are specified with sufficient accuracy. In a turbulent flow the boundary conditions are fluctuating in time, and this temporal behavior is unknown in a deterministic sense. This theoretical problem can be circumvented by using some statistical properties of the boundary conditions, such as their average value and r.m.s. fluctuations, which are often reasonably well known. It is then expected that the ensemble averaged solution of the unsteady transport equations does not depend much on the errors in the boundary conditions. The non-linear nature of the coupled partial differential equations, however, can still lead to chaotic behavior of the solution, which hampers an unambiguous interpretation of the results.

On the other hand, the wide range of length scales and time scales in a turbulent reacting flow can only be solved numerically with sufficient resolution if a very large number of discrete points in time and space is used. It can be estimated that this would require an enormous computational power and data storage capacity, which is far beyond the capability of present-day computers. But even if the computational power were available it is still uncertain whether numerical algorithms can be found which will converge to yield the desired solution.

The counterpart of the deterministic approach to turbulent reacting flow is the stochastic approach. The fluctuating quantities in the flow can be thought of as stochastic variables, the full statistical description of which involves the set of all correlation functions in time and space. As with the deterministic solution, the full statistical information cannot be found for practical problems. For many purposes, however, the one-point joint statistical description of all relevant variables will provide sufficient information. This implies that correlations between variables in physical space are excluded from this description. More general theory on the stochastic approach to turbulent reacting flows is given by Pope (1979, 1985), Borghi (1988) and Kollmann (1989). In this section some basic theoretical concepts of the statistical theory will be given, to be used for specific cases afterwards.
2.3. Probability theory

2.3.1 Univariate probability theory

If we consider the statistical properties of a single stochastic variable \( \phi \), we can define the distribution function of \( \phi \) in every point \((x, t)\) in time and space by:

\[
F_\phi(\psi; \mathbf{x}, t) \equiv \mathcal{P}(\phi < \psi; \mathbf{x}, t)
\]  \hspace{1cm} (2.35)

In this formula, \( \mathcal{P}(\phi < \psi; \mathbf{x}, t) \) denotes the probability of finding \( \phi < \psi \) at time \( t \) and location \( \mathbf{x} \). The probability density function \( f_\phi \) is subsequently defined as the derivative of \( F_\phi \):

\[
f_\phi(\psi) = \frac{dF_\phi(\psi)}{d\psi}
\]  \hspace{1cm} (2.36)

Using this definition, one sees that \( f_\phi(\psi) \, d\psi \) represents the probability of finding \( \psi \leq \phi < \psi + d\psi \).

Probability theory states that \( 0 \leq \mathcal{P} \leq 1 \), which leads to a number of basic properties of \( \mathcal{F} \) and \( f_\phi \):

\[
\begin{align*}
0 & \leq F_\phi(\psi) \leq 1 \\
f_\phi(\psi) & \geq 0 \\
\int_{-\infty}^{\infty} f_\phi(\psi) \, d\psi & = 1
\end{align*}
\]  \hspace{1cm} (2.37), (2.38), (2.39)

At this stage is noteworthy to mention that \( f_\phi \) is a function of time and space. In turbulent flows with stationary statistical properties of \( \phi \) in every point in space, the time dependence of \( f_\phi \) is dropped. For the practical applications described in this thesis that will be the case. In the sequel we will tacitly assume time-independent probability density functions only.

If the stochastic variable \( \phi \) takes a uniform value \( c \) over the physical domain of interest, the space dependence is dropped. The distribution function then reduces to:

\[
F_\phi(\psi) = \mathcal{H}(\psi - c)
\]  \hspace{1cm} (2.40)

for every point \( \mathbf{x} \) in space. \( \mathcal{H} \) is the Heaviside step function, defined by:

\[
\mathcal{H}(x) = \begin{cases} 0 & \text{if } x < 0 \\ 1 & \text{if } x \geq 0 \end{cases}
\]  \hspace{1cm} (2.41)

The corresponding PDF is the Dirac delta function:

\[
f_\phi(\psi) = \delta(\psi - c)
\]  \hspace{1cm} (2.42)

with the Dirac function formally defined by:

\[
\int_{-\epsilon}^{\epsilon} \delta(x) = 1 \text{ for every } \epsilon > 0
\]  \hspace{1cm} (2.43)
Chapter 2. Basic theory

The function $f_\phi$ (or $F_\phi$) contains all the one-point statistical properties of the variable $\phi$ in every point in space. Some important properties will be discussed below. The expectation or average of $\phi$ is denoted by $\mathcal{E}(\phi)$, $\langle \phi \rangle$ or $\bar{\phi}$ and is found by:

$$\langle \phi \rangle = \int_{-\infty}^{\infty} \psi f_\phi(\psi) \, d\psi$$  \hspace{1cm} (2.44)

The average $\langle \phi \rangle$ is also called the first moment of the PDF $f_\phi$. In general, the $n^{th}$ moment of a PDF is defined by:

$$\langle \phi^n \rangle = \int_{-\infty}^{\infty} \psi^n f_\phi(\psi) \, d\psi$$  \hspace{1cm} (2.45)

If the PDF is known, all moments can be obtained provided the integration converges. On the other hand, the PDF cannot be constructed from a finite number of its moments even if this number is very large. Only if an analytical expression for the PDF exists and is known, then a finite number of its moments may fully define the PDF.

With the expectation of $\phi$ we can use the Reynolds decomposition to define:

$$\phi = \langle \phi \rangle + \phi'$$  \hspace{1cm} (2.46)

where $\phi'$ is the fluctuating part of $\phi$ relative to the average value. For the fluctuations we can define the $n^{th}$ central moment by:

$$\langle \phi'^n \rangle = \int_{-\infty}^{\infty} (\psi - \langle \phi \rangle)^n f_\phi(\psi) \, d\psi$$  \hspace{1cm} (2.47)

By definition, the first central moment is always zero. The second central moment $\langle \phi'^2 \rangle$ is called the variance. The square root $\sigma$ of the variance is a measure for the width of the PDF. The third central moment is related to the asymmetry of the PDF and is called the skewness.

Finally, for any variable $Q$ which is a function of a stochastic variable $\phi$, we can derive its statistical properties by means of:

$$\langle Q \rangle = \int_{-\infty}^{\infty} Q(\psi) f_\phi(\psi) \, d\psi$$  \hspace{1cm} (2.48)

2.3.2 Multivariate probability theory

Although the univariate PDF of a single quantity $\phi$ already provides a great deal of information in turbulent flows, we are generally interested in correlations between relevant quantities. This involves the knowledge of the joint probability density functions of a set of stochastic variables. In accordance with the previous subsection, the probabilities are assumed to be time independent. We will only consider correlations in time between variables.
2.3. Probability theory

Suppose we have \( n \) stochastic quantities \( \phi_1, \phi_2, \ldots, \phi_n \), denoted by \( \Phi \). These quantities can be scalar quantities like temperature or species concentrations, but also vector components such as the \( u \)-velocity etc. Then it is possible to define the joint distribution function:

\[
F_{\Phi}(\psi) \equiv \mathcal{P}(\Phi < \psi)
\]

where \( \Phi < \psi \) is the abbreviated notation for \( \phi_1 < \psi_1, \ldots, \phi_n < \psi_n \). The joint PDF reads:

\[
f_{\Phi}(\psi) = \frac{\partial^n}{\partial \psi_1 \cdots \partial \psi_n} F_{\Phi}(\psi_1, \ldots, \psi_n)
\]

Hence:

\[
f_{\Phi}(\psi) \, d\psi = \mathcal{P}(\psi \leq \phi < \psi + d\psi)
\]

The basic properties of the univariate PDF can be expanded to the multivariate (joint) PDF:

\[
f_{\Phi}(\psi) \geq 0 \tag{2.52}
\]

\[
\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} f_{\Phi}(\psi) \, d\psi = 1 \tag{2.53}
\]

\[
\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} f_{\Phi}(\psi) \, d\psi_1 \cdots d\psi_{i-1} d\psi_{i+1} \cdots d\psi_n = f_{\phi_i}(\psi_i) \tag{2.54}
\]

It is observed that the marginal univariate PDF \( f_{\phi_i} \) can always be retrieved from the joint PDF upon integration over all other variables.

As with the univariate PDF, the statistical properties of any variable \( Q \) which is a function of \( \Phi \) are found by:

\[
\langle Q \rangle = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} Q(\psi) f_{\Phi}(\psi) \, d\psi
\]

(2.55)

From the joint PDF the correlations between any subset of variables can be obtained, for example:

\[
\langle \phi_1 \phi_2 \rangle = \langle \phi_1 \rangle \langle \phi_2 \rangle + \langle \phi_1^' \phi_2^' \rangle = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi_1 \psi_2 f_{\phi_1 \phi_2}(\psi_1, \psi_2) \, d\psi_1 d\psi_2 \tag{2.56}
\]

The correlation coefficient \( r_{12} \) of variables \( \phi_1 \) and \( \phi_2 \) is defined by:

\[
r_{12} = \frac{\langle \phi_1^' \phi_2^' \rangle}{\langle \phi_1^2 \rangle^{1/2} \langle \phi_2^2 \rangle^{1/2}} \tag{2.57}
\]

In general, \(-1 \leq r \leq 1\). If \(|r| = 1\) then \( \phi_1 \) and \( \phi_2 \) are said to be perfectly correlated. If \( r = 0 \) then the variables are uncorrelated.
2.3.3 Conditional probability

Conditional probability theory is of particular importance in the stochastic approach to turbulent reacting flows. The probability of finding event $A$ conditional upon event $B$ is defined as:

$$
P(A \mid B) = \frac{P(A \land B)}{P(B)} \quad (2.58)
$$

The conditional PDF for a quantity $\phi_1$ conditional upon $\phi_2$ can be written as:

$$f_{\phi_1 \mid \phi_2}(\psi_1 \mid \psi_2) = \frac{f_{\phi_1 \phi_2}(\psi_1, \psi_2)}{f_{\phi_2}(\psi_2)} \quad (2.59)
$$

This conditional PDF can be understood as follows. $f_{\phi_1 \mid \phi_2}(\psi_1 \mid \psi_2) \, d\psi_1$ represents the probability to find $\psi_1 \leq \phi < \psi_1 + d\psi_1$ upon the condition that $\phi_2 = \psi_2$. Rephrasing (2.59) shows:

$$f_{\phi_1 \phi_2}(\psi_1, \psi_2) = f_{\phi_1}(\psi_1) f_{\phi_2 \mid \phi_1}(\psi_2 \mid \psi_1) = f_{\phi_2}(\psi_2) f_{\phi_1 \mid \phi_2}(\psi_1 \mid \psi_2) \quad (2.60)
$$

If a quantity $Q$ is a function of $\phi_1$ and $\phi_2$, then the expectation of $Q$ conditional upon $\phi_2 = \psi_2$ is:

$$\langle Q \mid \phi_2 = \psi_2 \rangle = \int_{-\infty}^{\infty} Q(\psi_1, \psi_2) f_{\phi_1 \mid \phi_2}(\psi_1 \mid \psi_2) \, d\psi_1 \quad (2.61)
$$

The unconditional average $\langle Q \rangle$ then reads:

$$\langle Q \rangle = \int_{-\infty}^{\infty} \langle Q \mid \phi_2 = \psi_2 \rangle f_{\phi_2}(\psi_2) \, d\psi_2 \quad (2.62)
$$

If the variables $\phi_1$ and $\phi_2$ are statistically independent, the conditional PDFs reduce to the standard marginal PDFs:

$$f_{\phi_1 \phi_2}(\psi_1 \mid \psi_2) = f_{\phi_1}(\psi_1) \quad (2.63)
$$

$$f_{\phi_2 \mid \phi_1}(\psi_2 \mid \psi_1) = f_{\phi_2}(\psi_2) \quad (2.64)
$$

Substitution of these results in (2.60) shows that the joint PDF is reduced to the product of the marginal univariate PDFs:

$$f_{\phi_1 \phi_2}(\psi_1, \psi_2) = f_{\phi_1}(\psi_1) f_{\phi_2}(\psi_2) \quad (2.65)
$$

In other words, knowledge of the value of variable $\phi_1$ does not bear any information on the value of $\phi_2$ and vice versa. Thus statistical independence implies that the variables are uncorrelated, but the opposite is not necessarily true.

The theory of conditional probability is particularly useful when dealing with intermittent turbulent flows, in which distinct regions of low and high turbulence intensity can be identified. This will be discussed in further detail in Section 3.5.
2.4. Turbulence closure

2.3.4 Variable density and Favre averaging

Turbulent flows with variable density (especially turbulent flames) are often modeled by means of density-weighted or so-called Favre-averaged quantities (Reynolds, 1894; Favre, 1969; Bilger, 1975). Although the use of Favre-averaged quantities raises its specific modeling difficulties, the main advantage is that explicit density correlations are avoided in the ensemble- or Reynolds-averaged transport equations.

The Favre averaged value of a stochastic quantity $Q$ is defined as:

$$
\tilde{Q} = \frac{\langle \rho Q \rangle}{\langle \rho \rangle}
$$

(2.66)

The analog of the Reynolds decomposition is the Favre decomposition:

$$
Q = \tilde{Q} + Q''
$$

(2.67)

By definition, the Favre average of the Favre fluctuation $\tilde{Q}'' = 0$, but the Reynolds average of the Favre fluctuation $Q''$ is not equal to zero:

$$
\langle Q'' \rangle = -\frac{\langle \rho' Q' \rangle}{\langle \rho \rangle}
$$

(2.68)

The evaluation of Favre averaged quantities can be facilitated by using the Favre PDF, which can be written in terms of the common ensemble or Reynolds PDF:

$$
\tilde{f}_\phi(\psi) = f_\phi(\psi) \frac{\rho(\psi)}{\langle \rho \rangle}
$$

(2.69)

For every quantity $Q$ which is a function of $\phi$, its Favre averaged value can be retrieved from the Favre PDF:

$$
\tilde{Q} = \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} Q(\psi) \tilde{f}_\phi(\psi) \, d\psi
$$

(2.70)

The only exception to this rule is the Reynolds average of the density, which obeys:

$$
\frac{1}{\langle \rho \rangle} = \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} \frac{1}{\rho(\psi)} \tilde{f}_\phi(\psi) \, d\psi
$$

(2.71)

This concludes the basic stochastic theory, applications of which we shall discuss in later chapters.

2.4 Turbulence closure

2.4.1 Averaged equations and quantities

The conservation equations described in Section 2.2.1 cannot be solved analytically or numerically. In the present study we are interested mainly in the time averaged behavior
of stationary flames, however, and therefore the explicit time dependent behavior of the flow is not of prime concern. Hence, some suitable averaging procedure is applied to the conservation equations, in order to derive equations for time averaged quantities.

Taking the ensemble average of the Navier-Stokes equations and by applying the Favre decomposition, one obtains the following equations for stationary flow:

$$\frac{\partial}{\partial x_j} (\langle \rho \rangle \bar{v}_j) = 0$$  \hspace{1cm} (2.72)

$$\frac{\partial}{\partial x_j} (\langle \rho \rangle \bar{v}_j \bar{v}_i) = \frac{\partial}{\partial x_j} (\langle \tau_{ij} \rangle - \langle \rho \rangle \bar{v}_i \bar{v}_j') - \frac{\partial (\rho)}{\partial x_i} + \langle \rho \rangle g_i$$  \hspace{1cm} (2.73)

The correlations $\langle \rho \rangle \bar{v}_i' \bar{v}_j''$ have the dimension of a stress, and are called the Reynolds stresses. The Reynolds stresses are unknown variables in the model so far, and will have to be modeled. The $\tau_{ij}$ are the coefficients of the viscous stress tensor. Here the advantage of Favre decomposition becomes apparent, since all explicit density-velocity correlations are avoided in the above equations.

The mean density $\langle \rho \rangle$ is determined from the averaged equation of state, which reads:

$$\langle \rho \rangle = \langle \rho \rangle R^0 \sum_{i=1}^{N} \frac{\bar{Y}_i}{M_i}$$  \hspace{1cm} (2.74)

Again some unknown quantities $\bar{Y}_i \equiv \bar{Y}_i + T \bar{Y}_i''$ appear, which will be treated in Section 3.7.

The energy equation (2.3) is transformed into an equation for the Favre averaged enthalpy:

$$\frac{\partial}{\partial x_j} (\langle \rho \rangle \bar{v}_j \bar{h}) = \frac{\partial}{\partial x_j} \left( \langle \frac{\mu}{Pr} \frac{\partial h}{\partial x_j} \rangle - \langle \rho \rangle \bar{h}_i \bar{v}_j'' \right) + \langle \rho \rangle S_{\text{rad}}$$  \hspace{1cm} (2.75)

In this equation we have assumed equal Lewis numbers $\text{Le}_i = 1$ for all species, and we have neglected compressibility effects and viscous dissipation.

The calorific equation of state relates the temperature to the enthalpy:

$$\bar{h} = \sum_{i=1}^{N} \bar{h}_i \bar{Y}_i$$  \hspace{1cm} (2.76)

in which the $h_i$ are implicitly related to the temperature by means of (2.7).

Finally, the averaged species mass fractions obey:

$$\frac{\partial}{\partial x_j} (\langle \rho \rangle \bar{v}_j \bar{Y}_i) = \frac{\partial}{\partial x_j} \left( \langle \rho \rangle D \frac{\partial Y_i}{\partial x_j} \right) - \langle \rho \rangle Y_i'' \bar{v}_j'' + \langle \bar{\nu}_i \rangle$$  \hspace{1cm} (2.77)

where we have simplified molecular diffusion by assuming Fickian diffusion and by using equal diffusion coefficients $D_i = D$.

In effect, the basic conservation equations and equations of state have been manipulated to yield transport equations for the averaged flow variables. These new transport equations
2.4. Turbulence closure

contain many unknown correlations between fluctuating variables, for which a suitable
closure has to be constructed. The next section will discuss the closure models applied
in this thesis. The section does not deal, however, with the closure of the source terms
due to chemical reactions and radiative heat transfer, which will be treated separately in
Sections 3.7 and 2.5, respectively.

2.4.2 Turbulence closure model

The predominant unknown correlations appearing in the previous section are the Reynolds
stresses \( \langle \rho \rangle \nu_i^t \nu_j^t \) and the turbulent scalar fluxes \( \langle \rho \rangle \nu_i^t \phi'' \). At high Reynolds numbers, the
mean molecular fluxes are relatively unimportant compared to the turbulent fluxes, and
are modeled by:

\[
\left\langle \rho \bar{D} \frac{\partial \phi}{\partial x_i} \right\rangle = \langle \rho \rangle \bar{D} \frac{\partial \bar{\phi}}{\partial x_i}
\]  

(2.78)

Manipulation of the Navier-Stokes equations and the scalar transport equations will
yield new transport equations for the yet unknown turbulent stresses and fluxes, but at the
same time a variety of new unclosed terms emerges. Closure of the unknown terms at this
level of modeling is called second-moment closure or Reynolds-stress modeling (RSM).
The RSM has been developed over the last two decades (Launder, 1988; Launder et al.,
1975; Lumley, 1980). Improvements of the RSM are hampered by the vast complexity of
the unknown correlations in the second-moment equations. Usually these terms are
very difficult to measure, but recent developments in Direct Numerical Simulations (DNS)
of turbulent flows have provided another source of data for model development and
validation.

Nevertheless, the RSM has not been applied very often for reacting flows and the
major contributions in this field are usually restricted to relatively simple geometries and a
parabolic solution method (Chen and Lumley, 1984; Janicka, 1987; Dibble et al., 1987b;
Correa et al., 1984). In this study we do not use the RSM because emphasis is on the
prediction of the thermochemical properties of the flames, rather than the detailed
turbulence structure. For premixed turbulent flames and flames without a typical jet-like
mixing behavior (e.g. swirling flames), the RSM should be preferred over simpler models,
but this is not required here. Furthermore, developments in modeling of the turbulent
scalar fluxes and the scalar dissipation in the RSM is still a subject of major interest.
Finally, the implementation of the full RSM in a 3D CFD code or a 2D code with detailed
chemical kinetics is a prohibitive task and falls outside the scope of this thesis.

The flames studied here can be modeled reasonably well by the standard \( k-\varepsilon \) model,
which has been established for a wide class of flows. In the \( k-\varepsilon \) model, the modeling of
the turbulent fluxes has been pursued by using certain analogies with the corresponding
molecular fluxes, introducing the concept of an effective eddy viscosity (or diffusivity). In
contrast to the molecular transport properties, the eddy viscosity is not a fluid property but
a flow property. The success of the eddy viscosity concept therefore relies on its ability
to establish a physically relevant coupling between the mean flow field and its turbulent
mixing behavior.
The eddy viscosity model relates the effective turbulent diffusivity to a characteristic turbulent length scale \( \ell_t \) and a velocity scale \( v_t \):

\[
\mu_t \sim \langle \rho \rangle \ell_t v_t
\]  
(2.79)

The velocity scale is represented by the turbulent kinetic energy of the energy containing (large) eddies, \( \tilde{k} = \frac{1}{2} \sum v_i^2 \), whereas the length scale is the average size of the large eddies, estimated by:

\[
\ell_t \sim \frac{v_t^3}{\tilde{\xi}} \sim \frac{\tilde{k}^{3/2}}{\tilde{\xi}}
\]  
(2.80)

The eddy viscosity thus becomes:

\[
\mu_t = C_\mu \langle \rho \rangle \frac{\tilde{k}^2}{\tilde{\xi}}
\]  
(2.81)

where \( C_\mu = 0.09 \) is the standard value for the constant.

Introduction of the eddy viscosity yields a model for the Reynolds stresses:

\[
- \langle \rho \rangle v_i^m v_j^m = \mu_t \left( \frac{\partial \tilde{v}_i}{\partial x_j} + \frac{\partial \tilde{v}_j}{\partial x_i} \right) - \frac{2}{3} \delta_{ij} \left( \langle \rho \rangle \tilde{k} + \mu_t \frac{\partial \tilde{v}_k}{\partial x_k} \right)
\]  
(2.82)

Unknown quantities in this model are the turbulent kinetic energy \( \tilde{k} \) and its viscous dissipation rate \( \tilde{\xi} \), for which transport equations are derived in the next section.

Similarly, the scalar turbulent fluxes are modeled by assuming an effective eddy diffusivity, using the gradient transport model:

\[
- \langle \rho \rangle \phi v_i^m \phi^m = \frac{\mu_t}{\sigma_\phi} \frac{\partial \tilde{\phi}}{\partial x_i}
\]  
(2.83)

Here, \( \sigma_\phi \) is the effective turbulent Prandtl or Schmidt number for the scalar \( \phi \), which can be determined from experiments and computer optimization. Evidently, the above model for the scalar fluxes will only be valid if there is a strong coupling between the mixing of the velocity field and the mixing of the scalar field, and if so-called counter-gradient effects do not occur. This typically is the case for nonpremixed jet flames without swirl.

### 2.4.3 Modeled \( k-\epsilon \) equations

We will not repeat the derivation of the modeled \( k-\epsilon \) equations for variable-density flows here; they can be found in numerous textbooks (see e.g. Wilcox, 1993). The modeled \( \tilde{k} \)-equation reads:

\[
\frac{\partial}{\partial x_j} \left( \langle \rho \rangle \tilde{v}_j \tilde{k} \right) = \frac{\partial}{\partial x_j} \left[ \left( \langle \mu \rangle + \frac{\mu_t}{\sigma_k} \frac{\partial \tilde{k}}{\partial x_j} \right) + P_k + G_k - \langle \rho \rangle \tilde{\xi} \right]
\]  
(2.84)

with:

\[
P_k = -\langle \rho \rangle v_i^m v_j^m \frac{\partial \tilde{v}_i}{\partial x_j}
\]
2.5. Radiative heat transfer

\[ G_k \equiv -\langle v''_i \rangle \frac{\partial (p)}{\partial x_i} = -\frac{\mu_t}{\sigma_p (\rho)^2} \frac{\partial (p)}{\partial x_j} \frac{\partial (\rho)}{\partial x_j} \]

The terms on the r.h.s. represent (molecular and turbulent) diffusion processes, production by mean shear \( P_k \), production by buoyancy forces \( G_k \) and viscous dissipation of turbulence. For the Reynolds stresses, the expression of (2.82) has to be substituted.

The model equation for \( \bar{e} \) is:

\[ \frac{\partial}{\partial x_j} \left( (\rho) \bar{v}_j \bar{e} \right) = \frac{\partial}{\partial x_j} \left[ \left( (\mu) + \frac{\mu_t}{\sigma_e} \right) \frac{\partial \bar{e}}{\partial x_j} \right] + \frac{\bar{e}}{k} (C_{e1} P_k + C_{e2} G_k - C_{e3} (\rho) \bar{e}) \quad (2.85) \]

The constants appearing in the \( k-\epsilon \) equations are taken to have the standard values: \( \sigma_k = 1.0, \sigma_e = 1.3, \sigma_p = 0.7, C_{e1} = 1.44, C_{e2} = 1.92 \) and \( C_{e3} = 1.0 \).

For jet flows, the standard model constants do not produce the right spreading rates of momentum and scalar quantities. Sanders (1994) suggests to set the \( C_\mu \) constant to 0.06 instead of 0.09. Here, we use a somewhat more complex model, based on work of Launder et al. (1972). The constants \( C_\mu \) and \( C_{e2} \) are replaced by:

\[ C_\mu = 0.09 - 0.04 F_{\text{jet}} \]
\[ C_{e2} = 1.92 - 0.0667 F_{\text{jet}} \quad (2.86) \]

The function \( F_{\text{jet}} \) is zero in a Cartesian coordinate system. For an axisymmetrical jet, \( F_{\text{jet}} \) depends on the axial velocity gradient and the jet width:

\[ F_{\text{jet}} = \left\{ \frac{d_1/2}{1.6 \Delta u} \left( \frac{|d \bar{u}_{cl}|}{dx} - \frac{d \bar{u}_{cl}}{dx} \right) \right\}^{0.2} \quad (2.87) \]

Here, \( d_1/2 \) is the jet diameter defined by the location where \( \bar{u} = \frac{1}{2} (\bar{u}_{cl} - \bar{u}_\infty) \), \( \bar{u}_{cl} \) is the mean centerline velocity, \( \Delta u \equiv \bar{u}_{cl} - \bar{u}_\infty \) is the difference between the centerline velocity and the ambient velocity. The constants in this equation were adopted from Abou-Ellail and Salem (1990).

2.5 Radiative heat transfer

Radiative heat transfer is an important physical phenomenon in natural-gas flames and therefore it has to be accounted for in order to obtain reliable temperature predictions. In large-scale industrial furnaces, radiation may be responsible for over 90% of the total heat transfer of the flame to the furnace walls. Laboratory-scale flames are usually much smaller and colder, but radiation may still produce a significant temperature decrease compared to the adiabatic case. The general heat transfer equation is unsolvable for turbulent flames, and simplifications are used to model the radiation effects. In the sequel, we will discuss the basic assumptions used in the simulation models of this thesis. A detailed treatment of radiation effects in gaseous flames is presented by Wieringa (1992).
Chapter 2. Basic theory

The general equation for radiative heat transfer in a gaseous medium reads:

\[ \frac{\partial i'_\lambda(s)}{\partial s} = -(K^a_\lambda + K^s_\lambda)i'_\lambda(s) + K^a_\lambda i'_{b,\lambda} + \frac{K^a_\lambda}{4\pi} \int_0^\pi i'_\lambda(\Omega_i) \Phi_\lambda(\Omega_i, \Omega)d\Omega_i \]  \hspace{1cm} (2.88)

In this equation, \( i'_\lambda(s) \) is the spectral radiant intensity along a beam in the direction of \( s \), where \( s \) is a distance in the medium, and \( i'_{b,\lambda} \) is the spectral black-body intensity. \( K^a_\lambda \) and \( K^s_\lambda \) are the spectral absorption and scattering coefficient of the medium, respectively, and \( \Phi_\lambda(\Omega_i, \Omega) \) is the phase function of scattering from a solid angle \( \Omega_i \) into the direction of solid angle \( \Omega \). Here, the coordinate \( s \) runs in the direction of solid angle \( \Omega \). The black-body intensity \( i'_{b,\lambda} \) is related to the spectral emissive power \( E_{b,\lambda} \) by virtue of Planck’s formula:

\[ E_{b,\lambda} \equiv \pi i'_{b,\lambda} = \frac{c_1 \lambda^{-5}}{\exp(c_2/\lambda T) - 1} \]  \hspace{1cm} (2.89)

Here, \( \lambda \) is the wavelength, and \( c_1 = 3.742 \cdot 10^{-16} \text{ W} \cdot \text{m}^2 \) and \( c_2 = 1.439 \cdot 10^{-2} \text{ m} \cdot \text{K} \) are radiation constants.

The nature of the integro-differential equation (2.88) differs from the common convection-diffusion transport equations discussed before. The most important difference is that radiation generally is a non-local phenomenon, implying that other solution techniques have to be employed. In order to solve the radiation equation numerically, some simplifications are sought.

An important first simplification is to neglect effects of scattering. This is allowed here, since scattering is mainly caused by particles larger than the wavelengths of interest, and these particles are absent in natural-gas flames. Equation (2.88) can then be integrated to yield:

\[ i'_\lambda(s) = i'_\lambda(0)\tau_\lambda(0, s) + \int_0^s i'_{b,\lambda}(s') \frac{\partial \tau_\lambda(s', s)}{\partial s'} ds' \]  \hspace{1cm} (2.90)

The function \( \tau_\lambda(s', s) \) is the spectral transmissivity of the gas from \( s' \) to \( s \):

\[ \tau_\lambda(s', s) = \exp \left( -\int_{s'}^s K^a_\lambda(s'') ds'' \right) \]  \hspace{1cm} (2.91)

The spectral transmissivity is a function of species concentrations and temperature, and therefore it is not a constant in natural gas flames. This suggests that the spectral properties of flames are to be included in the radiation model. For our purposes, however, this would lead to excessive computing times, and as an important second simplification we assume the gas and bounding walls to have grey radiation properties: \( K^a_\lambda = K^a \), independent of \( \lambda \). Consequently, the transmissivity becomes:

\[ \tau(s', s) = \exp \left( -\int_{s'}^s K^a(s'') ds'' \right) \]  \hspace{1cm} (2.92)
2.5. Radiative heat transfer

If it is assumed that $K^a$ is uniform in space, the above integral can be evaluated directly, yielding $\tau(s', s) = \exp(-K^a|s' - s|)$.

Several approaches have been pursued to solve the radiative heat transfer problem for a non-scattering grey gas. Hotell’s zone method (HZN) (Hotell and Cohen, 1958; Hotell and Sarofim, 1963; Hotell and Sarofim, 1967) and the Discrete Transfer Method (DTM) (Lockwood and Shah, 1981) were used for the 3D furnace flows in a Cartesian geometry as well as the axisymmetrical flames.

The HZN is a fairly old and well-established method. It is based upon a subdivision of the domain of interest into a number of volume zones and area zones, using uniform properties and temperature in each zone. In our application, we assumed a uniform absorption coefficient $K^a$ for the whole radiation domain. The geometrical information required for the radiative heat transfer calculation can be computed in advance, which reduces the computational costs in actual simulations of radiation coupled with fluid flow. The method is not very flexible with respect to more complex geometries, however, and becomes less accurate if the assumption of a uniform absorption coefficient is violated.

In the DTM radiation is simulated by monitoring the emission and propagation of a discrete number of beams. It bears close resemblance to the Monte Carlo ray transfer method. Unlike the Monte Carlo method, however, the beams are not chosen randomly, but are selected in a deterministic fashion, thus reducing the computational effort considerably. If the directions of these ‘fixed’ beams and the number of beams are sufficiently well defined, the DTM offers the advantage to allow for spatially nonuniform properties and complex geometries, without excessive computing times.

If we rewrite the integral form of the radiative transfer equation (2.90) for a grey medium in vector notation, we obtain:

$$i'(r, \Omega) = i'(r', \Omega)\tau(r, r') + \int_{r'}^{r} K^a(r''')i''(r'', \Omega)\tau(r, r'')dr'''$$

(2.93)

Figure 2.1 illustrates the meaning of the position vectors $r$, $r'$ and $r'''$. The integration runs over all vectors $r'''$ on the straight line between $r'$ and $r$. The hemispherically incident flux arriving at boundary point $r$ is expressed by:

$$q^+(r) = \int_A q^-(r')\frac{\tau(r, r')\cos \theta\cos \theta'}{\pi||r - r'||^2}dA'$$

$$+ \int_V K^a(r'')E_b(r'')\frac{\tau(r, r'')\cos \theta}{\pi||r - r''||^2}dV''$$

(2.94)

Here, $q^-(r')$ is the leaving flux from a surface element $dA'$ at position $r'$; $dV''$ is an infinitesimal volume element at $r''$. The values of $\cos \theta$ and $\cos \theta'$ are defined by $|n \cdot \Omega|$ and $|n' \cdot \Omega|$. Since energy conservation holds at the boundaries, one has:

$$q^- = \varepsilon_w E_b + (1 - \varepsilon_w)q^+$$

(2.95)
with $\varepsilon_w$ the wall emissivity.

Using the above formulation, the radiative source term in the enthalpy equation can be written as the sum of absorption and emission:

$$\rho S_{\text{rad}}(r) = S_{\text{abs}}(r) - S_{\text{em}}(r);$$ \hspace{1cm} (2.96)

$$\rho S_{\text{abs}}(r) = K^a(r) \int_A q^-(r') \frac{\tau(r, r') \cos \theta'}{\pi ||r - r'||^2} dA' + K^a(r) \int_V K^a(r'') E_b(r'') \frac{\tau(r, r'')}{\pi ||r - r'||^2} dV'' \hspace{1cm} (2.97)

$$\rho S_{\text{em}}(r) = 4 K^a(r) E_b(r) \hspace{1cm} (2.98)$$

In the HZM the domain of interest in divided into $N_A$ surface elements $A_i$ and $N_V$ volume elements $V_k$. The heat exchange from one element to another is expressed by a set of geometrical factors, called direct-exchange areas. For exchange between surfaces $A_i$ and $A_j$ we have:

$$\bar{s}_{ij} \equiv \int_{A_i} \int_{A_j} \tau(r, r') \cos \theta \cos \theta' \frac{dA'}{\pi ||r - r'||^2} dA'dA;$$ \hspace{1cm} (2.99)

for exchange between surface $A_i$ and gas volume $V_k$:

$$\bar{s}_{ik} \equiv \int_{A_i} \int_{V_k} K^a(r'') \frac{\tau(r, r'') \cos \theta}{\pi ||r - r'||^2} dV'' dA;$$ \hspace{1cm} (2.100)
and for volume-volume exchange:

\[
\overline{g_kg_l} = \int_{V_k} \int_{V_l} K^a(r''')K^a(r''') \frac{\tau(r'', r''')}{\pi ||r'' - r'''||^2} dV'' dV'''.
\] (2.101)

The direct-exchange areas are symmetrical ($\overline{s_is_j} = \overline{s_js_i}$ etc.). From conservation of energy the compatibility equations follow:

\[
\sum_{j=1}^{N_A} \overline{s_is_j} + \sum_{k=1}^{N_V} \overline{s_is_k} = A_i \quad (2.102a)
\]

\[
\sum_{j=1}^{N_A} \overline{s_js_k} + \sum_{l=1}^{N_V} \overline{g_jg_k} = 4K_i^a V_k \quad (2.102b)
\]

The incident heat flux (2.94) at surface $A_i$ can be written as:

\[
A_iq_i^+ = \sum_{j=1}^{N_A} \overline{s_is_j} q_j^- + \sum_{k=1}^{N_V} \overline{s_is_k} E_{b,k} \quad (2.103)
\]

Using (2.95), we arrive at a matrix equation for the leaving fluxes $q_i^-:

\[
\sum_{j=1}^{N_A} \left( \frac{A_i}{1 - \varepsilon_{w,i}} \delta_{ij} \right) q_i^- = -\frac{\varepsilon_{w,i}}{1 - \varepsilon_{w,i}} A_i E_{b,i} - \sum_{k=1}^{N_V} \overline{s_is_k} E_{b,k} \quad (2.104)
\]

Here, $\delta_{ij}$ is the Kronecker delta, and it is assumed that the wall emissivity $\varepsilon_{w,i} < 1$. Equation (2.95) is valid for a surface zone with a prescribed wall temperature; if instead the wall heat flux $q_w$ is prescribed, the appropriate relationship becomes:

\[
q_i^- = q_i^+ - q_w, \quad (2.105)
\]

which yields:

\[
\sum_{j=1}^{N_A} \left( \frac{A_i}{1 - \varepsilon_{w,i}} \delta_{ij} \right) q_i^- = A_i q_w - \sum_{k=1}^{N_V} \overline{s_is_k} E_{b,k} \quad (2.106)
\]

In order to determine the temperature of such a surface, (2.95) can be employed. If the surface element is black ($\varepsilon_{w,i} = 1$), we can simply put $q_i^- = E_{b,i}$. The net heat flux leaving a surface element $A_i$ can be computed from:

\[
A_i(q_i^+ - q_i^-) = \sum_{j=1}^{N_A} \overline{s_is_j} q_j^- + \sum_{k=1}^{N_V} \overline{s_is_k} E_{b,k} - A_i q_i^- \quad (2.107)
\]

For the gas volumes, it is assumed that the temperatures are known. Hence, the leaving fluxes at the surface zones are computed by (2.104) and (2.106). Next, the source term in the enthalpy equation is obtained for each volume zone $V_k$:

\[
\rho_k S_{rad,k} V_k = \sum_{j=1}^{N_A} \overline{s_js_j} q_j^- + \sum_{l=1}^{N_V} \overline{g_jg_k} E_{b,l} - 4K_k^a E_{b,k} V_k \quad (2.108)
\]

Finally, the enthalpy equation can be solved to yield the new gas temperatures. In Section 4.5 further attention is paid to the numerical calculation of the direct exchange areas and the coupling with the CFD algorithm.
2.5.1 Discrete Transfer Method

The Discrete Transfer Method has been described in detail by Lockwood and Shah (1981) and Wieringa (1992). Important advantages of the DTM are that complex geometries can be handled more easily than with the HZM, and that local variations of the absorption coefficient \( K^a \) can be incorporated.

Like the HZM, the DTM starts by dividing the enclosure into a number of discrete volumes and surface zones. At each surface zone, the hemisphere is divided into a number of solid-angle elements, each of which is associated with a beam direction. For each beam direction, the incident flux is calculated, by tracing the beam back into the enclosure, to monitor its history through the volumes until the surface element from which it emerged has been reached. The initial energy of the beams at their starting surface is governed by the thermal boundary conditions of that surface.

For the radiant intensity of the beam travelling through a volume element from location \( r_{n-1} \) to \( r_n \), a recurrence relation holds:

\[
i'_n = i'_{n-1} \exp(-K^a \delta) + i'_0 (1 - \exp(-K^a \delta))
\] (2.109)

Here, \( K^a \) is the absorption coefficient of the gas between \( r_{n-1} \) and \( r_n \) and \( \delta = ||r_n - r_{n-1}|| \). The beam energy at the starting surface can be determined from:

\[
i'_0 = \frac{q_0}{\pi}
\] (2.110)

where index 0 denotes the starting point (or surface) of the beam under consideration. Here it has been assumed that the leaving flux \( q^- \) is known in advance, and that the surface is diffuse and isothermal.

By summation of all the beams \( k \) travelling towards a surface \( A_j \), the hemispherically incident flux is given by:

\[
q^+_j = \sum_k i'_k \cos \theta_k \Delta \Omega_k
\] (2.111)

where \( \theta_k \) is the angle between the beam and the normal vector to the surface, and \( \Delta \Omega_k \) is the solid angle represented by beam \( k \).

The local radiative source term for the enthalpy equation can be deduced from (2.109), by taking into account all beams that cross a given volume element, and by calculating the energy loss of each beam through the volume over a distance \( \delta \). Actually, each beam represents a solid angle which may cross several volume elements only partially. This will complicate the numerical evaluation of the radiative source term, and therefore, as pointed out by others (Wieringa, 1992; Lockwood and Shah, 1981), we assume that the energy of each solid angle is concentrated in the line along the beam. The radiative source term for a volume element \( V_m \) then becomes:

\[
\rho S_{rad} = \frac{1}{V_m} \sum_k (i'_{n-1} - i'_n) A_k \cos \theta_k \Delta \Omega_k
\] (2.112)

The summation runs over all beams \( k \) that pass through the volume element, and \( A_k \) is the surface element towards which the beam is directed.
2.5. Radiative heat transfer

The directions of the beams can be distributed arbitrarily among the hemisphere. However, biased results can be expected if the beam directions are not isotropically distributed and if energy conservation is violated. Wieringa (1992) formulated additional criteria for the beam directions in order to satisfy energy conservation and to reduce systematic errors as a result of uncareful selection of beam directions. The solid angle for each beam \( \theta_k \) is represented by the angle with the normal \( \theta_k \) and an polar angle \( \phi_k \). The \( \phi \)-directions can be distributed uniformly in the interval \([0, 2\pi]\). If the solid angle interval around each beam is described by the two angles \( \alpha_k \) and \( \alpha_{k-1} \), the value of \( \theta_k \) is given by:

\[
\cos \theta_k = \frac{1}{2}(\cos \alpha_{k-1} + \cos \alpha_k)
\]

(2.113)

In order to have equal solid angles \( \Delta \Omega \) for each beam, we adopted Wieringa’s recommendation to distribute the \( \alpha_k \) such that \( \cos \alpha_{k-1} = \cos \alpha_k \) is constant between adjacent solid angles. This is achieved by:

\[
\theta_k = \arccos \left(1 - \frac{2k - 1}{2N\theta}\right)
\]

(2.114)

with \( N\theta \) the number of subdivisions in \( \theta \)-direction.

2.5.2 Simplified radiation model

The modeling of radiative heat transfer can be simplified if the walls of the enclosure do not participate in the radiative heat exchange (the walls are cold with respect to the radiating part of the fluid), and if the mean beam length of the radiation is much longer than the characteristic dimensions of the radiating parts of the fluid. In other words, if the radiative source term is dominated by the heat loss term, and self-absorption of radiation by the gas is negligible, we can simplify the source term by:

\[
\rho S_{rad} = -4K^a(E_{b,\text{gas}} - E_{b,w})
\]

(2.115)

where \( K^a \) is the total grey absorption coefficient of the medium. In this equation the term \( E_{b,w} \) is retained, in order to yield a zero source term in the non-radiating parts of the fluid.

2.5.3 Inclusion of soot radiation

Soot is known to greatly enhance the intensity of heat radiation in the infrared part of the spectrum. Even although natural-gas flames have a relatively low carbon content, the formation of soot particulates may have a pronounced influence on the radiative heat transfer. In order to model the effect of soot on the radiation, the formation and consumption of soot has to be accounted for, which will be discussed in Section 3.9.

If the soot concentration is known, the total soot absorption coefficient \( K^a_{\text{soot}} \) can be computed from the spectral soot absorption coefficient, which is given by Mie theory. Here, we have adopted the approach of Boerstoel et al. (1994), who computed the grey soot absorption coefficient by a Planck-curve averaging procedure. In effect, we arrive at:

\[
K^a_{\text{soot}} = f(T)f_{v,\text{soot}}
\]

(2.116)
where $f_{v,\text{soot}}$ is the soot volume fraction, and $f(T)$ is the temperature dependent part of the grey absorption coefficient. More details are given by Boerstoel et al. (1994).

The total grey absorption coefficient of the medium is written as the sum of the gas absorption and the soot absorption:

$$K^a = K^a_{\text{gas}} + K^a_{\text{soot}}$$  \hspace{1cm} (2.117)

Even if a constant value of $K^a_{\text{gas}}$ is assumed, $K^a$ will be a function of space now, and therefore the Hottel zone model is ill-suited for the inclusion of soot radiation effects.
CHAPTER 3

Chemistry models for turbulent flames

3.1 Outline of this chapter

The numerical calculation of chemically reacting flows is complicated due to the non-linearity of the chemical reaction rates and the stiffness of the set of partial differential equations for species mass fractions and temperature. Sophisticated numerical techniques allow a full treatment of chemical reactions in laminar flame computations, but for turbulent flames such a complete description of the chemistry is computationally prohibitive. Therefore, simplified reaction models are sought in order to predict mean concentrations and temperature in turbulent reacting flows.

Chemical reaction kinetics have been included explicitly in a number of turbulent flame studies, using reduced reaction schemes and Monte Carlo joint PDFs (Pope, 1985), or full mechanisms and presumed-shape joint PDFs (Bockhorn, 1989). These approaches have been applied to relatively simple geometries, particularly an axisymmetric 2D configuration. For the calculation of 3D furnace flows of practical industrial interest, these joint-PDF methods are computationally too expensive, and a further reduction of the complexity of the chemical model is required.

The first section of this chapter attempts to put the various models into a broader perspective, in terms of regimes of turbulent diffusion flames. Several concepts used in this section, such as the mixture fraction variable and strained flamelets will be presented in more detail in subsequent sections.

Next, a number of conserved-scalar chemistry models are discussed which can be used to perform 2D or 3D flame calculations. The conserved-scalar models are attractive because they offer the possibility to describe the thermochemical field of a turbulent flame as a function of only one or two independent variables, at a much lower computational expense. Several chemistry models in the conserved-scalar formalism are presented here. In further sections, attention is given to the determination of mean thermochemical quantities, by applying an assumed PDF approach. Several theoretical aspects of the assumed PDF weighting are considered, including the description of intermittency effects.

Subsequently, the treatment of chemical kinetics in the so-called laminar flamelet models is presented. Laminar flamelets can be viewed as an intermediate between full kinetic models and purely conserved-scalar models. Premixed as well as diffusion flamelets are described in this chapter.

In the following section, the detailed chemical kinetics model for turbulent flames, as developed by Bockhorn (1989), will be outlined. Attention is given to the fundamentals of this theory, and particular improvements and modifications are discussed.

The final section deals with the modeling of thermal NO formation within the context of the conserved-scalar chemistry models.
3.2 Regimes of turbulent diffusion flames

In the literature, two major approaches exist to the modeling problem of turbulent fast-chemistry flames: the conserved-scalar model or laminar flamelet model on the one hand, and the distributed reaction zone model, which essentially disregards spatial or temporal coherent structures in turbulent flames and adopts a stochastic point of view, on the other hand. The work of Peters (1984, 1986, 1991) clearly supports the laminar flamelet concept, whereas the work of Bilger (1988) favours the concept of distributed reaction zones, to be treated by PDF closure. Recent studies by Bilger and co-workers (Bilger, 1988; Bilger, 1989; Bilger et al., 1990) have attempted to provide evidence to decide whether the conserved-scalar description of turbulent diffusion flames is valid and under which circumstances.

A phenomenological approach to the modeling of turbulent diffusion flames has been developed (Bilger, 1976a; Peters, 1991; Williams, 1986), in order to classify the regimes of such flames. A key issue in this theory is the comparison of time scales and length scales for the laminar and turbulent case. Following Peters (1991), we will discuss the relevant scales for laminar and turbulent flames.

Laminar case  Any diffusion flame will have a reaction zone close to the stoichiometric isopleth where \( \xi = \xi_{st} \). Here, \( \xi \) is the conserved scalar or mixture fraction, to be discussed in more detail in the next section. By definition, \( \xi = 0 \) in pure oxidizer (air) and \( \xi = 1 \) in pure fuel, and \( \xi_{st} \) corresponds to the stoichiometric ratio. On the fuel-lean and fuel-rich side the flame usually does not exist because of too low temperatures to sustain the highly temperature dependent chemical reactions. For simplicity, equal Lewis numbers are assumed for all species. The laminar flamelet description then leads to differential equations for species mass fractions and temperature, in terms of two independent scalars: the mixture fraction \( \xi \) and the scalar dissipation rate \( \chi_{st} = 2ID(\nabla \xi)^2 \) at \( \xi = \xi_{st} \).

The scalar dissipation rate is a property of laminar counterflow diffusion flames, and is related to the strain rate \( a \) and the value of \( \xi_{st} \) according to an approximate formula:

\[
\chi_{st} \approx 4a\xi_{st}^2 \left( \text{erfc}^{-1}(2\xi_{st}) \right)^2
\]

where \( \text{erfc}^{-1} \) is the inverse of the complementary error function. \( \text{erfc}(x) \equiv 1 - \text{erf}(x) = 2/\sqrt{\pi} \int_x^\infty \exp(-y^2)dy \). For a methane/air flame close to extinction, \( a_{\text{ext}} \approx 400 \text{ s}^{-1} \), and \( \xi_{st} = 0.055 \), yielding \( \chi_{\text{ext}} \approx 6.2 \text{ s}^{-1} \). This value can be used as an estimate of the characteristic chemical time scale \( \tau_c \) at stoichiometric conditions:

\[
\tau_c = \xi_{st}^2(1 - \xi_{st})^2/\chi_{\text{ext}}
\]

For methane flames, this gives \( \tau_c \approx 0.34 \text{ ms} \).

The characteristic length scale \( l_c \) of a laminar diffusion flame can be related to the width of the reaction zone in mixture fraction space (estimated to be about 0.3 \( \xi_{st} \)), and the corresponding gradient of the mixture fraction:

\[
l_c = 0.3\xi_{st}\sqrt{2ID/\chi_{st}}
\]
3.2. Regimes of turbulent diffusion flames

This formula shows that, in contrast to turbulent premixed flames, there is no length scale independent from the flow field in non-premixed flames, because the flame basically depends on the mixing of two initially unmixed reactant streams: the scalar dissipation rate $\chi$ is a function of time and space. Only the width of the reaction zone (of a flamelet) in mixture fraction space is independent of the flow field.

_Turbulent case._ The turbulent velocity scale of the energy containing eddies is estimated to be $v_t = \sqrt{2\tilde{k}/3}$, and the integral length scale is found from $\ell_t = v_t^3/\tilde{c}$. The corresponding integral time scale then follows from $\tau_t = 2/3(\tilde{k}/\tilde{c})$. Other integral scales to be considered for jet flames are the jet half-width $\delta_{1/2}$ and the excess centerline velocity $u_{cl} - u_{oc}$. These quantities scale with $x$ and $1/x$, respectively, yielding a time scale $\sim x^2$.

Intermediate scales are covered by the Taylor length scale $\ell_T$, which is the distance over which a fluid element is convected by a large eddy (with velocity $v_t$) during a Kolmogorov time $\tau_K$. For isotropic turbulence one arrives at $\ell_T = \ell_t/\sqrt{15/Re}$, with $Re_t = v_t\ell_t/\nu$ the turbulent Reynolds number.

The smallest fluid-mechanical scales are the Kolmogorov scales given by $\ell_K = (\nu^3/\tilde{c})^{1/4}$, $v_K = (\nu^3/\tilde{c})^{1/4}$ and $\tau_K = (\nu/\tilde{c})^{1/2}$. The Kolmogorov scales are also referred to as the dissipation scales, since on these scales the turbulent kinetic energy is dissipated by the viscosity of the fluid. In gaseous flames the length scales of (passive) scalars advected by the fluid are approximately equal to the hydrodynamic scales, because the molecular and turbulent Schmidt numbers are of order unity. Hence, Schmidt number effects typical for chemical reactions in condensed fluids are disregarded in this analysis.

_Comparison of length scales._ Based on the above concepts, Peters (1991) proposed a phase diagram for the regimes of turbulent diffusion flames (figure 3.1), different from the analysis given by Williams (1986). The averaged scalar dissipation can be used to couple the width of the reaction zone in mixture fraction space to a length scale in a turbulent field, assuming that the mean gradient of the mixture fraction is mainly determined by the fluctuations of the (instantaneous) gradient and not by the gradient of the mean mixture fraction field. For isotropic turbulence it may be derived that:

$$\bar{\ell}_c = 0.3 \frac{\xi_{st}''}{\xi_{st}'} \sqrt{\frac{6ID_k}{2\tilde{c}}}$$

(3.4)

where $\xi_{st}'' = (\xi_{st}^2)'^{1/2}$ at $\tilde{c} = \xi_{st}$.

_Comparison of time scales._ The Damköhler number $\text{Da}_t = \tau_t/\tau_c$ relates the chemical time scale to the large-eddy turnover time scale. If this number is small (i.e. in the order of unity), chemical reactions are slow compared even with the slowest turbulent processes, and the flame is determined by chemical kinetics; this is identified as the regime of distributed reaction zones. For $\text{Da}_t \ll 1$, well-stirred reactor conditions prevail.
A second Damköhler number is defined by $Da_K \equiv \tau_K / \tau_c$. If this number is decreased to unity, the smallest eddies will mix faster than the chemical reactions are able to respond, and partial premixing of the reaction zone will occur. Therefore, $Da_K = 1$ is considered to be the limiting line between distributed reaction zones and flamelets.

The ratio $Da_t : Da_K = Re_t$ will always be larger than 1 in a turbulent flame, and hence the horizontal axis in figure 3.1 is taken to be $Da_K$. For $Da_K > 1$ flamelets or coherent flame structures may exist. If the mean scalar dissipation rate $\chi > \chi_{ext}$, most of the flamelets will be extinguished by the strain rates imposed by the flow. At the vertical axis of figure 3.1 we use the r.m.s. value of mixture fraction fluctuations at stoichiometry, $\xi''_{st}$, scaled with $\xi_{st}(1 - \xi_{st})$. Separated flamelets will exist if the fluctuations $\xi''_{st}$ will exceed the reaction zone width in mixture fraction space.

### 3.3 Conserved-scalar chemistry models

#### 3.3.1 Literature survey

The conserved-scalar approach is a fundamental topic in turbulent flame studies. Many theoretical analyses treat the conserved-scalar description in detail (Bilger, 1976a; Bilger, 1977; Bilger, 1989; Borghi, 1988; Williams, 1985). The most basic conserved-scalar
3.3. Conserved-scalar chemistry models

model assumes an infinitely fast one-step global reaction (Burke and Schumann, 1928), and has been used in many studies of turbulent diffusion flames (Bush and Fendell, 1974; Kent and Bilger, 1977; Lin and O'Brien, 1974; Toor, 1962) and industrial furnace simulation (Carvalho, 1983; Post, 1988).

A somewhat more complicated model assumes chemical equilibrium instead of infinitely fast irreversible reactions (Becker, 1975; Kent and Bilger, 1977). The validity of the equilibrium assumption breaks down at lower flame temperatures where the reaction rates are not sufficiently fast to attain equilibrium. To remedy the deficiencies of the equilibrium model, semi-empirical models were developed. The flame-zone model (Abou-Ellail and Salem, 1989; Eickhoff and Grethe, 1979; Eickhoff and Grethe, 1982) presumes chemical equilibrium within the flame zone and frozen chemistry outside this zone. The width of the flame zone in conserved-scalar space is specified empirically, and raises fundamental problems due to the discontinuity at the flame-zone boundaries. A more elegant method has been developed by Bilger and Stärner (1983) who postulated a constrained-equilibrium model. By this model, realistic levels of CO and H₂ are predicted in hydrocarbon diffusion flames at lower temperatures.

The conserved-scalar models can be considered to be the limiting form of reduced kinetic mechanisms, by which the number of independent thermochemical variables is systematically reduced, by mathematical or chemical analysis. For natural gas/methane, much progress has been made in the last decade but the applicability of accurate four-step reduced mechanisms is still restricted to fairly simple 2D flows. For 3D furnace simulations, the conserved-scalar approach remains the preferred model, in terms of computational costs.

A number of models at an intermediate level of complexity between the conserved-scalar approach and multi-step chemical mechanisms should also be mentioned. A set of simple extensions and improvements of the conserved-scalar approach has been developed, such as mixedness-reactedness models (Bradley et al., 1990), and partial equilibrium or perturbation models (Bilger, 1980; Correa et al., 1988). Also, for a prescribed range of flame conditions, it is possible to assume a global reaction between fuel and oxidizer, attributing fit parameters to an Arrhenius-like expression of the global reaction rate (Humman et al., 1981). These methods, although attractive theoretically, are not discussed here.

3.3.2 Conserved scalar approach

By a number of assumptions known as the Shvab-Zel'dovich approximation and described in detail by Williams (1985), the unsteady transport equations for the species mass fractions \( Y_i \) and thermal enthalpy \( h_\theta \) become:

\[
\rho \frac{\partial Y_i}{\partial t} + (\rho v) \cdot \nabla Y_i = \nabla \cdot (\rho \mathbb{D} \nabla Y_i) = \dot{w}_i \tag{3.5}
\]

\[
\rho \frac{\partial h_\theta}{\partial t} + (\rho v) \cdot \nabla h_\theta = \nabla \cdot (\rho \mathbb{D} \nabla h_\theta) = - \sum_{i=1}^{N} h^{i \theta} \dot{w}_i \tag{3.6}
\]
where \( \rho \) is the density, \( \mathbf{v} \) the velocity, \( Y_i \) the mass fraction of species \( \mathcal{M}_i \), \( \mathcal{D} \) the molecular species diffusivity, \( \dot{W}_i \) the net chemical formation rate of species \( i \) and \( h_i^0 \) is the species standard enthalpy of formation. In these equations it is assumed that all species have equal diffusivities \( (\mathcal{D}_i = \mathcal{D}) \) and that the Lewis number \( \text{Le} = \lambda/\rho \mathcal{D} c_p \) is unity.

For a given irreversible reaction:

\[
\sum_{i=1}^{N} \nu'_i \mathcal{M}_i \rightarrow \sum_{i=1}^{N} \nu''_i \mathcal{M}_i \tag{3.7}
\]

one can define a scalar function \( \beta \) of the form:

\[
\beta = a_0 \left( h_\theta + \sum_{i=1}^{N} Y_i h_i^0 \right) + \sum_{i=1}^{N} a_i \left( \frac{Y_i}{M_i (\nu'_i - \nu''_i)} \right) \tag{3.8}
\]

with the restriction that \( \sum_{i=1}^{N} a_i = 0 \). By means of (3.5) and (3.6), it is formally shown that all chemical source terms in the transport equation for \( \beta \) cancel:

\[
\mathcal{L}(\beta) = 0 \tag{3.9}
\]

where \( \mathcal{L} \) is the linear transport operator defined by:

\[
\mathcal{L}(\phi) = \frac{\partial \phi}{\partial t} + (\rho \mathbf{v}) \cdot \nabla \phi - \nabla \cdot (\rho \mathcal{D} \nabla \phi) \tag{3.10}
\]

Hence, the constructed variable \( \beta \) is a conserved scalar in a reacting mixing flow. Every possible combination \( \beta \) is called a Shvab-Zel'dovich coupling function.

As shown by Bilger (1976a) the general expression for the conserved scalar \( \beta \) can be reduced to yield two special cases. The first case emerges by taking \( a_0 = 1 \) and \( a_i = 0 \):

\[
\beta = h \equiv h_\theta + \sum_{i=1}^{N} Y_i h_i^0 \tag{3.11}
\]

where \( h \) is the total enthalpy, which is conserved under chemical reactions. The second case is found by taking \( a_0 = 0 \) and \( a_i = (\nu'_i - \nu''_i) M_i n_{ki} \), yielding:

\[
Z_k = \sum_{i=1}^{N} n_{ki} Y_i M_k / M_i \tag{3.12}
\]

In this equation \( n_{ki} \) represents the number of atoms of element \( k \) in species \( i \), \( Z_k \) is the element mass fraction and \( M_k \) is the element molar mass. Since no atoms are created or destroyed under chemical reactions, \( Z_k \) is also a conserved scalar. It is important to note that both \( h \) and \( Z_k \) are independent from \( \nu'_i \) and \( \nu''_i \), implying that they are conserved at all times, whether the reactions are reversible or irreversible, and irrespective of the total number of species and reactions.
3.3. Conserved-scalar chemistry models

For a two-stream mixing problem every conserved scalar $\beta$ (defined by the coefficients $a_0$ and $a_i$) will exhibit the same similar behavior, provided the boundary conditions of $\bar{h}$ and $Y_i$ are compatible. This will generally be true if the flow is adiabatic, giving the boundary conditions $\beta = \beta_1$ in stream 1, $\beta = \beta_2$ in stream 2 and homogeneous Neumann boundary conditions at all other boundaries. Subsequently $\beta$ can be normalized by defining:

$$\xi = \frac{\beta - \beta_1}{\beta_2 - \beta_1}$$  \hspace{1cm} (3.13)

In this definition the actual choice for $\beta$ does not matter as long as $\beta_1 \neq \beta_2$. By definition $\xi = 0$ in stream 1 and $\xi = 1$ in stream 2.

From here on $\xi$ will be called the mixture fraction, which can be considered to be the mass fraction of atoms originating from stream 2. The $\xi$-field completely defines all other conserved scalar fields, such as the $\bar{h}$-field and the $Z_k$-field. The dependent thermochemical variables ($\rho, T, Y_i$) are related to mixture fraction by the chemistry model which at this stage still has to be specified. The concept of the conserved scalar can be applied to turbulent flames if the Damkohler number is sufficiently large ($Da_k > 1$), corresponding with the regimes of connected reaction zones and flamelets, depicted in figure 3.1 and discussed in the previous section.

Density is a function of mixture fraction if pressure variations are negligible, yielding:

$$\rho(\xi) = \frac{p M_m(\xi)}{R^0 T(\xi)}$$  \hspace{1cm} (3.14)

Here $p$ is the pressure and $M_m$ is the molar mass of the mixture, which is determined from the mixture composition. In all of our applications atmospheric pressure prevails, giving $p = p_{\text{atm}} = 101325$ Pa.

3.3.3 Treatment of enthalpy and temperature

The total enthalpy or stagnation enthalpy $h$ of a mixture is the sum of the chemical enthalpy $h_c$ and the thermal or sensible enthalpy $h_\theta$:

$$h = h_c + h_\theta = \sum_{i=1}^{N} Y_i h_i^0 + \sum_{i=1}^{N} Y_i h_{\theta,i}$$  \hspace{1cm} (3.15)

The standard enthalpy of formation $h_i^0$ of a species $i$ can be found in thermodynamic databases.

For practical purposes, one may also wish to use the so-called lower calorific value $h_{lc,i}$ of species $i$, which is the amount of heat released if 1 kg of species $i$ at standard conditions ($p^0 = 101325$ Pa, $T^0 = 298.15$ K) is completely oxidized to form CO$_2$ and H$_2$O, and then cooled down to the initial temperature and pressure. The H$_2$O which is formed in this process is assumed to be in the gas phase after cooling. In formula:

$$h_{lc,i} = h_i^0 - n_{C,i} \frac{M_{CO_2} h_{CO_2}^0}{M_i} - \frac{1}{2} n_{H,i} \frac{M_{H_2O} h_{H_2O}^0}{M_i}$$  \hspace{1cm} (3.16)
In general, \( h_{lc,i} \) will be positive for combustible species containing C-atoms or H-atoms, and zero for CO\(_2\), H\(_2\)O and all species which do not contain C-atoms or H-atoms. Thus, the total lower calorific value of the mixture represents the amount of heat which can be extracted if all species are completely oxidized. It is related to the chemical enthalpy by:

\[
h_c \equiv \sum_{i=1}^{N} h_{lc,i} = \sum_{i=1}^{N} Y_i h_i^0 - \left( \frac{Z_C M_{CO_2}}{M_C} \right) h_{CO_2}^0 - \left( \frac{Z_H M_{H_2O}}{2M_H} \right) h_{H_2O}^0
\]  

(3.17)

where we have used (3.12). Inspection of this equation reveals that the modified enthalpy \( h^* \equiv h_\theta + h_c \) also is a conserved scalar. In Table 3.1 we have listed the enthalpy of formation and the lower calorific values for a number of important species in natural gas combustion. The temperature \( T \) of the mixture is determined from the thermal enthalpy \( h_\theta \), using the relationship for constant pressure:

\[
dh_{\theta,i} = c_{p,i}(T) \, dT
\]  

(3.18)

If the species specific heats \( c_{p,i} \) would all be equal to a constant \( c_p \), then the temperature \( T \) would be a linear function of \( h_\theta \). In general, however, the species specific heats \( c_{p,i} \) are all different functions of temperature. As a result, the temperature has to be determined from:

\[
h_\theta = h - h_c = \sum_{i=1}^{N} Y_i \int_{T_0}^{T} c_{p,i}(\theta) \, d\theta
\]  

(3.19)

The mixture thermal enthalpy is a function of \( \xi \) alone, so the temperature can be calculated from the implicit equation given above. A Newton-Raphson iteration procedure will produce the correct flame temperatures as a function of \( \xi \).
3.3. \textit{Conserved-scalar chemistry models}

![Graph showing species mass fractions in the Burke-Schumann flame sheet. Symbols: --- inert species, \cdots fuel species, \cdots oxidizer species, \cdots product species.]

3.3.4 \textit{Burke-Schumann flame sheet model}

The simplest way to model the chemistry in diffusion flames is to assume an infinitely fast irreversible global reaction, yielding the so-called Burke-Schumann approximation (Burke and Schumann, 1928) or flame sheet model. In the flame sheet model, the combustion process is simplified as a one-step irreversible global reaction:

$$F + \nu' O_2 \rightarrow \text{products}$$ \hfill (3.20)

where $F$ denotes the \textquote{fuel} species and $\nu'$ is a stoichiometric coefficient. The reaction occurs at the isopleth where the mixture fraction has the stoichiometric value $\xi_{st}$. Outside this very thin flame sheet no reactions take place, and hot combustion products are mixed with the air or fuel stream. Thus all species mass fractions are simple piecewise linear functions of $\xi$ (see figure 3.2).

The mass fractions read:

\begin{align*}
\text{Inert species:} & \quad Y_{in} &= Y_{in,1} + (Y_{in,2} - Y_{in,1})\xi \hfill (3.21a) \\
\text{Fuel species:} & \quad Y_{fu} &= Y_{fu,2} \left( \frac{\xi - \xi_{st}}{1 - \xi_{st}} \right) \mathcal{H}(\xi - \xi_{st}) \hfill (3.21b) \\
\text{Oxidizer species:} & \quad Y_{ox} &= Y_{ox,1} \left( \frac{\xi_{st} - \xi}{\xi_{st}} \right) (1 - \mathcal{H}(\xi - \xi_{st})) \hfill (3.21c) \\
\text{Product species:} & \quad Y_{pr} &= 1 - Y_{fu} - Y_{ox} - Y_{in} \hfill (3.21d)
\end{align*}

where $\mathcal{H}(x)$ is the Heaviside step function. The value of $\xi_{st}$ can be calculated by regarding
Chapter 3. Chemistry models for turbulent flames

![Graph](image)

**Figure 3.3:** Species mass fractions in the two-step flame sheet model. Symbols: --- inert species, \(
\cdots\) fuel species, --- oxidizer species, \(\cdots\) product species (H\(_2\)O, CO\(_2\)), \(\Delta\) intermediate species (H\(_2\), CO).

the fuel and air composition and the one-step irreversible reaction:

\[
\xi_{sl} = \frac{Y_{O_2,1}}{\frac{\nu_{M_2}}{M_F} Y_{F,2} + Y_{O_2,1}}
\]  

(3.22)

A drawback of the flame sheet model is its inability to include the formation of intermediate species, mainly CO and H\(_2\). This can be remedied by assuming a global two-step reaction mechanism. The combustion of a general hydrocarbon fuel denoted by C\(_x\)H\(_y\) can then be formally described by:

\[
\begin{align*}
C_xH_y + \nu_1^fO_2 &\rightarrow x a \text{ CO}_2 + x (1 - a) \text{ CO} + \frac{y}{2} b \text{ H}_2\text{O} + y (1 - b) \text{ H}_2 \\
 c \text{ CO} + d \text{ H}_2 + \nu_2^fO_2 &\rightarrow c \text{ CO}_2 + d \text{ H}_2\text{O}
\end{align*}
\]

Both reactions are assumed to be infinitely fast and irreversible. The second oxidation step will only occur if the first step has been completed. Thus this model implies that two reaction sheets will exist: one at the \(\xi = \xi_{sl}\) isopleth (identical to the one-step reaction), and one at \(\xi = \xi_{ig}\). This is unrealistic from a chemical point of view: why should the second reaction always have to be preceded by the first reaction and why is the chemistry frozen for \(\xi_{sl} < \xi < \xi_{ig}\)? Nevertheless, this two-step model yields the desired realistic levels of intermediate species CO and H\(_2\), and the corresponding lower temperatures (see figure 3.3). The model can be tuned via the parameters \(a\) and \(b\).

Another drawback of the flame sheet model is the absence of radical species. The existence of radical species (e.g., OH, O, H) in the reaction zone gives lower flame...
temperatures. This can be modeled by an empirical correction function (Post, 1988), which effectively increases the mixture specific heat $c_{p,m}$ and thus reduces the temperature for a given enthalpy $h$. The correction function becomes effective for $T' > 1970$ K. At the very high temperatures prevailing in glass melting furnaces this correction is essential (figure 3.4) for realistic temperature predictions.

### 3.3.5 Chemical equilibrium model

The assumption of an infinitely fast one-step irreversible global reaction to describe fuel oxidation can be relaxed by assuming full chemical equilibrium for all species. This offers the possibility to include radicals and intermediate species into the simulation model. For example, natural gas combustion will involve more than 40 chemical species, many of which will be present in very low concentrations. The flame sheet model does not allow a reasonable prediction of these radical species, but equilibrium calculations will at least provide some information about the order of magnitude of their concentrations. This is particularly relevant with respect to the prediction of NO formation and fuel burn-out.

In general, the assumption of full chemical equilibrium is justified only if turbulent mixing times are much larger than chemical reaction times, or, in other words, at high Damköhler numbers. For the large-scale high-temperature flames in glass melting furnaces, this is approximately true. The Kolmogorov time scale $\tau_K$ in a typical large-scale furnace is estimated as $> 10^{-3}$ s, which is larger than the characteristic chemical time scale for most species. The assumption of chemical equilibrium will not be valid, however, for smaller flames and at lower temperatures, yielding a smaller Kolmogorov scale and
larger chemical time scales. To calculate chemical equilibrium efficiently in this study, the STANJAN code developed by Reynolds (1986) was used. Some modifications were made to enhance computational speed (Peeters et al., 1993).

3.3.6 Constrained-equilibrium model

Partial equilibrium

The full equilibrium model has been applied successfully for fast chemistry combustion, such as in hydrogen flames. For hydrocarbon flames the relatively slow burn-out of CO restricts the applicability of this approach. Treatment of CO kinetics in diffusion flames is hampered by the fact that CO is found to be in partial equilibrium in the high-temperature regions of the these flames, whereas explicit kinetics mainly play a role outside the visible flame region. Models are sought which entail this behavior.

In the high-temperature regions of a flame, many elementary reactions are active, the majority of which involve two reactants and two products. These so-called two-body reactions will leave the mole number density of the mixture unaltered. Some reactions, however, involve three reactants and two products or vice versa, and these will affect the mole number density. The main effect of the three-body reactions is to reduce the number of radicals in the flame zone. By considering the reaction rates of the elementary reactions in flames, it can be estimated that the two-body reactions between radicals are in partial equilibrium while the three-body recombination reactions are not, simply because collisions between three molecules have a relatively low probability. As a result, radical concentrations are in excess compared to full equilibrium concentrations, and the mole number of the reacting mixture will exceed its equilibrium value. This leads to the so-called partial equilibrium theory: all fast two-body reactions are assumed to be in chemical equilibrium, whereas the three-body recombination reactions are not. In its simplest form the mixture fraction \( \xi \) and the excess mole number \( n^* = n - n_{eq} \) are used to define the partial equilibrium composition. For \( n^* = 0 \) the model reduces to full equilibrium. The partial equilibrium model is particularly valid for lower temperatures, at which the three-body recombination reactions are too slow to attain equilibrium.

Constrained equilibrium

In diffusion flames, the chemical reactions mainly occur in a zone where the mixture fraction has a value close to its stoichiometric value. For too small or too large values of \( \xi \), the reaction rates drop quickly and the chemistry is 'frozen'. Hence the reality lies somewhere in between an infinitely thin flame sheet and a full equilibrium for all mixture fraction values. This knowledge has lead several investigators to develop a flame zone model.

Early attempts to construct a flame zone model were done by Libby and Economos (1963) and Eickhoff and Grethe (1979, 1982), but these models suffer from several deficiencies. Bilger and Stårner (1983) developed a model for hydrocarbon flames which involved a partial equilibrium approach with additional flame zone constraints. In this
study we did not employ the partial equilibrium part, and we only applied the flame zone constraints. The model of Bilger and Stårner treats the flame as a reaction zone located around the stoichiometric mixture fraction, supplemented by a fuel breakdown/pyrolysis sheet at $\xi = \xi_{ig} > \xi_{st}$. The pyrolysis sheet is assumed to be a one-step, irreversible, infinitely fast fuel decomposition reaction. On the rich side of this sheet no fuel is assumed to react.

Fuel hydrocarbons are pyrolyzed at the decomposition isopleth, yielding:

$$Y_{fu} = Y_{fu,2} \frac{(\xi - \xi_{ig})}{1 - \xi_{ig}} \mathcal{H}(\xi - \xi_{ig})$$

(3.23)

$\xi_{ig}$ is a model parameter which defines the position of the fuel decomposition flame sheet, and $Y_{fu}$ represents any hydrocarbon fuel species. At this decomposition flame sheet part of the fuel is assumed to be converted to intermediate hydrocarbons. For the intermediate hydrocarbons one has:

$$Y_{int} = \begin{cases} 
0 & \text{for } 0 \leq \xi < \xi_{st} \\
\frac{\xi - \xi_{st}}{1 - \xi_{st}} & \text{for } \xi_{st} \leq \xi \leq \xi_{ig} \\
\frac{\xi_{ig} - \xi_{st}}{1 - \xi_{st}} \left( \frac{1 - \xi}{1 - \xi_{ig}} \right) & \text{for } \xi_{ig} \leq \xi \leq 1
\end{cases}$$

(3.24)

where $e$ denotes the fraction of fuel hydrocarbon mass fraction which is converted to intermediate hydrocarbons at the pyrolysis flame sheet. At the stoichiometric isopleth $\xi = \xi_{st}$ all intermediate hydrocarbons are consumed. As a consequence, both the fuel and intermediate hydrocarbon mass fractions are piecewise linear functions of mixture fraction, similar to the two-step flame sheet model. This is depicted in figure 3.5. Input parameters to the model are the value of $\xi_{ig}$, the fraction $e$ and the intermediate hydrocarbon species. Bilger and Stårner took $\xi_{ig} = \xi_{st} + 0.018$, $e = 0.2$ and $C_2H_4$ for methane flames. Having defined the fuel decomposition model, the flame structure can be calculated as a function of mixture fraction. For any given value of $\xi$ the element mass fractions and the species mass fractions $Y_{fu}$ and $Y_{int}$ are known. Furthermore, the enthalpy is assumed to be prescribed. From these constraints it is possible to calculate the chemical equilibrium mass fractions of the remaining species (Peeters et al., 1993).

In figure 3.6 it can be seen that the constrained-equilibrium flame zone model differs considerably from the full chemistry model, yielding lower mass fractions of CO and H$_2$ for fuel rich mixtures ($\xi > \xi_{st}$). The imposed constraints on the hydrocarbon species extract C-atoms and H-atoms from the remaining mixture, whereas the amount of available O-atoms remains unaltered. This causes a shift from CO to CO$_2$ and from H$_2$ to H$_2$O.

### 3.3.7 Treatment of non-adiabaticity

In virtually all practical applications of turbulent combustion, the flow is strongly non-adiabatic. Locally the instantaneous thermal enthalpy can be about 50% lower than its...
adiabatic value. In large high-temperature flames the enthalpy loss is mainly caused by radiative heat transfer, but at lower temperatures and for laboratory-scale flames convection and heat conduction will contribute to larger extents.

For the calculation of the thermochemical field the non-adiabaticity introduces a severe complication. In the Shvab-Zel'dovich approximation the partial differential equations for $\xi$ and $h$ are similar, and with corresponding boundary conditions $h$ is a linear function of $\xi$. In the non-adiabatic case the enthalpy becomes a second independent variable which determines the thermochemical field. The transport equation for enthalpy contains a source term due to radiative heat transfer, and boundary conditions are also different from those of the mixture fraction. In general, every dependent thermochemical quantity will be a function both of the mixture fraction and the enthalpy:

$$\phi = \phi(\xi, h) \quad (3.25)$$

Although there is no practical difficulty to determine all thermochemical quantities as functions of $\xi$ and $h$, problems arise in the calculation of turbulent flows.

Due to the nonlinearity of the functions $\phi = \phi(\xi)$ in the adiabatic flame case, one has to use the probability density function for $\xi$ to evaluate the mean values of $\phi$. This is described in detail in Section 3.4. In the non-adiabatic case the joint PDF of $\xi$ and $h$ is required to calculate mean thermochemical quantities. If one employs a presumed-shape joint PDF which depends on a finite number of its lowest-order moments, the two-dimensional joint PDF will at least involve the knowledge of the mean and variance of $\xi$ and $h$, as well as their covariance. This poses serious problems, since the modeling of the partial differential equations for the (co)variance of $\xi$ and $h$ is a difficult task. Moreover, the evaluation of PDF-weighted variables would consume excessive amounts of computer time for 3D
3.3. Conserved-scalar chemistry models

![Graphs showing comparison of full-equilibrium model and constrained-equilibrium model applied to a methane flame. Solid line: full-equilibrium model; dotted line: constrained-equilibrium model.]

Figure 3.6: Comparison of full-equilibrium model and constrained-equilibrium model applied to a methane flame. Solid line: full-equilibrium model; dotted line: constrained-equilibrium model.

Simulations.

In view of the difficulties sketched above, a simplification is sought in order to retain the simple dependence \( h = h(\xi) \). Although this pseudo conserved-scalar description of non-adiabatic flames is certainly not valid in the general case, it proves to be a useful model. It seems reasonable to assume that at a given location in the flow with a given mean enthalpy \( \bar{h} \) deviating from the adiabatic enthalpy value \( h_1 + (h_2 - h_1)\xi \) by an amount \( \Delta h \), the local fluctuations of the instantaneous enthalpy \( h \) will deviate from the adiabatic values in about the same amount. This was first recognized by Salooja (1978), who presumed that locally the desired relationship \( \bar{h} = h(\xi) \) might be approximately true. Salooja used the locally computed mean values \( \bar{\xi} \) and \( \bar{h} \) to fit a linear function similar to the adiabatic relationship \( h = h(\xi) \):

\[
h = \bar{h} + (h_2 - h_1)(\xi - \bar{\xi})
\]

(3.26)

This is depicted in figure 3.7. In this manner, the local enthalpy behaves in much the same
way as the enthalpy in the adiabatic case.

As one can see, Salooja’s function produces $h$-values outside the interval $[h_1, h_2]$. This is not realistic, since due to the nature of the convection-diffusion equation for $h$, the radiative source terms and the boundary conditions will generally yield $h_1 \leq h \leq h_2$. These considerations were used by Megahed (1979), who assumed a piecewise linear profile for $h(\xi)$:

$$h = \begin{cases} h_1 + (\tilde{h} - h_1)\xi & \text{for } 0 \leq \xi < \tilde{\xi} \\ h_2 + \left(\frac{h_2 - \tilde{h}}{1 - \tilde{\xi}}\right)(\xi - 1) & \text{for } \tilde{\xi} \leq \xi \leq 1 \end{cases} \quad (3.27)$$

Inspection of the combinations $(\tilde{\xi}, \tilde{h})$ for 3D high-temperature furnace calculations showed that for a given point in the flow, the mean enthalpy of nearest neighbour points was often related in the piecewise linear fashion as assumed by Megahed. Therefore Megahed’s function, sketched in figure 3.7, seems more appropriate for furnace calculations than the function of Salooja. Further refinements of this model can be obtained by fitting other functions or polynomials.

As a result of this pseudo conserved-scalar approach, the numerical calculation of the mean thermochemical field can proceed according to an algorithm which strongly resembles the adiabatic case. This completes the description of the conserved-scalar model with inclusion of non-adiabaticity.
3.4 Assumed PDF closure for conserved-scalar models

3.4.1 Introduction

In the previous section models were discussed which relate the thermochemical variables of a two-stream mixing flow to a conserved scalar, the mixture fraction $\xi$, and the enthalpy $h$. Hence the complete one-point statistical information of the dependent thermochemical variables is known if the joint statistics of $\xi$ and $h$ are known.

To obtain average values of the thermochemical variables in a turbulent flow, one cannot simply put $\bar{\phi} = \phi(\bar{\xi}, \bar{h})$ since the functions $\phi(\xi, h)$ usually are highly nonlinear. Therefore the joint PDF $f_{\xi h}$ of $\xi$ and $h$ is required to compute the average $\bar{\phi}$. If we use an empirical model which relates the local enthalpy fluctuations to the local mixture fraction fluctuations, as discussed in Section 3.3.7, the enthalpy is eliminated as an independent variable, requiring the PDF of the mixture fraction alone:

$$
\bar{\phi} = \int_{0}^{1} \phi(\zeta, \bar{\xi}, \bar{h}) f_\xi(\zeta) \, d\zeta
$$

(3.28)

This equation is the starting point for the present investigation. For the sake of brevity we will write $\phi(\xi, \bar{\xi}, \bar{h}) = \phi(\xi)$.

In the sequel it is assumed that the relationship between $\phi$ and $\xi$ is known from the chemistry models discussed in the previous chapter. Furthermore, Favre averaged variables will be used throughout (Bilger, 1975; Favre, 1969). The Reynolds averaged density $\langle \rho \rangle$ is retrieved from the Favre PDF by:

$$
\langle \rho \rangle^{-1} = \int_{0}^{1} \rho(\zeta)^{-1} f_\xi(\zeta) \, d\zeta
$$

(3.29)

The PDF shape may vary considerably over the flow, as has been demonstrated by numerous experiments (see figure 3.8). Close to the fuel and air inlet, the PDF will be

![Diagram of PDF shapes in a mixing flow](image)

FIGURE 3.8: Various PDF shapes in a mixing flow
affected by an intermittent behaviour of the flow, resulting in Dirac $\delta$-function-like peaks near $\xi = 0$ or $\xi = 1$. Further downstream on the centreline of the flow, the PDF will tend to a Gaussian (normal) distribution, whereas in other regions bimodal PDF shapes exist.

In general, the PDF in a given mixing flow can be calculated in two ways. The first method, which we shall not treat in detail here, is to derive a transport equation for $f_\xi$ itself (Pope, 1985). This transport equation contains unknown terms which have to be modeled. Especially the modeling of the effect of molecular mixing on the PDF is difficult and still a fundamental problem in PDF theory. The modeled PDF equation can be solved by means of a Monte Carlo method, which is computationally expensive. The main advantage of the Monte Carlo PDF method is the absence of a priori presumptions on the actual PDF shape in any part of the flow. In recent years, Monte Carlo PDF methods have reached a state-of-the-art at which accurate numerical solutions can be obtained for a growing number of applications (Pope, 1985; Roekaerts, 1992), yet mostly restricted to 2D flows.

The second method presumes that the PDF can be described by a finite number of its moments, usually the zero (normalization), first (mean) and second (variance) moment. The moments can be computed from their respective modeled transport equations. In general it is not true that an arbitrary PDF can be fully represented by a finite number of its moments. Nevertheless, still reasonable results can be obtained with the presumed-shape PDF method (Elands, 1987; Libby, 1977). The presumed PDF method is computationally less expensive than the Monte Carlo PDF method, and therefore enjoys popularity for numerical simulations of complex turbulent flows, such as 3D furnace flows (Correa, 1984; Elgobashi and Pun, 1974).

### 3.4.2 Fundamentals of presumed PDF modeling

A major problem of the presumed PDF method is to compute the lower moments from their modeled transport equations. The usual turbulence closure concepts may be applied in the framework of the eddy viscosity model, yielding:

\[
\langle \rho \rangle \frac{\partial \tilde{\xi}}{\partial x_k} = \frac{\partial}{\partial x_k} \left( \langle \rho \rangle \frac{I_D}{\sigma_{\xi}} + \frac{\mu_1}{\sigma_{\xi}} \frac{\partial \tilde{\xi}}{\partial x_k} \right) + 3 \tilde{\varepsilon} \frac{\partial}{\partial x_k} \left( \frac{\mu_1}{\sigma_{\xi}} \frac{\partial \tilde{\xi}}{\partial x_k} \right) + C_{\varepsilon_1} \frac{\mu_1}{\sigma_{\xi}} \frac{\partial \tilde{\varepsilon}}{\partial x_k} - C_{\varepsilon_2} \langle \rho \rangle \frac{\tilde{\varepsilon}}{k} \tilde{\varepsilon} \quad (3.30)
\]

\[
\langle \rho \rangle \frac{\partial \tilde{\varepsilon} \tilde{n}_2}{\partial x_k} = \frac{\partial}{\partial x_k} \left( \langle \rho \rangle \frac{I_D}{\sigma_{\varepsilon_{\tilde{n}_2}}} + \frac{\mu_1}{\sigma_{\varepsilon_{\tilde{n}_2}}} \frac{\partial \tilde{\varepsilon} \tilde{n}_2}{\partial x_k} \right) + C_{\varepsilon_1} \frac{\mu_1}{\sigma_{\varepsilon_{\tilde{n}_2}}} \frac{\partial \tilde{\varepsilon}}{\partial x_k} + C_{\varepsilon_2} \langle \rho \rangle \frac{\tilde{\varepsilon}}{k} \tilde{\varepsilon} \tilde{n}_2 \quad (3.31)
\]

where the latter equation is taken from Abou-Ellail and Salem (1990). The model constants are listed in Table 3.2. Thus, the lower PDF moments can be computed in each point of the
flow. Here we will not go into further details concerning the turbulence closure of Favre averaged equations for scalar transport.

Another problem related to the presumed PDF method is to find a mathematical formula which captures all the different PDF shapes occurring in a mixing flow. In the past, several proposals have been made, the most important of which we shall discuss in subsequent sections. The parameters which appear in a given formula for the presumed-shape PDF are related to the lower-order moments of the PDF through the following relationships:

\[
1 = \int_0^1 \tilde{f}_\xi(\zeta) \, d\zeta
\]  \hspace{1cm} (3.33a)

\[
\bar{\zeta} = \int_0^1 \zeta \tilde{f}_\xi(\zeta) \, d\zeta
\]  \hspace{1cm} (3.33b)

\[
\bar{\zeta}^{\text{m2}} = \int_0^1 \zeta^2 \tilde{f}_\xi(\zeta) \, d\zeta - \bar{\zeta}^2
\]  \hspace{1cm} (3.33c)

These equations serve as implicit parameter equations. The mathematical PDF formula should match the experimental data as accurately as possible, but at the same time be as simple as possible for numerical reasons. In the next section we will confine ourselves to PDFs which are uniquely described by the above three equations. In the section on intermittency models we will discuss more complex presumed PDF models involving an additional higher moment, the skewness \( s \equiv \bar{\zeta}^{\text{m3}} \):

\[
\bar{\zeta}^{\text{m3}} = \int_0^1 \zeta^3 \tilde{f}_\xi(\zeta) \, d\zeta - 3\bar{\zeta} \bar{\zeta}^{\text{m2}} - \bar{\zeta}^3
\]  \hspace{1cm} (3.34)

### 3.4.3 Univariate PDF shapes

**Single Dirac PDF**

The single Dirac PDF is the simplest PDF form conceivable. It is described by:

\[
\tilde{f}_\xi(\zeta) = \delta(\zeta - \bar{\xi}).
\]  \hspace{1cm} (3.35)

As a consequence, we have \( \bar{\phi} = \phi(\bar{\xi}) \) which means that turbulent fluctuations are negligible. The single Dirac PDF shape will occur in the inlet streams of fuel and air, where the mixture fraction does not vary in time, and far away downstream of the mixing zone, where the flow field has become well-mixed again.
Double Dirac PDF

The double Dirac PDF is given by:

\[ f_\xi(\xi) = \alpha_0 \delta(\xi - \xi_0) + \alpha_1 \delta(\xi - \xi_1). \]  

(3.36)

For given values of \( \tilde{\xi} \) and \( \tilde{\xi}^{\prime 2} \), the double Dirac PDF is the most extreme way in which turbulent fluctuations may occur. The fluid remains essentially unmixed at the microscopic level, although the value of \( \xi \) in the separate streams may change. Consequently, this PDF shape is unrealistic in a physical sense, but it captures some basic features of turbulent fluctuations. The four PDF parameters \( \alpha_0, \alpha_1, \xi_0 \) and \( \xi_1 \) can be found in terms of \( \tilde{\xi} \) and \( \tilde{\xi}^{\prime 2} \). Several limiting cases are distinguished:

a) \( \tilde{\xi}^{\prime 2} = 0 \).

No fluctuations and the PDF reduces to the single Dirac function. This is formulated as \( \xi_0 = \xi_1 = \tilde{\xi} \) and \( \alpha_0 = \alpha_1 = \frac{1}{2} \).

b) \( \tilde{\xi}^{\prime 2} \leq \tilde{\xi}^2 \) and \( \tilde{\xi}^{\prime 2} \leq (1 - \tilde{\xi})^2 \).

Battlement without intermittency. No clipping of the PDF at \( \xi = 0 \) or \( \xi = 1 \). This is the standard case and is plotted in figure 3.9. This gives \( \alpha_0 = \alpha_1 = \frac{1}{2} \) and \( \xi_0 = \tilde{\xi} - \sqrt{\tilde{\xi}^{\prime 2}} \), \( \xi_1 = \tilde{\xi} + \sqrt{\tilde{\xi}^{\prime 2}} \).

c) \( \tilde{\xi}^{\prime 2} > \tilde{\xi}^2 \) and \( \tilde{\xi}^{\prime 2} \leq \tilde{\xi}(1 - \tilde{\xi}) \).

This case will only occur if \( \tilde{\xi} < \frac{1}{2} \) and fluctuations are so large that \( \xi_0 \) would become negative. Therefore the PDF is clipped at \( \xi = 0 \). In formula:

\[ \xi_0 = 0 \; ; \; \xi_1 = \tilde{\xi} + \frac{\tilde{\xi}^{\prime 2}}{\tilde{\xi}^{\prime 2}} \frac{\tilde{\xi}^{\prime 2}}{\xi} \]

\[ \alpha_0 = \frac{\tilde{\xi}^{\prime 2}}{\tilde{\xi}^{\prime 2} + \tilde{\xi}^2} \; ; \; \alpha_1 = 1 - \alpha_0 = \frac{\tilde{\xi}^2}{\tilde{\xi}^{\prime 2} + \tilde{\xi}^2} \]

d) \( \tilde{\xi}^{\prime 2} > (1 - \tilde{\xi})^2 \) and \( \tilde{\xi}^{\prime 2} \leq \tilde{\xi}(1 - \tilde{\xi}) \).

This case can only occur if \( \tilde{\xi} > \frac{1}{2} \) and fluctuations are so large that \( \xi_1 \) would become larger than 1. There is a strict analogy with case c. The PDF is now clipped at \( \xi = 1 \). In formula:

\[ \xi_0 = \tilde{\xi} - \frac{\tilde{\xi}^{\prime 2}}{1 - \tilde{\xi}} \; ; \; \xi_1 = 1 \]
3.4. Assumed PDF closure for conserved-scalar models

\[ \alpha_0 = \frac{(1 - \bar{\xi})^2}{\xi_{\text{in}}^2 + (1 - \bar{\xi})^2} ; \quad \alpha_1 = 1 - \alpha_0 = \frac{\xi_{\text{in}}^2}{\xi_{\text{in}}^2 + (1 - \bar{\xi})^2} \]

e) \xi_{\text{in}}^2 > \bar{\xi}(1 - \bar{\xi}).

Now, the fluctuations are so large that clipping at both ends of the allowed interval \([0, 1]\) is required. As a result, \(\xi_0 = 0\) and \(\xi_1 = 1\). Furthermore, we have \(\alpha_0 = 1 - \bar{\xi}\) and \(\alpha_1 = \bar{\xi}\).

**Top hat PDF**

The 'top hat' or rectangular PDF is described by:

\[
\tilde{f}_\xi(\zeta) = \alpha_0 \delta(\zeta - \xi_0) + \alpha_1 \delta(\zeta - \xi_1) + C \{ \mathcal{H}(\zeta - \xi_0) - \mathcal{H}(\zeta - \xi_1) \} \]  

(3.37)

where \(\mathcal{H}\) is the Heaviside step function. The PDF parameters to be determined are \(\alpha_0\), \(\alpha_1\), \(\xi_0\), \(\xi_1\) and \(C\). Six different cases can be distinguished, some of which are shown by figure 3.10:

a) \(\xi_{\text{in}}^2 = 0\): No turbulent fluctuations.

The PDF reduces to the single Dirac PDF, which is formally described by \(C = 0\); \(\alpha_0 = \alpha_1 = \frac{1}{2}\); \(\xi_0 = \xi_1 = \bar{\xi}\).

b) \(\xi_{\text{in}}^2 \leq \frac{1}{3} \bar{\xi}^2\): No intermittency effects.

This is the general case where fluctuations are relatively small, giving \(\alpha_0 = \alpha_1 = 0\). Applying the normalization condition yields \(C(\xi_1 - \xi_0) = 1\). Furthermore, we have:

\[
\bar{\xi} = \int_{\xi_0}^{\xi_1} \zeta \tilde{f}_\xi(\zeta) \, d\zeta = \frac{1}{2} C(\xi_1 - \xi_0)(\xi_1 + \xi_0) .
\]
Combining these two relationships gives $\tilde{\xi} = \frac{1}{2}(\xi_0 + \xi_1)$, as expected. The second moment is written as:

$$\tilde{\xi}^2 = -\tilde{\xi}^2 + C \int_{\xi_0}^{\xi_1} \xi^2 d\xi = -\tilde{\xi}^2 + \frac{1}{3}C(\xi_1^3 - \xi_0^3) = \frac{1}{12}(\xi_0 - \xi_1)^2$$

This gives:

$$\xi_0 = \tilde{\xi} - \sqrt{3\tilde{\xi}^2} ; \quad \xi_1 = \tilde{\xi} + \sqrt{3\tilde{\xi}^2}$$

$$C = \sqrt{12\tilde{\xi}^2}$$

c) $\frac{1}{3}\tilde{\xi}^2 \leq \tilde{\xi}^2 < \frac{2}{3}\tilde{\xi}^2 - \tilde{\xi}^2$.

Here we have intermittency at $\xi = 0$, but not at $\xi = 1$. This will only occur if fluctuations are moderately large and $\tilde{\xi} < \frac{1}{2}$. Now we have $\xi_0 = 0$ and $\alpha_1 = 0$. Applying the three conditions (3.33a), (3.33b), (3.33c), we find:

$$\alpha_0 = \frac{\tilde{\xi}^2 - \frac{1}{3}\tilde{\xi}^2}{\tilde{\xi}^2 + \tilde{\xi}^2}$$

$$\xi_1 = \frac{2\tilde{\xi}}{1 - \alpha_0}$$

$$C = \frac{1 - \alpha_0}{\xi_1} = \frac{(1 - \alpha_0)^2}{2\tilde{\xi}}$$

d) $\frac{2}{3}\tilde{\xi}^2 - \tilde{\xi}^2 < \tilde{\xi}^2 < \tilde{\xi}^2 - \tilde{\xi}^2$: Intermittency at both ends.

This will only occur if fluctuations are very large. As a result we have $\xi_0 = 0$, $\xi_1 = 1$, with which we obtain:

$$C = 6(\tilde{\xi} - \tilde{\xi}^2 - \tilde{\xi}^2)$$

$$\alpha_0 = 1 - \tilde{\xi} - \frac{1}{2}C ; \quad \alpha_1 = \tilde{\xi} - \frac{1}{2}C$$

e) $\tilde{\xi} - \tilde{\xi}^2 \leq \tilde{\xi}^2$:

Fully intermittent flow.

Fluctuations are so large that only Dirac spikes near the interval edges remain. This gives $C = 0$, $\xi_0 = 0$, $\xi_1 = 1$, $\alpha_0 = 1 - \tilde{\xi}$ and $\alpha_1 = \tilde{\xi}$.

f) $\frac{1}{3}(1 - \tilde{\xi})^2 < \tilde{\xi}^2 \leq \frac{4}{3}\tilde{\xi} - \tilde{\xi}^2 - \frac{1}{3}$.

This case is analogous to case c, but now we have $\tilde{\xi} > \frac{1}{2}$ and $\tilde{\xi}$ replaced with $1 - \tilde{\xi}$. Hence, $\alpha_0 = 0$, $\xi_1 = 1$. Moreover,

$$\xi_0 = \frac{3}{2}(\tilde{\xi} - \tilde{\xi}^2 - \tilde{\xi}^2) - \frac{1}{2}$$

$$\alpha_1 = 1 - C(1 - \xi_0) = 1 - 2\left(\frac{1 - \tilde{\xi}}{1 - \xi_0}\right)$$

$$C = \frac{2(1 - \tilde{\xi})}{(1 - \xi_0)^2}$$
3.4. Assumed PDF closure for conserved-scalar models

\[ \tilde{f}_\xi(\xi) = \frac{\xi^{a-1}(1 - \xi)^{b-1}}{\int_0^1 \xi^{a-1}(1 - \xi)^{b-1} d\xi} = \frac{\Gamma(a + b)}{\Gamma(a)\Gamma(b)} \xi^{a-1}(1 - \xi)^{b-1} \quad (3.38) \]

where \( \Gamma(a) \) is the gamma function defined as:

\[ \Gamma(a) = \int_0^\infty e^{-t}t^{a-1}dt, \quad a > 0. \quad (3.39) \]

The PDF parameters \( a \) and \( b \) uniquely depend on the first and second moment:

\[ a = \frac{\xi^2(1 - \tilde{\xi})}{\tilde{\xi}^2} - \tilde{\xi}, \quad (3.40) \]

\[ b = a \left( \frac{1 - \tilde{\xi}}{\xi} \right) = \frac{\tilde{\xi}(1 - \tilde{\xi})^2}{\tilde{\xi}^2} - (1 - \tilde{\xi}). \quad (3.41) \]

If \( \tilde{\xi} \) and \( \tilde{\xi}^{n2} \) are known, \( a \) and \( b \) can be calculated directly. Depending on the numerical values of \( a \) and \( b \), the \( \beta \)-function covers a wide range of different shapes, as illustrated by figure 3.11. For small fluctuations i.e. small \( \tilde{\xi}^{n2} \), \( a \) and \( b \) will become large and \( \tilde{f}_\xi(\xi) \) will resemble the single Dirac PDF \( \delta(\xi - \tilde{\xi}) \) or a Gaussian-like PDF. For large fluctuations, \( a \) and \( b \) will be small and the maximum value of \( \tilde{f}_\xi \) is shifted towards \( \xi = 0 \) or \( \xi = 1 \), depending on \( \tilde{\xi} \). For \( a < 1 \) the PDF has a singularity at \( \xi = 0 \); for \( b < 1 \) the PDF has a singularity at \( \xi = 1 \). For \( a, b > 1 \) the PDF will be zero at both interval boundaries \( \xi = 0, \xi = 1 \).
The location of the PDF maximum is given by:

\[ \xi_{\text{max}} = \frac{a - 1}{a + b - 2} = \frac{a - 1}{(a - 1) + (b - 1)}. \]

If \( a = b \) we have \( \xi_{\text{max}} = \frac{1}{2} \) and the PDF is symmetrical around \( \xi = \frac{1}{2} \). For \( a < b \) we have \( \xi_{\text{max}} > \frac{1}{2} \) and vice versa. If \( a = 1 \) or \( b = 1 \) a singularity appears which remains finite in the asymptotic limit of \( \xi \downarrow 0 \) and \( \xi \uparrow 1 \), respectively, and the PDF reduces to:

\[ a = 1 \Rightarrow \tilde{f}_\xi(0) = b \]

\[ b = 1 \Rightarrow \tilde{f}_\xi(1) = a \]

**Truncated Gaussian distribution**

The general shape of the truncated Gaussian PDF reads:

\[
\tilde{f}_\xi(\zeta) = \frac{1}{A\sigma \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{\zeta - \mu}{\sigma} \right)^2 \right] \{H(\zeta) - H(\zeta - 1)\} \tag{3.42}
\]

The PDF parameters are \( \mu \) and \( \sigma \). They are related to \( \tilde{\xi} \) and \( \tilde{\xi}^2 \) by virtue of the conditions (3.33b) and (3.33c). \( A \) is a normalization constant which is required since the PDF is confined to the interval \([0, 1]\) (see figure 3.12). It can be derived from the normalization condition (3.33a). Substitution of 3.42 yields an implicit set of equations for \( \mu \) and \( \sigma \):

\[ \tilde{\xi} = \mu + \frac{\sigma B}{A} \tag{3.43} \]

\[ \tilde{\xi}^2 = -\tilde{\xi}^2 + \mu^2 + \sigma^2 + \frac{\sigma \mu B}{A} - \frac{C}{A} \tag{3.44} \]
3.4. Assumed PDF closure for conserved-scalar models

where we have used:

\[ A = \frac{1}{2} \left[ \text{erf}(z_0) + \text{erf}(z_1) \right] = 1 \]  
\[ B = \frac{1}{\sqrt{2\pi}} \left( \exp(-z_0^2) - \exp(-z_1^2) \right) \]  
\[ C = \frac{\sigma}{\sqrt{2\pi}} \exp(-z_1^2) \]

Here and in the next paragraph \( z_0 \) and \( z_1 \) are defined by:

\[ z_0 = \frac{\mu}{\sigma \sqrt{2}} ; \quad z_1 = \frac{1 - \mu}{\sigma \sqrt{2}} \]

Clipped Gaussian distribution

The general shape of the clipped Gaussian PDF reads:

\[ \tilde{f}_\xi(\zeta) = \alpha_0 \delta(\zeta) + \alpha_1 \delta(\zeta - 1) \]
\[ + \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{\zeta - \mu}{\sigma} \right)^2 \right] \{ \mathcal{H}(\zeta) - \mathcal{H}(\zeta - 1) \} \]

Again, as with the truncated Gaussian distribution, the PDF parameters \( \mu \) and \( \sigma \) are related to \( \tilde{\zeta} \) and \( \tilde{\xi}^{1/2} \). As additional parameters we have the weights of the Dirac functions, \( \alpha_0 \) and \( \alpha_1 \). Since \( \mu \) and \( \sigma \) now are the parameters of the full (unclipped) Gaussian distribution, we have by definition:

\[ \alpha_0 = \int_{-\infty}^{0} \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{\zeta - \mu}{\sigma} \right)^2 \right] d\zeta = \frac{1}{2} \left[ 1 - \text{erf}(z_0) \right] \]
\[ \alpha_1 = \int_{1}^{\infty} \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{\zeta - \mu}{\sigma} \right)^2 \right] d\zeta = \frac{1}{2} \left[ 1 - \text{erf}(z_1) \right] \]

Consequently, \( \alpha_0 \) and \( \alpha_1 \) are fully determined by \( \mu \) and \( \sigma \). Applying the normalization condition and the PDF definition, i.e. (3.33a), (3.33b) and (3.33c), one obtains:

\[ \tilde{\xi} = \alpha_1 + \mu A + \sigma B \]
\[ \tilde{\xi}^{1/2} = -\xi^2 + \alpha_1 + (\mu^2 + \sigma^2)A + \sigma \mu B - C \]

where \( A, B, C, z_0, z_1 \) are the same as in (3.45-3.48). From figure 3.13 it is seen that for larger variances, the clipped Gaussian PDF differs from the truncated Gaussian PDF (cf. figure 3.12).
Chapter 3. Chemistry models for turbulent flames

3.5 Intermittency modeling

3.5.1 Introduction

Turbulent non-premixed flames often exhibit an intermittent behavior as a consequence of the high-speed fuel jet mixing with the low-speed air. Intermittency can be explained by considering the temporal behavior of a typical quantity (e.g. the mixture fraction) in the mixing region of a jet. Figure 3.14 shows a schematic time evolution of the mixture fraction close to the fuel jet. Most of the time the signal has a typically turbulent character, but at times fluctuations are absent. This intermittency has a strong influence on the shape of the PDFs of the fluctuating variables. Close to the inlet regions sharp delta spikes will occur, whereas further downstream the PDF will tend to a Gaussian (normal) distribution. In the flow two different regions can be distinguished: the turbulent zone and the non-turbulent zone. In more sophisticated descriptions even a third zone is considered: the super-layer which marks the transition from the turbulent zone to the non-turbulent zone.

As stated, the PDF of a mixing scalar can have a bimodal shape due to the contribution of the ‘turbulent’ and the ‘non-turbulent’ zones. Conditionally averaged quantities in the ‘turbulent’ zone, do not show such bimodal behavior and often have a near-Gaussian distribution. Therefore, when applying conditional averaging, it is possible to split the

Figure 3.13: Clipped Gaussian PDF for $\bar{\xi} = 0.1$ and $\bar{\xi}^m_2 = 6.2 \cdot 10^{-3}, 4.3 \cdot 10^{-4}$ and $3.0 \cdot 10^{-5}$.

Figure 3.14: Schematic intermittent signal in a turbulent flow
PDF in two distinct parts: a delta peak for the non-turbulent zone, a smooth distribution (near-Gaussian) for the turbulent zone. This may improve predictions of the mean thermochemical quantities.

### 3.5.2 Literature review

Experimental evidence for intermittent behaviour of turbulent flows was first obtained by Corrsin and Kistler (1954) for non-reacting flows. Since then, much experimental research has been done to study the intermittent nature of turbulent shear layers (Gutmark and Wygnanski, 1976; Hedley and Keffer, 1974; Wygnanski and Fiedler, 1970).

Theoretical work on the description of intermittency and conditional averaging was first done by Libby (1975, 1977) and Dopazo (1977). The latter derived exact equations for conditional moments and the intermittency factor $\gamma$. Further modeling was carried out by Chevray and Tutu (1978). Finally, Byggstøyl and Kollmann (1981) developed a complete closure model for the intermittency factor and the conditionally averaged quantities, based on the $k$-$\epsilon$ model of turbulence.

In recent years, attention has shifted towards higher-order (second-moment) closure schemes, in combination with modeling of turbulent non-premixed flames. In addition, detailed experiments have been carried out by a number of workers. The experimental technique of conditional sampling in turbulent combustion was further developed. A comprehensive review article on this subject was written by Libby et al. (1982).

Drake et al. (1984) experimentally studied the effects of intermittency, conditional averaging and Favre averaging in hydrogen jet diffusion flames. Further results were published by Drake and Pitz (1986, 1986). At the Sandia Laboratories methane flames have been investigated (Dibble et al., 1987b; Masri et al., 1988; Schefer and Dibble, 1985). A large number of experimental data on PDFs, conditional zone quantities, intermittency and density fluctuations has thus been collected.

Full second-moment closure schemes for turbulent non-premixed flames have now reached a state at which reasonably accurate predictions can be made for parabolic 2D flows. Intermittency was further modeled by many others (Chen, 1987; Chen et al., 1987; Chen and Lumley, 1984; Janicka and Kollmann, 1982; Janicka and Kollmann, 1985; Kollmann, 1983). Second-order models for variable-density flows without intermittency have also been developed (Dibble et al., 1987a; Janicka, 1984; Shih et al., 1987; Vandromme and Kollmann, 1982).

### 3.5.3 Intermittency theory

To describe intermittent behaviour, an indicator function $I(x, t)$ is defined as:

$$I(x, t) = \begin{cases} 1 & \text{turbulent zone} \\ 0 & \text{non-turbulent zone} \end{cases} \quad (3.52)$$

In practice, one requires a non-negative discriminator variable $D(x, t)$, with $D \geq \epsilon > 0$ corresponding to the turbulent zone at $(x, t)$ and $D < \epsilon$ to the non-turbulent zone. The
actual choice of the discriminator is of minor importance for our theoretical analysis, but not trivial for experiments. One may take the vorticity fluctuations as a discriminator variable:

$$D = \omega'_k \omega'_k. \quad (3.53)$$

The instantaneous surface $S$ which separates the turbulent zone from the non-turbulent zone is described as:

$$S(x, t) \equiv D(x, t) - \epsilon = 0. \quad (3.54)$$

In reality $S$ will have a finite thickness, comparable to the Kolmogorov microscale of the turbulent zone. For high turbulent-Reynolds numbers, however, $S$ will be sufficiently thin to permit a useful physical definition. The interface $S$ has a propagation speed given by:

$$u^S = \frac{d x^S}{d t}, \quad (3.55)$$

where $x^S$ is a point on $S$. The interface progression velocity relative to the moving fluid therefore is:

$$V n_i = v_i - v^S_i, \quad (3.56)$$

where $n$ is the unit vector normal to $S$, pointing into the turbulent zone. This definition is unambiguous, so that we can derive a transport equation for the indicator function $I$:

$$\rho \frac{\partial I}{\partial x_k} = \rho n_k \delta(S), \quad (3.57)$$

$$\rho \frac{\partial I}{\partial t} = -\rho v^S_k n_k \delta(S). \quad (3.58)$$

$I$ will change its value only at the interface $S$, which explains the $\delta$-function appearing in (3.57) and (3.58). Combining these two relationships yields:

$$\rho \frac{\partial I}{\partial t} + \rho v^S_k \frac{\partial I}{\partial x_k} = \rho V \delta(S). \quad (3.59)$$

The intermittency function $I$ can be Favre averaged to obtain the (Favre) intermittency factor $\bar{\gamma}$.

$$\bar{\gamma} \equiv \frac{\langle \rho I(x, t) \rangle}{\langle \rho \rangle}. \quad (3.60)$$

With this definition conditional-zone averages and fluctuations can be defined:

$$\bar{\phi}^{(1)} = \frac{\langle \rho I \phi \rangle}{\langle \rho \rangle \bar{\gamma}}, \quad (3.61)$$

$$\bar{\phi}^{(0)} = \frac{\langle \rho (1 - I) \phi \rangle}{\langle \rho \rangle (1 - \bar{\gamma})}, \quad (3.62)$$

$$\phi^{(1)} = \phi - \bar{\phi}^{(1)}, \quad (3.63)$$

$$\phi^{(0)} = \phi - \bar{\phi}^{(0)}. \quad (3.64)$$
3.5. Intermittency modeling

The superscripts \(^{(1)}\) and \(^{(0)}\) denote the turbulent zone and non-turbulent zone, respectively. By definition, the conditional-zone averages of \(\phi^{(1)}\) and \(\phi^{(0)}\) are zero.

Correlations between fluctuations are given by:

\[
\overline{\phi' \psi'}^{(1)} = \frac{\langle \rho I \phi^{(1)} \psi^{(1)} \rangle}{\langle \rho \rangle \bar{\gamma}},
\]

\[
\overline{\phi' \psi'}^{(0)} = \frac{\langle \rho (1 - I) \phi^{(0)} \psi^{(0)} \rangle}{\langle \rho \rangle (1 - \bar{\gamma})}.
\]

From these conditionally averaged quantities the usual unconditional (Favre) mean quantities can be recovered:

\[
\bar{\phi} = \bar{\gamma} \bar{\phi}^{(1)} + (1 - \bar{\gamma}) \bar{\phi}^{(0)},
\]

\[
\overline{\phi' \psi'} = \bar{\gamma} \overline{\phi' \psi'}^{(1)} + (1 - \bar{\gamma}) \overline{\phi' \psi'}^{(0)} + \bar{\gamma}(1 - \bar{\gamma}) \Delta \bar{\phi} \Delta \bar{\psi},
\]

where \(\Delta \bar{\phi} \equiv \bar{\phi}^{(1)} - \bar{\phi}^{(0)}\). The last term in (3.68) expresses the fact that the conventional correlation \(\phi' \psi'\) is not merely a linear combination of the two conditional-zone correlations. The term represents contributions from discrete jumps of first moments between the two conditional zones.

From the transport equation for the indicator function \(I\) a transport equation for the Favre averaged intermittency factor \(\bar{\gamma}\) can be derived:

\[
\langle \rho \rangle \frac{\partial \bar{\gamma}}{\partial t} + \langle \rho \rangle \bar{v}_k \frac{\partial \bar{\gamma}}{\partial x_k} = \frac{\partial}{\partial x_k} \left[ \langle \rho \rangle \bar{\gamma} (\bar{v}_k - \bar{v}_k^{(1)}) \right] + \langle \rho \rangle \bar{W}_\gamma.
\]

Here, \(\bar{W}_\gamma\) is the Favre averaged source term:

\[
\bar{W}_\gamma = \frac{\langle \rho V \delta(S) \rangle}{\langle \rho \rangle}.
\]

If the conditional and unconditional velocities are solved for, the only term to be modeled is the source term \(\bar{W}_\gamma\). In parabolic flow models, however, the cross-flow velocity component is often computed rather inaccurately. In that case, better results are obtained if the velocity difference \(\bar{v}_k - \bar{v}_k^{(1)}\) is modeled rather than calculated directly.

Lumley (1980) argued that the discontinuous jump between the conditional and unconditional velocities should be in the direction from the fluid with higher intermittency towards the fluid with lower intermittency. This suggests that the velocity jump is proportional to the gradient of intermittency. According to Chen (1987), a simple gradient-diffusion-like model is:

\[
\bar{v}_k - \bar{v}_k^{(1)} = C_\gamma \frac{\hat{k}^{(1)}}{\bar{\gamma}} \frac{(1 - \bar{\gamma})^2}{\bar{\gamma}} \frac{\partial \bar{\gamma}}{\partial x_k},
\]

where \(\hat{k}^{(1)} \equiv \frac{1}{2} \bar{\psi'}^2 \bar{v}'^{(1)}\) is the turbulent kinetic energy in the turbulent zone and \(C_\gamma = 0.14\) is a model constant inferred from experiments. Byggstøyl and Kollmann (1981) conceived a
somewhat different model, which we shall not discuss here. For complex turbulent flows, the equations for all mean velocity components will be solved and then no model for the cross-flow velocity jump will be needed.

The second term to be modeled is the source term \( \tilde{W}_\gamma \). First attempts to model this term were made by Libby (1975) and Chevray and Tutu (1978). Their models have several disadvantages, as was argued by Byggstøyl and Kollmann (1981). As an improvement, they have split up the source term into three separate parts:

\[
\tilde{W}_\gamma = \tilde{W}_\gamma^{(1)} + \tilde{W}_\gamma^{(2)} + \tilde{W}_\gamma^{(3)}
\]

where:

\[
\tilde{W}_\gamma^{(1)} = C_{\gamma 1} \tilde{\gamma}(1 - \tilde{\gamma}) \frac{1}{k^{(1)}} \overline{\nu^\prime \nu^\prime_{j}} \frac{\partial \bar{v}_i^{(1)}}{\partial x_j}
\]

\[
\tilde{W}_\gamma^{(2)} = C_{\gamma 2} \left( \frac{k^{(1)}}{\bar{c}^{(1)}} \right)^2 \frac{\partial \tilde{\gamma}}{\partial x_k} \frac{\partial \tilde{\gamma}}{\partial x_k}
\]

\[
\tilde{W}_\gamma^{(3)} = C_{\gamma 3} \tilde{\gamma}(1 - \tilde{\gamma}) \frac{\bar{c}^{(1)}}{k^{(1)}}
\]

The first part is a production term and expresses the fact that intermittency production should be proportional to production of turbulent kinetic energy. Furthermore, this term depends on \( \tilde{\gamma} \) itself, since the realizability condition \( 0 \leq \tilde{\gamma} \leq 1 \) should be satisfied at all times. Therefore, a factor \( \tilde{\gamma}(1 - \tilde{\gamma}) \), which is approximately equal to the crossing frequency of the turbulent-non-turbulent interface at a certain point in the flow, is added.

The second term states that intermittency production is proportional to the gradient of intermittency. In fully developed turbulent shear flow, a rapid variation of \( \tilde{\gamma} \) implies a slow movement of the turbulent fluid in the direction of \( \nabla \tilde{\gamma} \) but rapid orthogonal to it. This yields a strong anisotropy of the Reynolds stresses, which is counteracted by the pressure-strain correlation. Hence the second term can be interpreted as a nonlinear convection term representing a counterbalance effect due to intermittency anisotropy.

The third term \( \tilde{W}_\gamma^{(3)} \) is required to enforce realizability in a homogeneous turbulent flow, in which no production of kinetic energy and no intermittency gradients are present.

The above model for \( \tilde{W}_\gamma \) was developed by Byggstøyl and Kollmann (1981). We will use the version of Chen (1987) which has slightly different constants: \( C_{\gamma 1} = 1.75 (2.22) \), \( C_{\gamma 2} = 0.4 (0.6) \) and \( C_{\gamma 3} = 0.1 (0.1) \). In parentheses we have given the values of the constants suggested by Byggstøyl and Kollmann, who based their model on the \( k-\epsilon \) model of turbulence, whereas Chen used a Reynolds-stress turbulence closure.

### 3.5.4 Alternative intermittency model

In the previous sections the theoretical concepts of conditional averaging and related closure assumptions have been outlined. The fundamental approach leads to the simultaneous solution of transport equations for the conditional averages. To find such a solution is tedious and has mainly been applied to parabolic axisymmetric flows, where parabolic
3.5. Intermittency modeling

Partial differential equations can be solved at reasonable costs. The resulting PDF can then be found by linear combination of Dirac functions and a presumed-shape PDF, such as the $\beta$-function distribution.

Instead of solving for the modeled transport equation for $\tilde{\gamma}$, we can use the properties of the presumed-shape PDF of the mixture fraction. In the previous Section possible shapes of the univariate PDF were discussed, based on the first and second moment as independent input quantities. Consequently, all higher moments of the PDF are known if the lower moments are evaluated from their transport equations. Vice versa, if the third moment is solved separately, we can introduce an additional independent PDF parameter: the intermittency factor $\tilde{\gamma}$. This was recognized by Abou-Ellail and Salem (1990), who constructed a conditional turbulent mixture fraction PDF and an intermittency spike at $\xi = 0$ by solving the transport equations for $\tilde{\xi}$, $\tilde{\xi}^{\beta 2}$ and $\tilde{\xi}^{\beta 3}$. One has to realize that such a model is based on an indicator function proportional to the fluctuations of mixture fraction rather than vorticity fluctuations. Furthermore, the modeled transport equations for $\tilde{\xi}$, $\tilde{\xi}^{\beta 2}$ and especially $\tilde{\xi}^{\beta 3}$ have their specific difficulties not discussed here. Hence the model discussed below not only relies on the assumptions regarding the PDF shape, but also on the underlying turbulence closure model for the moment equations.

Using the definitions of conditional averages, and by employing the specific properties of the $\beta$-function PDF, one can find an algebraic relationship between $\tilde{\gamma}$ and the moments of the PDF. The composite PDF consists of a $\delta$-function representing the unmixed air, and a $\beta$-function for the conditional turbulent fluctuations of mixture fraction:

$$
\tilde{f}_\xi(\zeta) = (1 - \tilde{\gamma})\delta(\zeta) + \tilde{\gamma}f^{(1)}_\xi(\zeta)
$$

The parameters of the conditional $\beta$-function are obtained from the conditional moments:

$$
f^{(1)}_\xi(\zeta) = \frac{\Gamma(a + b)}{\Gamma(a)\Gamma(b)} \zeta^{a-1}(1 - \zeta)^{b-1}
$$

where:

$$
a = \tilde{\xi}^{(1)} \left[ \frac{\tilde{\xi}^{(1)}(1 - \tilde{\xi}^{(1)})}{\tilde{\xi}^{\beta 2(1)}} - 1 \right]
$$

$$
b = a(1 - \tilde{\xi}^{(1)})/\tilde{\xi}^{(1)}
$$

The conditional skewness $\tilde{\xi}^{\beta 3(1)}$ of the turbulent part $\tilde{f}_\xi^{(1)}$ of the PDF is related to the conditional lower moments:

$$
\tilde{\xi}^{\beta 3(1)} = \frac{2(\tilde{\xi}^{\beta 2(1)})^2(1 - 2\tilde{\xi}^{(1)})}{\tilde{\xi}^{(1)}(1 - \tilde{\xi}^{(1)}) + \tilde{\xi}^{\beta 2(1)}}
$$

In this model, only transport equations are solved for the unconditional moments $\tilde{\xi}$, $\tilde{\xi}^{\beta 2}$ and $\tilde{\xi}^{\beta 3}$, which are related to the conditional moments through the intermittency factor:

$$
\tilde{\xi} = \tilde{\gamma}\tilde{\xi}^{(1)}
$$
\[ \tilde{\xi}^2 + \tilde{\eta}^2 = \tilde{\gamma}(\tilde{\xi}^{(1)})^2 + \tilde{\eta}^{(1)} \]
\[ \tilde{\xi}^3 + 3 \tilde{\xi} \tilde{\eta}^2 + \tilde{\eta}^3 = \tilde{\gamma}(\tilde{\xi}^{(1)})^3 + 3 \tilde{\xi}^{(1)} \tilde{\eta}^{(1)} + \tilde{\eta}^{(1)} \]

By employing these algebraic relationships, an explicit formula for the intermittency factor as a function of the three unconditional moments can be derived:

\[ \tilde{\gamma} = \frac{2 \tilde{\xi}^2 \tilde{\eta}^{(1)} + \tilde{\xi} [\tilde{\eta}^{(2)}(4 \tilde{\xi}^2 - \tilde{\xi} - \tilde{\xi}^{(2)}) - \tilde{\xi}^3(1 - \tilde{\xi})]}{\tilde{\xi}^{(3)}(\tilde{\xi}^2 + \tilde{\xi} + \tilde{\xi}^{(2)}) + \tilde{\eta}^{(2)}(4 \tilde{\xi}^3 + 3 \tilde{\xi} \tilde{\eta}^{(2)} - \tilde{\xi}^2 - 2 \tilde{\xi}^{(2)} - \tilde{\xi}^4(1 - \tilde{\xi})} \] (3.78)

The above expression is valid under the assumption of a \( \beta \)-function PDF only; in case of Gaussian turbulent PDF a different formula would result.

The intermittency model of Abou-Ellail and Salem (1990) has been tested for a free methane jet flame in still air, showing an improved prediction of flame structure compared to the standard \( \beta \)-function PDF without explicit intermittency. Further numerical experiments have to be performed to apply the model to other, more complicated mixing flows.

As can readily be seen, certain problems may occur in practical numerical simulations which do not satisfy the realizability conditions. The nominator of (3.78) may attain non-physical values causing the intermittency factor to exceed its mathematical limits. Hence it is important to at least enforce:

\[ 0 \leq \tilde{\gamma} \leq \frac{\tilde{\xi}^2}{\tilde{\xi}^2 + \tilde{\xi}^{(2)}} \] (3.79)

At the boundaries of a turbulent jet the values of the lower moments will approach zero, which may lead to numerical problems in (3.78).

This concludes the treatment of intermittency modeling in relation to PDF models for non-reacting scalars.

### 3.6 Laminar flames

#### 3.6.1 Introduction

In recent years much emphasis has been given to the development of so-called laminar flamelet models (Bray, 1985; Peters, 1984; Peters, 1986). These models treat the reaction zone in a turbulent non-premixed flame as an ensemble of quasi-laminar 'flamelets'. The structure of such flamelets can be captured by two independent variables, the mixture fraction and the local rate of strain. Flamelet models are capable of predicting many fundamental features of turbulent diffusion flames, such as ignition and extinction phenomena, lift-off and blow-off. The validity of the model is still a subject of controversy in the literature (Bilger, 1988; Peters, 1991). For example, in many industrial furnaces the flame does not consist of a brush of thin flamelets, but exhibits distributed reaction zones. In section 3.2 a phenomenological foundation of the flamelet concept in relation to turbulent flames was presented.
3.6. Laminar flames

In this section two types of laminar flames are discussed, the premixed and non-premixed one-dimensional laminar flame. These flames constitute two important basic flame structures, and are believed to be 'building blocks' of many turbulent flames. Reliable numerical codes for laminar premixed and non-premixed 1D flames have been developed over the last decade and have become a powerful tool for further flame studies. Here we have used the codes PREMIX and OPPDIF developed by Sandia National Laboratories (Kee et al., 1985).

The present laminar flame calculations are used for three goals. The first aim is to investigate reaction mechanisms available from literature and to apply them to laminar flames in order to establish a suitable reaction scheme for methane and/or natural gas diffusion flames. Secondly, we want to perform sensitivity analysis on reaction rate parameters, in order to make comparisons with the detailed chemistry calculations for the turbulent axisymmetric flame. Finally, laminar diffusion flame ('flamelet') results can be compared with the conserved scalar models described previously, as developed for high-temperature 3D furnace calculations.

3.6.2 One-dimensional laminar premixed flames

Laminar premixed flames are a fundamental type of reacting flow, suitable for detailed experimental and numerical research. It is possible to conceive a flame geometry in which the governing equations can be regarded as essentially one-dimensional in space. Such equations can be solved accurately by sophisticated numerical codes, one of which is the PREMIX code (Kee et al., 1985).

Experimentally, 1D laminar premixed flames are investigated for calibration of laser-diagnostic equipment to be used in turbulent flames, such as used in the Heat Transfer Section. Accurate measurements on temperature and OH-radical concentrations have been performed, allowing a validation of the mathematical model.

The geometry under consideration is depicted in figure 3.15. The mixture of oxidizer and fuel is ignited at a water-cooled porous burner plate. The cooled plate prevents the flame from travelling upstream, and ensures a stable combustion process provided the flow velocities are not too high.

A fundamental property of premixed flames is the laminar burning speed, defined as the propagation velocity of the flame front in a quiescent premixed mixture. If the flow velocity of the mixture is exactly equal to the laminar burning speed, the flame front is stable in space and time. Such a stable freely propagating flame front is difficult to realize in an experiment, however, and hence the burner stabilized flame is studied more often.

**Governing differential equations**

On the axis of symmetry the flow is essential one-dimensional. The governing transport equations are then derived from the fundamental equations presented in Chapter 2. The continuity equation becomes:

\[
\frac{\partial}{\partial x}(\rho u) = 0
\]  
(3.80)
This implies that the total mass flow rate $\dot{M} = \rho u A$ is a constant at every $x$. $A$ is the cross-sectional area of the flame, which may be a function of $x$, but which is assumed to be constant hereafter.

The $x$-momentum equation then serves as an equation for pressure, and in case of atmospheric flames does not have to be solved ($p = p_{atm}$). The remaining conservation equations for energy and chemical species can be written as:

$$\rho u c_{p,m} \frac{dT}{dx} - \frac{d}{dx} \left( \rho \lambda \frac{dT}{dx} \right) + \sum_{i=1}^{N} \rho Y_i V_i c_{p,i} \frac{dT}{dx} + \sum_{i=1}^{N} M_i h_i \dot{w}_i - Q_{rad} = 0 \quad (3.81)$$

$$\rho u \frac{dY_i}{dx} + \frac{d}{dx} (\rho Y_i V_i) - M_i \dot{w}_i = 0 \quad (3.82)$$

For reasons of convenience the energy equation has been written as a temperature equation. The terms in this equation represent convection, conduction, differential heat diffusion, heat production due to reactions and radiation. Finally, the set of equations is closed by the ideal-gas equation of state, providing an equation for the local density:

$$\rho = \frac{p M_m}{R^0 T} \quad (3.83)$$

The transport properties of the species, i.e. thermal conductivities and diffusion coefficients are computed according to the CHEMKIN and TRANSPORT computer packages (Kee et al., 1986; Kee et al., 1989). The theory of molecular transport properties has been given in Chapter 2.

**Boundary conditions**

The boundary conditions are imposed at the burner $x = 0$ and far downstream $x \to \infty$. In practice, the computational domain is restricted to $x = L$, with $L$ sufficiently large. At
3.6. *Laminar flames*

\[ x = 0 \text{ we have:} \]

\[ \dot{M} = \dot{M}_0 \quad (3.84) \]
\[ T = T_0 \quad (3.85) \]
\[ Y_i = Y_{i,0} \quad (3.86) \]

At \( x = L \) homogeneous Neumann conditions are applied for all variables. For the mass flow rate \( \dot{M} \) no boundary condition is required. It turns out that the specification of \( Y_i = Y_{i,0} \) produces some problems. Due to the sharp gradients of some species mass fractions at \( x = 0 \), a back-flow of species towards the burner will occur, implying negative mass fractions for \( x < 0 \). In order to control the incoming species mass fluxes rather than their mass fractions, we use:

\[ \epsilon_{i,0} = Y_{i,0} + \frac{(\rho Y_i V_i A)_0}{M_0} \quad (3.87) \]

Here, \( \epsilon_i \) represents the mass flux fraction. Only if the molecular diffusion velocities \( V_i \) are zero the mass flux boundary conditions reduce to the mass fraction boundary conditions. By definition, \( \sum_{i=1}^{N} \epsilon_i = 1 \), but unlike the mass fractions the \( \epsilon_i \) may become \( < 0 \) or \( > 1 \).

### 3.6.3 One-dimensional laminar counterflow diffusion flames

Laminar counterflow diffusion flames have been widely used experimentally for the investigation of fundamental problems in combustion, such as the chemically controlled extinction limits of diffusion flames and the (one-dimensional) structure of diffusion flames. A review of numerous experiments for different flow geometries has been given by Tsuji (1982).

In the last decade considerable attention has been devoted to the numerical calculation of counterflow diffusion flames with the inclusion of detailed or reduced chemical kinetics and multicomponent molecular diffusion. Several groups have independently simulated the counterflow diffusion flames of methane on a porous cylinder (Tsuji and Yamaoka, 1969; Tsuji and Yamaoka, 1971). These results were published as the outcome of a GAMM workshop, and lead to reasonable agreement between various numerical methods employed by the different investigators. A comprehensive paper on this work has been presented by Dixon-Lewis et al. (1984). Major differences between experiment and numerical results are attributed to lack of radiation correction in the temperature measurements on the one hand and the two-dimensional character of the flow field on the other hand (Bloor et al., 1986). Chelliah et al. (1990) have calculated flat laminar counterflow diffusion flames and obtained even better agreement with experimental data.

In general the simulation of the counterflow diffusion flame constitutes a numerical problem which is simple enough to be treated as a quasi one-dimensional structure on the stagnation streamline, allowing detailed chemical kinetics and molecular transport to be incorporated accurately.
Chapter 3. Chemistry models for turbulent flames

![Image of a counterflow diffusion flame stabilized on a porous cylinder.](image)

**Figure 3.16:** Geometry of a counterflow diffusion flame stabilized on a porous cylinder.

**Governing differential equations**

The laminar counterflow diffusion flame consists of a laminar fuel flow, emanating from a porous cylinder with radius $R$, into a laminar air stream in the opposed direction, as depicted in figure 3.16. A stable reaction zone is established in the forward stagnation region of the cylinder. (A similar flow geometry can be obtained by two opposed round jets, but is not fundamentally different.) Both the fuel and the oxidizer diffuse towards the reaction zone with velocities proportional to the local concentration gradients. The flame zone is situated inside the boundary layer around the cylinder, but lies outside the stagnation point. Hence there is a convective back-flow of combustion products into the fuel-rich region of the flame. The flame is governed by a strong interaction between fluid dynamics (convection and diffusion) and chemical kinetics (reaction rates), producing a reaction zone structure which is a function of the overall velocity gradient (strain rate). Increasing the incoming air velocity $v_L$ for a fixed fuel velocity $v_0$ will give a higher velocity gradient, thus decreasing the fluid-dynamical mixing time: the flame front is stretched. At very low stretch and high Damköhler number the flame structure is insensitive to changes in the flame stretch. For lower Da or stronger flame stretch, non-equilibrium chemistry and even flame extinction will occur.

The complete derivation of the governing equations for the quasi 1D diffusion flame is presented elsewhere (Smooke and Giovangigli, 1991a) and will not be repeated here. The resulting equations closely resemble the ones given for the premixed flame, the most important difference being the explicit inclusion of the $y$-momentum equation in addition to the continuity equation.

Close to the stagnation point on the stagnation streamline, the two-dimensional flow resembles a potential flow. We define a stream function $\Psi(x, y) \equiv y F(x)$. The Cartesian continuity equation is satisfied if:

$$
\rho u = \frac{\partial \Psi}{\partial y} = F(x)
$$

(3.88)
3.6. Laminar flames

\[ \rho v = - \frac{\partial \Psi}{\partial x} = -y F'(x) \]  

(3.89)

The stagnation streamline is given by \( y = 0 \). On the stagnation streamline the symmetry of the flow dictates \( v = 0 \) and vanishing \( y \)-gradients, except for \( \partial v / \partial y \).

The pressure will be constant for low-Mach-number flow, but a non-negligible pressure gradient still remains in the momentum equations. It can be shown (Kee et al., 1988) that the pressure gradient \( \partial p / \partial y \) depends linearly on \( y \), and \( \partial p / \partial x = 0 \). Hence, the variable \( H \equiv 1 / y \left( \partial p / \partial y \right) \) is an eigenvalue of the flame, independent from \( x \). For a particular flame, \( H \) will be governed by the boundary values of the streamwise velocities, \( u_0 \) and \( u_L \).

The resulting set of differential equations reads:

\[ \frac{dF}{dx} = G \]  

(3.90)

\[ F \frac{d}{dx} \left( \frac{G}{\rho} \right) - \frac{G^2}{\rho} - \frac{d}{dx} \left( \mu \frac{d}{dx} \left( \frac{G}{\rho} \right) \right) - H = 0 \]  

(3.91)

\[ F \frac{dY_i}{dx} + \frac{d}{dx} (\rho Y_i V_i) - M_i \dot{\omega}_i = 0 \]  

(3.92)

\[ F \frac{c_p m}{dx} \frac{dT}{dx} - \frac{d}{dx} \left( \lambda \frac{dT}{dx} \right) + \rho \sum_{i=1}^{N} Y_i V_i c_{p,i} \frac{dT}{dx} + \sum_{i=1}^{N} M_i h_i \dot{\omega}_i - Q_{rad} = 0 \]  

(3.93)

These equations only depend on the streamwise coordinate \( x \). In case of a cylindrical coordinate system, i.e. for two opposed round jets rather than a porous-cylinder flame, we define \( F = \rho u \) and \( G = -\rho v / y \). In that case, the r.h.s. of (3.90) should be replaced by \( 2G \). All other equations remain unchanged. To close the set of equations, density is computed from the equation of state.

**Boundary conditions**

The boundary conditions for the laminar diffusion flame are as follows.

At the cylinder wall \( (x = 0) \):

\[ F = F_0 = \rho_0 u_0, \quad G_0 = 0, \quad T = T_0, \quad \epsilon_{i,0} = Y_{i,0} + \frac{(\rho Y_i V_i)_0}{\rho_0 u_0} \]  

(3.94)

At the free-stream edge \( (x = L) \):

\[ F = F_L = \rho_L u_L, \quad G_L = 0, \quad T = T_L, \quad Y_i = Y_{i,L} \]  

(3.95)

Actually, the boundary conditions for \( G \) are not exactly zero, but changing the conditions in agreement with experimental data yielded very little differences in the numerical results. In particular, the flame zone structure is insensitive to the boundary conditions for \( G \).

An important parameter in laminar diffusion flames is the velocity gradient \( a \). Increasing \( a \) will significantly alter the flame structure, and for values above a certain
limit \((a > a_{\text{ext}})\) the flame will extinguish due to the stretch induced by fluid dynamical forces. For a potential flow in Cartesian coordinates, in absence of combustion, we have \(F = -\rho a x\) and \(G = -\rho a\). Substitution into (3.91) yields \(H = \rho_{\infty} a_{\infty}^2\), where \(\infty\) is replaced by \(x = L\) in the numerical implementation. In this case, the boundary condition for \(G_L\) is dropped.

If \(H\) is computed as an eigenvalue for a given boundary condition \(G_L\), the value of \(a\) can be evaluated from the local velocity gradient. In the literature, some discussion exists whether \(a\) should be evaluated outside the flame zone on the oxidizer side, or at the point of stoichiometric mixture fraction (Smooke and Giovangigli, 1991a). In this study, we employed the former definition.

In case of two opposed round jets (cylindrical coordinates), we have \(F = -\rho a x\) and \(G = -\rho a/2\), yielding \(H = \rho_{\infty} a_{\infty}^2/4\) if the strain rate is to be prescribed.

### 3.7 Presumed-shape joint-PDF closure model

#### 3.7.1 Introduction

The conserved-scalar presumed-shape PDF model for turbulent diffusion flames (Bilger, 1976a) provides a reasonable description of many important combustion phenomena in high-temperature furnaces. Essentially, by assuming infinitely fast reactions, this type of closure does not account for direct influence of turbulent fluctuations on mean chemical reaction rates.

In general, however, Damköhler numbers will not be infinitely high and turbulent fluctuations of concentrations and temperature will affect the averaged reaction rates. In flames with lower temperatures, such as laboratory-scale natural gas flames, the effects of finite-rate chemistry have to be taken into account. Hence, transport equations have to be solved for all reacting species mass fractions. A major problem then is to find a suitable closure of the mean reaction rates.

In this Section, we will describe the closure method which was developed by Bockhorn (1989), and which accounts for turbulence-chemistry interactions by means of presumed-shape joint PDFs. This model is particularly suited for the description of distributed reaction zones (see section 3.2, but its validity can be extended to the regime of connected reaction zones and even the flamelet regime. To evaluate the mean reaction rates of all elementary reactions for a given flame, the joint PDF of the governing variables has to be known. For an arbitrary elementary reaction \(A + B \rightarrow C + D\) these variables are \(\rho\), \(Y_A\), \(Y_B\) and \(T\). Each elementary reaction thus requires a joint PDF of four independent stochastic variables. Density fluctuations can be eliminated as an independent quantity, rendering a joint PDF of three independent variables.

The joint PDF can be computed in various ways. The Monte Carlo method Pope (1985), attractive for its generality and lack of presumptions on the PDF shape, is infeasible because of the large number of independent variables to be dealt with in the case of detailed reaction mechanisms. In the presumed PDF method the joint PDF is assumed to have a known shape, \textit{in casu} a joint truncated Gaussian PDF, which is calculated from a finite set of its moments.
3.7. Presumed-shape joint-PDF closure model

To fully describe a multivariate joint PDF by a normal distribution, all of its lower moments (means, variances and covariances) have to be known. In the present description, modeled transport equations are solved for these moments.

The main advantage of the presumed-shape joint PDF method is that it allows for a detailed description of the combustion chemistry. In fact, the presumed PDF to be calculated does not involve the joint PDF for all the variables involved, but a separate PDF is defined for each elementary reaction rate to be closed. The maximum dimensionality of each individual PDF is three, whereas the total joint PDF would be of dimensionality $N + 1$, with $N$ being the number of reacting species. The presumed joint PDF approach does not rely on reduced reaction mechanisms, and may provide information on the validity of existing reduced mechanisms.

The computational effort of the presumed joint PDF method, has an $O(N^2)$ dependence on the number of reacting scalars in the chemical mechanism, since the number of covariances increases quadratically with $N$. Furthermore, there may be doubt whether the PDF actually has a joint normal distribution. Monte Carlo calculations (Chen and Kollmann, 1988) have shown that the joint PDF of reacting scalars can have a very irregular asymmetrical shape. On the other hand, experimental evidence reveals that in certain types of flames the joint PDFs of reacting scalars can indeed resemble a joint normal distribution (Hassel et al., 1993).

The ability of the presumed-shape joint PDF method to give a full chemistry description without any further chemical modeling requirements makes it an interesting alternative, compared with the conserved-scalar approach on the one hand and the Monte Carlo PDF/reduced mechanism approach on the other hand.

3.7.2 Modeling of turbulence-chemistry interactions

Introduction of the presumed joint PDF

In an axisymmetric geometry, the elliptic turbulent transport operator $\mathcal{L}_t$ is defined by:

$$
\mathcal{L}_t(\bar{\phi}) = \frac{\partial (\rho) \bar{u}_\phi}{\partial x} + \frac{1}{r} \frac{1}{\partial r} \left( \frac{\mu_t}{\sigma_\phi} \frac{\partial \bar{\phi}}{\partial x} \right) - \frac{1}{r} \frac{1}{\partial r} \left( \frac{\mu_t}{\sigma_\phi} \frac{\partial \bar{\phi}}{\partial r} \right)
$$

(3.96)

Here the eddy-viscosity concept has been applied to model turbulent transport of $\phi$, and $\sigma_\phi$ is a turbulent Prandtl or Schmidt number. Also, Favre averaging is used. The transport equation for any Favre averaged variable $\bar{\phi}$ can now be written as:

$$
\mathcal{L}_t(\bar{\phi}) = \langle \rho \rangle \bar{S}_\phi
$$

(3.97)

The conservation equation for the species mass fraction $\bar{Y}_i$ reads:

$$
\mathcal{L}_t(\bar{Y}_i) = \langle \rho \rangle \bar{S}_i, \ i = 1, \ldots, N
$$

(3.98)

In general, the net reaction rate $S_i$ can be written as the sum of the $K$ elementary reaction rates $\dot{\omega}_k$:

$$
S_i = M_i \sum_{k=1}^{K} (\nu''_{i,k} - \nu'_{i,k}) \frac{\dot{\omega}_k}{\rho}, \ i = 1, \ldots, N
$$

(3.99)
\[ \dot{\omega}_k = A_k T^{\beta_k} \exp \left( -\frac{T A_{\ell,k}}{T} \right) \prod_{j=1}^{N} \left( \frac{\rho Y_j}{M_j} \right)^{\nu_{j,k}} \]  

(3.100)

Forward and backward reaction rates are treated separately here. To find an expression for the mean elementary reaction rate \( (\dot{\omega}_k/\rho) \), the joint-PDF closure is applied, yielding:

\[ (\dot{\omega}_k/\rho) = \int_{0}^{1} dy_1 \int_{0}^{1} dy_2 \int_{0}^{\infty} d\theta \int_{0}^{\infty} d\eta \frac{1}{\eta} \omega_k(\eta, \theta, y_1, y_2) \tilde{f}_{\rho Y_1 Y_2}(\eta, \theta, y_1, y_2) \]  

(3.101)

Here, \( \eta, \theta, y_i \) represent the domain of all possible values of \( \rho, T, Y_i \), respectively. Since most elementary reactions involve only two different reactants, the \( Y_1 \) and \( Y_2 \) practically cover the general case. In low-Mach-number flames, the influence of pressure fluctuations on the chemistry can be neglected. Furthermore, density \( \rho \) can be eliminated as an independent variable by stating:

\[ \tilde{f}_{\rho Y_1 Y_2}(\eta, \theta, y_1, y_2) = \delta(\eta - \langle \rho \rangle) \tilde{f}_{Y_1 Y_2}(\theta, y_1, y_2) \]  

(3.102)

thus neglecting all density fluctuations. One may also attribute the density fluctuations to temperature fluctuations by virtue of the instantaneous ideal gas law:

\[ \rho = \frac{\langle p \rangle \langle M_m \rangle}{R \theta} \]  

(3.103)

where local variations of \( \langle p \rangle \) and \( \langle M_m \rangle \) are neglected. Thus the dimensionality of the joint PDF required to close a single elementary reaction will be reduced to three.

**Mathematical description of the joint PDF**

**PDF parameters** The joint PDF is specified as a \( n \)-dimensional Gaussian distribution:

\[ \tilde{f}_{\phi}(\psi_1, \ldots, \psi_n) = \frac{1}{(2\pi)^{n/2} \sqrt{|M|}} \exp \left[ -\frac{1}{2|M|} \sum_{i,j=1}^{n} |M_{ij}| (\psi_i - \mu_i)(\psi_j - \mu_j) \right] \]  

(3.104)

where \( |M| \neq 0 \) is the determinant of the moment matrix \( M \), and \( |M_{ij}| \) is the algebraic complement of element \((i, j)\) in \( M \) (Bockhorn, 1989; Fisz, 1980). In our standard case, \( n = 3 \).

The moment matrix \( M \) can be written as:

\[ M = \begin{pmatrix} \lambda_{11} \ldots \lambda_{1n} \\ \vdots \ \vdots \\ \lambda_{n1} \ldots \lambda_{nn} \end{pmatrix} \]  

(3.105)

where the individual elements are:

\[ \lambda_{ii} = \sigma_i^2 \]
3.7. Presumed-shape joint-PDF closure model

\[ \lambda_{ij} = \rho_{ij} \sigma_i \sigma_j \]

Here \( \sigma_i \) is the standard deviation of variable \( \psi_i \), and \( \rho_{ij} \) is the correlation coefficient of variables \( \psi_i \) and \( \psi_j \). Hence, \(|M|\) can be cast in the form:

\[ |M| = \prod_{i=1}^{n} \sigma_i^2 |R| \]  \hspace{1cm} (3.106)

with \( R \) given by:

\[ R = \begin{pmatrix}
1 & \rho_{12} & \ldots & \rho_{1n} \\
\rho_{21} & 1 & \ldots & \rho_{2n} \\
\vdots & \vdots & \ddots & \vdots \\
\rho_{n1} & \rho_{n2} & \ldots & 1
\end{pmatrix} \]  \hspace{1cm} (3.107)

In general, \( 0 \leq |R| \leq 1 \).

The elements \( \lambda_{ij} \) of the moment matrix \( M \) are functions of the means, variances and covariances of the variables \( T, Y_1, \ldots, Y_N \). In the present model, transport equations are to be solved for these \( \frac{1}{2} (N + 1)(N + 2) \) quantities.

The mass fractions vary between 0 and 1, and \( Y_1 + Y_2 \leq 1 \), whereas the temperature will lie between a minimum value \( T_0 \) (defined by the initial and boundary conditions) and a maximum value \( T_{ad} \), the adiabatic flame temperature (defined by the chemistry of the flame). Hence the space of allowed values of the variables is restricted, so the PDF moments will not be equal to the moments of the variables, similar to the one-dimensional Gaussian PDF for the mixture fraction: the joint PDF is a truncated PDF. However, if fluctuations are relatively small compared to the mean values, the influence of the truncation will be negligible. In general, the moments of the PDF can be determined from the means and (co-)variances of the variables, by means of some numerical algorithm similar to the one-dimensional truncated Gaussian PDF, e.g. a Newton-Raphson procedure.

PDF integration Supposing the moments of the PDF are available as functions of the means and covariances of temperature and mass fractions, the PDF shape is completely determined and (3.101) can be evaluated.

Bockhorn (1989) studied a few simple elementary reactions and several global reaction rates to illustrate the use of the joint PDF closure, and to estimate quantitatively the relative influence of temperature fluctuations, mass fraction fluctuations and correlation effects. In general, for any temperature dependent elementary reaction, turbulent fluctuations of temperature will dominate the mean reaction rate, because of the nonlinearity of the Arrhenius expression.

As a first approximation it may be assumed that temperature and mass fraction fluctuations are uncorrelated. The joint PDF will then be a product of marginal one-dimensional PDFs, which are easy to evaluate and integrate. The value of \( \left( \frac{\bar{\omega}_k}{\rho} \right) \) can be represented as:

\[ \left( \frac{\bar{\omega}_k}{\rho} \right) = \left( \frac{\bar{\omega}_k}{\rho} \right)_0 \times F_T(\bar{T}, \bar{T}' t, T_{A,k}) \times F_Y(\bar{Y}_1, \bar{Y}_1'^2) \times F_Y(\bar{Y}_2, \bar{Y}_2'^2) \]  \hspace{1cm} (3.108)
TABLE 3.3: Polynomial coefficients for the correction function $F_T$.

<table>
<thead>
<tr>
<th>$T_uT$</th>
<th>$a_T1$</th>
<th>$a_T2$</th>
<th>$a_T3$</th>
<th>$a_T4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–0.001</td>
<td>0.</td>
<td>0.</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>0.001–0.05</td>
<td>-0.34688</td>
<td>7.22071</td>
<td>0.0122</td>
<td>0.</td>
</tr>
<tr>
<td>0.05–0.15</td>
<td>-1.50712</td>
<td>12.31916</td>
<td>0.0276</td>
<td>0.0008</td>
</tr>
<tr>
<td>&gt; 0.15</td>
<td>-2.52064</td>
<td>8.97535</td>
<td>0.08483</td>
<td>0.00118</td>
</tr>
</tbody>
</table>

with:

$$
\left( \frac{\bar{\omega}_k}{\rho} \right)_0 = \frac{1}{\rho^* A_k \bar{T}^{\beta_k}} \exp \left( -\frac{T_{A,k}}{\bar{T}} \right) \prod_{j=1}^{N} \left( \frac{\rho^* \bar{Y}_j}{M_j} \right)^{\nu_{j,k}}
$$

(3.109)

and $\rho^* = \langle p \rangle (M_m)/(RT_k)$ or $\rho^* = \langle \rho \rangle$, depending on the model. The functions $F_T$ and $F_Y$ are equal to 1 if the fluctuations of $T$, $Y_1$ and $Y_2$ are zero. In that case the ‘laminar’ expression remains. For increasing turbulent intensity, the mean reaction rates will increase ($F_T \geq 1$, $F_Y \geq 1$). It turns out that $F_T \gg F_Y$ by several orders of magnitude, depending on the value of $T_{A,k}/\bar{T}$. Furthermore, $F_Y$ differs from 1 only if $Y_i$ has a stoichiometric coefficient $\nu_{i,k} \neq 1$. Often, $\nu_{i,k} = 1$ and $F_Y$ will play no role of importance. In the above, the exponent $\beta_k$ is not included explicitly. For moderate temperature fluctuations, its influence can be accounted for by taking $T_{A,k}^* = T_{A,k} - \beta_k \bar{T} \ln \bar{T}$ as an effective activation energy.

To facilitate the PDF integration as a function of its moments, the functions $F_T$ and $F_Y$ have been cast into a suitable polynomial form, the coefficients of which are precomputed by means of regression analysis:

$$
10 \log F_T = a_{T1} + a_{T2} T_uT + a_{T3} \frac{T_{A,k}}{\bar{T}} + a_{T4} \left[ \frac{T_{A,k}}{\bar{T}} \right]^2
$$

(3.110)

and:

$$
10 \log F_Y = a_{Y1} + a_{Y2} T_uY + a_{Y3} [T_uY]^2
$$

(3.111)

where $T_u$ is the turbulent intensity of variable $\phi$. The values of the coefficients are listed in tables 3.3–3.5.

Influence of correlations of variables In the previous subsection it was argued that temperature fluctuations will strongly dominate the result of (3.101). If the variables are statistically correlated, however, the mean reaction rate may be changed significantly too. The magnitude of the change mainly depends on the activation energy. Again, this is represented by means of correction functions to the laminar case (3.108).

The function $F_{TY}$ represents correlation of temperature and species mass fractions, and $F_{YY}$ represents mass fraction correlations. The correlation coefficients are defined
3.7. Presumed-shape joint-PDF closure model

Table 3.4: Polynomial coefficients for the correction function $F_Y$ for a second-order species dependence ($\nu = 2$).

<table>
<thead>
<tr>
<th>$Tu_Y$</th>
<th>$a_{Y1}$</th>
<th>$a_{Y2}$</th>
<th>$a_{Y3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–0.01</td>
<td>0.</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>0.01–0.1</td>
<td>0.</td>
<td>0.</td>
<td>0.43233</td>
</tr>
<tr>
<td>0.1–0.3</td>
<td>0.00041</td>
<td>0.</td>
<td>0.41157</td>
</tr>
<tr>
<td>&gt; 0.3</td>
<td>-0.03128</td>
<td>0.17735</td>
<td>0.16073</td>
</tr>
</tbody>
</table>

Table 3.5: Polynomial coefficients for the correction function $F_Y$ for a third-order species dependence ($\nu = 3$).

<table>
<thead>
<tr>
<th>$Tu_Y$</th>
<th>$a_{Y1}$</th>
<th>$a_{Y2}$</th>
<th>$a_{Y3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–0.01</td>
<td>0.</td>
<td>0.</td>
<td>0.</td>
</tr>
<tr>
<td>0.01–0.1</td>
<td>0.00002</td>
<td>0.</td>
<td>1.28432</td>
</tr>
<tr>
<td>0.1–0.3</td>
<td>0.00283</td>
<td>0.</td>
<td>1.11133</td>
</tr>
<tr>
<td>&gt; 0.3</td>
<td>-0.03864</td>
<td>0.305</td>
<td>0.52208</td>
</tr>
</tbody>
</table>

as:

$$\rho_{\psi\psi} = \frac{\hat{\psi}'' \hat{\psi}'''}{\sqrt{\hat{\psi}''^2 \hat{\psi}'''^2}}$$

(3.112)

and $-1 \leq \rho_{\psi\psi} \leq +1$ always. The correction functions have to be equal to 1 if the correlation is zero. However, contrary to the functions $F_T$ and $F_Y$, the functions $F_{TY}$ and $F_{YY}$ may attain values smaller than 1. If temperature and mass fraction have a positive correlation the mean reaction rate will increase, whereas a negative correlation produces a smaller mean reaction rate. The effects will be stronger if the turbulence intensities are high and if the reaction has a high activation energy. In a polynomial form we have:

$$10 \log F_{TY} = a_{TY1} + a_{TY2} Tu_T + a_{TY3} [Tu_T]^2$$

$$+ a_{TY4} \frac{T_A,k}{T} + a_{TY5} \left[\frac{T_A,k}{T}\right]^2 + a_{TY6} \left[\frac{T_A,k}{T}\right]^3$$

(3.113)

The coefficients of this polynomial are listed in table 3.6.

In the present model, no effects of mass fraction-mass fraction correlation have been included, since they are considered to be of minor importance. The final result of the joint-PDF integration thus becomes:

$$\left(\frac{\bar{\omega}_k}{\rho}\right) = \left(\frac{\bar{\omega}_k}{\rho}\right)_0 \times F_T(\bar{T}, \bar{T}^n, T_{A,k}) \times F_Y(\bar{Y}_1, \bar{Y}_1^n) \times F_Y(\bar{Y}_2, \bar{Y}_2^n)$$

$$\times F_{TY}(\bar{T}, \bar{T}^n, T_{A,k}) \times F_{TY}(\bar{T}, \bar{T}^n, T_{A,k})$$

(3.114)
TABLE 3.6: Polynomial coefficients for the correction function $F_{TY}$.

<table>
<thead>
<tr>
<th>$a_{TY1}$</th>
<th>-0.57761</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{TY2}$</td>
<td>9.64633</td>
</tr>
<tr>
<td>$a_{TY3}$</td>
<td>-26.12947</td>
</tr>
<tr>
<td>$a_{TY4}$</td>
<td>0.05987</td>
</tr>
<tr>
<td>$a_{TY5}$</td>
<td>-0.00129</td>
</tr>
<tr>
<td>$a_{TY6}$</td>
<td>0.00001</td>
</tr>
</tbody>
</table>

The above formula greatly reduces computational costs, since the direct numerical evaluation of multidimensional integrals can be very time consuming.

3.7.3 Closure model for the means and covariances

Mass fraction covariances

The transport equations for the Favre-averaged mass fractions $\bar{Y}_i$ have been described in the previous subsection. For the mass fraction covariances similar equations can be derived, which still contain some unknown correlations:

$$
\mathcal{L}_i(Y_i \bar{Y}_i') = C_{g1} \frac{\mu_i}{\sigma_{Y_i Y_j}} \left[ \left( \frac{\partial \bar{Y}_i}{\partial x} \frac{\partial \bar{Y}_j}{\partial x} \right) + \left( \frac{\partial \bar{Y}_i}{\partial r} \frac{\partial \bar{Y}_j}{\partial r} \right) \right] - C_{g2} \langle \rho \rangle \frac{\varepsilon}{k} Y_i \bar{Y}_i'' + \langle \rho \rangle Y_i \bar{S}_j + \langle \rho \rangle Y_i'' \bar{S}_i
$$

(3.115)

The model constants $C_{g1}$ and $C_{g2}$ are the same as used in the modeled transport equation for the mixture fraction variance. The source terms $Y_i \bar{S}_j$ are closed by the same joint PDF as the mean reaction rates $\bar{S}_i$:

$$
Y_i \bar{S}_j = \bar{Y}_i \bar{S}_j - \bar{Y}_i \bar{S}_j
$$

(3.116)

Effectively, in the formula for $Y_i \bar{S}_j$, the stoichiometric coefficient of species $i$ in all elementary reactions involving species $j$ is incremented by 1.

Mean temperature

To find the mean temperature, the transport equation for the mean enthalpy is solved:

$$
\mathcal{L}_i(\bar{h}) = \langle \rho \rangle \bar{S}_h
$$

(3.117)

The source term $\bar{S}_h$ represents the influence of radiation. In the adiabatic case $S_h = 0$. The instantaneous temperature is linked to the enthalpy by virtue of the caloric equation of state, involving the species specific heats. These $c_{p,i}$ are known in terms of temperature
3.7. Presumed-shape joint-PDF closure model

polynomials (2.15,2.16). Using Favre decomposition: \( T = \bar{T} + T'' \) and \( Y_i = \bar{Y}_i + Y''_i \), we can write the averaged caloric equation of state as:

\[
\hat{h} = \sum_{i=1}^{N} \left\{ \left( \sum_{n=0}^{P} a_{n,i} \bar{Y}_i \bar{T}^n \right) + \left( \sum_{n=1}^{P} a_{n,i} n(n-1) \frac{1}{2} \bar{Y}_i \bar{T}^{n-2} \bar{T}'' \right) \right\} \tag{3.118}
\]

This equation constitutes an implicit expression for \( \bar{T} \), provided all other moments in this equation are known. Moments of an order higher than 2 are neglected, since they are assumed to have little influence and they are difficult to model.

**Temperature variance**

The temperature variance \( \bar{h''} \) can be found from the enthalpy variance, for which the modeled transport equation reads:

\[
\mathcal{L}_t(\bar{h''}) = C_{g1} \frac{\mu_t}{\sigma_h} \left( \frac{\partial \bar{h}}{\partial x} \right)^2 + \left( \frac{\partial \bar{h}}{\partial r} \right)^2 - C_{g2} (\bar{\rho}) \bar{h''} + 2 \langle \rho \rangle \bar{h''} \bar{S}_h \tag{3.119}
\]

Again, the relationship between the temperature variance and the enthalpy variance is derived from the caloric equation of state. A very crude approximation would be:

\[
\bar{h''} = c_{p,m}^2 \bar{T''} \tag{3.120}
\]

where fluctuations of \( c_{p,m} \) are neglected. In flames, however, \( c_{p,m} \) varies considerably with temperature, and in analogy with the mean temperature we take:

\[
\bar{h''} = \sum_{i=1}^{N} \sum_{j=1}^{N} b_{ij} = \sum_{i=1}^{N} b_{ii} + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} b_{ij} \tag{3.121}
\]

where the \( b_{ij} \) read:

\[
\begin{align*}
b_{ij} = & \left( \sum_{n=0}^{P} a_{n,i} \bar{T}^n \right) \left( \sum_{n=0}^{P} a_{n,j} \bar{T}^n \right) \bar{Y}_i'' \bar{Y}_j'' \\
+ & \left( \sum_{n=0}^{P} a_{n,i} \bar{T}^n \right) \left( \sum_{n=1}^{P} a_{n,j} n \bar{T}^{n-1} \right) \bar{Y}_j \bar{Y}_i'' T'' \\
+ & \left( \sum_{n=1}^{P} a_{n,i} n \bar{T}^{n-1} \right) \left( \sum_{n=0}^{P} a_{n,j} \bar{T}^n \right) \bar{Y}_i \bar{Y}_j'' T'' \\
+ & \left( \sum_{n=1}^{P} a_{n,i} n \bar{T}^{n-1} \right) \left( \sum_{n=1}^{P} a_{n,j} n \bar{T}^{n-1} \right) (\bar{Y}_i \bar{Y}_j \bar{T}'') + Y_i'' T'' Y_j'' T''
\end{align*}
\]
\[ -\left( \sum_{n=1}^{P} a_{n,i} n \bar{T}_n \right) \left( \sum_{n=2}^{P} a_{n,j} n (n-1) \bar{T}_n \right) \tilde{Y}_i \tilde{Y}_j \bar{T}_n^2 \]
\[ -\left( \sum_{n=2}^{P} a_{n,i} \frac{n}{2} (n-1) \bar{T}_n \right) \left( \sum_{n=1}^{P} a_{n,j} n \bar{T}_n \right) \tilde{Y}_i \tilde{Y}_j \bar{T}_n^2 \]
\[ -\left( \sum_{n=2}^{P} a_{n,i} \frac{n}{2} (n-1) \bar{T}_n \right) \left( \sum_{n=2}^{P} a_{n,j} \frac{n}{2} (n-1) \bar{T}_n \right) \tilde{Y}_i \tilde{Y}_j \bar{T}_n^2 \] (3.122)

If the other covariances \( \tilde{Y}_i \tilde{Y}_j \) and \( \tilde{Y}_i \bar{T}_n \) are known, the temperature variance can be evaluated from the above equations. In a first approximation the covariances can be neglected, only retaining the mean mass fractions and their variances:

\[ b_{ij} = \left( \sum_{n=1}^{P} a_{n,i} n \bar{T}_n \right) \left( \sum_{n=1}^{P} a_{n,j} n \bar{T}_n \right) \bar{Y}_i \bar{Y}_j \bar{T}_n^2 \]
\[ -\left( \sum_{n=2}^{P} a_{n,i} \frac{n}{2} (n-1) \bar{T}_n \right) \left( \sum_{n=2}^{P} a_{n,j} \frac{n}{2} (n-1) \bar{T}_n \right) \bar{Y}_i \bar{Y}_j \bar{T}_n^2 \] (3.123)

for \( i \neq j \), and:

\[ b_{ii} = \left( \sum_{n=0}^{P} a_{n,j} n \bar{T}_n \right)^2 \bar{Y}_i \bar{T}_n^2 \]
\[ + \left( \sum_{n=1}^{P} a_{n,i} n \bar{T}_n \right)^2 \bar{Y}_i \bar{T}_n^2 \]
\[ -\left( \sum_{n=2}^{P} a_{n,i} \frac{n}{2} (n-1) \bar{T}_n \right)^2 \bar{Y}_i \bar{T}_n^2 \] (3.124)

for \( i = j \).

**Mass fraction-temperature covariance**

The final covariance to be determined is the covariance of species mass fractions and the temperature \( \bar{Y}_i \bar{T}_n \). Again the polynomial representation of \( \bar{h}_i \) can be used to derive up to second order:

\[ \bar{Y}_i \bar{h}_n = \sum_{j=1}^{N} \left( \sum_{n=1}^{P} a_{n,j} n \bar{T}_n \right) \bar{Y}_j \bar{Y}_i \bar{T}_n + \sum_{j=1}^{N} \left( \sum_{n=0}^{P} a_{n,j} n \bar{T}_n \right) \bar{Y}_i \bar{Y}_j \bar{T}_n \] (3.125)

For the covariance of species mass fractions and enthalpy a modeled transport equation is solved:

\[ \mathcal{L}_i(\bar{Y}_i \bar{h}_n) = C_{g1} \frac{\mu_l}{\sigma_{Y_i h}} \left[ \frac{\partial \bar{Y}_i}{\partial x} \frac{\partial \bar{h}}{\partial x} + \frac{\partial \bar{Y}_i}{\partial r} \frac{\partial \bar{h}}{\partial r} \right] \]
\[ - C_{g2}(\rho) \frac{\bar{E}}{k} \bar{Y}_i \bar{h}_n + \langle \rho \rangle \bar{Y}_i \bar{S}_h + \langle \rho \rangle \bar{h}_n \bar{S}_i \] (3.126)
3.8. Thermal nitric oxide formation

In first approximation, the source term correlations $Y"_i S_k$ and $h"_i S_i$ are assumed to be negligible compared to the other terms on the r.h.s. of (3.126). This closes the set of equations to be solved in order to determine the parameters of the Gaussian joint PDF.

Mean density

In the preceding subsections all the relevant (co)variances were modeled. The mean density still has to be determined in function of these moments. The ideal-gas equation of state can be Favre averaged, yielding:

$$\langle \rho \rangle = \langle p \rangle \left[ R^0 \sum_{i=1}^{N} \frac{\bar{T} \bar{Y}_i + Y"_i T"}{M_i} \right]^{-1}. \quad (3.127)$$

In combination with the modeled equations for mass continuity, momentum conservation and turbulence quantities $\bar{k}$ and $\bar{\varepsilon}$, the set of equations is closed and can be solved by a numerical procedure.

3.8 Thermal nitric oxide formation

3.8.1 Introduction

Hydrocarbon combustion often produces unwanted pollutant species. On the short term, the major combustion pollutant species arising in combustion of hydrocarbon fuels are CO, nitrogen oxides (NO$_x$), sulfur oxides (SO$_x$), organic compounds (containing CH chains) and particulates (e.g. soot). Because of its contribution to global warming, CO$_2$ may also be considered an unwanted product of combustion. If we want to minimize the emission of pollutant species, detailed knowledge of the pathways of formation and destruction is of crucial importance.

In natural gas combustion the situation is of less complexity than for other fossil fuels, like oil or coal. First of all, natural gas does not contain sulfur and large amounts of organic compounds. CO$_2$ is a natural combustion product, but since methane contains a large amount of hydrogen atoms, the emission of CO$_2$ by natural gas flames is less a problem that with other hydrocarbon fuels. The emissions of CO, partially burned or unburned hydrocarbons and soot can often be suppressed by tuning the combustion equipment such that sufficiently long residence times and high temperature are achieved, allowing a complete oxidation process.

The main pollutant of natural gas flames then is the formation of nitrogen oxides. Nitrogen oxides can be classified into three important groups: nitric oxide NO, nitrogen dioxide NO$_2$ and nitrous oxide N$_2$O. The formation of NO$_x$ is not an essential part of the combustion process itself, but emerges as a result of the highly reactive environment in the flame zone. In the literature the various pathways to NO$_x$ have been described in detail (Bowman, 1975; Bowman, 1991; Glarborg and Hadvig, 1991; Hanson and Salimian, 1984; Hayhurst and Vince, 1980; Miller and Bowman, 1989). From kinetic analysis it can be
shown that for high temperature natural gas combustion the formation of NO is the prime NO\(_x\) source.

The formation of NO can be split into three routes: ‘thermal’ NO, ‘prompt’ NO and fuel-bound NO. Since natural gas does not contain fuel-bound nitrogen, the latter route can be discarded. The prompt NO formation mainly occurs in fuel rich regions of the flames, where sufficient amounts of C-atoms are available. It is estimated that at the high temperatures prevailing in industrial furnaces, the prompt NO mechanism is of minor importance (Bowman, 1991). Hence, the thermal NO formation mechanism, as described by Zel’dovich (1946) is generally accepted to represent the major NO formation pathway in high-temperature furnaces.

In the sequel we will discuss the kinetics of thermal NO formation, its numerical prediction within the framework of the conserved scalar formalism, and the computation of mean NO formation rates in turbulent non-premixed flames.

### 3.8.2 Kinetics of thermal NO formation

Many industrial furnaces, e.g. glass melting furnaces, are operated at fuel-lean or near-stoichiometric conditions. In that case, the NO formation kinetics are described by the Zel’dovich mechanism:

\[
\begin{align*}
N_2 + O &\rightleftharpoons NO + N \\
N + O_2 &\rightleftharpoons NO + O \\
N + OH &\rightleftharpoons NO + H
\end{align*}
\]

The forward and reverse reaction rate constants have been determined experimentally with reasonable accuracy (see Appendix C). Here we will only summarize the constants used in the present study (Table 3.7), taken from Koster ((1993)), who mainly adopted the values given by Bockhorn ((1987)). There is a strong temperature dependence for reactions 1f and 2b. The rate limiting step is the reaction \(N_2 + O \rightarrow NO + N\) which has the highest activation energy. High temperatures will promote the formation of ‘thermal’ NO, as will the presence of sufficient oxygen and nitrogen atoms and molecules. This explains why thermal NO formation increases as the fuel burn-out is enhanced by supplying additional air and by increasing the flame temperature.
3.8. Thermal nitric oxide formation

The equilibrium constant for the four irreversible reactions 1f, 1b, 2f and 2b can be calculated directly from the reaction rates listed above:

\[
K_{eq} = \frac{k_{1f}k_{2f}}{k_{1b}k_{2b}} \tag{3.131}
\]

The resulting equilibrium constants for the various literature references (see Appendix C), show that although the specific constants may vary, the overall temperature dependence is almost the same in the region 1500 K < \( T < 2500 \) K, which is a characteristic range for many practical flames.

The Zel’dovich reactions are relatively slow; in the flame zone the NO concentrations will often lie below their equilibrium values at the local conditions. Beyond the flame zone the concentrations may exceed their local equilibrium values, because the destruction of NO is slow as well. Since the Damköhler number for NO formation is small, no direct conserved-scalar analogy can be made. The interaction between turbulent fluctuations and the average chemical formation rate of NO therefore will be strong, especially with respect to temperature fluctuations. A decomposition of the mean chemical source term by means of a series expansion of first, second and higher-order moments involving temperature and concentrations, has a poor convergence behaviour. Many higher-order moments need to be included before the series expansion can be truncated (if at all), and hence this method is intractable. Therefore, the only feasible method to obtain the mean chemical source terms accurately is by PDF closure.

3.8.3 Reduced reaction kinetics

Short Zel’dovich mechanism

Firstly, we will consider only the standard ‘short’ Zel’dovich mechanism, by assuming that the third reaction (3.130) has a negligible contribution. At a later stage we will add the third reaction to verify this assumption.

From the known forward and reverse reaction rates, we have:

\[
\frac{dC_{NO}}{dt} = k_{1f}C_{N_2}C_O + k_{2f}C_NC_{O_2} - k_{1b}C_{NO}C_N - k_{2b}C_{NO}C_O \tag{3.132}
\]

or:

\[
\rho S_{NO} = M_{NO} \frac{dC_{NO}}{dt} \tag{3.133}
\]

where in general:

\[
S_{NO} = S_{NO}(\rho, T, Y_{NO}, Y_{N_2}, Y_{O_2}, Y_O, Y_N) \tag{3.134}
\]

The quantity \( S_{NO} \) is a scaled formation rate with dimension \( s^{-1} \), and may be viewed as the reciprocal characteristic chemical time scale of net production or destruction of NO. The quantity \( \rho S_{NO} \) is the net source term in the transport equation for \( Y_{NO} \). From (3.134) it is seen that not only the mass fractions of the main species \( O_2 \) and \( N_2 \), but also of the radicals \( O \) and \( N \) are required in order to determine the instantaneous formation rate of
NO, assuming that the NO concentration is known. In the simple conserved-scalar flame sheet model no direct information on radical concentrations is included. To allow for reasonable predictions, a reduction of the chemistry description is pursued, as described by Peters (1991).

As a first approximation, since the forward reaction of (3.128) is the rate determining step, it is assumed that N-radicals are always in steady state, their rate of formation being much slower than their consumption rate:

$$\frac{dC_N}{dt} = k_{1f}C_O C_{N_2} + k_{2b}C_O C_{NO} - k_{1b}C_N C_{NO} - k_{2f}C_N C_{O_2} = 0$$

(3.135)

This yields the N-radical concentration as a function of the other species concentrations:

$$C_N = C_O \frac{k_{1f}C_{N_2} + k_{2b}C_{NO}}{k_{1b}C_{NO} + k_{2f}C_{O_2}}$$

(3.136)

For the O-radicals a similar approach is followed, albeit that we do not equilibrate the O-atom concentration from a partial equilibrium within the Zel'dovich mechanism itself. Rather we assume O-atoms to be in equilibrium with O$_2$ molecules through the dissociation/recombination reaction:

$$O_2 + M \rightleftharpoons O + O + M$$

(3.137)

In low-temperature flames the O-atom concentration is known to exceed its equilibrium value considerably, but for higher temperatures and increasing Damköhler numbers, the equilibrium assumption will become valid more and more. Since the Zel'dovich mechanism itself only is a valid simplification at high temperatures the aforementioned approximations seem reasonably well justified. This produces:

$$C_O = K_O C_{O_2}^{\frac{3}{2}}$$

(3.138)

where $K_O$ is the square root of the equilibrium constant for the dissociation/recombination reaction. Thus, the O-radical concentration is directly coupled to the O$_2$ concentration. In Appendix C we have listed various proposals for the constant $K_O$ taken from different literature sources.

Some investigators use a so-called super-equilibrium factor in the above expression for $C_O$ to account for non-equilibrium effects, but here we will refrain from doing so. No universal super-equilibrium factor exists, so it has to be re-determined for each separate case. This determination can only be carried out by careful comparison between experiment and model calculations, and is often hampered by possible sources of inaccuracy, such as experimental and numerical errors. The super-equilibrium factor may then serve as a final tuning parameter to match experimental and numerical data, which obscures a rigorous validation of the numerical model. For example, if the use of an inadequate PDF model for mixture fraction fluctuations produces too low levels of NO, this may be counterbalanced by a chemistry model which produces very high levels of NO. Thus, the use of a super-equilibrium factor (or not) can be based on coincidence instead of sound mathematical
modeling. Only for a limited class of similar problems the same super-equilibrium factor might be used, which may be valuable for certain trend predictions.

With the aid of the expression (3.136) for $C_N$ we can derive the modeled chemical source term for NO formation:

$$\frac{dC_{NO}}{dt} = 2C_O \frac{k_{1f}k_{2f}C_{N_2}C_{O_2} - k_{1b}k_{2b}C_{NO}^2}{k_{1b}C_{NO} + k_{2f}C_{O_2}}$$

(3.139)

This expression can be rewritten if we employ the relationship for the equilibrium concentration $C_{NO,eq} = K_{eq}C_{N_2}C_{O_2}$:

$$\frac{dC_{NO}}{dt} = 2C_O \frac{k_{1f}k_{2f}C_{N_2}C_{O_2}}{k_{1b}C_{NO} + k_{2f}C_{O_2}} \left(1 - \frac{C_{NO}^2}{C_{NO,eq}^2}\right)$$

(3.140)

In the limit of very low NO concentrations the NO formation rate can be approximated by:

$$\frac{dC_{NO}}{dt} \approx 2k_{1f}C_OC_{N_2} \approx 2k_{1f}K_{O}C_{O_2}^{\frac{1}{2}}C_{N_2}$$

(3.141)

In actual computations with, say, $C_{NO} \sim 1000$ ppm, this approximation is no longer justified, and the complete formula (3.139) should be used.

### 3.8.4 Conserved scalar formalism

Within the framework of the flame sheet chemistry model, all thermochemical quantities are directly related to the mixture fraction $\xi$. Non-adiabaticity effects are included by means of an empirical local relationship $h = h(\xi, \vec{\xi}, \vec{h})$. As a result, all concentrations and the temperature appearing in (3.139) are functions of $\xi$:

$$S_{NO} = S_{NO}(\xi, Y_{NO})$$

(3.142)

This serves as a starting point for the closure of the average reaction rate.

In figure 3.17 a comparison of the formation rate as a function of mixture fraction is given for three different chemistry models. The NO mass fraction is taken to be zero. Calculations have been performed for the combustion of natural gas at 300 K with preheated air at 1400 K, closely resembling the fuel and air streams in high-temperature glass melting furnaces. The stoichiometric mixture fraction for the natural gas fuel under consideration is 0.062. The O-atom concentration in the flame sheet model is inferred from (3.138), and is compared with the mass fraction profiles for the two equilibrium models in figure 3.18. Since in the flame sheet model $Y_{O_2} = 0$ for $\xi > \xi_{st}$, the largest differences in figure 3.17 occur for fuel rich conditions, and there is a strong similarity between the O-atom concentration and the NO formation rate.

The influence of non-adiabaticity is investigated in figure 3.19. For lower enthalpy (representing radiative heat loss) the instantaneous NO formation rate drops quickly, as a consequence of the large activation energy of reaction 1f.
As the NO mass fractions increases, the net formation rate will decrease and become zero for chemical equilibrium. The equilibrium concentration as a function of mixture fraction is plotted in figure 3.20. In figure 3.21 the net formation rate of NO is depicted for increasing concentration levels. In large scale furnaces the concentration may exceed 1000 ppm, showing that the reverse reaction rates become non-negligible.
3.8. Thermal nitric oxide formation

![Graph](image)

**Figure 3.19:** Influence of non-adiabaticity on thermal NO formation. (a) Flame sheet model (b) Full equilibrium model. Symbols: --- adiabatic case; —— 5% heat loss, - - - 10% heat loss, · · · 15% heat loss, △ 20% heat loss.

![Graph](image)

**Figure 3.20:** Equilibrium NO mass fraction as a function of mixture fraction, for natural gas combustion using air at 1400 K and fuel at 300 K, calculated by the one-step flame sheet model.

3.8.5 Extended Zel’dovich mechanism

The extended Zel’dovich mechanism involves the OH reaction (3.130). As no reliable approximation exists to relate the mass fractions of the OH- and H-radicals to the mixture fraction in the Burke-Schumann flame sheet model, the extended Zel’dovich model is only employed in combination with equilibrium chemistry models. These models provide the desired radical concentrations as functions of the mixture fraction.
The analog of (3.136) reads:

$$C_N = \frac{k_{1f}C_{N_2}C_O + k_{2b}C_{NO}C_O + k_{3b}C_{NO}C_H}{k_{1b}C_{NO} + k_{2f}C_O + k_{3f}C_{OH}}$$  \hspace{1cm} (3.143)

The counterpart of (3.139) becomes:

$$\frac{dC_{NO}}{dt} = 2C_O \frac{k_{1f}k_{2f}C_{N_2}C_O - k_{1b}k_{2b}C_{NO}^2}{k_{1b}C_{NO} + k_{2f}C_O + k_{3f}C_{OH}}$$

$$+ 2 \frac{k_{1b}k_{3f}C_{N_2}C_{OH}C_O - k_{1b}k_{3b}C_{NO}C_H}{k_{1b}C_{NO} + k_{2f}C_O + k_{3f}C_{OH}}$$  \hspace{1cm} (3.144)

In the asymptotic limit of very low NO concentration the above expression reduces to:

$$\frac{dC_{NO}}{dt} = 2C_O \frac{k_{1f}k_{2f}C_{N_2}C_O}{k_{2f}C_O + k_{3f}C_{OH}} + 2 \frac{k_{1f}k_{3f}C_{N_2}C_{OH}C_O}{k_{2f}C_O + k_{3f}C_{OH}} = 2k_{1f}C_OC_{N_2}$$  \hspace{1cm} (3.145)

which is identical to (3.141). In figure 3.22 we have compared the net NO formation rate of the extended Zel’dovich mechanism with the standard ‘short’ mechanism, for increasing values of $Y_{NO}$, using the full equilibrium chemistry model. As illustrated above, the short and extended mechanism are identical for zero $Y_{NO}$. For increasing $Y_{NO}$ the differences are small.

### 3.8.6 PDF closure for mean NO formation rate

The transport equation for the NO mass fraction can be modeled by means of Favre-averaging and the well-known $k$-$\epsilon$ model of turbulence, yielding for the steady state in
3.8. Thermal nitric oxide formation

\[ \frac{\partial \left( \delta \tilde{\nu}_k \tilde{Y}_{\text{NO}} \right)}{\partial x_k} = \frac{\partial}{\partial x_k} \left( \frac{\mu_t}{\sigma_y} \frac{\partial \tilde{Y}_{\text{NO}}}{\partial x_k} \right) + \langle \rho \rangle \tilde{S}_{\text{NO}} \]  

(3.146)

As shown in the previous sections, the modeled NO formation rate only depends on the mixture fraction $\xi$ and the NO concentration, for given initial temperature conditions of the fuel and the oxidizer. This offers the possibility to calculate the mean source term $\tilde{S}_{\text{NO}}$ by means of a two-dimensional joint Favre PDF of $\xi$ and $Y_{\text{NO}}$.

\[ \tilde{S}_{\text{NO}} = \int_0^1 \int_0^1 S_{\text{NO}}(\xi, y) \tilde{f}_Y(\xi, y) \, dy \, d\xi \]  

(3.147)

This presents difficulties, since the joint PDF $\tilde{f}_{\xi Y_{\text{NO}}}$ is an unknown function in our model so far. As a first important approximation, it is assumed that fluctuations of $\xi$ and $Y_{\text{NO}}$ are independent. This seems reasonable, as the kinetics of NO formation are slow. In that case, the joint PDF can be written as the product of the two marginal PDFs of $\xi$ and $Y_{\text{NO}}$:

\[ \tilde{f}_{\xi Y}(\xi, y) = \tilde{f}_\xi(\xi) \tilde{f}_Y(y) \]  

(3.148)

For convenience, we will drop the index $\text{NO}$ in the sequel, taking $Y \equiv Y_{\text{NO}}$. For $\tilde{f}_\xi$ we use the same PDF as for the global combustion model, applying the presumed-shape PDF model. The PDF for the NO mass fraction $\tilde{f}_Y$ can be modeled analogously to $\tilde{f}_\xi$. In other words, $\tilde{f}_Y$ is characterized by its first and second moment. Generally speaking, we have to solve the transport equation for $\tilde{Y}^{\eta_2}$ which closely resembles the transport equation for the mixture fraction variance $\tilde{\xi}^{\eta_2}$, with the exception that an additional correlation term $\tilde{Y}^{\eta_2} \tilde{S}$ enters the equation.
With the present model assumptions (mixture fraction, reduced NO kinetics), the correlation term \( \overline{Y''S} \) is closed through the PDF integration:

\[
\overline{Y''S} = \int \int_{0}^{1} (y - \overline{Y}) S(\zeta, y) \tilde{f}_\zeta(\zeta) \tilde{f}_Y(y) \, d\zeta \, dy 
\]  

(3.149)

This allows for the calculation of the marginal PDF \( \tilde{f}_Y \) and the evaluation of the integrals. As a first approximation, we consider the marginal PDF of \( Y_{\text{NO}} \) to be represented by a single \( \delta \)-function PDF, thus neglecting fluctuations in \( Y_{\text{NO}} \): \( \tilde{f}_Y = \delta(y - \overline{Y}) \). This saves a considerable amount of computing time, although the error in \( \tilde{f}_Y \) is expected to be small. The final simplified model for the joint PDF then reads:

\[
\tilde{f}_{\zeta Y} = \tilde{f}_\zeta \delta(y - \overline{Y})
\]  

(3.150)

with which the mean source term for NO formation can be easily calculated, since only the marginal PDF for the mixture fraction is required:

\[
\overline{S}_{\text{NO}} = \int_{0}^{1} \tilde{f}_\zeta(\zeta) S_{\text{NO}}(\zeta, \overline{Y}_{\text{NO}}) \, d\zeta
\]  

(3.151)

However, as we know that mean NO mass fractions usually are very small, there is a possibility for the marginal PDF \( \tilde{f}_Y \) to be skewed with a Dirac delta-function near \( Y = 0 \) if the fluctuations \( \overline{Y''} \) are relatively large. The assumption of negligible NO mass fraction fluctuations can be relaxed by calculating \( \overline{Y''^2} \), using a double Dirac delta-function model for the marginal PDF \( \tilde{f}_Y \):

\[
\tilde{f}_Y(y) = a_0 \delta(y - Y_0) + a_1 \delta(y - Y_1)
\]  

(3.152)

This yields:

\[
\overline{S} = a_0 \int_{0}^{1} S(\zeta, Y_0) \tilde{f}_\zeta(\zeta) \, d\zeta + a_1 \int_{0}^{1} S(\zeta, Y_1) \tilde{f}_\zeta(\zeta) \, d\zeta
\]  

(3.153)

and

\[
\overline{Y''S} = a_0 Y_0 \int_{0}^{1} S(\zeta, Y_0) \tilde{f}_\zeta(\zeta) \, d\zeta + a_1 Y_1 \int_{0}^{1} S(\zeta, Y_1) \tilde{f}_\zeta(\zeta) \, d\zeta - \overline{Y} \overline{S}
\]  

(3.154)

These equations show that the actual computational time for integration of the various source terms is doubled by the inclusion of a double Dirac delta-function PDF \( \tilde{f}_Y \). If a continuous marginal PDF \( \tilde{f}_Y \) is to be used, however, the required CPU time for PDF integration will increase with a factor \( N \), \( N \) being the number of integration intervals for the marginal PDF quadrature.

For numerical reasons, it is convenient to split the expression for \( \overline{S}_{\text{NO}} \) into a linear part in \( \overline{Y}_{\text{NO}} \) and a constant part, independent of \( \overline{Y}_{\text{NO}} \). This can be done easily by inspection of
3.9 Soot formation model

As discussed at the end of Chapter 2, soot radiation may play an important role in the radiative heat transfer in flames. Since the detailed chemistry of soot formation and oxidation is extremely complex, we have used empirical models to account for these phenomena. In this section we will briefly discuss the soot formation and oxidation models used for the modeling of soot in the laboratory-scale flames. More details on soot models, their validation and fine tuning are given by Boerstoel et al. (1994).

We used the model of Khan and Greeves (1974) for soot formation, and the Magnussen model (Magnussen and Hjertager, 1976) for soot oxidation. According to these models, the averaged soot mass fraction is given by a transport equation of the type:

\[ \mathcal{L}_t (\bar{Y}_{\text{soot}}) = \langle \rho \rangle \bar{S}^+_{\text{soot}} - \langle \rho \rangle \bar{S}^-_{\text{soot}} \]  

(3.155)

In the model of Khan and Greeves, the production term \( \langle \rho \rangle \bar{S}^+_{\text{soot}} \) is given by an expression which contains a global activation temperature:

\[ \langle \rho \rangle \bar{S}^+_{\text{soot}} = \left\{ C_t p_{\text{fu}} \phi^n \exp\left(-\frac{T_{A,\text{soot}}}{T}\right) \right\} \]  

(3.156)

where the model constants read:

\[ C_t = 0.01 \text{ kg/(N.m.s)} \]

\[ T_{A,\text{soot}} = 20150 \text{ K} \]

\[ n = 3 \]

The constants were taken from Boerstoel et al. (1994), who tuned these values for natural-gas combustion at high temperatures, and which also worked well for laboratory-scale flames. (The original model constants by Khan and Greeves were tuned for diesel engine combustion.) In (3.156) \( p_{\text{fu}} \equiv p X_{\text{fu}} \) is the partial pressure of the hydrocarbon fuel species, and \( \phi \) is the equivalence ratio, which is a monotonous function of the mixture fraction: \( \phi \equiv \xi/(1 - \xi) \times (1 - \xi_{\text{st}})/\xi_{\text{st}} \). By virtue of the conserved-scalar chemistry model, the soot formation term is written as a function of mixture fraction, and we can adopt a PDF closure to obtain the mean formation rate.

The soot oxidation model of Magnussen and Hjertager (1976) is the well-known Eddy-Break-Up model:

\[ \langle \rho \rangle \bar{S}^-_{\text{soot}} = C_{\text{ebu}} (\rho) \bar{Y}_{\text{soot}} \frac{\bar{\varepsilon}}{k} \times \min \left[ 1, \frac{\bar{Y}_{O_2}}{\bar{Y}_{\text{soot}} s_{\text{soot}} + \bar{Y}_{\text{fu}} s_{\text{fu}}} \right] \]  

(3.157)
where $s_{soot}$ and $s_{fu}$ are stoichiometric coefficients for the soot and fuel, respectively ($s_{soot} = 2.7$, $s_{fu} = 4.0$) and $C_{cBu}$ is a model parameter which is assigned the value of 4. This expression describes a mixing-controlled soot oxidation rate, without further kinetic effects. In regions where no oxygen is present, the soot oxidation rate will be zero.
CHAPTER 4

Numerical algorithms

4.1 Solution of 2D and 3D transport equations

4.1.1 Introduction

The modeled transport equations for Favre-averaged variables in turbulent flows constitute a set of coupled non-linear partial differential equations, closed by additional algebraic equations and boundary conditions. These equations cannot be solved analytically, and therefore a suitable numerical algorithm is employed to solve them on a computer. In the sequel the transport equations will be discretized by the finite-volume method (Patankar, 1980), which is a well-known method for the numerical modeling of turbulent flows. The basic principles of the finite-volume method can be found elsewhere (Patankar, 1980; Post, 1988; Bockhorn, 1989; Koster, 1993).

4.1.2 Discretization of general transport equation

For brevity, we will discuss discretizations for the Cartesian 2D case, which can be easily transformed to the axisymmetric geometry or the 3D case used in our furnace flow computations. The starting point for the finite volume method is the definition of a suitable distribution of grid cells covering the whole domain of interest. In this thesis, a rectilinear, non-uniform grid spacing is used, as illustrated in figure 4.1.

![Figure 4.1: Example of non-uniform 2D grid with grid node positions](image)

Each grid cell is completely characterized by the position of its cell walls, and the position of the grid node located inside the cell. In the present formulation, the cell walls

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are defined exactly in between two neighbouring grid nodes. Due to the non-uniformity of the grid, the opposite is not true: the grid nodes need not lie exactly in the center of the grid cell. Moreover, the positions of the velocity components are staggered with respect to the scalar grid points, such that they are located exactly on the scalar cell walls. This grid staggering is employed to avoid numerical instabilities in solving the Navier-Stokes equations (Patankar, 1980).

![Diagram of a 2D Cartesian finite volume grid cell, node positions and velocity grid staggering](image)

**Figure 4.2:** Nomenclature for a typical 2D Cartesian finite volume grid cell, node positions and velocity grid staggering

The transport equation for any scalar variable $\phi$ is integrated over each grid cell, using appropriate discretizations for the fluxes through the cell walls and for the source terms. We write the general transport equation in the form:

$$\frac{\partial \rho \phi}{\partial t} + \frac{\partial J_{\phi,k}}{\partial x_k} = \rho S_{\phi}$$ (4.1)

where $J_{\phi,k}$ denotes the total convective and diffusive flux of $\phi$ in the $x_k$-direction:

$$J_{\phi,k} = \rho u_k \phi - \Gamma_{\phi} \frac{\partial \phi}{\partial x_k}$$ (4.2)

Integration of (4.1) over a typical 2D grid cell, depicted in figure 4.2, yields:

$$(\rho_p \phi_p - \rho_v \phi_v) \frac{\Delta V}{\Delta t} + J_e A_e - J_w A_w + J_n A_n - J_s A_s = \rho \overline{S}_{\phi} \Delta V$$ (4.3)

The lowercase letters e, w, n, s denote the cell wall positions, whereas the uppercase letters P, E, W, N, S denote grid node positions, according to figure 4.2. $\Delta t$ is the time step, and the superscript $^\circ$ denotes a value at the previous time level. $\Delta V$ is the cell volume, and the $A_k$ are the cell wall areas.
4.1. Solution of 2D and 3D transport equations

Each total flux \( J_k \) represents the sum of the diffusive flux \( D_k \equiv -\Gamma \phi \partial \phi / \partial x_k \) and the convective flux \( C_k \equiv \rho u_k \phi \). Since we have defined the cell walls to be located exactly between two grid points, the values of \( \rho \) and \( \Gamma \) at the east wall are given by:

\[
\Gamma_e = \frac{2\Gamma_p \Gamma_e}{\Gamma_p + \Gamma_e} \\
\rho_e = \frac{1}{2} (\rho_p + \rho_e)
\]

Note that the average transport coefficient at the wall is the harmonic mean of the neighbouring points instead of the arithmetic mean. The velocity \( u_e \) is known exactly due to the staggered grid for the velocities. At the other cell walls a similar interpolation is used.

The essential step in arriving at a linear algebraic equation for \( \phi_e \) is the discretization of \( \phi \) and \( \partial \phi / \partial x_k \) at the cell walls. After expressing these quantities at the cell wall in terms of values at grid nodes, one arrives at the general discretized equation:

\[
a_p \phi_p = a_e \phi_e + a_w \phi_w + a_N \phi_N + a_s \phi_s + b_p
\] (4.4)

The values of the various coefficients depend on the discretization scheme. An important condition for the stability of the set of algebraic equations is the requirement that all matrix coefficients are positive; only the \( b_p \) coefficient may be negative.

If we define the cell Péclet number at the east wall as:

\[
\text{Pe}_e = \frac{\rho_e u_e \Delta x_e}{\Gamma_e}
\] (4.5)

we can use a number of discretization schemes based on this local cell Péclet number. In this thesis we used three different schemes, well-known in the literature: the upwind scheme, the central scheme and the hybrid scheme. All of these schemes have first order accuracy on a non-uniform grid. These schemes can be cast into a general form, yielding:

\[
a_e = D_e A(|\text{Pe}_e|) + \max(-C_e, 0) \\
a_w = D_w A(|\text{Pe}_w|) + \max(C_w, 0) \\
a_N = D_N A(|\text{Pe}_N|) + \max(-C_n, 0) \\
a_s = D_s A(|\text{Pe}_s|) + \max(C_s, 0)
\] (4.6)

The function \( A(|\text{Pe}|) \) reads:

\[
A(|\text{Pe}|) = \begin{cases} 
1 & \text{Upwind scheme} \\
1 - 0.5|\text{Pe}| & \text{Central scheme} \\
\max(1 - 0.5|\text{Pe}|, 0) & \text{Hybrid scheme}
\end{cases}
\] (4.7)

The choice for either of the above schemes will depend on the properties of the flow and the numerical stability of the set of linear algebraic equations. In case of a strongly convection-dominated problem, \textit{i.e.} high \(|\text{Pe}|\), the upwind scheme or the hybrid scheme are to be preferred, whereas for flows with only a moderate convective influence (\(|\text{Pe}| < 2\))
the central scheme and the hybrid scheme are considered to be superior. This is related to the fact that the central scheme has a strong tendency to become numerically unstable on relatively coarse grids (high \(|\text{Pe}|\)).

On first glance, the hybrid scheme seems to be attractive for the general case, since this scheme adjusts itself to the local circumstances: it switches from 'upwind'-like behaviour to a central scheme if \(|\text{Pe}|\) approaches zero. A drawback of the hybrid scheme, however, is the neglect of diffusion in the downstream direction, for large \(|\text{Pe}|\), in contrast to the real upwind scheme where the diffusive flux is always retained. As a result, no information can travel upstream in a convection-dominated flow without recirculation, which may lead to unrealistic solutions, for instance in the case of flame lift-off. However, if gradients in the downstream direction are not too large, the upwind scheme or the hybrid scheme combine numerical efficiency with sufficient accuracy.

Returning to (4.4), the coefficients \(a_p\) and \(b_p\) read:

\[
\begin{align*}
    a_p &= a_e + a_w + a_s + a_p^0 \quad (4.8) \\
    b_p &= \rho_S \Delta V + a_p^0 \phi_p^0 \quad (4.9) \\
    a_p^0 &= \frac{\rho_p \Delta V}{\Delta l} \quad (4.10)
\end{align*}
\]

The discretized source term has been simplified by \(\rho_S \Delta V\); more elaborate alternatives will be discussed in the next section.

### 4.1.3 Implementation of source terms

The right-hand side of (4.1) represents the source term in the transport equation for \(\phi\). In general, this source term can be integrated over the control volume using a suitable finite difference discretization of the constituent terms. The common way of doing this is by putting:

\[
\int_{\Delta V} \rho S_\phi dV = \bar{\rho S} \Delta V \quad (4.11)
\]

\(\bar{\rho S}\) represents the average value of \(\rho S_\phi\) over the control volume \(\Delta V\). If \(\rho S_\phi\) is a function of \(\phi\) itself, the source term can be linearized:

\[
\bar{\rho S} = S_c + S_p \phi_p \quad (4.12)
\]

where \(S_c\) is the constant part of \(\rho S_\phi\) and \(S_p\) the linear coefficient of \(\phi_p\). If \(S_p < 0\), we can incorporate this part into the coefficient \(a_p\), yielding the discretized equation:

\[
(a_p - S_p \Delta V)\phi_p = \sum_{nb} a_{nb} \phi_{nb} + b_p \quad (4.13)
\]

with \(b_p = S_c \Delta V\). If \(S_p > 0\), the source term is unstable with respect to perturbations in \(\phi\), and we are forced to write \(b_p = \bar{\rho S}_\phi \Delta V\), in order to stabilize the numerical solution.

In the transport equations for turbulence quantities like \(k\) and \(\epsilon\) and for chemically reacting species, one generally encounters source term expressions which depend on \(\phi\) in
a non-linear fashion. In that case several options are open to linearize the source term. Putting \( S_c = \overline{\rho S} \); \( S_p = 0 \) is allowed, but slows down the convergence. The method recommended by Patankar (1980) is a Newton-Raphson linearization:

\[
(rS\phi)^n = (rS)^{n-1} + \left( \frac{\partial rS}{\partial \phi} \right)^{n-1} (\phi_p^n - \phi_p^{n-1}) \tag{4.14}
\]

where \( n \) denotes the current iteration number. As a result, we obtain:

\[
S_c = (rS)^{n-1} - \left( \frac{\partial rS}{\partial \phi} \right)^{n-1} \phi_p^{n-1} \tag{4.15}
\]

\[
S_p = \left( \frac{\partial rS}{\partial \phi} \right)^{n-1} \]

In keeping with the above, the local slope \( \partial rS/\partial \phi \) should be negative, otherwise \( rS \) should be treated as a constant \( (S_c = \overline{\rho S}, S_p = 0) \). Sometimes the derivative \( \partial rS/\partial \phi \) is a complex analytical function of \( \phi \), and it is more convenient to use a simplification of the derivative to reduce computational costs.

**Turbulence quantities**

Often, the numerical solution procedure is unstable with respect to the turbulence quantities \( k \) and \( \epsilon \). This is not surprising in view of the strongly non-linear source terms in the \( k-\epsilon \) equations, and the strong coupling of these equations. Hence, source term manipulations may aid the numerical stability by means of implicit relaxation. The dissipation term \( \rho \epsilon \) in the \( k \)-equation does not depend on \( k \) itself. Nevertheless, after manipulation we use:

\[
S_c = P_k + G_k \tag{4.16}
\]

\[
S_p = -\frac{\rho \epsilon}{kn^{-1}} \tag{4.17}
\]

where \( n \) is the current iteration number. The linearized coefficient \( S_p < 0 \) enhances the stability of the set of linear equations.

**Chemically reacting species**

The transport equations for the chemically reacting species contain the averaged reaction rates. Generally, the net reaction rate can be split into a production term \( P_\phi > 0 \) and a destruction term \( D_\phi < 0 \):

\[
\rho S_\phi = P_\phi + D_\phi \tag{4.18}
\]

If \( \phi \) is a species mass fraction, the destruction term \( D_\phi \) more or less depends linearly on \( \phi \), since many elementary reaction rates have stoichiometric coefficients equal to 1. Therefore, to a good approximation we may put:

\[
S_c = P_\phi \tag{4.19}
\]

\[
S_p = \frac{D_\phi}{\phi_p^{n-1}} \tag{4.20}
\]
In the reaction zone of the flame, the transport equation may become strongly dominated by the chemical source terms. This is reflected in the discretized equation for \( \phi_p \), where the coefficients \( S_C \) and \( S_p \) will outweigh the coefficients \( a_p \) and \( a_{nb} \) by orders of magnitude. The local solution then becomes:

\[
\phi_p = -\frac{S_C}{S_p} = -\frac{P_\phi}{D_\phi} \phi_p^{n-1}
\]  

(4.21)

This leads to numerical instability if \( P_\phi \) and \( D_\phi \) are not (yet) of the same order of magnitude, in other words, if \( \phi \) has not yet attained local chemical equilibrium. Especially if \( D_\phi \ll P_\phi \), the new solution \( \phi_p^n \) can be orders of magnitude larger than the previous solution \( \phi_p^{n-1} \), which may trigger unwanted numerical oscillations.

Therefore, it is desirable to construct a numerical scheme that will not allow too large variations of a reacting quantity \( \phi \). This can be accomplished artificially by under-relaxation factors, by small time steps and by limiting the relative change of a reacting scalar between two successive iteration steps. Manipulation of the source terms, as discussed above, also contributes to further stabilization.

Note that for reacting scalars, splitting the net chemical source term into separate destruction and production terms will ensure non-negative mass fractions in every grid point, since all matrix coefficients will be positive. The present formulation is very similar to the general formula (4.14).

**Explicit relaxation**

The source terms for the chemically reacting species may exhibit strong variations between successive time steps or iteration levels. If we are interested in a stationary solution only, the source terms can be relaxed by a suitable relaxation factor \( \alpha \):

\[
\overline{\rho S} = \alpha \overline{\rho S^n} + (1 - \alpha) \overline{\rho S^{n-1}}
\]  

(4.22)

**4.1.4 Treatment of mass continuity and pressure**

A well known problem in solving the Navier-Stokes equations is that no differential equation for pressure is available. In the present algorithm, the pressure field is solved by using the continuity equation as an additional equation to obtain a correct pressure field. The SIMPLE (Semi-Implicit solution of Pressure Linked Equations) method, developed by Spalding and Patankar (1980) was used. Its merits and drawbacks have been discussed in many textbooks and papers, and will not be repeated here. We merely mention that the SIMPLE algorithm proved to be adequate for our applications, i.e. turbulent variable-density flow in a confined geometry.

Briefly, the SIMPLE method works as follows. On the staggered grid for the velocity components the corresponding matrix coefficients are calculated, using the given (hybrid) discretization scheme. The pressure enters the momentum equations in the source terms \(-\partial p/\partial x_i\), and is obtained from an estimated pressure field. Using this initial pressure field, the momentum equations are solved. Next, the pressure field is corrected in order to
preserve local mass continuity. This is achieved by a source term for the discretized pressure correction equation, which depends on the local mass continuity error. In case of a converged solution, this error will have become very small and the pressure correction becomes virtually zero. In effect, the pressure correction equation is solved. The previously calculated velocity field and the guessed pressure field are subsequently updated by the correction terms.

In the specific case of variable density flow, the iteration procedure is extended by an updating of the mean density field, which can be done by the conserved-scalar approach, or directly from the equation of state for an ideal gas. However, it was sometimes found to be advantageous to update the density field only once every 10 to 20 iterations, since the coupling of density and pressure field is mild: no compressibility effects are taken into account. To a good approximation, the mean pressure field differs only slightly from the standard atmospheric pressure, which is used in the expression for the mean density. Nevertheless, small pressure gradients will already exert a strong influence on the velocity field, and therefore the pressure correction procedure is necessary to ensure mass and momentum continuity.

4.1.5 Implementation of boundary conditions

General rules

The implementation of boundary conditions is carried out in two different ways. The FURNACE code employs virtual cells and grid nodes, in which case the numerical solution procedure of the set of discretized equations applies to the internal grid nodes only, thereby using the values at the virtual nodes. The matrix coefficients derived in the previous sections do not have to be adjusted to accommodate for the boundary conditions. After each iteration, the variables are updated at the virtual nodes, keeping the internal values fixed.

The BIGMIX code does not use virtual grid nodes, but the the outer nodes are located at the boundaries instead. In order to account for the boundary conditions, discretized equations are derived for the boundary grid nodes. If we have a point P in a near-wall cell \((i, j)\), with the wall located at the east cell wall, the general algebraic equation for variable \(\phi_{i,j}\) reads:

\[
a_p^{i,j} \phi_{i,j} = a_u^{i,j} \phi_{i+1,j} + a_w^{i,j} \phi_{i-1,j} + a_N^{i,j} \phi_{i,j+1} + a_S^{i,j} \phi_{i,j-1} + b_p^{i,j}
\] (4.23)

The discretized equation for grid node \((i+1, j)\) at the wall can be simplified to:

\[
a_p^{i+1,j} \phi_{i+1,j} = a_w^{i+1,j} \phi_{i,j} + b_p^{i+1,j}
\] (4.24)

This equation serves as an expression for \(\phi_{i+1,j}\), which is subsequently substituted into (4.23). Hence, the coefficients for (4.23) are replaced with:

\[
a_p^{i,j} = a_p^{i,j} - a_w^{i,j} a_w^{i+1,j} / a_p^{i+1,j}
\] (4.25)

\[
b_p^{i,j} = b_p^{i,j} + a_w^{i,j} b_p^{i+1,j} / a_p^{i+1,j}
\] (4.26)

\[
a_w^{i,j} = 0
\] (4.27)
where * denotes the new coefficients. If the boundary condition is of the Dirichlet type, we have \( a_i^{i+1,j} = 1, \ a_i^{i+1,j} = 0, \ b_i^{i+1,j} = \phi_{\text{wall}} \). If the boundary condition is of the Neumann type, we have \( a_i^{i+1,j} = 1, \ a_i^{i+1,j} = 1, \ b_i^{i+1,j} = (\partial \phi / \partial x)_{\text{wall}} \Delta x \), with \( \Delta x \equiv x_{i+1} - x_i \). This description is first order accurate, in accordance with the first order discretization of the inner cell equations on a non-uniform mesh. For the other near-wall cells similar implementations hold.

**Porosity method**

Both the **FURNACE** and **BIGMIX** codes employ a rectilinear grid. For the **BIGMIX** code this grid coincides with the geometry of the combustion chamber. The large-scale furnaces modeled by the **FURNACE** code, however, have an irregular shape, which does not match the rectangular grid cells. In particular, the gas pipe in the **IFRF** geometry is round, and the roof of the industrial glass melting furnace is curved. The problem of non-matching boundaries is resolved by the porosity method (Post, 1988). Each control volume is attributed a porosity \( P_{i,j,k} \), which represents the fraction of the control volume that is open for the fluid flow. Hence, an inner grid cell has porosity 1, whereas a grid cell in a blocked wall has porosity 0. Of course, the porosity formulation becomes active for partially open cells: \( 0 < P < 1 \). The cell volume \( \Delta V \) is replaced by \( P \Delta V \) in the discretized equations, and the internode distances are adjusted likewise. Furthermore, each cell wall has its own wall porosity \( P_w \), which is multiplied with the standard cell wall area to obtain the porosity corrected cell wall areas. It turns out that the porosity method is a rather time consuming algorithm in dealing with irregular boundaries on a rectangular mesh. Fortunately, for the glass melting furnaces considered, the flow along the curved walls is not very important, whereas the glass surface is flat and therefore treated exactly. Hence, the porosity method works sufficiently well for our simulation purposes.

**Wall functions**

The turbulent boundary layers along the walls of a combustion chamber or a furnace exhibit steep gradients. To resolve these gradients accurately, a fine mesh spacing is required at relatively high computational cost. In order to avoid this, wall functions are commonly applied in situations where the exact representation of the boundary layer is of minor importance. This is typically the case for the flows studied in this thesis, since the important regions (the flame zones) are located at a reasonable distance from the confinement walls.

The concept of wall functions in \( k-\epsilon \) turbulence modeling has been founded by Spalding and co-workers (Elgobashi et al., 1977). The basic idea is that for a fully developed turbulent boundary layer a universal velocity profile exists, of the form:

\[
    u^+ = \frac{1}{\kappa} \ln(y^+)
\]

where \( u^+ \) and \( y^+ \) are the non-dimensionalized velocity and distance to the wall, respec-
4.1. Solution of 2D and 3D transport equations

tively:

\[
\begin{align*}
    u^+ &= u/u_r \\
    y^+ &= \frac{\rho u_r y}{\mu}
\end{align*}
\]

The constant \( \kappa \) is the Von Kármán constant (\( \kappa = 0.41 \)) and the constant \( E = 9.0 \) for a smooth surface wall. The velocity scale \( u_r \) is the friction velocity, related to the wall shear stress via:

\[ \tau_w \equiv \rho u_r^2 \]  \hspace{1cm} (4.29)

Very close to the wall, the velocity profile is laminar and one has \( u^+ = y^+ \). The logarithmic profile and the linear profile are matched in the so-called buffer layer, for which no universal profile is defined here. The fully turbulent part extends from \( y^+ > 40 \). Equating the expressions for the logarithmic layer and the viscous sublayer yields \( y^+ = 11.27 \) at the connection point. In the numerical implementation, a viscous sublayer is assumed if the value of \( y^+ \) at the near-wall grid node is smaller than this threshold value, and a fully turbulent layer is assumed for \( y^+ > 11.27 \). It is generally advised to choose the near-wall grid node such that \( y^+ \) is sufficiently high, say \( y^+ > 30 \), for the fully turbulent profile to be well applicable.

The fully turbulent layer is characterized by a constant shear stress, i.e. independent of the distance to the wall. Furthermore, the production and dissipation of turbulent kinetic energy are believed to be in local equilibrium (\( P_k = \rho \epsilon \)). As a consequence, the turbulent kinetic energy \( k_p \) at a near-wall grid node P is related to the wall shear stress via:

\[ u_r = C_{1/4}^{1/4} k_p^{1/2} \]  \hspace{1cm} (4.30)

The proper expression for \( y_p^+ \) thus becomes:

\[ y_p^+ = \frac{\rho C_{1/4}^{1/4} k_p^{1/2} y_p}{\mu} \]  \hspace{1cm} (4.31)

where \( y_p \) is the distance of the near-wall grid node to the wall. In order to express the wall shear stress \( \tau_w \) as a function of known quantities at point P, we use:

\[ \tau_w = \frac{\rho u_p C_{1/4}^{1/4} k_p^{1/2}}{\frac{1}{\kappa} \ln(E y_p^+)} \]  \hspace{1cm} (4.32)

with \( y_p^+ \) given by (4.31).

**Pressure boundary conditions**

The pressure correction is a non-physical quantity, and only serves as an intermediate variable to obtain a physically realistic pressure field. Therefore, the boundary conditions for the pressure correction depend on the physical boundary conditions of velocity and pressure. If the pressure \( p \) is specified at a given boundary (usually at the outlet region),
the pressure correction \( p' \) will be zero at that boundary, which is a boundary condition of the homogeneous Dirichlet type. On the other hand, if the velocity normal to the boundary is specified (at walls, symmetry planes and inlet regions), no correction of the velocity is required, and homogeneous Neumann conditions apply.

4.1.6 Solution algorithm

The set of coupled algebraic equations can now be expressed in matrix form:

\[
A \phi = b
\]  
(4.33)

where \( \phi \) is the complete vector of all unknowns in all grid points. It is assumed that the boundary conditions have been absorbed in the coefficients for the inner grid cells, hence no explicit dependence of boundary values is required in the matrix equation. In the general case, the number of elements in the solution vector is much too large to allow a direct numerical solution.

As a first important step, the variables are solved sequentially rather than simultaneously. This reduces the number of unknowns in the vector \( \phi \) by a factor \( N \), \( N \) being the number of variables. For each variable, the resulting solution vector has length \( L \times M \), \( L \) and \( M \) being the number of internal grid cells in \( x \)- and \( y \)-direction, respectively. Usually, for discretizations involving at least several thousands of internal grid cells, this still is too much to be treated efficiently on present-day computers.

Therefore, the second reduction step is the adoption of a line-by-line solution technique, assuming \( \phi \)-values on adjacent grid lines to be known. The algorithm employed by the BIGMIX and FURNACE codes is referred to as the Thomas algorithm or tri-diagonal matrix algorithm (TDMA), described in numerous textbooks (Patanker, 1980). The TDMA solves the variables on a chosen grid line very efficiently but since the complete matrix equation is not solved simultaneously, the rate of convergence is diminished compared to direct methods. To accommodate for this behavior, an alternating direction implicit technique (ADI) is used, by sweeping to and forth through the computational domain, in various directions, using the same matrix coefficients. Thus, the influence of boundary conditions on internal grid cells is transferred more rapidly per iteration step. Depending on the problem, one may choose to perform sweeps in \( x \)-direction only, \emph{e.g.} in case of a (nearly) parabolic flow with a dominant flow direction. For recirculating flows, however, the ADI technique considerably enhances the rate of convergence.

The FURNACE code is a three-dimensional code; to improve the convergence behaviour, several variants of the TDMA are available: line TDMA, plane TDMA and space TDMA (Post, 1988). Solvers like the point-by-point Jacobi and Gauss-Seidel method are encoded as well, but were found to give slower convergence.

4.1.7 Solution of conserved-scalar flames

The standard chemistry model used by the FURNACE code as well as the BIGMIX code is the conserved-scalar model, in terms of the mixture fraction and the enthalpy. Since
4.1. Solution of 2D and 3D transport equations

Read user input parameters

Initialize geometry and constants

Initialize independent variables \((u, v, \xi, \text{etc.})\)

Initialize dependent variables \((T, Y_k, \text{etc.})\)

\(n = n + 1\)

Start iteration \(n\)

Update dependent variables

Solve hydrodynamical variables

Solve independent thermochemical variables

Apply convergence criteria

Generate final output

FIGURE 4.3: Flow diagram of solution algorithm for conserved-scalar flame model.

no chemical source terms appear in this model, the standard solution techniques are employed. Figure 4.3 depicts a flow chart for the iterative solution procedure for these flame models.

4.1.8 Solution of chemically reacting flow

When solving the fully kinetic model for turbulent flames, involving over 50 coupled transport equations for the reacting scalars, large numerical oscillations may occur. The simplest way to suppress these oscillations is the use of a (very) small false time step, smaller than the smallest (chemical) time scale of the problem. The number of time steps for a given problem is determined by the ratio of the largest relevant time scale and the smallest chemical time scale. In general, this may lead to excessive computing times, since the larger time scales usually occur in regions of relatively low turbulence intensities, where we are not particularly interested in resolving these time scales. Fortunately, the
source term linearization adds to the numerical stability of the problem. In effect, the actual allowed time step for the reacting scalars can be larger than would be dictated by the smallest chemical time scale. Moreover, an improvement of the time dependent solution for stationary problems is obtained by using different time steps for the variables. In this respect, the chemically reacting variables require smaller false time steps (usually $10^{-4}$ s) than the hydrodynamical variables ($10^{-2}$ s).

### 4.1.9 Convergence criteria

The convergence of the iteration process is monitored by various criteria. The most important criterion is the requirement that for every variable the sum of all absolute values of the local residuals in every grid cell becomes smaller than a specified threshold value. In order to allow a fair comparison between variables of different absolute magnitude (e.g. enthalpy and species mass fractions), the residuals are normalized with a suitably chosen constant, which equals the inlet flow rate of the product ($\rho u \xi$).

The absolute residual of a variable $\phi$ at a grid point $P$ is defined as:

$$ R_p = \left| \sum_{nb} a_{nb} \phi_{nb} + b_p - a_p \phi_p \right| \quad (4.34) $$

The normalized absolute residual $R^n_p$ is then defined as:

$$ R^n_p = \frac{\sum_{nb} a_{nb} \phi_{nb} + b_p - a_p \phi_p}{|M \phi_{ref}|} \quad (4.35) $$

Here, $M$ is the total inlet mass flow rate, and $\phi_{ref}$ is a typical value for $\phi$ over the entire computational domain. The convergence criterion can then be described by $\sum R^n_p < \delta_1$, where the summation runs over all internal grid cells and $\delta_1$ generally is in the order of $10^{-5}$.

The above definition is a necessary but sometimes insufficient criterion for full convergence. In case of reacting species, the local values of $\phi$ may differ from the reference value $\phi_{ref}$ by several orders of magnitude. In effect, the convergence criterion based on small absolute normalized residuals may overlook regions in the computational domain where $\phi \ll \phi_{ref}$. This may cause problems if $\phi$ is a radical species mass fraction, for which relatively small concentrations are still essential in describing the flame structure.

To accommodate for this discrepancy, a relative criterion is formulated, by demanding that:

$$ \left| \frac{\phi^n_p - \phi^{n-1}_p}{\phi^{n-1}_p} \right| < \delta_2 \quad (4.36) $$

with $\delta_2 \sim 10^{-4}$. The relative convergence criterion is applied only if $|\phi_p| > 10^{-8}$, in order to avoid floating point exceptions and slow convergence in regions where $\phi$ is
4.2. Solution method for 1D laminar flames

insignificantly small. Furthermore, the absolute residual is normalized according to:

\[ R^n_p = \frac{\left| \sum_{nb} a_{nb} \phi_{nb} + b_p - a_p \phi_p \right|}{\sum_{i,j} |a_{i,j} \phi_{i,j}|} \]  (4.37)

It is found that this way of normalization gives faster convergence compared to (4.35) for source-term dominated variables, such as \( k, \epsilon \) and reacting scalars.

The third criterion is based on the conservation laws of energy, mass and momentum. In this thesis we have studied confined flows mainly, and this allows us to use the overall mass and energy conservation. At every cross section normal to the main flow direction, the conservation laws are monitored and upon convergence it is checked that the deviation from exact conservation is less than \( 10^{-3}\% \) between each cross section. This is particularly important for overall conservation of the mixture fraction and the element mass fractions, which are linked to the thermochemical fields.

4.2 Solution method for 1D laminar flames

The numerical solution procedure for the 1D laminar flames is based on the solution strategy employed by the Sandia codes for premixed laminar flames (Kee et al., 1985). Rather than repeating the details of this strategy, only the basic features of the numerical method are presented here.

First of all, the boundary value problem is discretized by finite difference (or finite volume) approximations, yielding an algebraic set of equations. The initial approximations are made on a very coarse mesh with less than ten points. Once a converged solution has been obtained for this coarse mesh, the number of grid points is gradually increased in those regions where the gradient or the curvature of the species and temperature profiles are large. The initial estimate for the finer mesh is obtained by interpolating the coarse mesh solution. This procedure continues until the required specified resolution has been reached.

The system of algebraic equations is solved by the damped modified Newton algorithm. The radius of convergence of this Newton method is usually rather small, so that a solution can only be obtained if the initial guess is quite good already. If the Newton algorithm fails to converge, the solution procedure switches to time integration. After a limited number of time steps, the transient solution is used as a new starting point for the Newton algorithm. As the grid becomes finer the interpolated solution from the previous mesh will become a better starting estimate for the Newton method, and no additional time stepping is needed.

4.2.1 Modified damped Newton algorithm

After discretization of the ordinary differential equations on a given grid, we have a system of nonlinear algebraic equations, to be solved by means of the modified damped Newton
algorithm. Newton's method determines a sequence of iterations or approximate solutions that approach the true solution in a converging series. The approximate solution can be denoted by a vector $\phi$:

$$\phi = (F_1, G_1, T_1, Y_{1,1}, \ldots, Y_{N,1}, \ldots, F_M, G_M, T_M, Y_{1,M}, \ldots, Y_{N,M})^T$$

(4.38)

where $m = 1, \ldots, M$ denotes the mesh point ($M$ is the number of grid points, $N$ is the number of species). The above notation holds for laminar diffusion flames; in case of laminar premixed flames, the $F_m$ and $G_m$ are replaced by the local mass flow $M_m$. In general, the approximate solution $\phi$ does not exactly fulfill the true solution when substituted into the discretized equations, but it will equal a residual vector $F$. The purpose of the solution routine is to find a solution vector $\phi$ that satisfies:

$$F(\phi) = 0$$

(4.39)

The vector $F$ is composed of the residuals of the continuity equation, the momentum equation (for laminar diffusion flames), the temperature equation and the species conservation equations. The ordering of the $F$-vector is analogous to the ordering of $\phi$.

Provided the initial estimate $\phi^{(0)}$ is sufficiently good, Newton's method will give a sequence $\{\phi^{(n)}\}$ that converges rapidly to the solution of the nonlinear equations $F(\phi) = 0$. The standard form of the algorithm reads:

$$\phi^{(n+1)} = \phi^{(n)} - \left(\frac{\partial F}{\partial \phi}\right)^{-1} F(\phi^{(n)})$$

(4.40)

This form, however, is not suited for practical use. On the one hand, evaluation of the Jacobi matrices $J^{(n)} = \partial F / \partial \phi^{(n)}$ for each iteration $n$ is time consuming. Secondly, often a very accurate initial estimate $\phi^{(0)}$ is required to ensure convergence.

As a remedy, the Jacobi matrix $J^{(n)}$ is replaced by one from a previous iteration step in the algorithm in order to save computing time. Furthermore, the full step from $\phi^{(n)}$ to $\phi^{(n+1)}$ is damped by a damping parameter $\lambda^{(n)}$. The iteration thus becomes:

$$\phi^{(n+1)} = \phi^{(n)} - \lambda^{(n)} \left(J^{(n)}\right)^{-1} F(\phi^{(n)})$$

(4.41)

where $0 \leq \lambda^{(n)} \leq 1$ and $J^{(n)} = J^{(n-1)}$. The inverse Jacobi matrix in the above equation is not computed, but instead a system of linear equations $J^{(n)} \Delta \phi^{(n)} = -F(\phi^{(n)})$ is solved for the undamped correction vector $\Delta \phi^{(n)} \equiv \phi^{(n+1)} - \phi^{(n)}$.

The selection of the Jacobi matrix and the parameter $\lambda^{(n)}$ is governed by a look-ahead procedure. Having tentatively chosen the new solution vector $\phi^{(n+1)}$, the program uses this vector to calculate the next solution $\phi^{(n+2)}$. The vector $\phi^{(n+1)}$ is accepted as the new solution if the undamped steps decrease in magnitude:

$$\left|\left(J^{(n)}\right)^{-1} F(\phi^{(n+2)})\right| < \left|\left(J^{(n)}\right)^{-1} F(\phi^{(n+1)})\right|$$

(4.42)
4.2. Solution method for 1D laminar flames

In this manner, the iteration is prevented from stepping away from the initial region where there is good reason to believe the solution lies. If \( \phi^{(n+1)} \) fails this test, the algorithm retries the step with a halved damping parameter or a new Jacobi matrix. Initially, the parameter \( \lambda^{(n)} \) is chosen as large as possible with the constraint that \( \phi^{(n)} \) must not violate physical bounds upon the variables. For example, the temperature should always fall in a realistic range, and all mass fractions fall between zero and one.

The Newton iteration continues until the maximum norm of the undamped correction vector \( \Delta \phi^{(n)} \) is reduced to within the desired tolerance. Convergence is reached when:

\[
\| \Delta \phi \| \leq \max(A, R \| \phi \|)
\]  

(4.43)

where \( A \) is an absolute tolerance and \( R \) a relative tolerance. Both criteria are necessary, since \( A \) specifies the number of significant digits the solution should contain, and \( R \) excludes components smaller than \( A \) from the relative convergence criteria (otherwise machine precision would be required for intermediate species which may well be present in mass fractions smaller than \( 10^{-20} \)). Thus, \( A \) defines which species are taken into account when looking at the accuracy of the solution, and \( R \) will provide the number of accurate digits of the solution. Typically, \( R \) will be of the order \( 10^{-4} \), and \( A \) will be much smaller, say \( 10^{-10} \).

If damping cannot produce an acceptable correction, then a new Jacobi matrix is computed. If, using this new Jacobi matrix, the damped Newton step is still rejected, then the algorithm will switch to time stepping.

4.2.2 Jacobi matrix

The Jacobi matrix is a large banded block-tridiagonal matrix. In principle, analytic expressions for the Jacobi elements could be derived. This is a very difficult task and not very efficient, since the derivation would have to be repeated for any new physical or chemical model studied. Moreover, the modified Newton method works well with estimated (and hence less accurate) Jacobi matrices. Therefore, the Jacobi matrix is evaluated numerically by finite difference perturbations:

\[
J_{ij} \approx \frac{F_i(\phi_j + \delta) - F_i(\phi_j)}{\delta}
\]  

(4.44)

where \( \delta = r \phi_j + a \). Here \( r \) and \( a \) which denote the relative and absolute perturbations are chosen equal to the square root of the computer's unit roundoff.

From the above equation it is seen that with a single perturbation of an element \( \phi_j \) of the solution vector an entire column \( J_{ij}, i = 1, \ldots, M \times (N + 3) \) of the Jacobi matrix can be computed. Because the matrix is banded, several of its columns can be evaluated at once. When two or more columns share no non-zero rows, then they can be evaluated numerically by a single perturbation of the \( \phi \) vector. This is important for computational efficiency, since operations on the Jacobi matrix are the most expensive parts of the algorithm.
4.2.3 Adaptive gridding

Starting on a relatively coarse mesh has several important advantages. Firstly, the Newton algorithm is more likely to converge on a coarse mesh than on a finer mesh, bearing in mind that the initial guess will usually be rather inaccurate. Secondly, the number of variables is small, reducing computational costs per iteration.

Ultimately, the solution is to be obtained on a fine grid. As the solution is computed on each successively finer grid, the starting estimates obtained after interpolation of the previous results will become better and better, and the modified Newton method will work more efficiently with less iterations. Hence, although successively finer grids will require more time and memory capacity, the number of iterations for a finer grid will decrease as a result of improving initial estimates.

The adaptive placement of the grid points to refine the mesh is carried out in such a way that the total number of grid points needed to achieve the desired accuracy is minimized. Many grid points will fall in regions where gradients or curvature are large, and only a few grid points are placed in regions where gradients are almost zero. Gradients are resolved by bounding the variation in the solution components between mesh points as:

\[
|\phi_{n,m} - \phi_{n,m-1}| \leq \delta (\max \phi_n - \min \phi_n) \tag{4.45}
\]

where \(n\) refers to the variable and \(m\) to the grid point. Analogously, curvature in the solution is bounded as:

\[
\left| \left( \frac{d\phi_n}{d\eta} \right)_m - \left( \frac{d\phi_n}{d\eta} \right)_{m-1} \right| \leq \gamma \left( \max \frac{d\phi_n}{d\eta} - \min \frac{d\phi_n}{d\eta} \right) \tag{4.46}
\]

Each of the above expressions is evaluated between all of the neighbouring mesh points. If the inequality is not satisfied in a given subinterval, then a new grid point is placed at the midpoint of the interval. The parameters \(\delta\) and \(\gamma\) are the governing parameters for this adaptive gridding process. If a finer mesh has been generated an initial estimate for a renewed Newton step is obtained by linear interpolation from the solution on the coarse mesh onto the fine mesh. This adaptation is performed each time a converged solution has been computed, until on all mesh points the above inequalities are satisfied.

The above grid refinement procedure will only work for stationary problems. If the regions of steep gradients would move away as a result of some transient (physical or numerical) phenomenon, the algorithm would become very inefficient, leaving old grid points in regions where a coarser mesh would be sufficient. To circumvent this, a restart option was built into the OPPDIF code, allowing a new initial estimate to be interpolated from an intermediate solution obtained previously, with a rearrangement of grid points. An similar procedure was added to the PREMIX code. Using this option greatly reduced computational costs, when using previously obtained solutions as initial estimates for problems with new model parameters or boundary conditions.
4.2. Solution method for 1D laminar flames

4.2.4 Time stepping

The steady-state flame solution that is sought can always be regarded as the result of some physical transient process. Determining the steady solution by solving the transient equations is a very reliable but often slow method. Therefore the modified Newton method, which converges very rapidly (when it converges) is to be preferred. If the iteration does not converge, then a new (better) starting estimate has to be found.

Time stepping is used to go from one trial solution which lies outside the domain of convergence of Newton’s method to another trial solution which falls inside the domain of convergence. It is important to choose the number of time steps and the size of the time step such that the time stepping inter-mezzo is as efficient as possible. Adding the time derivatives to the ordinary differential equations yields a system of parabolic partial differential equations. The solution of this system is obtained via the backward Euler method, which is an implicit time stepping procedure.

The time dependent problem is solved by the same Newton method as the steady-state problem. The important difference is that the transient problem is much more likely to converge. For a sufficiently small time step, convergence should always be the case. The new solution \( \phi^{(n+1)} \) will approach the initial solution \( \phi^{(n)} \) if the time step approaches zero. Mathematically, this leads to a Jacobi matrix which has a factor \( 1/\Delta t \) on the diagonal. The condition number of the Jacobi matrix hence is reduced as the time step is decreased. If the condition number is lower, better convergence is achieved. Generally speaking we have a trade-off between convergence and progress towards the steady solution. For the laminar premixed flames, 100 consecutive time steps of around \( 10^{-5} \) seconds, are often sufficient before retrying the Newton method. For the laminar diffusion flames, more time steps are sometimes required, depending on the problem.

4.2.5 Sensitivity analysis

Sensitivity analysis yields information to qualitatively understand how the solution depends on a number of parameters in the model. Once the Jacobi matrix for the steady-state problem has been calculated, the sensitivity coefficients can be computed easily. In the present application, we are only interested in the first order sensitivity coefficients. The boundary value problem is rewritten in terms of the vector \( \alpha \) which contains all the relevant parameters on which a sensitivity analysis is to be performed:

\[
F(\phi; \alpha) = 0
\]  
(4.47)

In particular, \( \alpha \) may contain the pre-exponential factors in the Arrhenius expressions for the various elementary reactions of the reaction mechanism. Differentiation with respect to \( \alpha \) yields a matrix equation for the sensitivity coefficients:

\[
\frac{\partial F}{\partial \phi} \frac{\partial \phi}{\partial \alpha} + \frac{\partial F}{\partial \alpha} = 0
\]  
(4.48)

The first matrix is the Jacobi matrix \( J \) of the original system. The third matrix \( \partial F/\partial \alpha \) is the matrix of the partial derivatives of \( F \) with respect to the parameters. Each column of
this matrix indicates the dependence of the residual vector \( \mathbf{F} \) on a single parameter \( \alpha_l \). The sensitivity coefficients are defined as \( \frac{\partial \phi}{\partial \alpha} \). This matrix contains information on how each parameter affects the temperature, the velocities and the species mass fractions at each point in the flame (i.e. at each grid point). Each column again reveals the dependence of the solution vector on a particular parameter.

The Jacobian matrix \( \mathbf{J}^{(n)} \) is already available from the solution of the original boundary value problem. The parameter derivatives which constitute the third matrix in the above equation are computed by means of a perturbation method similar to the determination of the Jacobian matrix, as explained previously. Therefore, one obtains a linear system of equations, which can be solved column by column for the sensitivity coefficient matrix. Standard routines are available for this.

The raw sensitivity coefficients should better be manipulated before they are interpreted. First of all, we calculate normalized sensitivity coefficients in the form of logarithmic derivatives:

\[
\frac{\partial \ln Y_i}{\partial \ln \alpha_l} = \frac{\alpha_l}{Y_i} \frac{\partial Y_i}{\partial \alpha_l}
\]  

(4.49)

Moreover, it may be desirable to work in molar quantities rather than mass quantities. In that case, the coefficients are transformed into:

\[
\frac{\alpha_l}{X_i} \frac{\partial X_i}{\partial \alpha_l} = \frac{\alpha_l}{Y_i} \frac{\partial Y_i}{\partial \alpha_l} - \frac{\alpha_l M}{\bar{M}} \sum_{j=1}^{N} \frac{1}{M_j} \frac{\partial Y_i}{\partial \alpha_l}
\]  

(4.50)

where \( \bar{M} \) is the mean molecular weight of the mixture.

### 4.3 Numerical aspects of PDF integration

In numerical flame simulations the PDF parameters have to be determined numerically as a function of \( \xi \) and \( \xi^{n2} \), and the integration of (3.28) has to be carried out with sufficient accuracy. The determination of the PDF parameters for the single and double Dirac functions is simple, and the numerical evaluation of (3.28) is straightforward. The same holds for the top-hat PDF, which has a well-defined width. A suitable numerical integration scheme is the trapezoidal quadrature (Press \textit{et al.}, 1986) with about 100 intervals for four-digit accuracy. The numerics of the \( \beta \)-function and the Gaussian distributions are more complicated and will be treated below.

#### 4.3.1 Beta function integration

In order to integrate the \( \beta \)-function PDF over all \( \xi \)-values, the parameters \( a \) and \( b \) are found analytically from \( \tilde{\xi} \) and \( \xi^{n2} \). An efficient quadrature scheme is the Gauss-Legendre quadrature (Wormeck, 1983), which considerably reduces the required number of integration intervals. The Gauss-Legendre scheme is based on the transformation:

\[
\int_{-1}^{1} \psi(z) dz = \sum_{n=1}^{N} w_n \psi(z_n')
\]  

(4.51)
4.3. Numerical aspects of PDF integration

where \( w'_n \) and \( z'_n \) are the weights and roots of the Legendre polynomials.
Transformation to the interval \([0, 1]\) yields:

\[
\int_0^1 \psi(z) dz = \sum_{n=1}^N w_n \psi(z_n)
\]  
(4.52)

with \( w_n = \frac{1}{2} w'_n \) and \( z_n = \frac{1}{2} (z'_n + 1) \). For prescribed \( N \) the weights \( w_n \) and roots \( z_n \) can be computed in advance and will remain fixed independent of the PDF shape. To avoid numerical problems, it is convenient to use logarithmic values of all parameters:

\[
\bar{\phi} = \int_0^1 \tilde{f}_\xi(\zeta) \phi(\zeta) \, d\zeta = \frac{\Gamma(a + b)}{\Gamma(a) \Gamma(b)} \sum_{n=1}^N w_n z_n^{a-1}(1 - z_n)^{b-1} \phi(z_n)
\]

\[
= \exp \{ \ln \Gamma(a + b) - \ln \Gamma(a) - \ln \Gamma(b) \} \times \sum_{n=1}^N \phi(z_n) \exp \{ \ln w_n + (a - 1) \ln z_n + (b - 1) \ln(1 - z_n) \}
\]  
(4.53)

In this summation all terms are known in advance, except the values of \( a \) and \( b \), and the coupling function \( \phi(z_n) \) which depends on \( \bar{\xi} \) and \( \bar{h} \) in the non-adiabatic case. If \( \bar{\xi} \bar{h}^2 \) is smaller than a suitably chosen threshold number, then the \( \beta \)-function can be replaced by a Dirac function at \( \xi = \xi \).

If \( \bar{\xi} \bar{h}^2 \) is non-negligibly small the \( \beta \)-function will resemble a Gaussian distribution. The Gauss-Legendre scheme will only be accurate if the roots \( z_n \) are closely interspaced, so \( N \) has to be very large. A more efficient integration scheme then employs properties of the normal distribution, by defining an effective integration interval \([\xi - 5\sigma, \xi + 5\sigma]\), with \( \sigma = \sqrt{\bar{\xi} \bar{h}^2} \). Quadrature can then be carried out as for the top-hat PDF.

A third method of integration is to use an adaptive technique, which chooses the non-uniform intervals \( \xi_n \) depending on the curvature of the integrand function \( \phi(\xi) \times \tilde{f}_\xi(\zeta) \). In regions where the integrand has small curvature only a few coarse intervals are required to reach the desired accuracy of integration. In other regions a fine quadrature mesh may be needed. This adaptive method is very accurate for relatively few intervals, but it is computationally expensive. In the present study it was only used if the former two quadrature methods were found to be inaccurate for \( N \sim 200 \). The definitions (3.33a-3.33c) were used as test cases for the PDF integration scheme.

Near the boundaries of the integration domain problems may occur if \( a, b < 1 \). In that case the integrand will be unbounded as \( \xi \) approaches zero or unity, respectively. To perform the integration, some approximations are needed. A small interval \([0, \Delta]\) can be calculated apart from the rest of the integration domain. On this small interval, the function \( \phi(\xi) \) will be approximated by a linear function: \( \phi = \phi(\frac{1}{2}\Delta) + (\xi - \frac{1}{2}\Delta)\phi'(\frac{1}{2}\Delta) = p + q \xi \), which is admissible if \( \Delta \) is small enough. Furthermore, the term \((1 - \xi)^{b-1}\) can be approximated by a Taylor series expansion:

\[
(1 - \xi)^{b-1} = 1 - (b - 1)\xi + \mathcal{O}\left(\xi^2\right)
\]
With these approximations the integration can be carried out analytically, where second and higher order terms are neglected, yielding:

$$
\int_0^\Delta \phi(\zeta) \tilde{f}_\xi(\zeta) d\zeta = \frac{\Gamma(a+b)}{\Gamma(a)\Gamma(b)} \left\{ \frac{p}{a} + \left( \frac{q-(b-1)p}{a+1} \right) \Delta + \mathcal{O}(\Delta^2) \right\} \Delta^a \tag{4.54}
$$

Often a zeroth-order or first-order approximation will do, provided $\Delta$ is small enough. Near $\xi = 1$ a similar approach can be used, after applying a coordinate transformation by defining $\zeta' = 1 - \zeta$:

$$
\int_{1-\Delta}^1 \phi(\zeta) \tilde{f}_\xi(\zeta) d\zeta = \int_0^\Delta \phi(1 - \zeta') \tilde{f}_\xi(1 - \zeta') d\zeta' = \frac{\Gamma(a+b)}{\Gamma(a)\Gamma(b)} \int_0^\Delta \phi(1 - \zeta') \zeta'^{a-1} \Delta^b d\zeta' \tag{4.55}
$$

For finite $\Delta$ it is seen that both integrations (4.54) and (4.55) will yield a non-negligibly small contribution to the total PDF quadrature. This is due to the Dirac-function-like behaviour of the singular $\beta$-function near $\xi = 0$ or $\xi = 1$.

This particular treatment of cases where the integrand becomes singular near the interval edges can also be dealt with by the so-called open integration schemes, such as open midpoint integration (Press et al., 1986). In such schemes successive refinement is applied with a uniform grid spacing, where the function evaluations will be performed not at the interval boundaries but at their midpoints, hence no singularities will be encountered. A disadvantage of such a scheme, however, is that refinement will be applied to the whole integration domain, although it is required only at locations where the integrand has a very steep gradient. As a result this may lead to excessive computing times with many superfluous function evaluations. This example merely illustrates the fact that care has to be taken as to which quadrature procedure is best suited to obtain a quick and accurate solution. Often some analytical approximations and concepts can be very helpful.

### 4.3.2 Determination of the Gaussian PDF parameters

The parameters in the formula for the truncated or clipped normal distributions are defined by implicit equations. The set of non-linear parameter equations can be solved numerically. For this purpose the set is rewritten as:

$$
F_1(\mu, \sigma) \equiv \mu + \frac{\sigma B}{A} - \tilde{\xi} = 0 \tag{4.56}
$$

$$
F_2(\mu, \sigma) \equiv \mu^2 + \sigma^2 + \frac{\sigma \mu B}{A} - \frac{C}{A} - \tilde{\xi}^2 = 0 \tag{4.57}
$$

for the truncated Gaussian PDF, and analogously for the clipped PDF. This means that we have to find the roots of the functions $F_1$ and $F_2$. Several methods are available to
achieve this. It is emphasized, however, that no general formulation exists which will unambiguously converge to the correct solution.

If a good initial estimate of the solution is known, however, the iterative Newton-Raphson method will give quick convergence. Starting from an initial guess \( \mu = \xi, \sigma = \sqrt{\xi''^2} \), the correction terms for the iterative solution are:

\[
\Delta \sigma = \frac{F_1 \frac{\partial F_2}{\partial \mu} - F_2 \frac{\partial F_1}{\partial \mu}}{\frac{\partial F_1}{\partial \mu} \frac{\partial F_2}{\partial \sigma} - \frac{\partial F_1}{\partial \sigma} \frac{\partial F_2}{\partial \mu}} \tag{4.58}
\]

\[
\Delta \mu = \frac{-F_1 - \frac{\partial F_1}{\partial \sigma} \Delta \sigma}{\frac{\partial F_1}{\partial \mu}} \tag{4.59}
\]

Consequently, \( \mu \) and \( \sigma \) can be determined if \( \xi \) and \( \xi''^2 \) are known.

If a good initial guess for \( \mu \) and \( \sigma \) is not available, the Newton-Raphson iteration procedure will diverge. This will often be the case if \( \xi \) lies close to 0 or 1 and \( \xi''^2 \) is relatively large, causing the truncated Gaussian PDF to have a long tail and a \( \mu \) which falls outside the domain of interest \( 0 \leq \xi \leq 1 \). In that case a more robust method is available. We define:

\[
\mu_m = \mu_0 + m \Delta \mu
\]

\[
\sigma_n = \sigma_0 + n \Delta \sigma
\]

where \( m \in \{0, M\} \) and \( n \in \{0, N\} \). This discretization produces a set of combinations \((\mu_m, \sigma_n)\), with \( 0 \leq m \leq M \) and \( 0 \leq n \leq N \). Since we know that \( \sigma \geq 0 \), it seems logical to take \( \sigma_0 = 0 \), and \( N \) and \( \Delta \sigma \) should cover a realistic range of possible \( \sigma \)-values. For \( \mu \) we generally cannot state that \( \mu \geq 0 \), so \( \mu_0 \) should be taken smaller than zero. The number of steps \( M \) and the step size \( \Delta \mu \) should be chosen such that \( \mu_M = \mu_0 + M \Delta \mu = 1 + \mu_0 \), since we may anticipate symmetry at \( \xi = 0 \) and \( \xi = 1 \).

Now we define the residual of \( F_1 \) for each possible combination as \( R_{m,n}^1 = F_1(\mu_m, \sigma_n) \). For a given \( m \), we search for a value \( \sigma_{n_1} \) such that \( R_{m,n_1}^1 = 0 \) or \( \text{sign}(R_{m,n_1}^1) = -\text{sign}(R_{m,n_1+1}^1) \). In practice, the root \( R_1 = 0 \) will lie between \((\mu_m, \sigma_{n_1})\) and \((\mu_m, \sigma_{n_1+1})\). By means of interpolation between \( \sigma_{n_1} \) and \( \sigma_{n_1+1} \) we can find with great accuracy the exact solution \( \sigma_m^1 \) belonging to \( \mu_m \), such that \( R_{m,n_1+1}^1 \) is arbitrarily close to zero. The accuracy depends on the interpolation scheme and the choice for \( \Delta \sigma \). Now we have constructed a set of points \((\mu_m, \sigma_m^1)\) which constitute roots of the function \( F_1 \) for \( 0 \leq m \leq M \).

Secondly, we calculate all residuals \( R_{m,n}^2 = F_2(\mu_m, \sigma_n) \) of the function \( F_2 \). For given \( m \), we search the value \( n_2 \) for which \( R_{m,n}^2 \) changes sign or is equal to zero, just as we did for \( R_{m,n}^1 \). With this new \( n_2 \), we can determine \( \sigma_m^2 \) such that \( R_{m,n_2}^2 \) is very close to zero. In other words, we have constructed a set of points \((\mu_m, \sigma_m^2)\) with \( m \in \{0, M\} \) which are roots of \( F_2 \). As a result we have two one-dimensional tables, being the roots of \( F_1 \) and \( F_2 \), respectively.
In order to find simultaneous roots for \( F_1 \) and \( F_2 \), which in fact is the wanted solution of the set of non-linear equations, we now determine the value \( m_0 \) for which \(|\sigma_{m_0}^1 - \sigma_{m_0}^2|\) is minimal. Then \((\mu_{m_0}, \sigma_{m_0}^1)\) or equivalently \((\mu_{m_0}, \sigma_{m_0}^2)\) is the solution of \( F_1 = F_2 = 0 \).

This whole procedure is rather tedious, but straightforward. Numerically speaking there are no problems, but for each grid point where we have a different combination \((\xi, \xi'')\) the functions \( F_1 \) and \( F_2 \) are different, so the tabulation of \( \sigma^1 \) and \( \sigma^2 \) has to be performed once after time.

It is possible, however, to save a considerable amount of computing time, by defining new functions \( \tilde{F}_1 \) and \( \tilde{F}_2 \):

\[
\tilde{F}_1(\mu, \sigma) = F_1(\mu, \sigma) + \xi
\]
\[
\tilde{F}_2(\mu, \sigma) = F_2(\mu, \sigma) + \xi'' + \xi'''
\]  

Consequently, \( \tilde{F}_1 \) and \( \tilde{F}_2 \) are no longer explicit functions of \( \xi \) and \( \xi'' \), but they only depend on \( \mu \) and \( \sigma \). Now, we construct tables for the residuals of \( \tilde{F}_1 \) and \( \tilde{F}_2 \) rather than for those of \( F_1 \) and \( F_2 \) and the same tables can be used over and over again for each combination \((\xi, \xi'')\). For given \( \xi \) and \( \xi'' \) the solution is found at the locations where \( \tilde{F}_1^{m,n} = \tilde{F}_2^{m,n} \). If given\( \xi \) and \( \xi'' \) the solution is found at the locations where \( \tilde{F}_1^{m,n} = \tilde{F}_2^{m,n} \). This can be done by a quick two-dimensional search algorithm.

The values of \( M, N, \Delta \mu \) and \( \Delta \sigma \) should be chosen such that the whole domain of possible combinations \((\mu, \sigma)\) is covered with a relatively fine grid. The tabulation of independent roots of \( \tilde{F}_1 \) and \( \tilde{F}_2 \) can be done entirely in the preprocessing. The actual determination of the correct PDF parameters is then reduced to a relatively quick and simple search algorithm and interpolation procedure. As a refinement, the interpolation can be skipped, and the estimated solution \((\mu, \sigma)\) can be used as an initial guess for the Newton-Raphson iteration.

It turned out that this method works well if \( \xi'' \) is not too large. In the most extreme cases floating point problems will occur and the truncated Gaussian PDF was replaced by the clipped Gaussian PDF. The main difference of the clipped Gaussian distribution compared to the truncated distribution lies in the fact that \( \mu \) will usually fall inside the interval \([0,1]\), even if \( \xi'' \) is very large (see figure 3.13).

### 4.3.3 Integration of the Gaussian distribution

For finite \( \mu \) and \( \sigma \) no difficulties will arise, since the PDF shows no singularities. Therefore a trapezoidal integration scheme will be suitable, similar to the top-hat PDF or non-singular \( \beta \)-function. The PDF parameter \( \mu \) reveals the location of the PDF maximum, and \( \sigma \) indicates the width of the distribution. This can be used to our advantage when integrating the distribution. The major part of the PDF will fall inside the interval \( \xi \in [\mu - 5\sigma, \mu + 5\sigma] \).

Hence it is numerically efficient to replace the original integration interval \([0,1]\) by the interval given above. An important advantage of this approach is that it adjusts the quadrature interval in such a way that the PDF peak is integrated accurately, even if the peak is very thin.
The error made as a result of this interval truncation usually is very small, except when \( \mu \leq 0 \) or \( \mu \geq 1 \). This will sometimes be the case for the truncated Gaussian distribution, in which case the quadrature interval has to be enlarged suitably. Based on the considerations discussed above, the quadrature algorithm has been implemented in such a way that accurate results are obtained without excessive computing times. The Gauss-Legendre integration scheme was found to be inefficient for the integration of the normal distributions.

### 4.4 Adaptive tabulation of flame properties

#### 4.4.1 Introduction

Even although the assumption of a conserved-scalar chemistry model greatly simplifies the numerical effort in the simulation of turbulent diffusion flames, CPU times can still be prohibitive when dealing with a large number of grid cells. A substantial improvement is achieved when look-up tables are employed for the dependent thermochemical variables as functions of the conserved scalar. In the case of non-adiabatic non-premixed flames, the independent variables are the mixture fraction \( \xi \) and the enthalpy \( h \). Within the context of the presumed PDF closure, any mean thermochemical quantity is derived from:

\[
\bar{\phi} = \int_{h_{\text{min}}}^{h_{\text{max}}} \int_{0}^{1} \tilde{f}_{\xi h}(\zeta, \eta) \phi(\zeta, \eta) \, d\zeta \, d\eta
\]  

(4.62)

Here \( \tilde{f}_{\xi h} \) represents the Favre joint PDF of mixture fraction and enthalpy. As described in Chapter 3, the 2D integration is replaced by a 1D integration, using the local relationship:

\[
h = h(\xi, \tilde{\xi}, \tilde{h})
\]  

(4.63)

This yields:

\[
\bar{\phi} = \int_{0}^{1} \tilde{f}_{\xi}(\zeta) \phi(\zeta, \tilde{\xi}, \tilde{h}) \, d\zeta
\]  

(4.64)

It is possible to construct a 2D look-up table for the instantaneous function \( \phi = \phi(\xi, h) \), and to evaluate the integral (4.64) during the numerical simulation in every grid cell and for every iteration. This already saves an enormous amount of CPU time, in the order of a factor 10 or even more (for equilibrium chemistry models). However, the total numerical effort involved in the evaluation of the PDF integration still is huge, especially for the more complex PDF shapes such as the \( \beta \)-function.

Here, we decided to take the tabulation one step further, and to construct a table for the mean thermochemical quantities:

\[
\bar{\phi} = \mathcal{F}(\tilde{\xi}, \tilde{h}, \tilde{\phi})
\]  

(4.65)

Hence a 3D table is used to store \( \bar{\phi} \) prior to the iterative flow field simulation. Having selected a given PDF type and a chemistry model, the 3D tabulation is carried out as
a preprocessing step. Since many variables are tabulated simultaneously, all behaving differently in the space of allowed values of \((\xi, h, \xi')\), special consideration has been devoted to a flexible and efficient tabulation and look-up algorithm.

For natural-gas combustion, the expected variables to be stored in the table are the mean mixture properties, such as temperature, temperature variance, black body emissivity, density, mixture molar mass, mixture species diffusivity, heat conductivity, specific heat, and the species properties, such as average mass fractions, mole fractions, concentrations and their variances. When storing all of these properties in a table, at least 50 different properties can thus be identified for a moderately sized problem with no more than 10 species.

A relatively fine grid spacing is required to allow for a sufficiently accurate multi-linear interpolation. It is estimated that the number of grid points in a 3D table will exceed 100,000 if a simple multi-linear interpolation routine is to be used, on a tensor product tabulation grid. For the problem size sketched above, the table would at least involve over 40 Mb of storage space.

Such a large storage capacity claim is undesirable for practical calculations. We found that an adaptive tabulation strategy saves a large amount of storage space and tabulation time. The next subsection describes in detail the mathematical and numerical aspects of building such an adaptive table, and the features of an accompanying look-up scheme.

### 4.4.2 General adaptive tabulation algorithm

The adaptive tabulation algorithm presented here is based on the algorithm described by Norris and Pope (1991). Its aim is to ensure overall interpolation accuracy for all properties stored in the table, with a minimum number of grid nodes. The physical and chemical models underlying the property calculation as functions of the independent variables are assumed to be known. As presented here, the algorithm will work for an arbitrary function which satisfies the basic constraints explained below. The prime criterion for grid refinement is the curvature (second derivative) of the function \(f(\xi)\) within the 'physical' domain of interest. This criterion is related to the use of a multi-linear interpolation scheme afterwards. If the interpolation would be of higher order accuracy, the refinement criterion should be adjusted for higher order derivatives as well.

If multi-linear interpolation is adopted, the possible errors due to the interpolation scheme will be zero if the function \(f\) has a constant gradient \(\nabla f\). A small number of grid nodes will be sufficient for an exact representation of the function \(f\). For a function with \(\nabla^2 f \neq 0\) the grid node inter-spacing will determine the interpolation accuracy.

To translate these simple notions into a mathematical and numerical algorithm, some 'physical' information is required. First of all, the number of independent variables \(N\) defines the \(N\)-dimensional hyper-space in which the function \(f(\xi)\) is to be tabulated. Next, the function \(f\) must be known analytically or numerically within a prescribed 'physical' domain in \(\xi\)-space. This physical domain need not be rectangular. The function \(f\) and its gradient \(\nabla f\) should behave continuously within the physical domain. Finally, the function must not become unbounded near the boundaries of the physical domain.
4.4. Adaptive tabulation of flame properties

The adaptive tabulation algorithm works on a given ‘computational’ domain in \( x \)-space. The computational domain is assumed to be rectangular, and does not have to coincide with the physical domain. There are two ways of defining the computational domain. The first is a rectangle in which (partly) overlaps the ‘physical’ domain. In that case, some functional value must be defined for \( x \)-values which fall outside the ‘physical’ domain. The second method maps the allowed physical domain onto a rectangle by suitable mapping function. This is only possible if such a mapping function can be defined analytically. If not, the first method can be used.

The computational domain is subdivided into a prescribed number of uniform grid cells, the so-called coarse initial grid. The cell’s angular points (vertices) constitute the actual table. For each initial grid node \( n \), characterized by its position \( x_n \) in the hyper-space, the desired properties \( f_p(x) \) are computed and stored.

During the iterative tabulation procedure, each cell is checked for a possible subdivision into two smaller ‘child’ cells. The decision for cell splitting is based on the curvature of all the functions \( f_p \) in all diagonal directions of the cell. If all the cell’s vertices fall outside the physical domain of interest, any cell splitting is useless and the cell is skipped for further refinement. The user has to specify the threshold curvature level for each property \( f_p \) separately. If the criteria for all properties and all directions are satisfied, the cell is left unchanged, and no splitting is done. However, if at least one of the criteria in at least one of the diagonal directions is violated, then the cell is to be further refined.

As all cells are assumed to be rectangular boxes in hyper-space, cell splitting will only be carried out in one of the lateral directions, in order to preserve the rectangular cell structure. To determine the splitting direction for a ‘splittable’ cell, the curvature is evaluated in the lateral directions. The largest curvature will determine the splitting direction. The new cells are added to the list of grid cells, as are the new grid nodes. For each new node the properties are stored in the table.

This process is repeated again and again until every cell meets all the curvature criteria. Only newly added cells are checked after every refinement step, the old cells having already been investigated. To avoid an indefinite refinement procedure, the maximum number of refinement levels is specified by the user. Finally, a table of grid node positions \( x_n \) and properties \( f_p(x_n) \) is constructed. The cells are merely structures within the set of grid nodes, needed for the splitting procedure and for the look-up algorithm to be used afterwards. In the numerical algorithm, pointers are associated with each cell and each node, to be able to retrieve the dependencies and structures of cells and nodes.

Per grid point, the computational effort involved in this adaptive tabulation procedure definitely is larger than for a simple uniformly spaced grid. Additional information has to be stored, and the look-up algorithm will require extra time compared to the uniform case. The advantages will outweigh the drawbacks, however, if properties with a strong dependence on the independent variables are to be stored and if the table dimension becomes larger than 2. The next section will treat the numerical algorithm in more detail.
4.4.3 Detailed algorithm description

Grid and cell structure

Before proceeding to the actual description of the algorithm, some basic conventions and notions used will be discussed here. The basic structures in the algorithm are called a 'node' and a 'cell'. The nodes and cells are interrelated in the sense that the exact shape and location of the cell in $\mathbf{x}$-space is defined completely by the positions of its vertex nodes. In the sequel we will assume the cell to be a rectangular box in hyper-space, which will facilitate the description. In general, however, the cells do not necessarily have to be boxes, but may also have other shapes, such as pyramids, prisms, tetrahedrons etc. Special splitting rules may be defined for these structures.

The basic variable which predefines the cell structure is the number of its vertices. If the number of independent variables is $N$, being the dimension of the $\mathbf{x}$-space, then the number of cell vertices $N_v = 2^N$, the number of diagonal directions $N_d = 2^{N-1}$ and the number of lateral directions is $N$. The ordering of the vertices is done by a binary representation, as depicted in figure 4.4. The last binary digit in the representation denotes the $x_1$-direction, the last-but-one digit denotes the $x_2$-direction and so forth. The ordering is non-unique, but has several advantages as we shall see later. From the binary number the decimal vertex number $v$ can easily be retrieved:

$$ v = 1 + \sum_{i=1}^{N} b_i 2^{i-1} $$ (4.66)

For example, in a 3D table, the binary number 000 represents vertex number 1, 111 represents vertex number 8 and 110 represents vertex number 7 ($= 1 + 1 \cdot 2^2 + 1 \cdot 2^1 + 0 \cdot 2^0$).

As stated before, the cells form a structure superlying the node structure. From a set of grid nodes many different cells can be constructed. All the relevant information about the shape and size of the individual cells can be obtained from the positions of its vertex nodes. To each node a unique index number $n$ is attributed, and for each node its position $\mathbf{x}_n$ and the corresponding properties $f_p(\mathbf{x}_n), p = 1, \ldots, P$ are calculated and stored ($P$
being the number of properties). Analogously, each cell has a unique index number \( k \). The cell is defined by a cross reference table of node numbers \( n_{v,k}, v = 1, \ldots, 2^N \), where the specific following order of cell vertex nodes is used (4.66).

**Initial cell structure**

The initial structure of cells and grid nodes is defined in terms of the computational \( \bar{x} \)-space, which is a rectangular box, and a given number of cells in each direction. The initial coarse cells therefore are all of uniform size. The grid nodes lie at the cell vertices. The same grid node can serve as a vertex node for more than one cell. Thus, the total number of grid nodes on the initial table is kept as small as possible.

Each cell is attributed an integer number \( c_{1k} \) representing the cell number of its first child cell. If the cell has no child cells, then \( c_{1k} = 0 \). By convention, we define the cell number of the second child cell \( c_{2k} \) to be equal to \( c_{1k} + 1 \), hence this number does not have to be stored. On the initial grid, all child cell numbers are zero. The node locations \( \bar{x}_n \) and the properties \( f_p(\bar{x}_n) \) are then computed and stored in the table.

**Curvature criteria**

Once the initial grid has been established, each coarse cell is checked for subdivision. Before any subdivision is carried out, the current cell is verified to fall (partly) within the physical \( \bar{x} \)-domain. If not, then the cell is deemed ‘external’, and is skipped for subdivision. If the cell contains at least one vertex node in the physical \( \bar{x} \)-space, the cell is deemed ‘internal’ and is checked for possible subdivision.

The curvature criteria are checked in the diagonal directions of the cell. If \( v_{1d} \) denotes a cell’s vertex number on a diagonal, then the opposite vertex number \( v_{2d} \) on the diagonal obeys:

\[
v_{1d} + v_{2d} = N_v + 1
\]  
(4.67)

The total number of diagonals is \( N_d = N_v/2 \). The curvature \( C \) of property \( p \) for a given diagonal direction \( d \) is defined to be:

\[
C_{p,d} = |f_p(\bar{x}_{1d}) - 2f_p(\bar{x}_c) + f_p(\bar{x}_{2d})|
\]  
(4.68)

In order to evaluate the \( C_p \), the cell center position \( \bar{x}_c = \frac{1}{2}(\bar{x}_{1d} + \bar{x}_{2d}) \) and the corresponding properties have to be computed. For all diagonal directions \( d = 1, \ldots, N_d \) the criteria \( C_{p,d} < \epsilon_p \) are verified for all properties \( p = 1, \ldots, P \). Of course the \( \epsilon_p \) should all fulfill \( \epsilon_p > 0 \). If at least one of the \( C_{p,d} \) violates its criterion, the cell is further divided into two new cells, otherwise the cell is skipped. Thus, the curvature criteria involve only one new property evaluation, irrespective of the table dimension \( N \).

**Cell refinement**

If a cell is to be subdivided, the curvature is determined for the \( N \) lateral directions. This involves the evaluation of properties on the cell’s axes, i.e. on the cell’s mid-faces. The
number of mid-face nodes $N_m = 2N$. The curvature of the property $p$ on which the cell splitting decision was made is then calculated in the $N$ directions. In the direction of the largest curvature the cell will be split.

The number of new nodes to be added to the node list equals $N_v/2 = 2^{N-1}$. The positions of the new nodes can easily be inferred from the splitting direction and the positions of the cell vertex nodes. The positions of the new nodes are checked to already exist in the old node list, in order to avoid table redundancy. Only for the really new nodes the properties have to be computed and stored.

The ‘old’ cell is called a ‘parent’ cell. The parent cell has two ‘child’ cells, as defined by the old vertex nodes and the newly added nodes. The first child cell is adjacent to the parent cell’s origin (vertex node $v = 1$) by definition; the second child cell is the other new cell. In this strict following order the new cells are added to the cell list. The node IDs of the new cells’ vertices are retrieved from the vertex node ID numbers of the parent cell and the node ID numbers of the new nodes. Finally, the cell refinement is completed and the next cell is checked.

After each refinement iteration, only the newly added cells are checked for further subdivision. The prescribed number of refinement levels and the various curvature criteria $c_p$ for the properties will both determine the final size of the table. The maximum number of cells to be added during each refinement step is twice the number of cells added in the previous step. If the adaptive tabulation procedure is initialized with a very coarse grid, the number of new grid cells will increase exponentially at each new level of refinement, then reach a maximum, and finally decrease until no further cells are added.

Problems at boundaries

The boundaries of the physically allowed $x$-space may give some difficulties if the property functions $f_p$ do not behave properly at the boundaries. If the physical domain has an irregular (non-rectangular) shape, some computational (coarse) grid nodes will represent non-physical values, and their corresponding properties have to be computed differently, e.g. by projection onto the boundary of the allowed domain. Hence, the gradients of the properties will exhibit a discontinuity at the boundary between the physical and the non-physical domain, resulting in an excessive and unnecessary grid refinement. This difficulty can be overcome in several ways.

By the first method, we define a so-called ‘grey’ zone near the irregular boundaries, where the refinement criteria are not enforced. The ‘grey’ region between the restricted physical domain and the complete physical domain is deemed ‘external’ for the cell-splitting algorithm. As a result, the total number of cells and grid nodes will be reduced considerably, at the expense of poor interpolation accuracy near the boundaries of the physical domain.

The second method is elegant but more complex: the allowed physical domain is transformed onto a rectangle in computational space. The existence of a suitable transformation is not the subject of this thesis; there is a strong analogy, however, with the problem of boundary-fitted mesh generation for complex multi-dimensional regions in
4.4. Adaptive tabulation of flame properties

CFD. For our purposes, it is sufficient to note that a transformation exists if the allowed physical domain has a convex shape. Each coordinate direction $x_i$ is transformed to a new variable $\eta_i$, according to $\eta_i = (x_i - x_{i,min})/(x_{i,max} - x_{i,min})$. In principle, the values of $x_{i,min}$ and $x_{i,max}$ may be functions of $x_j$, $j = 1, \ldots, i - 1$. The tabulation algorithm is modified accordingly, since the refinement is now applied to cells of the transformed grid. In the look-up procedure, the physical point $x$ is transformed prior to look-up and interpolation, which implies that the transformation parameters have to be stored along with the table. This increases the computational cost of the look-up scheme, but it saves the unnecessary storage of many grid nodes near the boundaries.

4.4.4 Table look-up algorithm

In the previous section the adaptive tabulation technique was outlined. The algorithm is designed with the look-up procedure in mind. Therefore, the tabulation starts with a coarse uniform grid, and no coarse nodes are ever removed from the table in regions where they seem redundant. This greatly facilitates the look-up scheme.

The look-up algorithm works in two modes. In the first mode, the coarse cell is determined in which the point $x$ lies. Since the size of the computational domain and the number of coarse grid cells in all directions are known in advance, this can be done efficiently. In order to avoid errors, the point $x$ is assumed to fall within the computational domain. If this is not the case, the point is projected onto the nearest domain boundary. As soon as the coarse grid cell has been found, the algorithm switches to the second mode.

In the second mode, the current grid cell is checked to have child cells. If the cell has no child cells, then this mode is left and the algorithm proceeds to the interpolation step. If the cell has child cells, the new cell in which the point $x$ lies is identified. In turn, the new cell is examined for having any child cells. This procedure is repeated until a grid cell with no child cells is reached.

Although this look-up process involves some more arithmetic operations in comparison with uniform rectangular grids, the CPU time involved is acceptably small. The speed of the look-up procedure is enhanced if the fraction of childless coarse grid cells is increased, which is achieved by choosing a finer coarse grid. If the initial grid is too fine, the aim of the adaptive tabulation procedure is violated and a uniform table is to be preferred. Once the right cell has been determined, the properties are reconstructed by multi-linear interpolation (Press et al., 1986)

4.4.5 Some examples for non-premixed flames

As discussed in the introductory section of this report, the self-adaptive tabulation technique is applied here to flame property tabulation in terms of the conserved-scalar chemistry model for non-premixed flames, in conjunction with the presumed PDF closure. In this section some particular examples are shown to illustrate the advantages of the adaptive tabulation procedure.
One-dimensional case

We have tabulated the adiabatic flame temperature $T(\xi)$ as a function of mixture fraction, for a typical natural-gas flame using the Burke-Schumann flame sheet model (Peeters et al., 1993). The function $T(\xi)$ is depicted in figure 4.5. The coarse initial grid has 20 cells

<table>
<thead>
<tr>
<th>refinement level</th>
<th>criterion 10 K</th>
<th>criterion 1 K</th>
<th>criterion 0.1 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cells</td>
<td>nodes</td>
<td>cells</td>
</tr>
<tr>
<td>0</td>
<td>20</td>
<td>21</td>
<td>20</td>
</tr>
<tr>
<td>1</td>
<td>24</td>
<td>23</td>
<td>44</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>26</td>
<td>58</td>
</tr>
<tr>
<td>3</td>
<td>38</td>
<td>30</td>
<td>68</td>
</tr>
<tr>
<td>4</td>
<td>88</td>
<td>55</td>
<td>226</td>
</tr>
<tr>
<td>5</td>
<td>104</td>
<td>63</td>
<td>266</td>
</tr>
<tr>
<td>6</td>
<td>108</td>
<td>65</td>
<td>346</td>
</tr>
<tr>
<td>7</td>
<td>110</td>
<td>66</td>
<td>364</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
and 21 nodes; the final grid will depend on the curvature criterion. In Table 4.1 we have listed the final number of cells and nodes for various curvature criteria, using the function of figure 4.5.

Figure 4.6 depicts the final grid nodes for the three curvature criteria of Table 4.1. Due to the sharp maximum of the function, the nodes are distributed very non-uniformly. Here the advantage of the tabulation method becomes apparent if one considers the number of nodes required on a uniform grid to achieve the same level of accuracy. In the case of 1 K accuracy, the number of refinement levels is 7, and the smallest cell is a factor 1/128 smaller than the original coarse cells. Hence \(1 + 20 \times 128 = 2561\) uniform grid nodes instead of 66 will be needed to have comparable accuracy.

**Two-dimensional case**

The next example shows the convergence behaviour of the tabulation procedure during the tabulation of temperature as a function of two variables, the mixture fraction \(\xi\) and the enthalpy \(h\). For convenience, we use the transformed enthalpy \(h^* \equiv h - h_{ad}\), such that \(h^* = 0\) corresponds to the adiabatic (1D) case.

The physically allowed domain of \((\xi, h)\)-values has the shape of a distorted triangle, depicted in figure 4.7. The boundary of the physical domain consists of the adiabatic line \(h^* = 0\) and the line \(h^*(\xi)\) where \(T\) is equal to the inert mixing value. In other words, the lower limit represents the case of maximum enthalpy loss by the flame. Outside this domain the temperatures attain unrealistic values. Since the physical domain cannot be covered by a rectangular grid, problems are expected near the irregularly shaped boundary. Two different methods have been compared. The first method is the standard method and uses a computational domain which overlaps the physical domain. The second method uses coordinate transformation: the enthalpy \(h^*\) is transformed to a variable \(\eta(\xi)\) which is scaled between the lowest and highest \(h^*\) allowed for each given value of \(\xi\): \(\eta_i = (h^*_i - h^*_{\text{min}})/(h^*_{\text{max}} - h^*_{\text{min}})\). This transformation is possible because the allowed physical domain has a convex shape.
Chapter 4. Numerical algorithms

**Figure 4.7:** Computational domain vs. physically allowed domain for tabulation of flame properties as a function of mixture fraction and enthalpy. Unshaded area: allowed physical domain.

**Table 4.2:** Adaptive tabulation of temperature as a function of mixture fraction and enthalpy, using the constrained-equilibrium model.

<table>
<thead>
<tr>
<th>refinement level</th>
<th>cells</th>
<th>nodes</th>
<th>refinement level</th>
<th>cells</th>
<th>nodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>121</td>
<td>9</td>
<td>2168</td>
<td>1432</td>
</tr>
<tr>
<td>1</td>
<td>258</td>
<td>209</td>
<td>10</td>
<td>2260</td>
<td>1482</td>
</tr>
<tr>
<td>2</td>
<td>440</td>
<td>325</td>
<td>11</td>
<td>2314</td>
<td>1515</td>
</tr>
<tr>
<td>3</td>
<td>662</td>
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<td>1534</td>
</tr>
<tr>
<td>4</td>
<td>894</td>
<td>615</td>
<td>13</td>
<td>2360</td>
<td>1544</td>
</tr>
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</tr>
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<td>7</td>
<td>1810</td>
<td>1209</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2030</td>
<td>1345</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In Table 4.2 the successive refinement history is tabulated if a curvature criterion of 5 K is employed. The tabulation algorithm started with a uniform grid of 10 × 10 cells. As one can see, the number of grid points grows at a slower rate than the number of cells, because different cells can share the same vertex nodes. After 15 iteration steps, the smallest cell has an area which is a fraction $2^{-15} = 1/32768$ of the coarse initial cells. Uniform tabulation would lead to 3276800 cells and a comparable amount of grid nodes. Again the self-adaptive tabulation will save large amounts of computer storage, at the expense of a more elaborate look-up procedure.
Three-dimensional case

As a final example, the average temperature, integrated by a clipped Gaussian PDF, as a function of mean mixture fraction $\tilde{\xi}$, mixture fraction variance $\tilde{\xi}^{\prime 2}$ and mean enthalpy $\tilde{h}$ is tabulated with an accuracy of 10 K. The allowed physical domain in the space of the independent variables is a combination of a triangle in $\tilde{\xi}$-$\tilde{h}$-plane and a parabola in the $\tilde{\xi}$-$\tilde{\xi}^{\prime 2}$-plane. Again a suitable grey area has been defined to avoid too many grid cells near the edges. This is shown in figure 4.8 for the $\tilde{\xi}$-$\tilde{\xi}^{\prime 2}$-plane.

<table>
<thead>
<tr>
<th>refinement level</th>
<th>cells</th>
<th>nodes</th>
<th>refinement level</th>
<th>cells</th>
<th>nodes</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1331</td>
<td>10</td>
<td>18674</td>
<td>15763</td>
</tr>
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<td>1</td>
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<td>2146</td>
<td>11</td>
<td>19996</td>
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</tr>
<tr>
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<td>3467</td>
<td>12</td>
<td>21282</td>
<td>17970</td>
</tr>
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<td>6048</td>
<td>5205</td>
<td>13</td>
<td>22466</td>
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<tr>
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<td>7006</td>
<td>14</td>
<td>23520</td>
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</tr>
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<td>10286</td>
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<td>6</td>
<td>12286</td>
<td>10376</td>
<td>:</td>
<td>:</td>
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<td>40</td>
<td>29408</td>
<td>25698</td>
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<td>8</td>
<td>15750</td>
<td>13275</td>
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<td>29410</td>
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</tr>
<tr>
<td>9</td>
<td>17292</td>
<td>14583</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In Table 4.3 the tabulation history has been given for the tabulation of the mean temper-
nature as a function of mean mixture fraction, mixture fraction variance and mean enthalpy. A curvature criterion of 10 K was used, implying that linear interpolation would give an error of at most 5 K when employing this table in actual flame calculations. The example shows that the number of cells outweighs the number of grid points. Nevertheless, the number of grid points is still very large, as is the number of refinement levels. Apparently the mean temperature is a rather severe test case because of the sharp temperature peak near stoichiometry. Other thermochemical variables can also be stored in the table, but as they have a different curvature behavior, the 3D table will become even larger than the one in this example.

4.5 Implementation of radiation models

The radiation models discussed in the Section 2.5 have to be coupled with the FVM for the enthalpy transport equation. Here, we will briefly discuss some important aspects of the coupling algorithm, and some relevant details of the various methods are highlighted.

4.5.1 Hottel zone method

The numerical problems associated with the HZM are twofold: first of all, the direct-exchange areas have to be computed for a given discretization of Hottel volumes and surfaces, and secondly, a coupling has to be made with the FVM, in order to evaluate the source term in the mean enthalpy equation. The latter problem is not trivial, because for computational efficiency we use a Hottel grid that is much coarser than the FVM grid.

Calculation of direct-exchange areas

The direct-exchange areas generally are complex multi-dimensional integrals, the numerical evaluation of which is not a trivial exercise. For the Cartesian 3D case, Siddal (1986) developed a transformation in order to replace the 4-, 5- and 6-dimensional integrals by summations over one-dimensional integrals. These rules cannot be translated easily to the cylindrical 2D case. Instead, we used symmetry properties of the integrals for $\bar{s}_s \bar{s}_j$, $s_i \bar{g}_k$ and $g_k \bar{g}_j$, because the radiation field is taken to be axisymmetric, and the Hottel zone discretization is uniform.

In figure 4.9 a uniform grid is shown with the real cylindrical enclosure. The figure shows there are two different types of surface zones: top and bottom surface rings denoted by $e$ and side surface rings denoted by $w$. The volume rings are denoted by $g$. In the two-dimensional grid a surface ring $e$ is represented by a horizontal line at the boundary of the grid, a surface ring $w$ by a vertical line at the boundary of the grid and a volume ring $g$ by a rectangular surface within the grid. The vertical line at the left side of the grid represents the axis of symmetry. Six different types of direct-exchange area's are identified:

surface-surface exchange: $\bar{e}e$, $\bar{e}w$, $\bar{w}w$
4.5. Implementation of radiation models

![Diagram](image)

**Figure 4.9:** Two dimensional grid with cylindrical geometry, top and bottom surface zones are denoted by $e$, side surface zones by $w$ and volume zones by $g$.

Surface-volume exchange: $\frac{e}{g}$, $\frac{w}{g}$

Volume-volume exchange: $\frac{g}{g}$

In the literature very little can be found on the Hottel zone method for a cylindrical geometry. Only by Hottel and Sarofim (1967) a table of direct-exchange areas, calculated by Erkku, for a cylindrical uniform grid with square zones is given. However, the calculation method is not described. In this study a uniform grid is used, but the zones are not square. Also, Erkku's direct-exchange areas are given for a few different absorption coefficients only. This implies that the values calculated by Erkku can not be used for the flames examined here. However, the tabulated values are used to check the accuracy of the calculation method described below.

In this study a rather straightforward numerical method is used to calculate the direct-exchange areas. First, every zone is divided into a number of small rings which are
assumed to be infinitesimal. In figure 4.10 a bottom zone $e_i$ and a volume zone $g_j$ are divided into a number of small rings. Two infinitesimal assumed rings, one denoted by $de_k$, an infinitesimal surface ring and the other by $dg_l$, an infinitesimal volume ring, are drawn three-dimensional. Now, we first calculate the infinitesimal direct-exchange areas $de_kdg_l$ from all the small rings $de_k$ to the small rings $dg_l$. When all these direct-exchange areas from one small ring to another are calculated the complete direct-exchange area can be found by summation over all the infinitesimal direct-exchange areas, as described below.

From (2.100) we can write for the complete direct-exchange area $e_ig_j$:

$$
e_ig_j = \int_{A_i} \int_{V_j} \frac{K^i \cos \theta \exp(-K^i s)}{\pi s^2} dV_j dA_i$$  (4.69)

The infinitesimal area $dA_i$ and the infinitesimal volume $dV_j$ can be expressed as:

$$dA_i = r_c dr_c d\phi_c$$  (4.70)

and

$$dV_j = r_g dr_g d\phi_g dx_g$$  (4.71)
4.5. **Implementation of radiation models**

in which \( \theta \) is the angle between the surface normal at \( dA \) and \( s \), \( r_e \) and \( r_g \) are the \( r \)-coordinates in the \( e \) and \( g \) zone and \( \phi_e \) and \( \phi_g \) are the azimuthal angles. The term \( \cos \theta \) can be written as:

\[
\cos \theta = \frac{x_g}{s}
\]  

(4.72)

in which \( x_g \) is the axial \( x \)-coordinate in the volume zone \( g \). Substituting this in (4.69) we obtain:

\[
\overline{e_i g_j} = \int_{A_i} \int_{V_j} \frac{K^a r_e r_g x_g \exp(-K^a s)}{\pi s^3} dr_e dr_g d\phi_e d\phi_g
\]  

(4.73)

in which the distance between \( dA \) and \( dV \), denoted by \( s \), is given by:

\[
s = \sqrt{x_g^2 + r_g^2 + r_e^2 - 2 r_e r_g \cos \phi_e}
\]  

(4.74)

Because of axisymmetry, integration (from 0 to \( 2\pi \)) over \( \phi \) has to be performed only once. The infinitesimal direct-exchange area \( \overline{d e_k d g_l} \) can be calculated with the following integral:

\[
\overline{d e_k d g_l} = 2 K^a \int_0^{2\pi} \exp(-K^a s) r_e r_g x_g dr_e dr_g dx_g d\phi
\]  

(4.75)

Discretization of (4.75) gives:

\[
\overline{d e_k d g_l} = 2 K^a \sum_{m=1}^{N_\phi} \exp(-K^a s) r_e r_g x_g \Delta r_e \Delta r_g \Delta x_g \Delta \phi
\]  

(4.76)

in which \( N_\phi \) is the number of intervals into which the angle \( 2\pi \) is divided. Every calculation step the number \( N_\phi \) is increased, until the integral has reached a certain accuracy.

When all the small direct-exchange areas are calculated accurately, the direct-exchange area \( \overline{e_i g_j} \) can be found by the following summation:

\[
\overline{e_i g_j} = \sum_{k=1}^{N_e} \sum_{l=1}^{N_g} \overline{d e_k d g_l}
\]  

(4.77)

in which \( N_e \) and \( N_g \) are the numbers of small zones into which the zones \( e_i \) and \( g_j \) are divided, respectively.

The next step is to divide the zones into smaller zones by increasing the numbers \( N_e \) and \( N_g \). A new calculation of the infinitesimal direct-exchange areas is now performed from which the new direct-exchange area \( \overline{e_i g_j} \) is calculated. This is repeated till the difference between the old and new direct-exchange area is sufficiently small.

The procedure described above, to calculate the direct-exchange area \( \overline{e_i g_j} \) between the zones \( e_i \) and \( g_j \), can be summarized as follows:

1. Divide the zones \( e_i \) and \( g_j \) into \( N_e \) and \( N_g \) small zones.

2. Calculate the small direct-exchange areas \( \overline{d e_k d g_l} \).
   
   (a) Divide the angle \( 2\pi \) into \( N_\phi \) parts.
(b) Perform the calculation with (4.75).
(c) Stop if the required accuracy is reached, or repeat the calculation with a larger number of parts $N_{\phi}$ (go to 2a).

3. Calculate the direct-exchange area $\mathcal{E}_{i,\phi}$ using (4.77).

4. Stop if the required accuracy for the direct-exchange area $\mathcal{E}_{i,\phi}$ is reached, or repeat this calculation with larger numbers of small zones $N_{e}$ and $N_{\phi}$ (go to 1).

For the calculation of the other direct-exchange areas the procedure of the calculation is identical.

**Direct exchange area for a volume zone to itself**

A problem arises with the calculation of the direct exchange area for a volume ring to itself. When this direct-exchange area is formed from a number of infinitesimal direct-exchange areas, some of these are infinitesimal direct-exchange areas to themselves.

From (2.101) the infinitesimal direct-exchange area $dg_i dg_i$ for a small volume zone $dg_i$ to itself can be expressed as:

$$
\frac{dg_i dg_i}{s^2} = 2K^2 \int_0^{2\pi} \frac{\exp(-K^2 s^2)}{s^2} (dr_g)^2 (dx_g)^2 d\phi
$$

in which $s$ can be expressed as:

$$
 s = \sqrt{2r_g^2 (1 - \cos \phi)}
$$

Despite the fact that the six-fold volume integral (2.101) does exist, this is an integral that will not converge.

In order to obtain the direct-exchange area for a volume zone to itself the summation rule for the volume zones (2.102), described in Chapter 2, is used.

**Smoothing of direct-exchange areas**

Because a uniform grid is considered, the volume zones in a column all have the same direct-exchange area to themselves. This can be used to check the accuracy of using the summation rule. Small differences could occur because the summation does not use the same direct-exchange areas for every volume zone.

The final direct-exchange area $g_i \mathcal{E}_{g_i}$ for the volume zone $g_i$ to itself is calculated by averaging the direct-exchange areas for the volume zones in a column.

When all direct-exchange areas are calculated we wish to obtain energy conservation. That means the two summation rules described in Chapter 2 both have to be satisfied exactly. Due to the accumulation of errors the complete set of direct-exchange areas will not immediately satisfy the constraints of these summation rules.

The method used in this study is a least-squares smoothing method which is described in detail by Larsen and Howell (1986). All the direct-exchange areas are smoothed.
simultaneously and the required corrections are distributed among all the direct-exchange areas in proportion to their original magnitude. The method was already implemented in the FURNACE code and could be used for the cylindrical case without adapting it.

4.5.2 Discrete Transfer Model

Like the Hotte zone model the Discrete Transfer Method is originally developed for a three-dimensional geometry. In this study calculations are performed in a two-dimensional grid. So, we have to link the two-dimensional grid to the three-dimensional geometry. To do this, from every surface zone beams are sent in a number of directions divided over the hemisphere.

![Cylindrical geometry with two beams.](image)

FIGURE 4.11: Cylindrical geometry with two beams.

Consider a bottom surface zone $A_i$ as shown in figure 4.11. One method of sending the beams is to divide the surface ring $A_i$ into small parts $dA_k$, from where the beams depart into the hemisphere. However, due to axisymmetry the contributions of all small
surfaces \( dA_k \) are equal. Hence, it is sufficient to send beams from one point of the surface ring \( A_i \) only. In the two-dimensional grid this can be visualized by sending beams from the midpoints of the surface zones.

In figure 4.11 two beams are sent from the third bottom surface zone. One beam is sent in the grid plane. Models exist in which only beams are sent in this plane only. Then, however, a false representation of the radiation in the hemisphere is obtained. The second beam shown in figure 4.11 leaves the grid plane it departs from. The task is now to follow the beam through the cylinder and translate the route through the three-dimensional geometry into the two-dimensional grid plane.

In section 2.5 the equation for the calculation of the source term (2.112) is derived. From this equation it follows that we need to know the distance that a beam crosses a zone. In FURNACE the trajectories of the beam directions are calculated every iteration step. This is not necessary because the trajectories of the beams do not change during the iteration steps. Therefore, in the BIGMIX code the beams are followed only once. This saves a considerable amount of CPU time for every iteration step.

For each surface zone, every beam that is sent is followed through the cylinder. Every time a zone is crossed the distance travelled through the zone and the number of the zone are stored. To calculate the travelled distances in the crossed zones, for each surface zone, the following procedure is used:

1. Project the beam with angle \( \phi \) and \( \theta \), sent from a surface zone, onto the horizontal plane. An example of this projection is shown in figure 4.12.

2. Calculate in this horizontal plane the intersections of the projected beams with the circles.

3. Follow the beam through the cylinder until the boundary is reached:
   
   (a) Check if the next intersection with a zone boundary is an intersection with a new circle or a new vertical layer of zones.
   (b) Calculate the distance crossed in the zone.
   (c) Store the number of the zone crossed and the distance travelled through the zone.
   (d) Check if the boundary surface is reached, if not, then repeat 3.

4. Store the boundary point \( R \) that is reached.

5. Repeat 1 for the next beam till all beams are traced.

**Total and partial symmetry**

After choosing a division of beams in the hemisphere, there are two manners of calculation. We can make maximum use of the symmetry denoted by *total symmetry* or partial use of the symmetry, denoted by *partial symmetry*. This is illustrated in figure 4.12. Here
4.5. Implementation of radiation models

Figure 4.12: Top view of cylindrical geometry, showing four beams emitted from a point on a bottom surface zone, with total symmetry (a) and partial symmetry (b)

Four beams are used to represent the distribution of beams in the hemisphere. The beams, projected on the horizontal plane, are sent from the third bottom surface zone as shown in figure 4.11. There are two possibilities to send the four beams: in figure 4.12 (a) there is total use of symmetry, in figure 4.12 (b) there is partial use of symmetry. In the latter case relatively more beams pass through the centreline of the cylinder.

4.5.3 Accuracy

The accuracy of the DTM depends on the number of beams sent and the number of zones in the enclosure. To test the method some test cases can be performed. A critical test is the one where different boundary conditions for different surfaces exist and the gas is optically thin. In this case the incident fluxes depend on the starting points of the beams.

A test case that resembles the test case for a rectangular geometry, described by Wieringa (1992), is the following: A cylindrical enclosure with height \( h \) and radius \( r \) is shown in figure 4.13. All the walls are black (\( \epsilon_w = 1 \)) and the gas is transparent. Two different cases can be examined:

- Case 1 shown in figure 4.13 (a): only the bottom surface has an emissive power \( E = 1 \) W/m\(^2\), the other surfaces have \( E = 0 \) W/m\(^2\).

- Case 2 shown in figure 4.13 (b): only the side surface \( A_3 \) has \( E = 1 \) W/m\(^2\), the other surfaces have \( E = 0 \) W/m\(^2\).

The total heat flows through the surfaces can now be calculated exactly because the gas is transparent (Modest, 1993). In which \( R, X \) and \( H \) are defined as: Knowing the heat flows through the surfaces exactly, these values can be compared with the results of the DTM calculations.
4.5.4 Linking of radiation grid and FVM grid

For the radiation calculations the boundaries of the radiation enclosure are assumed to be transparent so all incoming heat flows to the environment. Therefore, the boundary surface has a temperature of \( T_w = 295 \text{ K} \) and the emissivity of the wall is \( \epsilon_w = 1 \). This boundary condition gives the opportunity to use a smaller enclosure than the real cylindrical combustion chamber, as described in the next section.

The influence of the inlet pipe, whose emissivity is not equal to one, is neglected. As the inlet pipe has a very small surface, only a small error has been introduced.

In order to calculate the flow correctly the FVM grid is bounded by the walls of the cylinder. Also, because the inlet pipe of the burner is very small, the grid has to be very fine in that area. Therefore, BIGMIX uses a stretched nonuniform rectilinear grid instead of a uniform grid.

In the DTM and Hottel calculations the grid does not have to be bounded by the real cylindrical enclosure, because of the boundary condition described in the previous section. The region of interest is the part where the flame is found. This means a smaller grid can be used. The FVM grid has a height of 1.5 m and a radius of 0.29 m, whereas the DTM and Hottel grid have a radius of 0.1 m with the same height as the FVM grid.

The radiation calculations have to be linked to the FVM grid. From the equations described in Chapter 3 it follows that the blackbody emissive power \( E_b \), computed by the BIGMIX code, is needed. Also, after the radiation calculations by the DTM or HZM, the radiative source term has to be distributed over the FVM cells. This is done with the method developed by Kuyper (1994).

Assume we have a large radiation cell \( k \) with volume \( V_k \) and FVM cells denoted with
4.5. Implementation of radiation models

Then, the blackbody emissive power \( E_{b,k} \) can be obtained from the FVM grid with:

\[
E_{b,k} = \sum_{i=1}^{N_F} E_{b,i} V_i
\]  

(4.80)

in which \( N_F \) is the number of FVM cells in the radiation volume zone \( V_k \) and \( E_{b,i} \) is the blackbody emissive power in the FVM cell \( i \).

The source term can be divided in an absorbed and an emitted part. These parts are distributed differently. The absorbed part has to be scaled by the volumes and the emitted part has to be scaled by the emissive power of the FVM cells. For the source term in the FVM cell \( P \) we obtain:

\[
S_{R,P} V_P = V_k S_{R,abs} \frac{V_P}{V_k} - V_k S_{R,em} \frac{E_{b,P} V_P}{\sum_{i=1}^{N_F} E_{b,i} V_i}
\]  

(4.81)

In this distribution the hot parts will emit more energy than the cold parts, but both will absorb an equal amount of energy.
CHAPTER 5

Laminar flame calculations

In this chapter results of 1D laminar flame calculations are presented. The results will be used for several purposes.

Firstly, laminar diffusion flames (laminar flamelets) can in a sense be considered as an extension of conserved-scalar models with infinitely fast reactions. It is interesting to see how the relatively simple flame sheet and equilibrium models compare with the laminar flamelets, in order to validate those models.

Secondly, laminar flames are useful to study reaction pathways in absence of turbulent flow. A comparison with the turbulent flame calculations with detailed chemistry may show whether there are significant differences between turbulent and laminar flame chemistry. In this chapter results are presented on reaction pathways and sensitivity of the flame structure to the reaction rate constants.

Thirdly, the sensitivity data can be used to reduce large reaction mechanisms, by discarding unimportant reactions. For example, it is interesting to see whether Groningen natural gas can be considered as diluted methane, for this would greatly reduce the number of species in the chemical mechanism. The shortened mechanisms are then to be used in the turbulent diffusion flame model with detailed chemistry.

The chapter starts, however, with a selection of relevant reaction mechanisms and a validation of the computer code used. The validation of the code was done primarily by comparison with measurements and is particularly important for the calibration of absolute OH-concentration LIF measurements performed in the Heat Transfer Section (De Vries, 1994).

5.1 Selection of reaction mechanisms

In the literature, many reaction mechanisms for hydrocarbon combustion have been reported. Here we are interested mainly in methane combustion, with an extension to some higher alkanes (ethane, propane, butane) present in Groningen natural gas and the IFRF natural gas. Two types of mechanisms were used: full mechanisms and skeletal mechanisms.

Skeletal mechanisms can be derived from full mechanisms by assuming certain flame conditions, subsequently discarding species and reactions from the complete scheme. In the literature, skeletal mechanisms have been tested to produce the same overall behavior as their ‘parent’ full mechanisms, but within a smaller range of applicability. As put forward by Peters (1991), most skeletal mechanisms for hydrocarbon combustion have been derived for fuel-lean to stoichiometric conditions only. Hence it is expected that the lack of C₂-species in these mechanisms will become apparent in fuel-rich flames. Furthermore, one has to be aware of the fact that even the full mechanisms do not cover all
5.1. Selection of reaction mechanisms

| Table 5.1: Summary of species involved in the tested reaction mechanisms. |
|-----------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| CH₄, O₂, CO₂, H₂O, N₂,     | full Glarborg | full Warnatz   | C₁/C₂ Warnatz | C₁ Warnatz     | C₁ Kee         | skeletal Smooke |
| H₂O, H₂O, OH, H₂O₂, H₂O₂,  | ×              | ×              | ×              | ×              | ×              | ×              |
| CH₃, CH₂O, HCO, CO         | ×              | ×              | ×              | ×              | ×              | ×              |
| CH₃O                       | ×              | ×              | ×              | ×              |                |                |
| CH₂CH                     | ×              | ×              | ×              | ×              |                |                |
| C                          |                |                |                |                |                |                |
| CH₂(s), CH₂OH              | ×              | ×              | ×              |                |                |                |
| CH₃OH                      |                |                |                |                |                |                |
| C₂H₆, C₂H₅, C₂H₄, C₂H₃,   | ×              | ×              |                |                |                |                |
| C₂H₅, C₂H₂, HCCO, CH₂CO   | ×              | ×              |                |                |                |                |
| CH₃CO, CH₃CHO, CH₂CHO      |                |                | ×              |                |                |                |
| C₃H₃, C₃H₂, C₄H₂          | ×              | ×              |                |                |                |                |
| C₃H₆, i-C₃H₇, n-C₃H₇,     |                |                | ×              |                |                |                |
| C₃H₆, C₃H₄                 |                |                |                |                |                |                |
| p-C₄H₉, s-C₄H₉, C₄H₆, C₄H₃,|                |                |                |                |                | ×              |

Possible combustion phenomena. Baulch et al. (1992) have shown the range of validity of many elementary reaction rate constants, with an estimate of their uncertainty. It is not uncommon to have uncertainties of a factor 2 for the pre-exponential constants. Therefore the mechanisms in the literature should be judged as an whole, rather than as assemblies parts of which can be combined to construct a new mechanism.

As stated before, we are interested in combustion at atmospheric pressure only. Two full mechanisms for hydrocarbon combustion were tested: the mechanism of Glarborg and Hadvig (1991) (full-Glarborg) and of Warnatz (Boersma, 1993) (full-Warnatz). Warnatz' mechanism is a subset of the very large reaction kinetics database constructed over the last decade by Warnatz and others, and is believed to capture the most important reactions with sufficient accuracy. In the present application a few unimportant reactions and species were discarded, mainly C₃- and C₄-species, since they were not available in the thermodynamic and transport-property databases. Glarborg's mechanism has been derived especially for natural gas combustion, but was only tested for shock-tube combustion, a perfectly stirred reactor and low-pressure flames (Glarborg and Hadvig, 1991).

In this work one skeletal mechanism and three 'short' mechanisms are used: the mechanism of Kee et al. (1985) (C₁-Kee) as delivered with the PREMIX code and used merely as a reference case, the skeletal mechanism of Smooke and Giovangigli (1991a) (skel-Smooke) which is an often quoted standard mechanism for methane combustion, and two short mechanisms derived from the full Warnatz mechanism by allowing C₁-species only (C₁-Warnatz) or allowing C₁ and C₂-species only (C₁/C₂-Warnatz), respectively.
The skel-Smooke mechanism was modified by changing the pressure dependent reaction \( \text{CH}_4 + (M) = \text{CH}_3 + \text{H} + (M) \) for the specific case of atmospheric pressure (Smooke and Giovangigli, 1991a). The skel-Smooke mechanism is specified in Appendix B, and in the sequel will be tested in premixed and non-premixed flames. Table 5.1 summarizes the species used by the various mechanisms.

### 5.2 Laminar premixed flame results

#### 5.2.1 Numerical accuracy of the laminar flame code

The numerical code (Kee et al., 1985) used to solve the 1D transport equations with detailed chemistry and multicomponent transport (see Chapter 2) has been validated by others and it has been shown to yield reliable results for a large number of different flames (Smooke and Giovangigli, 1991a). Therefore in this work only limited attention was paid to the improvement of numerical efficiency and accuracy. Here, we briefly mention a number of relevant numerical parameters used to obtain the solutions discussed in the sequel of this chapter.

Table 5.2 shows how several important quantities vary as a function of different models and parameters. The grid independence was checked by sharpening the criteria for further
5.2. Laminar premixed flame results

grid refinement, based on curvature and gradients of variables in each grid cell. The adaptive gridding algorithm does not remove grid nodes, but only adds nodes in regions where the refinement criteria are not (yet) satisfied. After a sequence of successive refinements the desired accuracy is attained. The dimensionless parameters $\epsilon_{\text{grad}} = 0.15$ and $\epsilon_{\text{curv}} = 0.25$ produced about 70 grid nodes in the computational domain $x \in [0, 10]$ (cm), sufficient to establish grid independence.

The flame zone extends only up to $x = 0.1$ mm. Since we were also interested in the region beyond this narrow zone, additional grid nodes were specified for $x > 0.1$ mm. The case of $N_p = 70$ was obtained with extra nodes in the downstream region, giving lower OH mole fraction at $x = 2$ cm. This improved the accuracy of the prediction of OH-concentrations in the downstream region.

Three different discretization schemes were used: finite difference with an upwind scheme, finite volume with an upwind scheme, and finite difference with a central scheme for convection. Diffusive processes were always discretized by a central scheme. In the premixed flame there is a dominant convection term in the positive $x$-direction. Therefore the upwind scheme produced accurate results compared to the higher-order central scheme.

5.2.2 Selection of test cases

Four different atmospheric premixed flames were tested:

A : Freely propagating stoichiometric methane flame.

B : Burner-stabilized methane flame with equivalence ratio $\phi = 0.88$ and inlet velocity $u_0 = 14.1$ cm/s.

C : Burner-stabilized methane flame with $\phi = 1.17$ and $u_0 = 13.5$ cm/s.

D : Burner-stabilized stoichiometric methane flame with $u_0 = 11.2$ cm/s.

Flame A is of interest since the laminar burning velocity is an important overall parameter of a freely propagating premixed flame. Hence flame A constitutes a severe test case for the numerical scheme as well as the reaction mechanism. The other three flames refer to the measurements performed in the so-called flat-flame burners, which are employed to calibrate the OH-concentration measurements by LIF (Laser Induced Fluorescence) in turbulent flames. Flames B and C have been reported by De Vries (1994), flame D has been measured by Kaiser et al. (1986).

All test flames are at atmospheric pressure, in agreement with the experiments. In atmospheric flames the reaction zone is about 1 mm thick, and it is almost impossible to measure its internal structure. Therefore in the literature most experiments involve low-pressure flames with a thicker reaction zone. For the three burner-stabilized flames B–D we are mainly interested in the post-flame region, and the flame zone is believed to be accurately represented by the numerical algorithm; the validation only concerns the post-flame region. Experimental data comprise thermocouple temperature measurements and LIF OH-concentration measurements.
TABLE 5.3: Calculated flame speeds for a stoichiometric atmospheric methane flame. The skel-Smooke0 mechanism equals the skel-Smooke mechanism but has no correction of the reaction
\[ \text{CH}_4 + (M) \rightarrow \text{CH}_3 + \text{H} + (M). \]

<table>
<thead>
<tr>
<th>mechanism</th>
<th>source</th>
<th>flame speed (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>full-Glarborg</td>
<td>present study</td>
<td>43.7</td>
</tr>
<tr>
<td>full-Warnatz</td>
<td>present study</td>
<td>36.6</td>
</tr>
<tr>
<td>C(_1/C_2)-Warnatz</td>
<td>Boersma (1993)</td>
<td>36.6</td>
</tr>
<tr>
<td>C(_1/C_2)-Warnatz</td>
<td>present study</td>
<td>36.7</td>
</tr>
<tr>
<td>C(_1)-Warnatz</td>
<td>Boersma (1993)</td>
<td>37.1</td>
</tr>
<tr>
<td>C(_1)-Warnatz</td>
<td>present study</td>
<td>37.1</td>
</tr>
<tr>
<td>skel-Smooke0</td>
<td>Smooke and Giovangigli (1991a)</td>
<td>43.</td>
</tr>
<tr>
<td>skel-Smooke0</td>
<td>Rogg (1991)</td>
<td>57.</td>
</tr>
<tr>
<td>skel-Smooke0</td>
<td>Peters (1991)</td>
<td>40.</td>
</tr>
<tr>
<td>skel-Smooke0</td>
<td>present study</td>
<td>40.1</td>
</tr>
<tr>
<td>skel-Smooke</td>
<td>Smooke and Giovangigli (1991a)</td>
<td>38.</td>
</tr>
<tr>
<td>skel-Smooke</td>
<td>present study</td>
<td>36.4</td>
</tr>
<tr>
<td>C(_1)-Kee</td>
<td>Kee et al. (1985)</td>
<td>40.5</td>
</tr>
<tr>
<td>C(_1)-Kee</td>
<td>present study</td>
<td>35.4</td>
</tr>
</tbody>
</table>

In practical flames, radiation will play a role in the post-flame region. As a result of heat losses, the flame will cool down and reaction rates will drop quicker than in the adiabatic case, yielding a ‘frozen’ composition rather than an equilibrium composition. Therefore radiation was included in the burner-stabilized test cases.

The main quantities we are interested in are temperature, major combustion species (hydrocarbons, CO, CO\(_2\), H\(_2\), H\(_2\)O), OH-concentration (for comparison with LIF experiments) and O-concentration (important in thermal NO-formation).

5.2.3 Test results laminar premixed flames

Flame A: Freely propagating stoichiometric flame

The adiabatic freely-propagating stoichiometric flame is important mainly because of the determination of the laminar flame speed (or burning velocity). This important property of premixed mixtures has been measured to be about 37 cm/s under stoichiometric atmospheric conditions (Warnatz, 1981).

In the literature many attempts have been made to reproduce this value numerically (Dixon-Lewis et al., 1984). It turned out that numerical results heavily depend not only on the numerical algorithm and grid refinement, but also on the employed chemical mechanism, see Table 5.3. An important observation to be made is the sensitivity of the skel-Smooke mechanism to the corrected recombination reaction \[ \text{CH}_4 + (M) = \text{CH}_3 + \text{H} + (M). \] giving considerable improvement of results (Smooke and Giovangigli, 1991a).
TABLE 5.4: Some relevant quantities in a freely propagating stoichiometric premixed methane flame.

<table>
<thead>
<tr>
<th>mechanism</th>
<th>$T_{\text{max}}$ (K)</th>
<th>$X_{\text{CO, max}}$ ($\times 10^2$)</th>
<th>$X_{\text{O, max}}$ ($\times 10^3$)</th>
<th>$X_{\text{OH, max}}$ ($\times 10^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>full-Glarborg</td>
<td>2198</td>
<td>5.01</td>
<td>3.04</td>
<td>7.50</td>
</tr>
<tr>
<td>full-Warnatz</td>
<td>2176</td>
<td>4.18</td>
<td>2.94</td>
<td>7.27</td>
</tr>
<tr>
<td>C1/C2-Warnatz</td>
<td>2175</td>
<td>4.18</td>
<td>2.95</td>
<td>7.27</td>
</tr>
<tr>
<td>C1-Warnatz</td>
<td>2178</td>
<td>4.20</td>
<td>3.00</td>
<td>7.31</td>
</tr>
<tr>
<td>skel-Smooke</td>
<td>2205</td>
<td>4.76</td>
<td>3.28</td>
<td>7.26</td>
</tr>
<tr>
<td>C1-Kee</td>
<td>2194</td>
<td>4.90</td>
<td>3.40</td>
<td>7.60</td>
</tr>
</tbody>
</table>

By correction is meant a change of the rate constants according to Warnatz (Smooke and Giovangigli, 1991a), explicitly assuming atmospheric pressure. See also Table B.1 in Appendix B.

The present study shows that all tested mechanisms agree reasonably well with each other, but the C1-Kee mechanism yields a relatively low flame speed, and the full full-Glarborg mechanism produces a too high flame speed compared to experiments. The results reported by Boersma (1993) are reproduced, using a different numerical code, however. The results of Kee et al. (1985), obtained with the same numerical code, could not be reproduced due to some changes in the discretization and the thermodynamic database used. The full Warnatz mechanism does not perform significantly better than the skeletal mechanisms C1/C2-Warnatz and C1-Warnatz. Apparently the formation of C2-species is irrelevant for the flame speed in stoichiometric flames.

Table 5.4 shows some characteristic quantities for the different mechanisms. The maximum temperature, which should be equal to the adiabatic flame temperature, is sensitive to the grid spacing far downstream of the flame zone, and is attained for very large $x$-values. In the present study, the computational domain was restricted to 10 cm downstream, which somewhat accounts for the observed differences between the mechanisms. The Warnatz mechanisms produce a rather low maximum temperature and maximum CO mole fraction, but other differences are small. Especially the maximum OH mole fraction is insensitive to the mechanism. The equilibrium OH mole fraction for this flame is about $2.4\times10^{-3}$, showing the existence of superequilibrium radical concentrations in these premixed flames.

In general, the results give confidence that no severe errors were made in the numerical solution procedure, but at the same time demonstrate how sensitive results may be to changes in the reaction mechanism.

Flame B: Burner-stabilized lean flame

Unlike the freely propagating flame discussed in the preceding subsection, the burner-stabilized flames are all calculated with a radiation heat loss term in the energy equation (3.81). The optically thin limit of radiative heat transfer has been employed to derive
a simple formula for the radiative source term:

\[ Q_{\text{rad}} = -4K\sigma T^4 + 2K_0\sigma T_0^4 + 2K_\infty\sigma T_\infty^4 \]  

(5.1)

where \( \sigma \) is the Stefan-Boltzmann constant and \( K \) is the local extinction coefficient of the gas mixture. The value of \( K \) is computed from the local mixture composition, according to the formula of Hubbard and Tien (1978). Downstream, the flame senses its own radiation, which is expressed by substituting \( T_\infty = T_L \) into (5.1), instead of taking the ambient value \( T_\infty = T_{\text{ambient}} = 300 \) K. Here \( T_L \) is the flame temperature at the end \( (x = x_L) \) of the computational domain, which is considerably higher than 300 K. This modification yields a less pronounced temperature decrease of about 125 K at \( x = 3 \) cm compared to 180 K for the case \( T_\infty = 300 \) K. The temperature profile for larger \( x \)-values is not studied here, since in practice the ambient air will mix with the hot combustion gases, penetrating onto the flame centerline for \( x > 5 \) cm and causing a rapid temperature decrease.

![Figure 5.1: Comparison of temperature profiles in the near-burner zone for flame B (\( \phi = 0.88 \)).](image)

Figures 5.1-5.3 give the profiles of the most important quantities in the neighbourhood of the burner. In addition to the graphical information some numerical values are presented in Table 5.5. We observe differences between the mechanisms in the order of 10\% or less, except for the full-Glarborg mechanism. For the three Warnatz mechanisms, the CO maximum is somewhat lower than for the Smooke and Kee mechanisms.

**Flame C: Burner-stabilized rich flame**

Figures 5.4-5.6 show the profiles of the most important quantities in the neighbourhood of the burner. From the figures and from Table 5.6 it is found that the C\(_1\)-Kee mechanism deviates slightly and the full-Glarborg mechanism considerably from the other mechanisms.
5.2. Laminar premixed flame results

**Figure 5.2:** Comparison of major-species profiles in the near-burner zone for flame B ($\phi = 0.88$). For symbols see Figure 5.1.

**Figure 5.3:** Comparison of radical species profiles in the near-burner zone for flame B ($\phi = 0.88$). For symbols see Figure 5.1.

For the Glarborg mechanism this is consistent with earlier observations. The *skel-Smooke* mechanism did not converge for this fuel-rich flame, which may be due to the fact that the mechanism is believed to be reliable for lean to stoichiometric flames only ($0.6 \leq \phi \leq 1$) (Smooke and Giovangigli, 1991a).
Chapter 5. Laminar flame calculations

![Graph showing temperature profiles](image)

**Figure 5.4:** Comparison of temperature profiles in the near-burner zone for flame C ($\phi = 1.17$).

The flame structure appears to be rather insensitive to the inclusion of C$_2$-species in the mechanism, by inspection of the three Warnatz mechanisms. Probably a much higher equivalence ratio has to be defined in order to get a substantial influence of the C$_2$-species.

**Flame D: Burner-stabilized stoichiometric flame**

Like flame A, flame D is a stoichiometric flame, but the main difference is the presence of the stabilizing burner, yielding a lower flame temperature. In effect, this flame does not compare with flame A, but with the fuel-lean flame B. Figures 5.7-5.9 show the profiles of the most important quantities in the neighbourhood of the burner. As can be seen from Figure 5.7, the *full-Glarborg* mechanism yields a higher temperature gradient at the burner, causing more conductive heat losses and therefore a lower temperature further

**Table 5.5:** Some relevant quantities in a burner-stabilized lean methane flame with equivalence ratio $\phi = 0.88$ (Flame B).

<table>
<thead>
<tr>
<th>mechanism</th>
<th>$T_{\text{max}}$ (K)</th>
<th>$X_{\text{CO,max}} \times 10^2$</th>
<th>$X_{\text{H}_2,\text{max}} \times 10^2$</th>
<th>$X_{\text{O,max}} \times 10^3$</th>
<th>$X_{\text{OH, max}} \times 10^3$</th>
<th>$X_{\text{OH},1.6\text{cm}} \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>full-Glarborg</em></td>
<td>1791.</td>
<td>2.70</td>
<td>0.59</td>
<td>1.32</td>
<td>3.46</td>
<td>5.41</td>
</tr>
<tr>
<td><em>full-Warnatz</em></td>
<td>1861.</td>
<td>2.29</td>
<td>0.77</td>
<td>1.59</td>
<td>4.11</td>
<td>6.98</td>
</tr>
<tr>
<td>C$_1$/C$_2$-Warnatz</td>
<td>1860.</td>
<td>2.28</td>
<td>0.77</td>
<td>1.59</td>
<td>4.10</td>
<td>6.95</td>
</tr>
<tr>
<td>C$_1$-Warnatz</td>
<td>1860.</td>
<td>2.37</td>
<td>0.80</td>
<td>1.60</td>
<td>4.10</td>
<td>6.95</td>
</tr>
<tr>
<td>skel-Smooke</td>
<td>1866.</td>
<td>2.70</td>
<td>0.76</td>
<td>1.69</td>
<td>4.03</td>
<td>7.48</td>
</tr>
<tr>
<td>C$_1$-Kee</td>
<td>1851.</td>
<td>2.77</td>
<td>0.90</td>
<td>1.78</td>
<td>4.18</td>
<td>8.50</td>
</tr>
</tbody>
</table>
5.2. Laminar premixed flame results

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>$T_{\text{max}}$ (K)</th>
<th>$X_{\text{CO,max}} \times 10^2$</th>
<th>$X_{\text{H}_2,\text{max}} \times 10^2$</th>
<th>$X_{\text{O}_2,\text{max}} \times 10^4$</th>
<th>$X_{\text{OH,max}} \times 10^3$</th>
<th>$X_{\text{OH,1.5cm}} \times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full-Glarborg</td>
<td>1754.</td>
<td>5.02</td>
<td>2.93</td>
<td>2.56</td>
<td>1.60</td>
<td>0.77</td>
</tr>
<tr>
<td>Full-Warnatz</td>
<td>1847.</td>
<td>4.50</td>
<td>2.78</td>
<td>3.38</td>
<td>2.11</td>
<td>1.22</td>
</tr>
<tr>
<td>C1/C2-Warnatz</td>
<td>1851.</td>
<td>4.50</td>
<td>2.78</td>
<td>3.22</td>
<td>2.10</td>
<td>1.19</td>
</tr>
<tr>
<td>C1-Warnatz</td>
<td>1854.</td>
<td>4.67</td>
<td>2.80</td>
<td>3.33</td>
<td>2.13</td>
<td>1.22</td>
</tr>
<tr>
<td>C1-Kee</td>
<td>1844.</td>
<td>5.06</td>
<td>2.90</td>
<td>4.63</td>
<td>2.49</td>
<td>1.51</td>
</tr>
<tr>
<td>Skel-Smooke</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

away from the burner.

Comparison with experiments

The temperature and OH-concentration are compared with measurements (Kaiser et al., 1986; Vries, 1994). Unfortunately, an accurate validation of the reaction zone structure is impossible, since the experimental techniques (LIF, thermocouples) cannot reach the near-burner zone.

Figure 5.10 shows the comparison between experiments of De Vries and our numerical results, for flame B and C. The temperature profile of the full-Glarborg mechanism matches the experimental data accurately for $x > 0.5$ cm, but the difference with the other mechanisms is relatively large, about 75 to 100 K. Taking into account the experimental

![Figure 5.5: Comparison of major-species profiles in the near-burner zone for flame C ($\phi = 1.17$). For symbols see Figure 5.4.](image-url)
Figure 5.6: Comparison of radical species profiles in the near-burner zone for flame C ($\phi = 1.17$). For symbols see Figure 5.4.

Figure 5.7: Comparison of temperature profiles in the near-burner zone for flame D ($\phi = 1.0$).

uncertainty (about 50 K), the other mechanisms are not fully compatible with the measurements. However, the thermocouple measurements depend heavily on correction formulae for radiative and conductive heat losses. To give an impression of these effects, we have included recent data by Van den Bercken (1995) using thermocouples and Mantzaras
5.2. Laminar premixed flame results

![Graph showing species profiles](image)

**Figure 5.8:** Comparison of major-species profiles in the near-burner zone for flame D ($\phi = 1.0$). For symbols see Figure 5.7.

![Graph showing radical species profiles](image)

**Figure 5.9:** Comparison of radical species profiles in the near-burner zone for flame D ($\phi = 1.0$). For symbols see Figure 5.7.

(1995) using Coherent Anti-Stokes Raman Spectroscopy, showing that the measurements by De Vries are possibly too low.

The OH-concentration measurements of De Vries (1994) are only qualitative, in the sense that no absolute gauging is possible for LIF concentration measurements. For
convenience, we have scaled the measured data to match the numerical data for \( x = 2.5 \) cm. The figures show that the decrease of the OH-concentration towards equilibrium values in the downstream region matches the numerical data fairly well.

For flame D, the experimental temperature data of Kaiser et al. (1986), depicted in Figure 5.11 do not agree with none of mechanisms for \( x < 0.7 \) cm, further downstream there is excellent agreement. Overall, the OH-profiles fit remarkably well. Again, the difference with the experimental temperature profile may be due to the radiation correction for the thermocouple signal and even catalytic effects in the reaction zone, since the data of Kaiser et al. (1986) even exceed the adiabatic flame temperature (also plotted) for this flame.

\[ \begin{align*}
\text{(a)} & \quad \text{no radiation} \\
\text{(b)} & \quad \left(10^{16} \text{ mole} \text{ cm}^{-3}\right) \\
\text{(c)} & \quad \text{no radiation} \\
\text{(d)} & \quad \left(10^{15} \text{ mole} \text{ cm}^{-3}\right)
\end{align*} \]

**Figure 5.10:** Comparison of numerical results and measurements of De Vries. (a) Flame B, temperature, (b) Flame B, OH concentration, (c) Flame C, temperature, (d) Flame C, OH concentration. For symbols see Figure 5.7; measurement data: • thermocouple data by De Vries, × thermocouple data by Van den Bercken, * CARS data by Mantzaras.
5.2. Laminar premixed flame results

![Graphs showing temperature and OH concentration profiles](image)

**Figure 5.11:** Comparison of numerical results for flame D and measurements of Kaiser et al. for temperature (a) and OH concentration (b). For symbols see Figure 5.7.

### 5.2.4 Implications for LIF calibration

The test results provide information which is relevant for calibration of absolute OH-concentration LIF measurements. As shown in the preceding subsections, the global flame structure is well predicted by the various mechanisms, hence a calibration with numerical results seems possible. However, the OH concentration profiles appear to be rather sensitive to the used mechanism. Depending on the equivalence ratio and the $x$-coordinate, differences can be larger than 15%. By omitting the C$_1$-Kee and full-Glarborg mechanisms this error can be reduced to less than 10%.

The test flames B and C show that the temperature profile obtained with the full-Glarborg mechanism differs substantially from the other mechanisms. For flame D, the C$_1$-Kee mechanism produces too high OH concentrations, whereas the full-Glarborg mechanism yields too low OH concentrations. Therefore, the skel-Smooke mechanism or one of the Warnatz mechanisms are recommended for calibration with numerical simulations.

Moreover, the inclusion of a radiation model considerably alters the results, giving lower temperatures in the burn-out region and correspondingly lower OH concentrations. Nevertheless, radiation has to be included to obtain agreement with temperature measurements. To be less dependent on the radiation model, it would be preferable to calibrate in a region of the flame where radiation plays no significant role. The superequilibrium radical concentrations in the narrow flame zone are insensitive to the radiation model, but LIF calibration can only be carried out in the downstream region, a few centimetres away from the burner. Figure 5.12 shows the OH profiles for flame B, using the full-Warnatz mechanism with and without radiation. It is seen that the OH profiles start to deviate for $x > 0.5$ cm, approximately. This suggests that calibration should be performed close to the burner. However, such a calibration would introduce large errors due to the experimental uncertainty in the height $x$ above the burner. The slope of the OH-profile close to the burner suggests that calibration be performed for larger $x$-values, where the profile
Figure 5.12: OH concentration profiles for a lean premixed flame (flame B), using the full-Warnatz mechanism with and without radiation.

Figure 5.13: OH concentration profiles for a lean premixed flame (flame B), using the full-Warnatz mechanism for different equivalence ratios.

runs more or less horizontal. Then radiation modeling will be a possible source of errors in the numerical calculation.

Peak OH concentrations are lower in the fuel-rich flame, and at \( x > 1 \) cm these concentrations have decayed faster than in the fuel-lean case. Furthermore, the reaction mechanisms show larger deviations in the fuel-rich flames, where \( \text{C}_2 \)-reactions may become important. For calibration purposes, a fuel-lean flame is recommended, yielding stronger LIF signal and less uncertainty due to the reaction mechanism. A larger inflow velocity \( u_0 \) will reduce diffusive heat losses to the cooled burner, yielding higher flame temperature and OH concentration, but a too high \( u_0 \) will blow off the flame.

The measured equivalence ratio can have about 5% uncertainty. Therefore, we calculated fuel-lean flames with \( \phi = 0.83, 0.88, 0.93 \) respectively, for the full-Warnatz mechanism. Figure 5.13 shows that for \( x \approx 2.5 \) cm the predicted OH concentrations differ by about 15%, and this difference does not change much for smaller or larger \( x \)-values.

The influence of the burner temperature on the flame structure was found to be negligible for burner temperatures between 300 and 400 K. A higher inlet temperature produces a higher flame temperature, but diffusive heat losses to the burner will diminish due to the temperature dependence of the heat conductivity coefficient, giving a counterbalancing effect.

Concluding this section: calibration of LIF measurements seems possible for a fuel-lean flame, using a Warnatz reaction mechanism or the skel-Smooke mechanism, at a location of \( x \approx 2.5 \) cm above the burner. Numerical uncertainties in this case are estimated to be about 15% due to the reaction mechanism and the radiation model, whereas 5% inaccuracy in the experimental equivalence ratio adds another 15% uncertainty, yielding a total error of 30%.
5.3 Laminar diffusion flame results

5.3.1 Numerical validation of the code

As for the laminar premixed flame, the diffusion flame code has been tested for its numerical accuracy by changing the grid refinement parameters, the discretization scheme and the molecular transport model. The difference between the premixed flame code and the diffusion flame code lies in the additional momentum equation for the diffusion flame, and the different boundary conditions. In laminar diffusion flames, extinction plays an important role at high strain rates. In the validation test runs we took $a = 100 \text{ s}^{-1}$ and $v_0 = 50 \text{ cm/s}$, well away from the extinction limit for methane flames. As observed by Dixon-Lewis et al. (1984), the flame extinction limit heavily depends on the grid. For each case the extinction limit was calculated independently, by incrementing the strain rate in steps of 10 $\text{s}^{-1}$.

Only the skel-Smooke mechanism was used in these test cases. The reference test case had an upwind finite-difference discretization scheme, mixture-averaged transport properties, and grid refinement parameters $\epsilon_{\text{grad}} = 0.15$, $\epsilon_{\text{curv}} = 0.25$. No radiation was included and the Tsuji-geometry was used. For this case the extinction limit was $a_{\text{ext}} = 380 \text{ s}^{-1}$, which compares well with the experimentally observed limit of 350 to 400 $\text{s}^{-1}$ (Chelliah et al., 1990).

Table 5.7 shows that the reference case differs only slightly from the solutions on a coarser or a finer grid. The extinction limit does not change strongly when decreasing $\epsilon_{\text{grad}}$ and $\epsilon_{\text{curv}}$. Compared to the premixed flame simulations, about 20 more grid points are required to obtain accurate results.

Changing the discretization method to hybrid finite-difference or upwind finite-volume for the convection term, did not significantly alter the results. Close to the reaction zone the velocities are small, and convection is rather unimportant. The upwind finite-difference scheme appeared to converge more rapidly, and was therefore selected for the test cases described below.

The variation of molecular transport models showed to have a stronger effect on the flame than for the premixed flame. Inclusion of multi-component diffusion and thermal diffusion (Soret effect) reduced the maximum temperature, and the extinction limit decreased by about 20 $\text{s}^{-1}$. Further simplifications suggested by Smooke and Giovangigli (1991a) concern the neglect of the enthalpy flux in the temperature equation, and the introduction of fixed values for the species Lewis numbers (although not all equal to 1). These models again yield some more differences. As a consequence, it was concluded to use the more accurate multicomponent diffusion model for subsequent test cases.

For the numerical validation described above, radiation plays no role of importance. Only at lower strain rates, giving a thicker flame, radiation will lower the flame temperature, with $\Delta T \approx 100 \text{ K}$ at $a = 10 \text{ s}^{-1}$. Even in the preheated air flame, the inclusion of radiation decreased the maximum temperature by no more than 20 K, an effect which becomes smaller at higher strain rates.
TABLE 5.7: Numerical accuracy test of diffusion flame calculations. Methane diffusion flame, Tsuji-burner geometry, \( a = 100 \text{ s}^{-1} \), \( u_0 = 50 \text{ cm/s} \). No radiation included. Mechanism by Smooke and Giovangigli (1991a). Reference case: mixture-averaged transport model, finite-difference upwind scheme, 99 grid nodes, refinement criteria \( \epsilon_{\text{grad}} = 0.15 \), \( \epsilon_{\text{curv}} = 0.25 \).

<table>
<thead>
<tr>
<th>( \epsilon_{\text{grad}} )</th>
<th>( \epsilon_{\text{curv}} )</th>
<th>( N_p )</th>
<th>( T_{\text{max}} ) (K)</th>
<th>( X_{H_{\text{max}}} \times 10^3 )</th>
<th>( X_{CO_{\text{max}}} \times 10^2 )</th>
<th>( X_{O_2, \xi=0.1} \times 10^3 )</th>
<th>( a_{\text{ext}} ) s(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>0.25</td>
<td>99</td>
<td>2051</td>
<td>2.74</td>
<td>3.22</td>
<td>2.56</td>
<td>380.</td>
</tr>
<tr>
<td>0.10</td>
<td>0.15</td>
<td>139</td>
<td>2051</td>
<td>2.74</td>
<td>3.26</td>
<td>2.61</td>
<td>370.</td>
</tr>
<tr>
<td>0.25</td>
<td>0.35</td>
<td>81</td>
<td>2058</td>
<td>2.77</td>
<td>3.23</td>
<td>2.44</td>
<td>380.</td>
</tr>
</tbody>
</table>

**Discretization dependence**

<table>
<thead>
<tr>
<th>model</th>
<th>( T_{\text{max}} ) (K)</th>
<th>( X_{H_{\text{max}}} \times 10^3 )</th>
<th>( X_{CO_{\text{max}}} \times 10^2 )</th>
<th>( X_{O_2, \xi=0.1} \times 10^3 )</th>
<th>( a_{\text{ext}} ) s(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>upwind finite-difference</td>
<td>2051</td>
<td>2.74</td>
<td>3.22</td>
<td>2.56</td>
<td>380.</td>
</tr>
<tr>
<td>upwind finite-volume</td>
<td>2051</td>
<td>2.77</td>
<td>3.26</td>
<td>2.59</td>
<td>370.</td>
</tr>
<tr>
<td>hybrid finite-difference</td>
<td>2051</td>
<td>2.74</td>
<td>3.24</td>
<td>2.59</td>
<td>380.</td>
</tr>
</tbody>
</table>

**Transport model dependence**

<table>
<thead>
<tr>
<th>model</th>
<th>( T_{\text{max}} ) (K)</th>
<th>( X_{H_{\text{max}}} \times 10^3 )</th>
<th>( X_{CO_{\text{max}}} \times 10^2 )</th>
<th>( X_{O_2, \xi=0.1} \times 10^3 )</th>
<th>( a_{\text{ext}} ) s(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>mixture averaged</td>
<td>2051</td>
<td>2.74</td>
<td>3.22</td>
<td>2.56</td>
<td>380.</td>
</tr>
<tr>
<td>multcomp., thermal dif.</td>
<td>2026</td>
<td>2.68</td>
<td>3.11</td>
<td>2.96</td>
<td>360.</td>
</tr>
<tr>
<td>mixture averaged, no h-flux</td>
<td>2092</td>
<td>3.00</td>
<td>3.42</td>
<td>1.36</td>
<td>410.</td>
</tr>
<tr>
<td>fixed species Lewis numbers</td>
<td>2025</td>
<td>2.65</td>
<td>3.19</td>
<td>3.25</td>
<td>350.</td>
</tr>
</tbody>
</table>

5.3.2 **Selection of test cases**

For the Tsuji-burner configuration the following three diffusion flame test cases were chosen:

E : Strained methane flame with \( a = 100 \text{ s}^{-1} \), \( u_0 = 50 \text{ cm/s} \) and fuel and air temperature 300 K.

F : Strained methane flame with \( a = 100 \text{ s}^{-1} \), \( u_0 = 15 \text{ cm/s} \), fuel temperature 300 K and preheated air at 1400 K.

G : Strained methane flame with \( a \) high enough to be close to extinction, \( u_0 = 50 \text{ cm/s} \), and fuel and air temperature 300 K.

Flame E represents a standard flame described in the literature, and is useful for further comparison. Flame F differs from flame E in the air temperature. For numerical convenience only, the inlet velocity \( u_0 \) has been adjusted to stabilize the reaction zone.
at about the same distance from the burner as in flame E. Pre-heated air is often used in industrial applications of natural gas diffusion flames, and it is worthwhile to investigate the influence on the laminar flamelet behavior. Flame G resembles flame E, but is examined close to extinction, in order to verify the sensitivity of reaction kinetics.

The fuel inlet velocity \( u_0 \) has been chosen to establish a flame zone suitably far away from the cylindrical burner to have negligible influence of diffusive heat losses to the burner, but still such that the computational domain can be kept suitably narrow. By specifying \( u_0 \) and \( a \), the air velocity \( u_l \) is implicitly fixed.

In the test cases, we are especially interested in the major quantities, such as \( T \), CO, CO\(_2\), CH\(_4\), O\(_2\), H\(_2\) and H\(_2\)O, besides the radicals OH and O which are important for the thermal NO formation. The extinction limit is an important overall parameter, playing much the same role as the flame speed for the premixed flame case. Profiles will be plotted against mixture fraction \( \xi \) instead of the spatial coordinate \( x \), to allow comparison with conserved-scalar models afterwards. The mixture fraction is determined by means of (Smooke and Giovangigli, 1991a):

\[
\xi = \frac{2Z_C/W_C + \frac{1}{2}Z_{H}/W_H + (Z_{O_L} - Z_O)/W_O}{2Z_{C,0}/W_C + \frac{1}{2}Z_{H,0}/W_H + Z_{O_L,0}/W_O} \tag{5.2}
\]

where \( Z_i \) represents the mass fraction of element \( i \) and \( W_i \) its molar mass. This formula is non-trivial, because the multi-component diffusion causes different elements to diffuse with different diffusion velocities. The above formula preserves the stoichiometric mixture fraction, and is valid for any hydrocarbon diffusion flame. The stoichiometric mixture fraction for the methane/air flames is 0.055.

### 5.3.3 Test results laminar diffusion flames

**Flame E: Standard strained diffusion flame**

Figures 5.14–5.15 show the most important scalars for flame E. The overall behavior of the mechanisms is the same, but some important differences are to be observed.

The Warnatz mechanisms are almost coinciding, corroborating the earlier observations in the premixed flames that neglecting C\(_2\)-species and higher alkanes does not significantly alter the results, as far as the major species are concerned.

The *full*-Glarborg mechanism produces too low temperatures compared to all other mechanisms. The prediction of CO and CO\(_2\)-levels is rather sensitive to the applied mechanism, as is the case for the radical mole fractions. Figure 5.16 shows that the location of the OH-maximum falls between the O-maximum (on the lean side) and the H-maximum (on the rich side).

Table 5.8 presents numerical values to be compared with calculations reported by others (Dixon-Lewis *et al.*., 1984; Smooke and Giovangigli, 1991a) and with measurements by Tsuji (1982).
Chapter 5. Laminar flame calculations

Figure 5.14: Comparison of temperature profiles in a moderately strained counterflow diffusion flame (Flame E).

Figure 5.15: Comparison of major species profiles in a moderately strained counterflow diffusion flame (Flame E). For symbols see Figure 5.14.

Flame F: Strained diffusion flame with preheated air

Figures 5.17–5.19 and Table 5.9 show the most important scalars for flame F. The first observation to be made is the fact that differences between the mechanisms are now more pronounced than for flame E. The high temperature of flame F causes reverse reactions
5.3. Laminar diffusion flame results

![Graph showing radical species profiles in a moderately strained counterflow diffusion flame (Flame E). For symbols see Figure 5.14.](image)

**Figure 5.16**: Comparison of radical species profiles in a moderately strained counterflow diffusion flame (Flame E). For symbols see Figure 5.14.

**Table 5.8**: Comparison of laminar flamelet results with literature values for flame E.

<table>
<thead>
<tr>
<th>mechanism</th>
<th>(T_{\text{max}}) (K)</th>
<th>(X_{\text{CO,\text{max}}}) ((\times 10^3))</th>
<th>(X_{\text{O,\text{max}}}) ((\times 10^3))</th>
<th>(X_{\text{OH,\text{max}}}) ((\times 10^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>skel-Smooke</td>
<td>2016</td>
<td>3.29</td>
<td>2.63</td>
<td>5.98</td>
</tr>
<tr>
<td>C(_1)-Kee</td>
<td>2007</td>
<td>4.55</td>
<td>2.83</td>
<td>6.21</td>
</tr>
<tr>
<td>full-Glarborg</td>
<td>1961</td>
<td>5.50</td>
<td>3.18</td>
<td>6.88</td>
</tr>
<tr>
<td>full-Warnatz</td>
<td>2008</td>
<td>4.01</td>
<td>2.78</td>
<td>6.50</td>
</tr>
<tr>
<td>C(_1)/C(_2)-Warnatz</td>
<td>2009</td>
<td>4.02</td>
<td>2.78</td>
<td>6.50</td>
</tr>
<tr>
<td>C(_1)-Warnatz</td>
<td>2026</td>
<td>4.92</td>
<td>2.90</td>
<td>6.45</td>
</tr>
</tbody>
</table>

**Experimental**

| Tsuji (1982)                | 1800                     | 4.0                                           |                                               |                                               |

**Other numerical data**

| Warnatz and Behrendt\(^1\)  | 1879                     | 4.56                                          | 3.13                                          | 5.84                                          |
| Dixon-Lewis et al.\(^1\)     | 1994                     | 3.94                                          | 3.11                                          | 6.48                                          |
| Fukutani and Jinno \(^1\)    | 2047                     | 4.09                                          | 2.59                                          | 6.24                                          |
| Miller et al.\(^1\)          | 1991                     | 4.71                                          | 3.14                                          | 6.29                                          |
| Peters et al.\(^1\)          | 1904                     | 3.36                                          | 2.70                                          | 5.97                                          |
| Smooke and Giovangigli (1991b)| 2067                     | 3.34                                          |                                               |                                               |
| skel-Smooke with simplifications | 2039                  | 3.79                                          | 2.93                                          | 6.36                                          |

\(^1\)Taken from Dixon-Lewis et al. (1984).
**Figure 5.17:** Comparison of temperature profiles in a moderately strained counterflow diffusion flame (Flame F).

**Figure 5.18:** Comparison of major-species profiles in a moderately strained counterflow diffusion flame (Flame F). For symbols see Figure 5.17.

...to become active. The skeletal mechanism generally have not been derived for high-temperature flames, hence some discrepancies may be anticipated. For example, in the *skel-Smooke* mechanism the reverse reaction rates had to be included in those cases where only irreversible forward reactions were specified. The reverse rates are evaluated from the...
5.3. Laminar diffusion flame results

![Graph showing radical species profiles in a moderately strained counterflow diffusion flame (Flame F).](image)

**Figure 5.19:** Comparison of radical species profiles in a moderately strained counterflow diffusion flame (Flame F). For symbols see Figure 5.17.

<table>
<thead>
<tr>
<th>mechanism</th>
<th>$T_{\text{max}}$ (K)</th>
<th>$X_{\text{CO},\text{max}}$ ($\times 10^2$)</th>
<th>$X_{\text{H}_2,\text{max}}$ ($\times 10^2$)</th>
<th>$X_{\text{O},\text{max}}$ ($\times 10^3$)</th>
<th>$X_{\text{OH},\text{max}}$ ($\times 10^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>full-Glarborg</td>
<td>2539</td>
<td>10.2</td>
<td>10.00</td>
<td>7.10</td>
<td>19.3</td>
</tr>
<tr>
<td>full-Warnatz</td>
<td>2531</td>
<td>8.2</td>
<td>8.36</td>
<td>6.54</td>
<td>18.3</td>
</tr>
<tr>
<td>C$_1$/C$_2$-Warnatz</td>
<td>2532</td>
<td>8.2</td>
<td>8.36</td>
<td>6.56</td>
<td>18.3</td>
</tr>
<tr>
<td>C$_1$-Warnatz</td>
<td>2545</td>
<td>11.1</td>
<td>9.08</td>
<td>7.06</td>
<td>19.1</td>
</tr>
<tr>
<td>skel-Smooke</td>
<td>2541</td>
<td>8.2</td>
<td>6.53</td>
<td>6.80</td>
<td>17.4</td>
</tr>
<tr>
<td>C$_1$-Kee</td>
<td>2528</td>
<td>10.0</td>
<td>7.53</td>
<td>7.10</td>
<td>18.3</td>
</tr>
</tbody>
</table>

**Table 5.9:** Comparison of laminar flamelet results for different mechanisms using preheated air at 1400 K (Flame F).

forward rates and the corresponding equilibrium constant for each reaction. Without this modification the \textit{skek-Smooke} mechanism produced a maximum flame temperature which was 200 K higher. This supports the idea that in the preheated air flame the chemistry is closer to equilibrium.

With respect to the profiles of the major species, Figure 5.18 shows good agreement for the O$_2$ mole fraction. The oxidation of CH$_4$, however, differs for the mechanisms with and without C$_2$-species, the latter mechanisms exhibiting a slower fuel decomposition rate. The profiles for CO$_2$ and CO deviate considerably, the C$_1$-Kee, full-Glarborg and C$_1$-Warnatz mechanisms giving higher CO mole fractions on the fuel-rich side compared to the full-Warnatz, C$_1$/C$_2$-Warnatz and skel-Smooke mechanisms. These variations are consistent with the differences between the temperature profiles, which are in the order of 100 to 200 K.
TABLE 5.10: Extinction limits for laminar diffusion flame using different mechanisms.

<table>
<thead>
<tr>
<th>mechanism</th>
<th>$a_{\text{ext}}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>full-Glarborg</td>
<td>600</td>
</tr>
<tr>
<td>full-Warnatz</td>
<td>520</td>
</tr>
<tr>
<td>$C_1/C_2$-Warnatz</td>
<td>540</td>
</tr>
<tr>
<td>$C_1$-Warnatz</td>
<td>560</td>
</tr>
<tr>
<td>skel-Smooke</td>
<td>380</td>
</tr>
<tr>
<td>$C_1$-Kee</td>
<td>400</td>
</tr>
</tbody>
</table>

Comparison with flame E reveals that the mechanisms do not show the same trends in both flames. In flame F, the skel-Smooke mechanism, for example, produces the same amount of CO as the full-Warnatz mechanism, whereas the mechanisms behave differently in flame E. Generally, the CO maximum is a factor 1.5 to 1.75 higher in the hot-air flame, which implies that at high temperatures the equilibrium chemistry tends to reduce CO$_2$ to CO.

Differences are smaller for the radical species profiles, depicted in Figure 5.19. The maximum OH mole fraction is shifted slightly towards the fuel-lean side, i.e., for $\xi < \xi_{\text{at}}$. Overall, the maximum radical concentrations are much higher than for the cold-air diffusion flame, by a factor of 2.5 to 3. In conjunction with the higher temperatures, this explains why thermal NO formation rates are much higher in these high-temperature flames compared to cold-air flames.

Flame G: Strained diffusion flame near extinction

Table 5.10 expresses the large differences between the various mechanisms. Clearly, only the $C_1$-Kee and the skel-Smooke mechanism are able to reproduce the experimental value of 350 to 400 s$^{-1}$. Most probably, this is due to the fact that these mechanisms have been tested especially to perform well under highly-strained conditions. For example, the correction of only one pressure-dependent reaction in the skel-Smooke mechanism reduces the extinction limit by 80 s$^{-1}$. The Warnatz mechanisms and the full-Glarborg mechanism might be improved likewise for this purpose.

The above values were obtained with the mixture-averaged transport model to speed up the calculations. The test runs discussed previously show that multicomponent transport will lead to a downward adjustment of the extinction limits by about 20 to 30 s$^{-1}$.

5.4 Comparison with conserved-scalar models

The results obtained for flames E and F can be compared with the simple conserved-scalar chemistry models, i.e., the full-equilibrium and the constrained-equilibrium model presented in §§3.3.5 and 3.3.6, and the two-step flame sheet model with parameters $a = 0.5$ and $b = 0.5$. It is interesting to see how well these models compare with flamelet models, and what the effect of the strain rate will be. In the sequel, the skel-Smooke mechanism
TABLE 5.11: Comparison of flamelets and simple conserved-scalar models for flame E.

<table>
<thead>
<tr>
<th>model</th>
<th>$T_{\text{max}}$ (K)</th>
<th>$Y_{\text{CO, max}} \times 10^2$</th>
<th>$\xi_{\text{CO, max}}$</th>
<th>$Y_{\text{H}_2, \text{max}} \times 10^3$</th>
<th>$\xi_{\text{H}_2, \text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>flamelet $a = 10 \text{ s}^{-1}$</td>
<td>2152</td>
<td>3.27</td>
<td>0.087</td>
<td>1.61</td>
<td>0.110</td>
</tr>
<tr>
<td>flamelet $a = 100 \text{ s}^{-1}$</td>
<td>2051</td>
<td>3.38</td>
<td>0.083</td>
<td>1.28</td>
<td>0.097</td>
</tr>
<tr>
<td>flamelet $a = 300 \text{ s}^{-1}$</td>
<td>1903</td>
<td>4.29</td>
<td>0.088</td>
<td>1.19</td>
<td>0.093</td>
</tr>
<tr>
<td>full equilibrium</td>
<td>2233</td>
<td>22.40</td>
<td>0.163</td>
<td>31.40</td>
<td>0.163</td>
</tr>
<tr>
<td>constrained equilibrium</td>
<td>2229</td>
<td>6.20</td>
<td>0.073</td>
<td>3.51</td>
<td>0.314</td>
</tr>
<tr>
<td>tuned constr. eq.</td>
<td>2233</td>
<td>3.84</td>
<td>0.064</td>
<td>1.81</td>
<td>0.395</td>
</tr>
<tr>
<td>flame sheet, $a = 0.5$, $b = 0.5$</td>
<td>2246</td>
<td>7.41</td>
<td>0.085</td>
<td>10.07</td>
<td>0.085</td>
</tr>
<tr>
<td>tuned flame sheet, $a = 0.65$, $b = 0.9$</td>
<td>2246</td>
<td>3.85</td>
<td>0.064</td>
<td>1.58</td>
<td>0.064</td>
</tr>
</tbody>
</table>

has been used to generate the flamelet profiles, since this mechanism performs well under many circumstances, and it converges quickly. Still, no radiation has been taken into account.

5.4.1 Methane/air flame with cold air

Figure 5.20 and Table 5.11 compare several profiles for the flame E case. Increasing the flamelet strain rate causes a temperature decrease, an effect which cannot be accounted for by the simple conserved-scalar models. Around $\xi = \xi_{\text{st}}$, the equilibrium temperature is higher than the flamelet temperature by over 100 K.

The full-equilibrium model yields far too low temperatures and too high CO concentration at fuel-rich conditions, and therefore is not realistic in low-temperature natural gas flames. The constrained-equilibrium model is able to reproduce the overall flamelet behavior much better. This is not surprising, since Bilger and Stårner developed the model for this purpose.

The two-step flame sheet model and the constrained-equilibrium model can be adapted to attain better agreement with the flamelet profiles. For the two-step flame sheet model this is achieved by defining the CO:CO$_2$-ratio and the H$_2$:H$_2$O-ratio for the first global oxidation step. The constrained-equilibrium model can be tuned by changing the value of $\xi_{\text{ig}}$, which in the standard case was defined as $\xi_{\text{ig}} = \xi_{\text{st}} + 0.018$. 
Chapter 5. Laminar flame calculations

**Figure 5.20:** Comparison of flamelet profiles and simple conserved-scalar models, for temperature and several species mass fractions. (Flame E). Solid line: 2-step flame sheet; dotted line: full equilibrium; dashed line: constrained equilibrium. Flamelet data: \( o \ a = 10 \text{ s}^{-1}, \times \ a = 100 \text{ s}^{-1}, \Delta \ a = 300 \text{ s}^{-1} \).

In the table, we have listed the results for the improved constrained-equilibrium model, by discarding the intermediate hydrocarbons and taking \( \xi_{\text{ig}} = \xi_{\text{st}} + 0.008 \). The tuned model is only applicable for \( T_{\text{air}} = 300 \text{ K} \), and yields better agreement for the CO profile. The two-step flame sheet model can be tuned to yield the same global behavior as the constrained-equilibrium model, using \( a = 0.65 \) and \( b = 0.9 \). The flamelet model shows CO leakage towards the lean side, which is not predicted by the simple conserved-scalar models. Generally, the flamelet models exhibit a maximum H\(_2\) mass fraction not coinciding with the CO maximum, implying that H\(_2\) is formed and consumed more quickly than CO. This chemical kinetic effect is not reproduced by the simple models, which predict coinciding CO and H\(_2\) maxima.

It is observed that the OH radical is not far from equilibrium in this low-temperature flame, but the O radical (important for NO formation) is predicted to be in superequilibrium concentrations by the flamelet model. This explains the so-called superequilibrium factors...
used in the literature to model thermal NO formation by means of a simple conserved-scalar model without direct radical concentration information. Furthermore, the flamelet profiles for the radical species are shifted somewhat to the lean side, as a result of convective and diffusive transport processes.

### 5.4.2 Methane/air flame with preheated air

In Figure 5.21 and Table 5.12 the same comparison is depicted for the flame F case with preheated air. The temperature profiles agree well near $\xi = \xi_u$, but on the rich side the constrained-equilibrium model gives a higher temperature than the flamelet model, by about 100 K. This is consistent with the CO level, which is lower in the constrained equilibrium model. The flamelet profiles for CO show higher maximum values for increasing strain rate, which is just opposite to the flame E case at lower temperatures.

Optimized values in the two-step flame sheet model for the flame F case are $a = 0.65$ and $b = 0.9$, but these may have to be changed for other air temperatures for the case of radiative heat losses. The constrained-equilibrium model is tuned by taking $\xi_{\text{sg}} = \xi_u + 0.035$.

The prediction of radical concentrations by the constrained-equilibrium model agrees qualitatively and quantitatively much better with the flamelet model compared to the flame E case. Still, the flamelet profiles are shifted towards to lean side. The superequilibrium
factor of the O radical profiles now is about 2, compared to 3 to 5 for flame E.

5.5 Natural gas versus diluted methane

The major component of natural gas is CH₄. The exact composition of natural gas, however, differs for each country and location. In order to verify whether natural gas can be taken as diluted methane, we have simplified the composition of the gas by discarding all higher alkanes. In Table 5.13 we have given the composition of Groningen natural gas, and the two simplified versions, called gas2 and gas1 in the sequel. The reduction of the set of species was carried out under the constraint that the calorific value of the gas remained unchanged, hence the mole fractions have been adapted a little bit. Gas2 contains only methane and ethane as fuel species, whereas gas1 contains only methane.

Table 5.14 compares the calculated results for a stoichiometric freely propagating flame (flame A). The data for pure methane have been listed as well. The laminar flame speeds of pure methane and gas2 are almost the same. Apparently the inclusion of ethane (with
### Table 5.13: Simplification of Groningen natural gas and IFRF gas by discarding higher alkanes.

<table>
<thead>
<tr>
<th>species</th>
<th>Groningen gas2 CH₄, C₂H₆</th>
<th>Groningen gas1 CH₄</th>
<th>IFRF gas CH₄, C₂H₆</th>
<th>IFRF gas CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>0.8129</td>
<td>0.8095</td>
<td>0.8527</td>
<td>0.8525</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.0287</td>
<td>0.0389</td>
<td>-</td>
<td>0.0560</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>0.0038</td>
<td>-</td>
<td>-</td>
<td>0.0121</td>
</tr>
<tr>
<td>C₅H₁₀</td>
<td>0.0015</td>
<td>-</td>
<td>-</td>
<td>0.0067</td>
</tr>
<tr>
<td>C₅H₁₂</td>
<td>0.0004</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C₆H₁₄</td>
<td>0.0005</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N₂</td>
<td>0.1432</td>
<td>0.1426</td>
<td>0.1386</td>
<td>0.0713</td>
</tr>
<tr>
<td>O₂</td>
<td>0.0001</td>
<td>0.0001</td>
<td>0.0001</td>
<td>-</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0089</td>
<td>0.0089</td>
<td>0.0086</td>
<td>0.0013</td>
</tr>
</tbody>
</table>

### Table 5.14: Comparison of properties of flame A (freely propagating stoichiometric premixed flame) with pure methane and simplified Groningen natural gas.

<table>
<thead>
<tr>
<th>fuel</th>
<th>mechanism</th>
<th>sₜ (cm/s)</th>
<th>T_max (K)</th>
<th>X_CO_max (×10²)</th>
<th>X_O_max (×10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>full-Warnatz</td>
<td>36.6</td>
<td>2176</td>
<td>4.18</td>
<td>2.94</td>
</tr>
<tr>
<td>gas2</td>
<td>full-Warnatz</td>
<td>36.4</td>
<td>2199</td>
<td>4.17</td>
<td>2.92</td>
</tr>
<tr>
<td>gas2</td>
<td>C₁/C₂-Warnatz</td>
<td>36.5</td>
<td>2198</td>
<td>4.17</td>
<td>2.93</td>
</tr>
<tr>
<td>gas1</td>
<td>C₁-Warnatz</td>
<td>34.4</td>
<td>2154</td>
<td>4.04</td>
<td>2.76</td>
</tr>
</tbody>
</table>

### Table 5.15: Comparison of pure methane and simplified Groningen natural gas for flames E and F (diffusion flames with cold and preheated air).

<table>
<thead>
<tr>
<th>fuel</th>
<th>mechanism</th>
<th>Flame E</th>
<th>Flame F</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T_max (K)</td>
<td>X_CO_max (×10²)</td>
<td>X_O_max (×10³)</td>
</tr>
<tr>
<td>methane</td>
<td>2008</td>
<td>3.78</td>
<td>2.78</td>
</tr>
<tr>
<td>gas2</td>
<td>1983</td>
<td>3.68</td>
<td>2.66</td>
</tr>
<tr>
<td>gas2</td>
<td>2018</td>
<td>3.70</td>
<td>2.67</td>
</tr>
<tr>
<td>gas1</td>
<td>1988</td>
<td>3.62</td>
<td>2.64</td>
</tr>
</tbody>
</table>

A higher flame speed than methane) and the dilution by nitrogen are counterbalancing effects. If the ethane is removed from gas2 we obtain gas1, which has a lower flame speed than pure methane. For the sake of completeness we have calculated the gas2 fuel with the full Warnatz mechanism and the C₁/C₂-Warnatz mechanism, showing negligible differences.

A similar comparison for the different fuels is presented in Table 5.15, where the diffusion flamelets E and F have been computed. Again, the differences between pure
methane and natural gas are virtually negligible. As a consequence, we may expect that a representation of natural gas by diluted methane (gas 1), calculated by the simplified C$_1$-Warnatz mechanism will yield reliable results.

### 5.6 Sensitivity analysis and reaction pathways

The calculated premixed and counterflow diffusion flame profiles can be further analyzed by inspecting the reaction pathways for the formation and destruction of species, and by performing a sensitivity analysis of results with respect to variations in the rate constants. The information thus obtained can then be used for further reduction of reaction mechanisms. The introduction of subsequent simplifications of reaction mechanisms generally limits the applicability of the simplified mechanism. One could even continue and derive a reduced mechanism by means of partial equilibrium and steady state assumptions, but this is not carried out here, since the application of the joint-PDF closure model (see Section 3.7) only works for a set of elementary reactions.

In the reaction pathway analysis, the C$_1$/C$_2$-Warnatz mechanism was used to investigate the C-reaction structure, for a number of different flames. As put forward by Warnatz (1984), the C$_2$-chain oxidation becomes important for rich flames, because of the recombination of CH$_3$ to C$_2$H$_6$ or C$_2$H$_4$. The present results for lean premixed flames and laminar diffusion flamellets show that in general the C$_2$-chain oxidation is of minor importance. If one were interested in modeling of soot formation in hydrocarbon flames the C$_2$-chain analysis would become important, and large differences between the mechanisms will occur. This observation cannot be extrapolated to the case of high-temperature flames with preheated air, since the prediction of CO profiles for the flame F case proved to be sensitive to the inclusion of C$_2$-oxidation reactions.

<table>
<thead>
<tr>
<th>nr.</th>
<th>reaction</th>
<th>relative sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H+O$_2$⇌OH+O</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>OH+H$_2$⇌H$_2$O+H</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>H+OH+M⇌H$_2$O+M</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>H+O$_2$+M⇌HO$_2$+M</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>CO+OH⇌CO$_2$+H</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>CHO+M⇌CO+H+M</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>CHO+H⇌CO+H$_2$</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>CH$_3$+O⇌CH$_2$O+H</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>CH$_3$+H⇌CH$_4$</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>CH$_4$+H⇌CH$_3$+H$_2$</td>
<td></td>
</tr>
<tr>
<td>78</td>
<td>CH$_3$OH⇌CH$_3$+OH</td>
<td></td>
</tr>
</tbody>
</table>

$\text{\textcolor{black}{\text{\cellcolor{gray}}}} = 0.090$

**Figure 5.22:** Sensitivity of laminar flame speed for the flame A case, using the C$_1$/C$_2$-Warnatz mechanism.
5.6. Sensitivity analysis and reaction pathways

<table>
<thead>
<tr>
<th>nr.</th>
<th>reaction</th>
<th>relative sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H+O₂⇆OH+O</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>OH+H₂⇆H₂O+H</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>H+O₂+M⇆HO₂+M</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>CO+OH⇆CO₂+H</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>CHO+M⇆CO+H+M</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>CH₂+O₂⇆CO+OH+H</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>CH₃+O⇆CH₂O+H</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>CH₃+H⇆CH₄</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>CH₃+OH⇆CH₃O+H</td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>CH₄+H⇆CH₃+H₂</td>
<td></td>
</tr>
<tr>
<td>78</td>
<td>CH₃OH⇆CH₃+OH</td>
<td></td>
</tr>
<tr>
<td>105</td>
<td>C₂H₃⇆C₂H₂+H</td>
<td></td>
</tr>
</tbody>
</table>

\[ \xi = 0.075 \]

**Figure 5.23:** Sensitivity of temperature at \( \xi = \xi_{st} \) for the flame G case, using the C₁/C₂-Warnatz mechanism.

<table>
<thead>
<tr>
<th>nr.</th>
<th>reaction</th>
<th>relative sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H+O₂⇆OH+O</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>OH+H₂⇆H₂O+H</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>H+O₂+M⇆HO₂+M</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>CO+OH⇆CO₂+H</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>CHO+M⇆CO+H+M</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>CH₂+O₂⇆CO₂+H₂</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>CH₃+H⇆CH₄</td>
<td></td>
</tr>
<tr>
<td>74</td>
<td>CH₄+OH⇆CH₃+H₂O</td>
<td></td>
</tr>
<tr>
<td>78</td>
<td>CH₃OH⇆CH₃+OH</td>
<td></td>
</tr>
</tbody>
</table>

\[ \xi = 0.046 \]

**Figure 5.24:** Sensitivity of CO at its maximum value for the flame A case, using the C₁/C₂-Warnatz mechanism.

Instead of giving all the sensitivity coefficients at different grid nodes for the various species and reactions, only a brief summary of the results is given here. The results are presented for the C₁/C₂-Warnatz mechanism, but most findings hold for other mechanisms as well. Figure 5.22 shows the sensitivity of the laminar flame speed for the most important reaction rates in the C₁/C₂-Warnatz mechanism. Clearly the fast H₂/O₂ shuffle reactions have a large influence on the flame speed, but some three-body recombination reactions, the CO oxidation chain and the fuel decomposition to CH₃ are important as well. These findings are similar to the sensitivity of the temperature at \( \xi = \xi_{st} \) for a counterflow diffusion flame near extinction (Flame G), as shown in Figure 5.23.

An investigation of the sensitivity of CO mass fractions reveals that more reactions
### Table 5.16: The most important reaction rates for the flame A and flame G case.

<table>
<thead>
<tr>
<th>reaction</th>
<th>skel-Smooke</th>
<th>C$_1$/C$_2$-Warnatz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A$ (cm$^3$mol$^{-1}$s$^{-1}$)</td>
<td>$\beta$</td>
</tr>
<tr>
<td>H + O$_2$ $\rightarrow$ OH + O</td>
<td>$2.0 \times 10^{14}$</td>
<td>0.0</td>
</tr>
<tr>
<td>CO + OH $\rightarrow$ CO$_2$ + H</td>
<td>$1.5 \times 10^{14}$</td>
<td>1.3</td>
</tr>
<tr>
<td>H + O$_2$ + M $\rightarrow$ HO$_2$ + M</td>
<td>$2.3 \times 10^{18}$</td>
<td>-0.8</td>
</tr>
<tr>
<td>CH$_3$ + H $\rightarrow$ CH$_4$</td>
<td>$1.9 \times 10^{36}$</td>
<td>-7.0</td>
</tr>
</tbody>
</table>

become important in the region where CO has its maximum, for the premixed flames as well as the diffusion flames. Figures 5.24 and 5.25 show some examples. For other species and radicals, different observations can be made. In all cases, however, temperature is a very important quantity, and therefore the reactions which control the temperature also largely determine the radical pool concentrations. To conclude this section, Table 5.16 gives the most important reactions in the C$_1$/C$_2$-Warnatz and the skel-Smooke mechanism, for the flame A and flame G cases.
5.7 Conclusions

To conclude this chapter, the observations and discussions of the previous sections are summarized.

The numerical codes used to simulate the laminar premixed and counterflow diffusion flames were found to be accurate and proved to be a useful tool to study in detail the chemistry of natural gas combustion.

As a spin-off of the premixed burner-stabilized flame simulations, it was shown that calibration of absolute OH concentration LIF measurements is possible, but that the relative uncertainty is rather large ($\approx 30\%$). If more detailed temperature measurements were available, one could be more conclusive about the influence of radiation on the laminar flame. Thermocouple measurements seem to be very sensitive to the flame structure, surface catalysis and radiation, which makes it difficult to calibrate these instruments for measurements within the reaction zone. Beyond the reaction zone, however, thermocouples and Coherent Anti-Stokes Raman Spectroscopy (CARS) can be used, and the most recent experimental data show an error not larger than 50 K. This error seems to be of the same order of magnitude of modeling errors, which involve flame radiation and the boundary conditions at the burner surface.

Comparison between laminar flamelet results and the simple conserved scalar models shows that for temperature and main species concentrations and for OH-radical concentrations, the predictions of the constrained-equilibrium model resembles the laminar flamelet data reasonably well, even for the case of preheated air. The O-radical prediction, however, deviates substantially, explaining the use of so-called superequilibrium factors in models for thermal NO formation. Fortunately, this superequilibrium level strongly decreases in the case of preheated air. The OH radical profiles of the equilibrium models do not differ very much from the flamelet profiles, suggesting that OH radicals are in partial equilibrium, even for the 300 K air-temperature case. The constrained-equilibrium model and the two-step flame sheet model can be tuned to resemble the flamelet data even more accurately. Different tuning parameters are required for the preheated air case. The full-equilibrium model and the one-step flame sheet model are to be rejected for further simulation purposes, since they predict unrealistic CO-levels and temperature.

Of the various mechanisms tested, the skel-Smooke mechanism is attractive because it is a small mechanism and it produces reasonable results for lean-to-stoichiometric premixed flames and for the diffusion flamelets. The predictions of the C$_1$-Kee mechanism deviate slightly from those of the skel-Smooke mechanism, but the C$_1$-Kee mechanism performs better for fuel-rich premixed flames. Of the full mechanisms, the full-Warnatz mechanism was superior to the full-Glarborg mechanism, which could be explained by the fact that the latter mechanism has not been developed for the atmospheric laminar flames discussed in this chapter.

Sensitivity analysis has revealed that the full full-Warnatz mechanism can be successfully reduced to the C$_1$-Warnatz mechanism, containing less species and reactions. This is due to the fact that the C$_2$-chemistry is rather unimportant in the flames investigated, except for fuel-rich conditions. The C$_1$-Warnatz mechanism can be reduced even further
by discarding unimportant species and reactions for the specific laminar flames studied. The correct prediction of CO in preheated air flames, however, requires the inclusion of $C_2$-species in the mechanism, and the prediction of soot formation processes always requires $C_2$-chemistry.

The complex mixture of hydrocarbons in natural gas can be successfully reduced to diluted methane, with the constraint that the lower calorific value of the diluted methane should match the original natural gas. In conjunction with the above, the skel-Smooke mechanism and the $C_1$-Warnatz mechanism are recommended for use in the joint-PDF closure model, if one wishes to study OH radicals. For better prediction of CO (and temperature) and for those cases where $C_2$-species are important, particularly for soot formation, the $C_1/C_2$-Warnatz mechanism is recommended.
CHAPTER 6

Results on axisymmetric diffusion flames

This chapter deals with the numerical simulation of axisymmetric turbulent diffusion flames, with emphasis on the different chemistry models discussed in Chapter 3. The calculations performed are aimed mainly at the simulation of the Delft piloted diffusion flame burner developed in our group, using a set of different boundary and inlet conditions.

6.1 Introduction

The literature on atmospheric turbulent diffusion flames is abundant, and can be cast into many categories, regarding theory as well as experiments. Theoretical and numerical studies have approached the task of turbulent diffusion flame modeling from various sides. The next section will discuss some important aspects of the theory of turbulent diffusion flames with application to the specific flames studied in this chapter.

In experimental studies, a wide variety of measurement techniques is used, such as laser-Doppler anemometry (LDA) and hot-wire techniques for velocity and turbulence quantities, sampling probe measurements, Raman spectroscopy and laser-induced fluorescence (LIF) measurements of species concentrations, and thermocouple measurements and coherent anti-Stokes Raman spectroscopy (CARS) for temperature. Besides these experimental methods, there is a large choice of flow geometries and fuel compositions, all leading to different overall flame characteristics. In the next section we will describe the specific geometry of the experimental set-up of turbulent diffusion flame, hereafter called the Delft piloted diffusion flame burner. In later sections, results of calculations of this flow geometry will be presented.

6.1.1 Burner geometry

The Delft piloted diffusion flame burner was designed to yield a stable axisymmetric turbulent non-premixed flame, burning natural gas (or methane) in a co-flowing air stream. The fuel jet exit has an inner diameter of 6 mm, and the fuel pipe is about 1 m long, sufficient to establish a fully developed turbulent flow at the nozzle. Two air streams are involved. The primary air is issued from an annulus around the fuel nozzle, with an inner diameter of 15 mm and an outer diameter of 45 mm. The velocity of the primary air can be varied independently, and can be preheated up to over 700 K.

Figure 6.1 shows a top view of the burner. The burner rim has a finite thickness of 4.5 mm, on which 12 pilot flames are located, issued from 12 holes of 0.5 mm width, and lying on a ring of 7 mm diameter. The pilot flames were premixed flames of a stoichiometric air/H₂/acetylene mixture, with a C:H ratio equal to that of the natural gas (about 4:1), a composition suggested earlier by Stårner and Bilger (1985).
In addition to the stabilizing influence of the pilot flames, there is also a small recirculation zone just above the burner rim, which has a stabilizing effect. In the experiments it turned out that the bluff-body-like influence of the rim was not sufficient to stabilize the flame under all circumstances, but that the pilot flames always produced a stable flame attached to the nozzle, for the range of fuel and primary air velocities investigated. However, further downstream the flame may still exhibit local extinction as a result of strain induced by the shear layer.

The annular air is surrounded by a low speed co-flowing air stream of about 0.3 m/s, just sufficient to avoid an external recirculation zone. This secondary air is provided by a throat, yielding low turbulence levels at the combustion chamber entrance, and a reasonably flat velocity profile. The secondary air is always kept at room temperature (295 K).

The burner chamber, depicted in figure 6.2, was octagonal with a separation of 57 cm between the sides, and was 90 cm long. In the calculations we used an axisymmetrical chamber of 58 cm diameter, and 150 cm length. It is assumed that the combustion chamber walls are located far enough away from the flame to allow such a simplification of the geometry. The extended computational domain was used to minimize effects of the homogeneous Neumann boundary conditions applied at the outlet.
Figure 6.2: Cross section of burner chamber used for laboratory-scale diffusion flames.
TABLE 6.1: Inlet conditions for six different flames.

<table>
<thead>
<tr>
<th>flame</th>
<th>$\Phi_m$ (g/s)</th>
<th>$U$ (m/s)</th>
<th>$T$ (K)</th>
<th>Re</th>
<th>$\Phi_m$ (g/s)</th>
<th>$U$ (m/s)</th>
<th>$T$ (K)</th>
<th>Re</th>
<th>$L_f$ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.24</td>
<td>11.0</td>
<td>295</td>
<td>4900</td>
<td>3.69</td>
<td>2.2</td>
<td>295</td>
<td>4400</td>
<td>0.87</td>
</tr>
<tr>
<td>II</td>
<td>0.34</td>
<td>15.4</td>
<td>295</td>
<td>6800</td>
<td>5.17</td>
<td>3.1</td>
<td>295</td>
<td>6200</td>
<td>0.90</td>
</tr>
<tr>
<td>III</td>
<td>0.48</td>
<td>21.9</td>
<td>295</td>
<td>9700</td>
<td>7.38</td>
<td>4.4</td>
<td>295</td>
<td>8800</td>
<td>0.85</td>
</tr>
<tr>
<td>IV</td>
<td>0.48</td>
<td>21.9</td>
<td>295</td>
<td>9700</td>
<td>13.39</td>
<td>8.0</td>
<td>295</td>
<td>16000</td>
<td>0.70</td>
</tr>
<tr>
<td>V</td>
<td>0.48</td>
<td>50.4</td>
<td>675</td>
<td>5300</td>
<td>7.38</td>
<td>11.2</td>
<td>654</td>
<td>5500</td>
<td>0.67</td>
</tr>
<tr>
<td>VI</td>
<td>0.48</td>
<td>49.6</td>
<td>664</td>
<td>5300</td>
<td>13.39</td>
<td>20.4</td>
<td>688</td>
<td>9300</td>
<td>0.52</td>
</tr>
</tbody>
</table>

6.1.2 Flow conditions

In a series of experiments by De Vries (1994) and Stroomer (1995), six different flames were studied by varying the inlet conditions of the fuel and primary air. The calculations described in the sequel have employed the same inlet conditions in order to allow comparison of results. The inlet conditions were varied by changing the flow rate of the fuel and primary air stream, and by using preheated primary air. Due to the rather long fuel pipe, about 1 m, the preheated primary air also caused a preheating of the fuel, which could not be avoided in the experiments. Table 6.1 summarizes the major experimental inlet conditions for the six different flames.

Apart from the six different flames, additional experiments were performed on the non-reacting equivalent of flame III, called jet I. In these experiments, the natural-gas fuel jet was replaced with an air jet of the same volume flow, which was used to study the difference between the turbulence structure of the reacting case and the non-reacting case. Furthermore, the non-reacting jet provided accurate data for the validation of the turbulence model and the numerical code.

6.2 Validation of the numerical code

The numerical code used for this investigation was adopted from Bockhorn (Bockhorn, 1989), and is based on the CORA2 computer code for axisymmetrical combustion chamber flows, developed at Imperial College by Srivatsa (1977). Over the years, the code has been validated for axisymmetric jet flows and flames, especially by Bockhorn who modeled CO/air and H$_2$/air flames with successfully.

Our flow geometry, however, has the peculiar feature of two coaxial jets in a low-speed co-flowing stream, a configuration which has not yet been described in the literature in detail. Therefore, some further validation of the numerical and mathematical model is carried out, to establish its accuracy. For this purpose, three cases are studied: an axisymmetric laminar jet, an axisymmetric non-reacting free turbulent jet and the non-reacting cold-flow jet described as jet I.
6.2. Validation of the numerical code

The laminar jet data are compared with theoretical data derived from asymptotic similarity analysis, whereas the turbulent jet data are compared with the measurements of Antonia and Bilger (1973, 1976). They have investigated the mixing of a passive scalar in an axisymmetric jet in a co-flowing stream, using a wind tunnel confinement. Apart from turbulence data, they also measured concentration profiles and probability density functions, which can be tested by our code as well. Emphasis is on the prediction of the self-similar region of mean velocity and mean concentration, the jet spreading rate, the centreline velocity decay, the intermittency function, and turbulent fluctuations of the quantities.

Other studies on non-reacting jets (free or confined, uniform or variable density, plane or axisymmetric, buoyant or non-buoyant) have been reported in numerous papers, and all have provided some information relevant to our case. However, they will not be discussed here in detail, mainly because this study is not concerned primarily with non-reacting mixing of jets or advanced turbulence modeling. The test cases described above merely are a tool to establish the validity of model assumptions and numerical schemes.

6.2.1 Laminar jet data

For a laminar jet in a free environment, similarity analysis (Sanders, 1994) shows that the half-width spreading rate is a function of the Reynolds number only:

\[ S_{1/2} = \frac{5.945}{Re} \]

where \( Re = \rho_0 u_0 D / \mu_0 \) (the index 0 refers to nozzle inlet conditions). Because of entrainment of ambient fluid, the mass flux \( \dot{M} \) grows linearly with downstream distance \( x \). Therefore, the mass-entrainment parameter \( E \) is a constant:

\[ E = \frac{1}{M_0} \frac{d\dot{M}}{dx} \]

For our laminar jet calculations, we used a jet Reynolds number of 650. The numerical grid extended 10 diameters in radial and 100 diameters in axial direction. A uniform radial grid was used near the nozzle, and a stretching function was applied towards the free edge; in axial direction a stretched grid with a constant stretching factor was used. The fluid was air, with \( \rho = 1.19 \text{ kg/m}^3 \) and \( \mu = 1.84 \times 10^{-5} \text{ kg/m/s} \). The numerical solution method was the standard elliptic ADI method described in Chapter 4.

Boundary conditions A uniform velocity profile was imposed at the inlet plane, and symmetry boundary conditions were used for \( r = 0 \). At the outlet boundary, homogeneous Neumann boundary conditions were applied for all variables. As a consequence of mass continuity, the condition \( \partial u / \partial x \) at the outlet plane enforced \( v = 0 \) at the outlet. At the free edge Dirichlet conditions were imposed, using the prevailing ambient values for the axial velocity. (For a free round jet, the ambient axial velocity is zero.) The free-edge boundary
condition for the radial velocity was derived from the continuity equation. If the free-edge boundary is located sufficiently far away from the mixing region of the jet, the velocity gradients $\partial u/\partial r$ and $\partial u/\partial x$ will both be zero. Hence, the proper boundary condition for the $v$-velocity is $\partial(rv)/\partial r = 0$, which is not equal to a Neumann condition. For all boundaries homogeneous Neumann conditions were used for the pressure correction. The ambient pressure was taken to be 101325 Pa, imposed at the common corner point of the free edge and the outlet boundary, to serve as an 'anchor point' for the absolute pressure. Gravitational forces were neglected.

The outlet boundary conditions influence the jet development, since at the outlet plane the spreading rate is forced to zero. When comparing the numerical results with similarity data, this should be kept in mind. In order to enhance the convergence, a low-speed coflow was used with a velocity of 2% of the nozzle bulk velocity. This coflow does not have a significant effect on the jet spreading rate, as will be shown in the sequel. Figure 6.3 shows the streamline contours for the laminar jet with $Re = 650$ without a coflow and with a low-speed coflow. These streamline patterns are quite different, but the jet's behaviour appears to be virtually unchanged.

**Grid dependence and discretization scheme** The first-order upwind scheme is notorious for its false (or numerical) diffusion. If the streamlines are skewed with respect to the numerical grid, artificial diffusion is induced, which can be described by a false-diffusion coefficient $\Gamma_{\text{false}}$. For a rectilinear grid cell, one can derive:

$$R_{\text{false}} = \frac{\Gamma_{\text{false}}}{\Gamma} = \frac{|V|\Delta x \Delta y \sin 2\theta}{4\Gamma(\Delta x \sin^3 \theta + \Delta y \cos^3 \theta)} \quad (6.3)$$
Here $\theta$ is the angle between the $x$-axis and the velocity vector, and $|V|$ is the norm of the velocity vector. For a uniform grid ($\Delta x = \Delta y$) it can easily be shown that the false diffusion ratio $R_{\text{false}}$ has a maximum for $\theta = \pi/4$. If $\Delta x \gg \Delta y$, we find that $R_{\text{false}}$ depends linearly on the cell size $\Delta y$. In general, the influence of false diffusion can be reduced by choosing a finer mesh, but more importantly, by using a higher-order discretization scheme.

In the case of a free jet with low-speed coflow, the streamlines are well aligned with the mesh lines, except near the inlet. Hence, this configuration suffers to a lesser extent from false diffusion effects. Without the coflow, strong numerical diffusion will occur in the regions where the horizontal streamlines coming from the free edge are bent into the axial direction of the jet. Figure 6.5 shows the false diffusion ratio for the free laminar jet without coflow, for a coarse mesh of $50 \times 20$ grid cells, whereas figure 6.6 shows the ratio at the same axial locations for a $150 \times 60$ mesh. It is clearly seen that false diffusion becomes insignificant further away from the nozzle, and that grid refinement reduces the false diffusion. Moreover, the regions of strong false diffusion are concentrated at the edge of the jet, where velocities are small. Therefore, the influence of false diffusion on the jet development remains limited.

The jet development towards similarity is described by the spreading rate parameter $S_{1/2}^\eta$. In figure 6.7 the spreading rate for several different grids and discretization schemes is depicted. The theoretical spreading rate of $9.1 \times 10^{-3}$ is predicted fairly accurately for $x/D > 50$, even on the coarsest mesh suffering from false diffusion. For smaller distances away from the nozzle, the constant spreading rate has not yet established itself.

Another test for the validity of the numerical code is the similarity profile, presented in figure 6.8. The velocity $u^*$ is scaled with the centerline value and the ambient velocity, giving $u^* = 1$ at the centerline and $u^* = 0$ for $\eta \to \infty$. The radial coordinate is scaled with the jet half-width $y_{1/2}$, so that $u^*(\eta = 1) = 0.5$ by definition. Similarity is observed
except for the profile nearest to the nozzle.

From the computations on the laminar free jet, we conclude that the numerical code is The jet development towards similarity is described by the spreading

### 6.2.2 Turbulent free jet data

The second test case for the validation of the numerical code is the non-reacting turbulent round jet. Turbulent round jets have been described abundantly in the literature, both experimentally and numerically. We do not present a detailed literature survey on the subject here, but we only emphasize some relevant experimental and numerical data.
6.2. Validation of the numerical code

Figure 6.7: Spreading rate of a free laminar jet at Re = 650, computed on different grids, using different discretization schemes. (a) 50 x 20 mesh, upwind scheme, no coflow. (b) 150 x 60 mesh, upwind scheme, no coflow. (c) 150 x 60 mesh, upwind scheme, with coflow. (d) 150 x 60 mesh, hybrid scheme, with coflow.

Figure 6.8: Similarity profiles for the axial velocity, computed for a free laminar jet at Re = 650, using a 150 x 60 mesh with the upwind discretization scheme.

In the literature, several aspects of non-reacting jets are discussed. Like the laminar jet, similarity analysis has been used to establish general scaling laws for round jet development. Important issue are the influence of density variations on these scaling laws, the influence of coflow, and the mixing behaviour of a conserved (passive) scalar. The review papers by Gouldin et al. (1986) and Sislain et al. (1988) provide details on this, both experimentally and numerically. Fundamental experimental investigations on turbulence structure and scalar mixing have been conducted by Wygnanski and co-workers.
Chapter 6. Results on axisymmetric diffusion flames


More recent work has been published by Pitts (1991), Panchapakesan and Lumley (1993a, 1993b), Antonia and Kim (1993), Sanders (1994). Of relevance to our case are the general scaling laws. For a turbulent free round jet (without coflow), the centerline velocity $u_{cl}$ is found to be inversely proportional to the distance from the nozzle:

$$
\frac{u_0}{u_{cl}} = K_u \left( \frac{x - x_0}{D} \right)
$$

(6.4)

Here, $u_0$ is the nozzle bulk velocity, and $x_0$ is some offset value for the axial coordinate, which is smaller than $5D$. Experimental data suggest $K_u \approx 0.170$, but there is some 10% scatter between various authors. A more detailed discussion is given by Van der Meer (1987).

The spreading rate of the turbulent jet is independent of axial distance $x$ and (unlike laminar jets) independent of the Reynolds number. In other words, there exists a similarity region where the radial coordinate is scaled with the axial distance $x$. The experimental data give $0.086 < S_{1/2}^u < 0.096$ (Sanders, 1994). The value of $S_{1/2}^u$ is equal to $\frac{1}{2} K_u$. The velocity fluctuation intensity on the jet axis is found to be a constant.

For the conserved scalar similar scaling laws hold:

$$
\frac{\xi_0}{\xi_{cl}} = K_\xi \left( \frac{x - x_0}{D} \right)
$$

(6.5)

and the scalar fluctuation intensity on the axis is a constant. The spreading rate of the conserved scalar $S_{1/2}^\xi$ is equal to $\frac{1}{2} K_\xi$, and from experiments one can deduce $S_{1/2}^\xi = 0.200$ with an uncertainty of about 15%. Again, the intensity of the scalar fluctuations on the centerline is approximately constant.

For our code validation, we have used the same geometry as for the laminar jet in the previous subsection. Since the turbulent jet has a much faster spreading than the laminar jet, we had to extend the computational domain in radial direction from 10 to 22.5 nozzle diameters in order to ensure that the free-edge boundary is sufficiently far away from the jet. Again, we investigated the dependence of our numerical results on the grid and the discretization scheme. We employed Launder's round-jet correction formula (2.86).

Figure 6.9 shows the streamlines for the free turbulent jet. The corresponding spreading rate is depicted in figure 6.10. Here we see that the jet attains a constant spreading rate up to $x/D = 50$, beyond which the spreading rate collapses to reach zero at the outlet boundary, located at $x/D = 100$. The reason for this is that the axial velocity of the jet decreases much faster than in the case of a laminar jet. Hence, far away from the nozzle the numerical grid becomes too coarse to describe the similarity properly. This grid dependence shown by figure 6.10 is evident if we compare case (a) and (b). The difference between the upwind and hybrid discretization scheme is not very strong, although on the finest mesh the hybrid scheme effectively uses central discretization in radial direction, and upwind
6.2. Validation of the numerical code

Figure 6.9: Streamline contours for turbulent free jet with Re = 32500, computed on a 150 × 60 mesh, using the upwind scheme. Radial direction enlarged by a factor of two.

Figure 6.10: Spreading rate of a free turbulent jet at Re = 32500, computed on different grids, using different discretization schemes. (a) 50 × 20 mesh, upwind scheme. (b) 150 × 60 mesh, upwind scheme. (d) 150 × 60 mesh, hybrid scheme.

discretization in axial direction. This again shows that numerical diffusion is not a very important issue in this type of flow, simply because the bulk of the flow has streamlines parallel to the grid orientation.

6.2.3 Simulation of jet 1

The experiments by Stroomer (1995), using Laser-Doppler anemometry (LDA) in order to measure mean velocities and turbulence quantities in jet 1, constitute a more severe test case for the turbulence model employed for the flame simulations. As discussed in
Section 6.1.1, the flow consists of three main inlets: a central fuel jet, primary annular air and low-speed coflowing air. In the cold-flow experiments, the fuel is replaced by air, yielding a constant-density jet in a double coflow.

In order to perform detailed comparisons of experimental and numerical results, it is essential to use inlet boundary conditions in the calculations which match the experiments as closely as possible, a problem which we address now first. Stroomer measured profiles of mean velocities and turbulence quantities at 3 mm above the burner, where the inlet profiles are hardly altered by the mixing processes in the combustion chamber. We first consider the low-speed coflow, for which it was found that this flow has very little influence on the overall jet mixing behavior. Therefore, a uniform axial velocity of 0.4 m/s was used as inlet boundary condition. No direct measurements were available. The inlet boundary condition for the turbulent kinetic energy was estimated by assuming a 3% turbulence intensity: \( \frac{2}{3} k = (0.03 U)^2 \). The viscous dissipation rate was obtained from the standard formula for well-developed pipe flow \( \epsilon = C_{\mu}^{3/4} k^{3/2} / (0.03 D) \) where \( D \) represents the hydraulic diameter of the coflow region.

Secondly, we estimated the inlet profile of the annular air flow numerically by calculating the flow in a 1-m long annulus pipe with the same dimensions as the primary-air annulus. Using the standard \( k-\epsilon \) model with wall functions and a 50 \( \times \) 10 grid, a fully developed turbulent annular air flow was computed assuming a bulk velocity of 4.5 m/s. Figure 6.11 compares the mean axial velocity with the measured profile at 3 mm above the annulus. The profile was measured for flame III, but the annular air flow conditions were the same for flame III and jet I. Despite some minor differences, it can be concluded that the experimental data closely resemble the fully-developed profile. Note that the computed velocity maximum is located closer to the inner radius of the annulus than to the outer radius. This is caused by the fact that the outer wall of the annulus has a larger circumferential area than the inner wall, and therefore has a stronger viscous effect on the
flow. The experiments are not entirely symmetrical, which may be caused by a very small asymmetry in the burner setup. Moreover, the measured maximum velocity is located almost exactly in between the inner and outer radius of the annulus. On average, the bulk velocity of the annular flow is well represented by 4.5 m/s.

The turbulent kinetic energy is depicted in figure 6.12. The computations predict a higher turbulent kinetic energy near the outer radius, which matches well with the experiments. Again, a slight asymmetry is observed in the experiments. We conclude that, for our further modeling purposes, a fully-developed annular flow be used as inlet boundary condition.

Finally, we consider the primary jet flow. The fuel pipe in the experiments has an inner diameter of 8 mm. Close to the burner outlet, a contraction has been placed to allow for pilot flames, yielding an outlet pipe diameter of 6 mm. Although the contraction is introduced gradually by a small 7° angle with the symmetry axis of the pipe, the pipe area is reduced by 44%, which causes an acceleration of the flow. Consequently, the turbulent velocity profile is flattened and the turbulence intensity is lower because the production of turbulent kinetic energy is retarded: the mean velocity is increased, whereas \( k \) still is consistent with the wider pipe flow upstream. Figure 6.13 shows the comparison of a fully developed pipe flow computation for a 1-m long fuel pipe, using \( 50 \times 10 \) grid points and a bulk velocity of 20.9 m/s and 16 m/s, respectively, and experimental data at 3 mm above the burner. (N.B. The data for the reacting flow have been used, as the nonreacting flow data did not include profiles very near the burner. However, the flame hardly affects the annular outflow so close to the nozzle.) The comparison shows that the mean-velocity profile at the burner nozzle resembles fully-developed pipe flow, although the measured profile is somewhat flatter. Figure 6.14 corroborates the suggestion that the contraction produces a lower relative turbulence intensity \( (\frac{k}{\overline{U}^2})^{1/2} \). The relatively high maximum values of turbulent kinetic energy near the pipe wall are absent in the
Chapter 6. Results on axisymmetric diffusion flames

Figure 6.13: Comparison of mean axial velocity between developed turbulent flow in a pipe of 6 mm diameter for bulk velocities of 20.9 m/s (---) and 16 m/s (---), and experimental data obtained at $x = 3$ mm above the pipe ($\times$).

Figure 6.14: Comparison of turbulent kinetic energy between developed turbulent flow in a pipe of 6 mm diameter for bulk velocities of 20.9 m/s (---) and 16 m/s (---), and experimental data obtained at $x = 3$ mm above the pipe ($\times$).

experiments, and the measured centerline level falls below the fully-developed results even for a bulk velocity of 16 m/s (which apparently is certainly too low according to figure 6.13). The measured level of $k$ is fairly constant for $r < 3$ mm; the data for $r > 3$ mm are not relevant here, since they are already affected by the burner rim and the presence of pilot flames. From these comparisons we decided to employ uniform inlet profiles for mean $u$-velocity, turbulent kinetic energy and viscous dissipation rate, assuming an inlet turbulence intensity of $\left(\frac{2}{3} k/U^2\right)^{1/2} = 0.06$ and an integral length scale proportional to the pipe diameter of 8 mm upstream of the contraction at the nozzle, rather than the 6-mm
diameter at the nozzle itself.

Having established the proper inlet boundary conditions for the cold-flow simulations, the standard $k$-$\epsilon$ model was used to model the cold jet development. At the combustion chamber walls, standard wall functions for $U$, $k$ and $\epsilon$ were adopted. At the burner rim, which has a width of 4.5 mm, the standard wall functions cannot be applied since the grid point near the wall has a dimensionless distance $y^+$ to the wall much smaller than 5. Besides, the wall functions have been developed for forced-convection boundary layers, whereas near the burner rim no well-developed boundary layer exists. Hence, the proper boundary conditions at the burner rim is the no-slip condition for $v$-velocity and $k$ and $\epsilon$ are calculated right up to the wall with $k_{wall} = 0$ and $\epsilon_{wall} = \infty$. In practise, a very large real number was used instead of $\infty$ for $\epsilon$.

From the measured cold-flow centerline velocity decay, an inlet bulk velocity of $\bar{u} = 21.6$ m/s was inferred, which complies within experimental error with the value of 21.9 m/s of De Vries (1994). This velocity was used for the uniform inlet profile of the central jet. Figure 6.15 shows the computed and measured axial velocity decay. On a coarse $50 \times 50$ grid (with only 3 grid cells in the central jet region) the potential core of the jet cannot be reproduced. Grid refinement showed that the results become grid independent on a finer $100 \times 75$ mesh, with 6 cells in the central inlet region. However, the standard $k$-$\epsilon$ model clearly fails in predicting the axial velocity decay. The used round-jet correction model (2.86) effectively decreases the eddy viscosity, yielding a velocity decay in excellent agreement with the experiments. This is also illustrated by the radial velocity profiles (figure 6.16) showing good correspondence between measurements and calculations. The value of the similarity parameter $K_u$ defined by (6.4) is not constant for this flow; it varies between 0.10 and 0.12. This shows that the three-stream jet flow behaves differently from the ideal single jet with or without coflow, described in the
Chapter 6. Results on axisymmetric diffusion flames

![Graph](image)

**Figure 6.16:** Radial profiles of mean axial velocity for the nonreacting jet with double coflow, compared between calculations and experiments. Computations: — $x = 50$ mm, $x = 150$ mm, $x = 250$ mm. Experimental data: $x = 50$ mm, $x = 150$ mm, $x = 250$ mm.

![Graph](image)

**Figure 6.17:** Centerline turbulent kinetic energy for the nonreacting jet with double coflow, compared between calculations and experiments. Lines: $\cdots$ 50 × 50 mesh, $\cdots$ 100 × 75 mesh, — 100 × 75 mesh with round-jet correction. Symbols: ○ experiments.

Previous section.

Figure 6.17 shows the centerline turbulent kinetic energy. The kinetic energy attains a maximum value at about 10 diameters downstream of the burner. The model without the round-jet correction largely overpredicts the experimental data. The corrected model, however, shows good qualitative agreement with the measurements, although the calculated turbulent kinetic energy decays too slowly. Parameter variations on the constants in Launder's correction formula (2.86) revealed that the axial decay of mean velocity and
6.2. Validation of the numerical code

Figure 6.18: Centerline rms velocity fluctuations for the nonreacting jet with double coflow, compared between calculations and experiments. Calculations: — $u_{rms}$, — $v_{rms}$. Experiments: ○ $u_{rms}$, × $v_{rms}$.

Figure 6.19: Radial profiles of rms $u$-velocity fluctuations for the nonreacting jet with double coflow, compared between calculations and experiments. Computations: — $x = 50$ mm, — $x = 150$ mm, · · · $x = 250$ mm. Experimental data: ○ $x = 50$ mm, × $x = 150$ mm, Δ $x = 250$ mm.

turbulent kinetic energy are insensitive to moderate changes of these constants. Therefore it was decided to use Launder’s original model constants for the flame simulations. In addition, variations of the inlet boundary conditions for the viscous dissipation rate $\epsilon$ have no significant effect on the $k$-profile.

In the mixing region, the values of $k$ and $\epsilon$ are strongly source-term dominated, which explains why the round-jet correction model works well. By adjusting the values of $C_\mu$ and $C_c2$, the local production and dissipation of turbulence are influenced, thus
causing a lower turbulent viscosity. Given the inability of the $k$-$\epsilon$ model to mimic detailed turbulence characteristics of mixing flows, it is not surprising to find discrepancies between predictions and measurements of turbulence quantities. This is reflected by root-mean-square (rms) values of the axial and radial velocity components, depicted in figure 6.18. The experiments show strong anisotropy near the burner, whereas the model results remain close to isotropy. Further downstream the turbulence decays towards isotropy. The radial profiles of the rms $u$-velocity fluctuations, however, are qualitatively in line with the measured data (figure 6.19).

The mixing behavior of the jet in double coflow is illustrated by figure 6.20, showing the turbulent Reynolds number $Re_t \equiv k^2/(\epsilon \nu)$ which is a measure of the eddy viscosity. It is clear that the mixing of the central jet with the annular flow does not cause a strong turbulent mixing, but rather the mixing layer between the annular flow and the low-speed coflow dominates the turbulent mixing field.

Concluding this section, we find that the fairly simple $k$-$\epsilon$ turbulence model, improved with Launder's round-jet correction model, is a sufficiently accurate tool to predict the mixing behavior of the free turbulent round jet as well as the cold-flow equivalent of the double-coflow turbulent diffusion flame.

6.3 Conserved-scalar closure model results

6.3.1 Mean flow field

In the previous section the validity of the numerical model and grid independence have been checked for nonreacting jet flows. In this section the reacting-flow simulation results will be discussed. We focus on the flame III case, which is the basic flame configuration
for the experiments. The model used for the calculations discussed in this section is the constrained-equilibrium model with a $\beta$-function PDF for mixture fraction (see §§3.3.6 and 3.4.3), using the corrected $k$-$\varepsilon$ model and assuming adiabatic flow. The boundary conditions for $\xi$ are $\xi = 1$ in the fuel stream, $\xi = 0$ in the air streams and zero Neumann conditions at all other boundaries. For the variance $\xi^{1/2}$ zero Neumann conditions were imposed at the outlet, and zero Dirichlet conditions in all three inlet streams and at the walls.

At first sight, there is a strong similarity between the flow fields of the non-reacting and reacting cases. The fuel jet is mixed with the surrounding annular air flow, and the annular air mixes with the low-speed coflow. Nevertheless, there are some important differences to be aware of. The effects of varying density and molecular viscosity, together with the influence of pilot flames used to stabilize the flame in the experiments, alter the jet mixing, especially close to the burner.

Without pilot flames, a very small recirculation zone appears just above the burner rim, as in the nonreacting case. In the presence of the pilot flames, however, the recirculation is distorted and shifted away from the axis. The details of the flow just above the burner rim are difficult to model, firstly because the pilot flames are not axisymmetric but are a three-dimensional phenomenon, and secondly because the flow structure is complicated. A very fine numerical grid is required, and the influence of higher molecular viscosity inside the hot parts of the flow has to be taken into account. Furthermore, it is doubtful whether the $k$-$\varepsilon$ model will be able to describe the strongly anisotropic turbulence near the burner rim. By contrast, our purpose is to model the flow around the burner rim as accurately as possible, but rather to have a good description of the mean flow further away from the burner.

The pilot flames have a cold-flow bulk velocity of 12 m/s, according to De Vries (1994). The total area of the 12 pilot flames is 2.36 mm$^2$. In our axisymmetrical geometry, the pilot flames cannot be issued from 12 pinholes, but we approximate them by a concentric slit burner with a diameter of 7 mm. The total area of the slit will match the experiments if the slit is 0.11 mm wide, which can only be achieved by a very fine numerical grid. Given the very high temperature of the pilot flames, the 12 m/s cold-flow velocity will produce a pilot flame velocity of about 100 m/s. This can hardly be modeled properly by the numerical code. Therefore, we decided to use a slit-shaped pilot flame of larger width between $y = 3.5$ and $y = 4$ mm, yielding a lower exit velocity of 23 m/s. The purpose of the pilot flames is to prevent the flame from lifting or even blowing off. When using a conserved-scalar model like the constrained-equilibrium model, no lift-off will occur since local extinction is impossible. Hence, the modeling of the pilot flames will hardly affect the flame predictions of the conserved-scalar model. For the detailed-kinetics model, however, the pilot flames are essential to prevent lift-off.

If the flame is completely attached to the burner rim, the reaction zone will have a higher molecular viscosity and lower density than the surrounding flow. In the reaction zone, the flow is accelerated by the thermal expansion, and the mixing of the central fuel jet with the surrounding annular air is damped. This causes a major difference between the cold-flow jet mixing and the flame. The central fuel jet is more or less shielded by
Chapter 6. Results on axisymmetric diffusion flames

Figure 6.21: Comparison between calculations (---) and experiments (○) for the centerline mean axial velocity in flame III.

Figure 6.22: Comparison between computed and measured radial profiles of the mean axial velocity in flame III.

a thin layer of quickly expanding gas and high molecular viscosity. In this shield flow the radial velocity fluctuations, which are mainly responsible for turbulent transport in radial direction, are damped by the axial acceleration. As a consequence, the experiments produce an increase of mean axial velocity on the centerline, which is not correctly modeled by the $k$-$\epsilon$ model with round-jet correction, since this model predicts an almost isotropic distribution of normal Reynolds stresses.

The centerline profile of the mean axial velocity is depicted in figure 6.21. Close to the burner, the experiments show an increase of the centerline velocity, which is not reproduced by the calculations. This is probably caused by the high-speed pilot flame jets, which have an estimated velocity of 100 m/s, and which act as a quickly expanding
and highly viscous, low-turbulent shield around the fuel jet. The jet centerline velocity increases because the mixing with the annular air is not very intense close to the burner, a behavior which differs from the cold-flow case. It should be noted that in the simulations the pilot flames were approximated by a round slit rather than separate tiny jets, which partly accounts for differences with the measurements as well. The overall decay of the centerline velocity is qualitatively predicted by the model, however.

Similar observations can be made for the calculated radial profiles of the mean $u$-velocity (figure 6.22), which match the experiments closely, except for $x = 50$ mm above the burner. At that location the jet mixing is overpredicted, whereas the experiments suggest an axial increase of the mean $u$-velocity. Further downstream, the computed profiles are slightly narrower than the experimental profiles, but the overall performance of the turbulence model is good. Part of the difference may be attributed to the comparison of Favre-averaged calculations with Reynolds-averaged measurements: $\tilde{u} = \langle u \rangle + \langle \rho' u' \rangle / \langle \rho \rangle$. Because the correlation $\langle \rho' u' \rangle$ generally is negative in flames, we may expect slight underprediction of the mean axial velocity. Similar to the nonreacting case, the parameters $K_u$ and $K_\xi$ are not constants. We find that $0.08 < K_u < 0.11$ and $0.06 < K_\xi < 0.12$. Towards the outlet of the combustion chamber both $K_u$ and $K_\xi$ increase, and $K_\xi$ becomes larger than $K_u$. There is no direct similarity between $K_u$ and $K_\xi$, which is caused by the different inlet boundary conditions for $\tilde{u}$ and $\tilde{\xi}$.

The centerline turbulent kinetic energy (figure 6.23) shows an initial decay in the first few diameters above the nozzle. Further downstream, turbulence is mixed onto the centerline and $\tilde{k}$ increases. This behavior is qualitatively reproduced by the model, although the local maximum is predicted too low. For $x > 0.2$ m, the centerline value of $\tilde{k}$ is in line with the experiments. The $k$-$\epsilon$ model treats the normal Reynolds stresses as if they were isotropic, which was already found for the nonreacting jet case. The r.m.s. values of the velocity fluctuations are depicted in figure 6.24, showing that initially the radial
velocity fluctuations are damped with respect to the axial velocity fluctuations. Further downstream, the distribution of the normal stresses becomes more isotropic. The predicted radial profiles for the \( u \)-velocity fluctuations, shown in figure 6.25, are qualitatively in good agreement with the measurements, as are the profiles for the turbulent kinetic energy. The anisotropy of the normal stresses explains why the jet mixing is overpredicted at \( x = 50 \text{ mm} \). In the \( k-\epsilon \) model the radial turbulent mixing is proportional to \( \frac{k^2}{\epsilon} \), but the Reynolds-stress model which takes into account the anisotropy of turbulence implies proportionality with \( \frac{\nu^2 k}{\epsilon} \). Only in regions where the turbulence is more or less isotropic these two quantities will behave similar, but in this case, especially near the burner, radial
fluctuations of the velocity component are damped as a consequence of the reaction zone.

6.3.2 Thermo-chemical fields

Temperatures

In figure 6.26 the mean profiles of the temperatures measured by De Vries (1994) are compared with numerical results. Correspondence between the measured and simulated temperatures is very good, taking into account the experimental accuracy of ±70 K. In laminar flames, the thermocouple measurements may suffer from catalytic effects near the reaction zone, but in a turbulent flame the thermocouple will be situated in the instantaneous reaction zone only a fraction of the time. Inspection of the radial location of maximum temperature reveals that the spreading of the reaction zone is somewhat underpredicted by the model, but both the shape of the profiles and the radial peak temperatures agree well with the experiments.

![Temperature Profiles](image)

**Figure 6.26:** Comparison of measured mean temperatures and numerical results. Lines denote calculated values, symbols denote experimental data.

**OH concentrations**

Radial profiles of the average OH concentration $c_{OH}$ are shown in figure 6.27, for $x = 50, 150$ and $250 \text{ mm}$. On the centreline, the average OH concentration and its standard deviation does not increase significantly up to $x = 250 \text{ mm}$. Therefore, the reaction zone does not reach the jet axis for $x$ smaller than $250 \text{ mm}$. The measured maximum average OH concentrations are about $4 \times 10^{15} \text{ cm}^{-3}$ and remain fairly constant with $x$.

Predictions of the OH concentrations by the constrained equilibrium model do not take into account super-equilibrium levels of OH. The predicted concentrations therefore are too low. The shape of the predicted profiles does not fully match the experiments. To investigate the sensitivity of predictions on the assumed PDF shape, we replaced
Figure 6.27: Radial mean OH concentration profiles. Lines denote calculated values, symbols denote experimental data.

The $\beta$-function mixture fraction PDF by a top-hat distribution. This deteriorates the mean temperature prediction as well as the OH prediction: both quantities show lower maximum values, and OH-profile shapes deviate even stronger from the experiments. We conclude that the conserved-scalar model with a $\beta$-function PDF performs well for mean temperature predictions, but fails to represent the shape of the measured mean OH profiles. It is unlikely that substituting the $\beta$-function PDF by any other PDF shape will significantly improve OH predictions without harming the mean temperature predictions. The observed differences cannot be attributed to the assumed PDF shape, but are inherent to the conserved-scalar chemistry model for OH.

Looking at the trend for larger downstream distance $x$, the experiments show a decay of maximum average OH values, whereas the conserved-scalar model gives a maximum OH level at the flame tip where $\tilde{\xi} = \xi_t$ and fluctuation levels are small. The experiments disagree with such a trend, even for $x > 250$ mm. Two mechanisms can be held responsible for this effect. First, soot radiation causes a lower flame temperature, which will reduce the maximum OH concentration further downstream of the nozzle. More importantly, strain rate effects are higher near the nozzle, and laminar flamelet calculations show that OH concentrations are highest for moderate strain rates (or scalar dissipation rates). If the strain rate is small, the function $Y_{OH}(\xi)$ will resemble the constrained-equilibrium model. For very high strain rates, the OH concentration decreases, and above the extinction limit, the concentration will be zero. For intermediate values ($a \approx 100$ s$^{-1}$), OH concentrations are significantly higher than the equilibrium concentrations. This is also shown in figure 5.20.

The distribution functions of the peak OH concentration in every instantaneous radial profile, exhibit a most probable instantaneous peak concentration of $12 \times 10^{15}$ cm$^{-3}$, see figure 6.28. The distribution functions all have a bimodal shape, with a peak near $c_{OH,max} = 0$, indicating the existence of local extinction. The low probability of finding peak OH concentrations between 2 and $7 \times 10^{15}$ cm$^{-3}$ suggests that concentration fluctua-
6.3. Conserved-scalar closure model results

![Graph showing PDF of maximum OH concentration](image)

**Figure 6.28:** PDF of maximum OH concentration found in instantaneous one-dimensional LIF measurements, at various x-values: -- x = 50 mm, --- x = 150 mm, · · · x = 250 mm.

...tions at a fixed position in space are mainly due to turbulent displacements of the reaction zone or to local extinction.

Laminar flamelets are believed to describe the OH chemistry in a more realistic manner than the constrained-equilibrium models by which no effects of strain rate or scalar dissipation is taken into account. The laminar flamelet data of figure 5.20 are equivalent to peak OH concentrations of $20 \times 10^{15}$ cm$^{-3}$, indicating a difference with the measured values of a factor of 1.6.

Returning to the radial mean OH profiles, it is interesting to see whether a laminar flamelet model would predict the experimental shape of these profiles. In the flamelet model, OH depends on $\xi$ similarly to the constrained-equilibrium model (figure 5.20). Hence, the use of a flamelet model (retaining the scalar mixing model) will not improve the width of the predicted radial mean OH profiles, but it will yield higher absolute values, more in line with the experiments.

6.3.3 Intermittency effects

In Chapter 3 models were discussed which account for the influence of large-scale intermittency on local PDF shapes of mixture fraction $\xi$. As stated before, the $\beta$-function covers many different PDF shapes, but it cannot represent a bimodal PDF, with an intermittency spike near $\xi = 0$ and a continuous part for $\xi > 0$. If the $\beta$-function has a singularity near $\xi = 0$ and/or $\xi = 1$, there can be no local maximum for $0 < \xi < 1$. Therefore, we expect to see some influence of an intermittency factor near the outer edge of the jet flow. We
apply the models of Kent and Bilger (1977) and Abou-Elail and Salem (1990) for the \( \beta \)-function PDF with intermittency, and compare results with the \( \beta \)-function PDF without intermittency.

In figure 6.29 several profiles of the intermittency factor \( \tilde{\gamma} \) are compared for the two models, at several axial locations. It must be mentioned, however, that the model of Abou-Elail and Salem did not converge. Results published by Abou-Elail and Salem (1990) show that the modeled skewness equation (3.32) works well for a single jet in a low-speed coflow, which was confirmed by test calculations performed with our own model implementation. For a jet surrounded by a turbulent annular coflow, however, there is no direct link between mixing layer turbulence and turbulent fluctuations of the conserved scalar \( \xi \). Several mixing regions exist in our particular flame configuration. Moreover, close to the burner rim the high-speed pilot flames cause some additional disturbances of the flow field. Consequently, complex models by which gradients of the conditionally-averaged velocity are employed in source terms for the intermittency factor \( \tilde{\gamma} \), will fail to give reliable results. Here, the conserved scalar \( \xi \) shows some intermittent structures, even though one cannot discern clearly a non-turbulent and a turbulent zone in the flow field.

Bearing this in mind, the unconverged solution of the Abou-Elail and Salem model was further compared with the Kent and Bilger model. Figure 6.29 shows that further away from the burner, the model of Abou-Elail starts to deviate considerably from the Kent and Bilger model. The profile of \( \tilde{\gamma} \) becomes narrower for larger \( x \)-values, which is in contradiction with our expectations. Figure 6.30 shows that the predictions by both the Abou-Elail model and the Kent and Bilger model deviate considerably from the standard model results, which agreed well with the experiments. The profile is too narrow, and the maximum temperature is underpredicted by about 250 K. Further downstream, the
6.3. Conserved-scalar closure model results

![Diagram](image)

**Figure 6.30:** Comparison mean temperature predicted by intermittency models, with results computed by the standard model and with experimental data, at $x = 0.25$ m.

Differences between the models become smaller, but the inclusion of intermittency does not yield results which are superior to the standard $\beta$-function PDF.

### 6.3.4 PDF shapes

It is interesting to see how the PDF shapes of the dependent thermochemical quantities behave as a function of the radial coordinate, for a given axial location. Here we take $x = 0.15$ m, because the prediction of mean velocity and temperature agrees well with the experimental results. In figure 6.31, we show the PDF shapes of the mixture fraction, the temperature and the OH concentration, at radial positions which correspond with the centerline, the point of maximum mean temperature, and the point where the mean temperature has the steepest gradient. The PDF shapes of the dependent variables are obtained numerically, using $\hat{f}_\xi(\xi) d\xi = \hat{f}_\phi(\phi(\xi)) d\phi$. Because $T$ and $N_{OH}$ are non-monotonous functions of $\xi$, we cannot calculate $\hat{f}_\phi = \hat{f}_\xi/(d\phi/d\xi)$ directly. Therefore, a simple numerical bin-method is used instead.

From figure 6.31, we see that the mixture fraction PDF has a different shape at the three radial positions; neither of the PDFs is completely symmetric around the mean. The dependent variables, however, show a completely different behavior.

The temperature PDFs have a bimodal shape at the off-axis radial locations. Hence, the predicted shape of the temperature PDF may be bimodal, even although the $\beta$-function PDF used for the mixture fraction cannot exhibit bimodality by itself. On the centerline, the temperature PDF resembles a Gaussian shape. The sharp peak of the temperature PDF for values close to $T_{\text{max}}$ is caused by the constrained-equilibrium model: at the point $\xi = \xi_{ig}$, the derivative of the function $T(\xi)$ has a discontinuity. This is reflected by a discontinuous jump of the temperature PDF.

The PDFs for the OH number density show a nearly flat distribution for the off-axis
FIGURE 6.31: PDF shapes of mixture fraction (a), temperature (b) and OH number density (c) at \( x = 0.15 \) m, for three radial locations corresponding with centerline (—), maximum mean temperature (⋯) and steepest temperature gradient (−−−).

positions; on the centerline, the PDF is practically a \( \delta \)-function at \( N_{OH} = 0 \). The OH PDFs from the experiments by De Vries (1994), taken at different axial locations, show good qualitative agreement with the numerically obtained PDF shapes: a high peak near \( c = 0 \) and a long flat tail. In the experiments higher absolute concentrations were found, and the peak near \( c = 0 \) was broadened because of noise influences.

Recent CARS temperature measurements obtained by Mantzaras (1995) are used to look at the temperature PDFs in more detail. Figure 6.32 shows a comparison of the measured and computed temperature PDFs at different radial locations, for \( x = 0.15 \) m above the burner, where the mean temperature profiles already showed good agreement. For \( r = 0 \) and \( r = 1.75 \) mm the computed data were translated slightly to improve the comparison of the PDF shapes. Here we see that the different shapes of the PDF as observed in the experiments are reproduced excellently by the model. This suggests not only that the conserved-scalar chemistry model applies very well to this particular flame, but moreover
FIGURE 6.32: Comparison of measured and computed temperature PDFs, at $x = 0.15$ m, for various radial locations. Histograms represent the experiments, lines the computations. (a) $r = 0$ mm, computed PDF shifted by 60 K; (b) $r = 1.75$ mm, computed PDF shifted by 60 K; (c) $r = 6.5$ mm; (d) $r = 8.25$ mm; (e) $r = 11.25$ mm; (f) $r = 15$ mm.
that the constrained-equilibrium chemistry model combined with the \( \beta \)-function mixture fraction PDF captures the thermochemical field very well.

6.4 Flame radiation and soot formation

6.4.1 Introduction

In the previous sections emphasis lay on the comparison of predictions with measurements taken relatively close to the burner. Further away from the inlet regions, radiation has an important effect in flames. This section studies the radiative properties of the Flame-C-case in more detail, in order to investigate the importance of radiative heat transfer for our axisymmetric diffusion flames. We described several models for radiative heat exchange in Chapters 2 and 4:

1. A simplified model in which self-absorption of radiation by the flame itself is neglected. This model is computationally cheap. It will only be valid if the mean beam length of the radiation is long in comparison with the dimensions of the hot region of the flame, and if the walls are not emitting substantially. Therefore, the simplified model is applicable to the laboratory jet flames of this chapter.

2. The Hottel zone model (HZM) This model is accurate, provided the flow does not exhibit strong temperature gradients and the local extinction coefficient is more or less a constant over the entire domain of interest.

3. The Discrete Transfer method (DTM) The DTM is computationally more expensive than the other two models. It suffers from systematic inaccuracies, because only a limited number of beam directions are followed, and the beam directions remain fixed during the iterative calculation process. However, the DTM has the advantage that it allows for the local extinction coefficient to be a function of space. Therefore, it is suited for the inclusion of soot formation models, which may produce locally high values of the extinction coefficient. The DTM can be expanded relatively easily to complex geometries.

This section is divided into a part where the developed methods are analyzed and a part where the results of the simulations of the axisymmetrical turbulent diffusion flame are presented. First, the method of calculating the direct-exchange areas, as used in the Hottel zone method, is checked. The calculated direct-exchange areas are compared for the geometry used by Erkku (Hottel and Sarofim, 1967). The influence of different boundary conditions on heat fluxes calculated with the Discrete Transfer Method are examined by two test cases. Also, the influence of the number of beams and the number of zones is investigated. For a given temperature field, the source terms and heat fluxes are compared using the different models described above. From this, a choice is made concerning the methods of radiation modelling used in the complete flow calculations of the turbulent flame. Finally, the results of the complete flow calculations, in which the radiation calculations are coupled with the transport equations, are presented.
6.4. Flame radiation and soot formation

![Diagram of a uniform grid with volume zones g, side surface zones w and top or bottom surface zones e.]

**Figure 6.33**: Uniform grid Erkku with volume zones $g$, side surface zones $w$ and top or bottom surface zones $e$.

<table>
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<th>DEA</th>
<th>$K^a$ m$^{-1}$</th>
<th>calculated m$^2$</th>
<th>$\delta_{calc}$ 10$^{-4}$</th>
<th>Erkku m$^2$</th>
<th>$\delta_{Erkku}$ 10$^{-4}$</th>
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</thead>
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<td>4.03</td>
<td>$2.551 \cdot 10^{-1}$</td>
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<td>$1.2121 \cdot 10^{-1}$</td>
<td>9.48</td>
<td>$1.211 \cdot 10^{-1}$</td>
<td>9.08</td>
</tr>
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<td>$g_{2}g_{13}$</td>
<td>0.1</td>
<td>$2.7053 \cdot 10^{-2}$</td>
<td>7.71</td>
<td>$2.706 \cdot 10^{-2}$</td>
<td>2.70</td>
</tr>
<tr>
<td>$w_{1}w_{4}$</td>
<td>0.1</td>
<td>$8.0126 \cdot 10^{-1}$</td>
<td>1.83</td>
<td>$8.014 \cdot 10^{-1}$</td>
<td>1.75</td>
</tr>
<tr>
<td>$e_{2}w_{4}$</td>
<td>0.1</td>
<td>$6.5421 \cdot 10^{-1}$</td>
<td>2.06</td>
<td>$6.541 \cdot 10^{-1}$</td>
<td>1.68</td>
</tr>
<tr>
<td>$e_{2}e_{9}$</td>
<td>0.25</td>
<td>$1.6397 \cdot 10^{-2}$</td>
<td>3.24</td>
<td>$1.640 \cdot 10^{-2}$</td>
<td>2.07</td>
</tr>
</tbody>
</table>

**Table 6.2**: Direct-exchange areas (DEA) and relative differences compared to the values of Erkku for a given absorption coefficient $K^a$. The direct-exchange area $e_{2}e_{9}$ is given for $K^a = 0.25$ m$^{-1}$ because the value for $K^a = 0.1$ m$^{-1}$ was omitted in Erkku’s table (Hottel and Sarofim, 1967).

### 6.4.2 Direct-exchange areas compared with Erkku values

To check the calculation method for the direct-exchange areas used in the Hottel zone method, as described in Section 4.5, the direct exchange areas were calculated for Erkku’s
geometry, who used a uniform cylindrical $5 \times 12$ grid. The volumes $g$ are numbered upwards starting from the left column. The bottom and top zones $e$ are numbered from the left to the right, beginning with the bottom zones. The side surface zones $w$ are numbered upwards. Several zones are indicated in figure 6.33. The direct-exchange areas between these zones are shown in table 6.2. These are randomly chosen direct-exchange areas to compare the values to those calculated by Erkku.

As described in Section 4.5, the direct-exchange areas are calculated by subdivision of the zones into smaller zones. After each evaluation of the direct-exchange areas, the number of small zones is increased. This is repeated until the difference between the last obtained value and the previous value is smaller than a given criterion. The obtained accuracy of the calculation is expressed by the relative difference $\delta_{\text{calc}}$:

$$\delta_{\text{calc}} = \left| \frac{\text{new value} - \text{old value}}{\text{new value}} \right|$$

The relative difference compared with the value of Erkku is defined as:

$$\delta_{\text{Erkku}} = \left| \frac{\text{Erkku} - \text{converged value}}{\text{Erkku}} \right|$$

These relative differences are also shown in table 6.2. The direct-exchange areas were calculated until a relative difference of $\delta_{\text{calc}} < 10^{-3}$ was reached.

The calculated values show excellent agreement with Erkku’s values. Furthermore, the relative difference with Erkku’s values is smaller than the relative difference used in the convergence criterion. Therefore we conclude that our numerical integration method is accurate.

**Table 6.3:** Direct-exchange areas for the rings to themselves compared to the values of Erkku for $K^a = 0.1 \text{ m}^{-1}$

<table>
<thead>
<tr>
<th>DEA</th>
<th>calculated $m^2$</th>
<th>Erkku $m^2$</th>
<th>$\delta_{\text{Erkku}}$ $10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_1g_1$</td>
<td>7.763·10^{-2}</td>
<td>7.760·10^{-2}</td>
<td>2.11</td>
</tr>
<tr>
<td>$g_1g_3$</td>
<td>2.584·10^{-1}</td>
<td>2.580·10^{-1}</td>
<td>1.73</td>
</tr>
<tr>
<td>$g_2g_1$</td>
<td>4.311·10^{-1}</td>
<td>4.303·10^{-1}</td>
<td>1.93</td>
</tr>
<tr>
<td>$g_3g_3$</td>
<td>6.021·10^{-1}</td>
<td>6.026·10^{-1}</td>
<td>0.70</td>
</tr>
<tr>
<td>$g_4g_4$</td>
<td>7.725·10^{-1}</td>
<td>7.738·10^{-1}</td>
<td>1.58</td>
</tr>
</tbody>
</table>

**Direct-exchange areas for the rings to themselves**

The direct-exchange areas for the rings to themselves are calculated with the volume summation rule (2.102). Therefore, only the relative difference compared to Erkku’s value can be calculated. The calculations are less accurate compared to the other direct-exchange areas because the summation yields an accumulation of errors. Table 6.3 gives the values of the direct-exchange areas for the rings to themselves.
The summation rule can only be used if the accuracy of the individual direct-exchange areas used in the summation is sufficient. Compared to the values given by Erkku the relative difference lies within 0.25%. Therefore we conclude that the accumulation of errors in the summation does not cause a large error in the direct-exchange areas for the rings to themselves.

6.4.3 Test cases for the Discrete Transfer Method

The two test cases for the DTM as described in Chapter 4, are discussed for the cylindrical geometry with a height of \( h = 2 \) m and a bottom area of \( A_1 = 1 \) m\(^2\). The number of beams and the number of grid zones are varied to check the influence of the discretization.

Case 1: Emitting bottom surface

In the first test case the bottom surface has an emissive power of \( E = 1 \) W/m\(^2\), and the total heat flow through the bottom is \( Q_{\text{bottom}} = -1 \) W. We define the heat flow to be positive if heat flows out of the enclosure. The total heat flows \( Q_{\text{top}} \) and \( Q_{\text{side}} \) through the top surface and the side surface, respectively, can be calculated exactly (Modest, 1993). Summing all the heat flows we have to obtain \( \Sigma Q_i = 0 \).

<table>
<thead>
<tr>
<th>( N_r )</th>
<th>( N_z )</th>
<th>( N_b )</th>
<th>total symmetry</th>
<th>partial symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>( Q_{\text{top}} ) W</td>
<td>( Q_{\text{side}} ) W</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>64</td>
<td>0.0589</td>
<td>0.6647</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>128</td>
<td>0.0605</td>
<td>0.7754</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>256</td>
<td>0.0605</td>
<td>0.4950</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>512</td>
<td>0.0608</td>
<td>0.4570</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>64</td>
<td>0.0549</td>
<td>0.7685</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>128</td>
<td>0.0748</td>
<td>0.8101</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>256</td>
<td>0.0620</td>
<td>0.9581</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>512</td>
<td>0.0720</td>
<td>0.9531</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>64</td>
<td>0.0492</td>
<td>0.9388</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>128</td>
<td>0.0665</td>
<td>0.9195</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>256</td>
<td>0.0604</td>
<td>0.9534</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>512</td>
<td>0.0703</td>
<td>0.9517</td>
</tr>
<tr>
<td>exact</td>
<td></td>
<td></td>
<td>0.0680</td>
<td>0.9310</td>
</tr>
</tbody>
</table>

In Table 6.4 the results are shown for different numbers of beams and different numbers of wall surface zones. \( N_r \) denotes the number of zones in the radial direction, \( N_z \) the
number of zones in the axial direction and $N_b$, the number of beams per zone. Both total symmetry and partial symmetry are compared.

![Figure 6.34: Heat flow through top surface $Q_{\text{top}}$ vs. the number of beams $N_b$ in case 1 for different grids and beam orientations. Dashed lines correspond to the total symmetry beam distribution, solid lines correspond to partial symmetry. The dotted line represents the exact solution. Symbols: ◦ 1 x 1 grid; Δ 4 x 4 grid; ○ 10 x 10 grid.](image)

![Figure 6.35: Heat flow through side surface $Q_{\text{side}}$ vs. the number of beams $N_b$ in case 1 for different grids and beam orientations. Lines and symbols are the same as in figure 6.34.](image)

The results in table 6.4 are presented graphically in figures 6.34 and 6.35. In these figures the results are plotted also for 4 and 16 beams per zone. We see that in general the accuracy is improved by increasing the number of beams and the number of surface
zones. For large numbers of beams or surface zones, however, the numerical solution fluctuates around the exact solution. This is attributed to the systematic error associated with the fixed beam directions. For a Cartesian geometry, Wieringa (1992) made the same observations. Only in the limit of many beams distributed properly, the systematic error can be reduced.

Differences between total symmetry and partial symmetry do not show that one of the two gives a systematically better solution. In case of the heat flow through the top, total symmetry gives the most accurate solution. The best solution for the heat flow through the side surface is found using partial symmetry.

Case 2: Emitting side surface

In the second test case the side surface has an emissive power of \( E = 1 \text{ W/m}^2 \), and the other surfaces are black and cold. We expect to find results similar to case 1, because the DTM is in fact a method that calculates the exchange factors from the surfaces to each other by sending beams to all the surfaces. The geometry is not changed compared to the first test case, so the exchange factors are the same.

The exchange factors have to obey the summation relation and the law of reciprocity as described in Chapter 4. As a consequence of these conditions the exchange factor for the bottom surface to the top surface can be calculated directly from the exchange factor for the side surface to the top surface and vice versa. Hence, the two different test cases are linked according to:

\[
Q_{\text{top, case 2}} = 1 - Q_{\text{top, case 1}} \\
Q_{\text{side, case 2}} = -2 Q_{\text{side, case 1}}
\]
The results of the DTM calculations (see figures 6.36 and 6.37) are in agreement with these relations. Moreover, the figures show that in case 2 the relative imprecision of the heat flow $Q_{\text{top}}$ is smaller compared with $Q_{\text{top}}$ calculated for case 1.

6.4.4 Source term calculations

In order to simulate the axisymmetrical turbulent flame with radiative heat transfer we have to obtain the source term for the enthalpy equation. This source term is derived from the mean blackbody emissive power field $\langle \sigma T^4 \rangle$. First, the source term is calculated for a given $\langle \sigma T^4 \rangle$ field of the flame, without making a feedback to the enthalpy equation at this stage. Here, we have used the results of the adiabatic flame III case, as described previously in this chapter.

For numerical convenience, the DTM and Hottel zone method are not applied on the same grid as the FVM grid on which the enthalpy equation is solved. Therefore the source terms calculated on the radiation grid have to be redistributed over the FVM grid. Consequences of this distribution are investigated. The absorption coefficient used for all models is $K^a = 0.1 \text{ m}^{-1}$. This value is based on earlier studies of furnace simulations (Koster, 1993; Wieringa, 1992).

Hottel zone method

Two different uniform grids were used to calculate the source term with the Hottel zone method, a $5 \times 10$ grid and a $10 \times 50$ grid. Here, the first number denotes the number of zones in the radial $r$-direction and the second number denotes the number of zones in the axial $x$-direction. The direct exchange areas were calculated for both grids until a relative difference of $\delta_{\text{calc}} < 10^{-3}$ was reached.
6.4. Flame radiation and soot formation

TABLE 6.5: Heat flows calculated with Hottel zone method for two different grids with $K^* = 0.1 \text{ m}^{-1}$

<table>
<thead>
<tr>
<th>Grid</th>
<th>$Q_{\text{top}}$ W</th>
<th>$Q_{\text{bottom}}$ W</th>
<th>$Q_{\text{side}}$ W</th>
<th>$Q_{\text{out}}$ W</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 x 10</td>
<td>23.46</td>
<td>9.71</td>
<td>1227.20</td>
<td>1260.37</td>
</tr>
<tr>
<td>10 x 50</td>
<td>22.71</td>
<td>8.89</td>
<td>1228.50</td>
<td>1260.10</td>
</tr>
</tbody>
</table>

The results of the source term calculations on the HZM grids show that the coarser Hottel grid cannot resolve the thin structure of the hot reaction zone near the burner. After redistribution of the source term, however, the two Hottel grids yield virtually the same source term on the FVM grid. This is a result of the distribution method as described in Chapter 4, which treats the emitted part of the radiative source term without smoothing. The FVM cells with a high temperature account for a relatively high contribution to the emitted part of the source term calculated in the radiation zone. As a consequence, the FVM source term derived from the 5 x 10 radiation grid still has the thin structure near the burner, because in the present flame the radiation is strongly dominated by emission, and not by absorption in the flame itself.

In table 6.5 the heat flows $Q_{\text{top}}$, $Q_{\text{side}}$ and $Q_{\text{bottom}}$ through the top, side and bottom walls are shown together with the total outgoing heat flow $Q_{\text{out}}$. The table illustrates that the differences between the 5 x 10 grid and the 10 x 50 grid are very small. We conclude that grid refinement is not necessary in this case.

Discrete Transfer Method

Turning to the DTM we can follow the same procedure as with the HZM. First, the total outgoing heat flow $Q_{\text{out}}$ is calculated for different numbers of beams, both using total symmetry and partial symmetry, using a 5 x 10 grid. Initially, the distribution of beams according to Wieringa (1992) was used (see table 6.6). The results of these calculations are shown in figure 6.38.

The dotted line represents the value calculated with the Hottel zone method. The figure shows that even for 512 beams a considerable difference between partial symmetry and total symmetry exists. This is a consequence of the beam distribution according to the FURNACE code.

The azimuthal angle $\phi = 2\pi$ and the polar angle $\theta = \pi/2$ are divided into $N_{\phi}$ and $N_{\theta}$ intervals, respectively. In this study an alternative distribution is used to examine the influence of the beam distribution on the total heat flow. Still, the condition as described in (2.113) has to be satisfied. We expect a finer division of the azimuthal angle $\phi = 2\pi$ to decrease the difference between partial symmetry and total symmetry. The new division of the hemisphere is illustrated in table 6.6.

Here, for each number of beams $N_{\phi}$, the intervals $N_{\phi}$ and $N_{\theta}$ are given. Both the distribution used in FURNACE and the new distribution are shown. For the new distribution
Figure 6.38: Total outgoing heat flow $Q_{out}$ vs. number of beams $N_b$ for FURNACE and new distribution calculated on a $5 \times 10$ grid.

Table 6.6: Distribution of beams in the hemisphere, with $N_b$ is the total number of beams sent from each surface zone, $N_\phi$ the number of intervals of the azimuthal angle $\phi = 2\pi$ and $N_\theta$ the number of intervals of the polar angle $\theta = \pi/2$.

<table>
<thead>
<tr>
<th>$N_b$</th>
<th>FURNACE</th>
<th>NEW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_\phi$</td>
<td>$N_\phi$</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>16</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>40</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>64</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>128</td>
<td>8</td>
<td>16</td>
</tr>
<tr>
<td>256</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>512</td>
<td>16</td>
<td>32</td>
</tr>
<tr>
<td>1024</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Also a subdivision of the hemisphere into 40 and 1024 beams is given, the division into 64 beams is omitted.

The results of calculating the outgoing heat flow with the new distribution are shown in figure 6.38. Differences between partial symmetry and total symmetry are negligible for $N_b = 512$ beams and 1024 beams. The outgoing heat flow $Q_{out}$ remains below the value calculated with the Hottel zone method.

Calculations have been performed for a $10 \times 50$ grid as well. The results of the outgoing heat flow $Q_{out}$ are shown in figure 6.39 compared with the results of the $5 \times 10$ grid. The finer grid does not yield results which differ significantly from the $5 \times 10$ grid.
To obtain a good impression of the source term fields calculated with the Discrete Transfer Method, the source term magnitude is plotted in figure 6.40. In figure 6.40 (a) the source term for \( N_b = 512 \) and partial symmetry of the radiation grid is shown for the grid \( 5 \times 10 \) (a1) and \( 10 \times 50 \) (a2). Near the centerline the source term is lower than calculated with the Hottel zone method. This difference is illustrated even better by the source term field after redistribution over the FVM grid. In figure 6.40 (b) the source term fields obtained on the \( 5 \times 10 \) grid (b1) and from the \( 10 \times 50 \) grid (b2) are shown.

At the vertical line where the boundary of the inner radiation zones is located a discontinuity occurs. The discontinuity is caused by the fact that the source term on the radiation grid is too low near the centerline, since only few DTM beams pass near the centerline. Therefore, the FVM cells have to redistribute a source term, which is too low, over hotter cells than the FVM cells lying in the radiation zone further away from the centerline. The magnitude of the discontinuities is reduced when increasing the number of beams \( N_b \). This is shown by figure 6.40 (b2) where a refined radiation grid is used.

In figure 6.40 (c) the results, after redistribution over the FVMgrid, are shown for total symmetry on a \( 5 \times 10 \) grid. The total symmetry results show the same discontinuous behavior as the partial symmetry results. Again, increasing the number of beams leads to smaller discontinuities.

Table 6.7 shows the minimum number of beams \( N_{\text{min}} \) crossing the volumes in the middle near the centerline. The results are in agreement with the results of the source term calculations; the more beams pass through the volume zones near the centerline, the smaller the discontinuity becomes.

In figure 6.41 the source term fields for 512 and 1024 beams using partial symmetry are compared. In both cases a \( 5 \times 10 \) radiation grid is used. Figure 6.41 (a) shows the source term calculated on the radiation grid. It shows that the source term calculated using
Figure 6.40: Source term fields DTM (a) for radiation grid with 512 beams partial symmetry, (b) after distribution over FVM grid, (c) for 512 and 1024 beams total symmetry, $\Delta S_R = -33$ kW/m$^3$
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Figure 6.41: Source term fields DTM (a) for radiation grid with 512 and 1024 beams partial symmetry, (b) after distribution over FVM grid, (c) 1024 beams compared with Hottel, \( \Delta S_R = -33 \) kW/m³.
Chapter 6. Results on axisymmetric diffusion flames

TABLE 6.7: Minimum number of beams through the middle volume zones near the symmetry axis for $5 \times 10$ grid.

<table>
<thead>
<tr>
<th>$N_b$</th>
<th>symmetry</th>
<th>$N_{\text{min}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>512</td>
<td>partial</td>
<td>66</td>
</tr>
<tr>
<td>512</td>
<td>total</td>
<td>68</td>
</tr>
<tr>
<td>1024</td>
<td>partial</td>
<td>154</td>
</tr>
<tr>
<td>1024</td>
<td>total</td>
<td>144</td>
</tr>
</tbody>
</table>

$N_b = 1024$ (a2) agrees better with the HZM results than the source term calculated with $N_b = 512$ (a1). After redistribution over the FVM grid only a small discontinuity remains as shown in (b2).

In figure 6.41 (c) the result of the HZM calculations (c1) and the result of the DTM calculation with $N_b = 1024$ (c2) are compared. There is a reasonable agreement, although the total heat flow $Q_{\text{out}}$, calculated by the DTM is a little lower than with the HZM as shown more clearly in figure 6.38.

The best results are obtained for $N_b = 1024$ using partial symmetry. In this case the largest number of beams crossing the volume zones near the centerline is obtained, as shown in table 6.7.

Heat fluxes through the boundaries

The heat fluxes calculated with the Discrete Transfer Method are examined for $N_b = 512$ and $N_b = 1024$, using partial symmetry. Different grids were used for the HZM and the DTM calculations, except for the DTM calculation with $N_b = 1024$. Here, we only show results of calculations on the radiation grid; the heat fluxes are not redistributed over the FVM grid.

It appears that most of the heat flows through the side surface, as shown previously by the HZM calculations. The results for the heat flux through the side surface $q_{\text{side}}$ of the HZM calculations are compared with the DTM results in figure 6.42. The HZM and DTM results agree excellently. The results obtained with the $10 \times 50$ grid do not differ much from the results obtained with the $5 \times 10$ grid.

In table 6.8 the total heat flows through the side, top and bottom surfaces are shown. The table illustrates once more that the different models produce about the same results. The total heat flow calculated on the fine DTM grid is slightly smaller than the heat flow calculated on the more coarse grid. This is caused by the relative number of beams that pass the center of the flame: the use of more and smaller surface zones implies that more beams have to be sent to reach the same relative amount of beams in the center.

The calculated heat fluxes through the top and the bottom surface are shown in figures 6.43 and 6.44. Here, the differences in the calculated heat fluxes are larger compared to the results of the heat flux through the side wall. The DTM calculations with 1024 beams agree best with the HZM results. The contribution of the heat fluxes through
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![Graph showing side wall heat flux vs. distance x.](image)

**Figure 6.42:** Side wall heat flux $q_{side}$ vs. distance $x$, obtained with HZM and DTM using different grids and beam distributions.

<table>
<thead>
<tr>
<th>grid</th>
<th>method</th>
<th>$Q_{top}$ W</th>
<th>$Q_{bottom}$ W</th>
<th>$Q_{side}$ W</th>
<th>$Q_{out}$ W</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10$</td>
<td>HZM</td>
<td>23.46</td>
<td>9.71</td>
<td>1227.20</td>
<td>1260.37</td>
</tr>
<tr>
<td>$10 \times 50$</td>
<td>HZM</td>
<td>22.71</td>
<td>8.89</td>
<td>1228.50</td>
<td>1260.10</td>
</tr>
<tr>
<td>$5 \times 10$</td>
<td>DTM 512</td>
<td>18.15</td>
<td>3.99</td>
<td>1216.07</td>
<td>1238.21</td>
</tr>
<tr>
<td>$10 \times 50$</td>
<td>DTM 512</td>
<td>17.32</td>
<td>3.11</td>
<td>1203.35</td>
<td>1223.77</td>
</tr>
<tr>
<td>$5 \times 10$</td>
<td>DTM 1024</td>
<td>19.95</td>
<td>5.79</td>
<td>1216.94</td>
<td>1242.68</td>
</tr>
</tbody>
</table>

**Table 6.8:** Total heat flows through the surfaces calculated with the DTM and Hottel zone method for two different grids with $K^* = 0.1$ m$^{-1}$.

the top and bottom surfaces to the total outgoing heat flow are relatively small, since most of the heat flows through the side surface. Thus, small differences in the heat fluxes through the bottom and top surfaces do not have much influence on the total radiation calculations for this particular flame. It must be kept in mind, however, that the choice $K^* = 0.1$ m$^{-1}$ is rather ad hoc and probably has a much larger influence on the predicted radiation field than the numerical accuracy of the models used.

### 6.4.5 Coupling of radiative heat transfer with fluid flow

The results presented in the previous subsections give an impression of the accuracy of the source term calculations by the DTM and the HZM. Refinement of the uniform radiation grid does not change results significantly, and therefore we used a $5 \times 10$ radiation grid for the radiating flame calculations. A comparison is made among the HZM, the DTM and
the simplified radiation model.

Calculations are performed for flame III with and without soot formation. In the calculations with soot formation, only the DTM and the simplified method can be used, because our HZM assumes a uniform absorption coefficient. For the flame gases, a constant absorption coefficient of $K^a = 0.1 \text{ m}^{-1}$ is used.

The radiation calculations took 15% of the total computing time, when using the most accurate Discrete Transfer Method with 1024 beams for each surface zone. Adding the
soot formation model gave only 3% increase in CPU time.

The following calculations are discussed:

- No radiation
- Simplified method
- DTM 512 beams partial symmetry
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![Graph](image)

**Figure 6.47:** Centreline profile of the absorption coefficient $K^*$ vs. the distance $x$, with soot formation included.

- DTM 1024 beams *partial symmetry*
- HZM
- Simplified method with soot formation
- DTM 1024 beams *partial symmetry* with soot formation

**Results without soot formation**

For the flame without soot formation, the results for the maximum temperature $T_{\text{max}}$ and the total outgoing heat flow $Q_{\text{out}}$ are shown in table 6.9. Differences between the results of the different radiation models are very small. The slightly higher temperature found with the DTM using 512 beams is caused by the value of the source term near the centerline which is too low, as already explained in the previous section.

A remarkable agreement of the simplified results and the results obtained with the other radiation models is found. This means that in absence of soot, no error is made by neglecting the radiative interaction within the flame.

In figures 6.45 and 6.46 radial temperature profiles at different heights in the flame are shown. Figure 6.45 shows the radial profile at a height of 0.35 m. The differences between no radiation and the radiation models are still rather small. At a higher position in the flame the differences increase, as can be seen in figure 6.46. Here the radial temperature profile at a height of 0.65 m is given. In both figures can be seen that the mean temperature obtained with the simplified method does not differ much from the temperatures obtained with the other models. With the Hotzel zone method exactly the same result is obtained as with the simplified method.
6.4. Flame radiation and soot formation

![Graph showing mean temperature \( \tilde{T} \) vs. radial distance \( y \) at height \( x = 0.35 \) m in the flame, with soot formation included.]

**Figure 6.48**: Mean temperature \( \tilde{T} \) vs. radial distance \( y \) at height \( x = 0.35 \) m in the flame, with soot formation included.

<table>
<thead>
<tr>
<th>method</th>
<th>( T_{\text{max}} )</th>
<th>( Q_{\text{out}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZM</td>
<td>1886</td>
<td>1239.39</td>
</tr>
<tr>
<td>DTM 512 beams</td>
<td>1890</td>
<td>1220.66</td>
</tr>
<tr>
<td>DTM 1024 beams</td>
<td>1888</td>
<td>1224.24</td>
</tr>
<tr>
<td>Simplified</td>
<td>1886</td>
<td>1267.45</td>
</tr>
<tr>
<td>no radiation</td>
<td>1925</td>
<td>—</td>
</tr>
</tbody>
</table>

**Table 6.9**: Results of complete flow calculations for different methods without soot formation, using \( K^a = 0.1 \) m\(^{-1}\).

**Results with soot formation**

Because of the influence of the soot concentration in the flame the absorption coefficient will locally have a higher value. In figure 6.47 the centerline profile of the absorption coefficient is shown. The absorption coefficient differs between the minimum value \( K_{\text{min}}^a = 0.1 \) m\(^{-1}\) and the maximum value \( K_{\text{max}}^a \approx 0.5 \) m\(^{-1}\).

Results of the maximum temperature \( T_{\text{max}} \) and the total outward heat flow \( Q_{\text{out}} \) are shown in table 6.10. The table shows that the difference between the DTM method and the simplified method is only marginal. In the calculations without soot this difference was even smaller. This means that with the presence of soot, causing higher absorption coefficients, the radiative interaction in the flame will become slightly more important. The formation of NO\(_x\), which is very sensitive on the temperature field, may show somewhat larger differences.
Table 6.10: Results of complete flow calculations for different methods with soot formation.

<table>
<thead>
<tr>
<th>method</th>
<th>$T_{\text{max}}$</th>
<th>$Q_{\text{out}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTM 1024 beams</td>
<td>1856</td>
<td>1429.01</td>
</tr>
<tr>
<td>Simplified</td>
<td>1846</td>
<td>1490.62</td>
</tr>
<tr>
<td>no radiation</td>
<td>1925</td>
<td>—</td>
</tr>
</tbody>
</table>

Figure 6.49: Mean temperature $\tilde{T}$ vs. radial distance $y$ at height $x = 0.65$ m in the flame.
With soot formation.

Profiles of the temperature field are shown in figures 6.48 and 6.49. In figure 6.48 the radial temperature profile at $x = 0.35$ m is shown. At this distance the difference with no radiation is still small but larger compared with the case of no soot formation. Differences between the simplified method and DTM are still very small. The lower part of the flame does not absorb much radiation emitted by other parts of the flame. Figure 6.47 shows that below 0.35 m the absorption coefficient already is increased, however, this is only in a small region near the centerline of the flame.

At $x = 0.65$ m the differences are larger, at this position the maximum temperature is obtained. It appears there is a marginal difference between the DTM and the simplified method, if we take into account the experimental uncertainty of about 70 K in the temperature measurements.

As made visible in the radial temperature profiles the differences between no radiation and radiation modelling occur only above a certain height in the flame. This can well be demonstrated by the temperature profile along the centerline of the flame shown in figure 6.50. Considerable differences are found for $x > 0.3$ m. This is a result of the fact...
that at the bottom side the flame has a very thin structure, so there radiative heat transfer will not play an important role. Also the combustion is very clean at the lower part of the flames which means there is little formation of soot and the absorption coefficient will be relatively small.

<table>
<thead>
<tr>
<th>method</th>
<th>$Q_{\text{top}}$ (W)</th>
<th>$Q_{\text{bottom}}$ (W)</th>
<th>$Q_{\text{side}}$ (W)</th>
<th>$Q_{\text{out}}$ (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTM no soot</td>
<td>18.51</td>
<td>5.79</td>
<td>1199.93</td>
<td>1224.24</td>
</tr>
<tr>
<td>DTM soot</td>
<td>17.96</td>
<td>8.16</td>
<td>1402.89</td>
<td>1429.01</td>
</tr>
</tbody>
</table>

Heat fluxes through the boundaries

The heat flows are compared for the situation with and without soot formation. In Table 6.11 the total heat flows through the boundary surfaces are shown for the DTM calculations with and without soot. The total heat flow $Q_{\text{out}}$ is increased by 16% when including soot formation. Still, most of the heat flows through the side boundary surface.

The differences between the heat flux through the side boundary surface with and without soot formation are shown in Figure 6.51. The figure shows that relatively more heat flows out of the lower part of the side surface. Thus, the presence of soot has influence on both the total heat flow and the flux distribution.
Chapter 6. Results on axisymmetric diffusion flames

\[2.75\]
\[2.20\]
\[1.65\]
\[1.10\]
\[0.55\]

\(q_{\text{side}}\) vs. axial distance \(x\) with and without soot formation.

\[\begin{array}{c}
0 & 15 & 30 & 45 & 60 & 75 & 90 & 105 & 120 & 135 & 150 \\
\hline
x (cm) & & & & & & & & & & \\
\end{array}\]

\[\begin{array}{c}
\text{DTM no soot} \\
\text{DTM soot} \\
\end{array}\]

**Figure 6.51:** Heat flux \(q_{\text{side}}\) vs. axial distance \(x\) with and without soot formation.

\[2000\]
\[1650\]
\[1300\]
\[950\]

\(\bar{T}\) vs. \(y\).

**Figure 6.52:** Measured temperatures compared with the numerical results of no radiation and DTM with soot, \(\bar{T}\) vs. \(y\).

### 6.4.6 Comparison of numerical and experimental data

In this section measured temperatures will be compared with the results of the numerical simulations. Experimental results are available up to a height of \(x = 0.25\) m. The temperatures were measured with thermocouples and corrected for radiative and conductive heat losses.

Experimental radial temperature profiles at different heights are shown in figure 6.52 together with the numerical results. Here the results are shown of the DTM calculation
with soot formation and of the calculation without radiation modelling. As can be seen in the figure the plots completely overlap. This is in agreement with figure 6.50 where differences are only found above a height of approximately 0.3 m. Unfortunately, at this moment no experimental results at high locations in the flame are available.

The difference between the calculated and the measured values increases slowly with $x$. This difference does not decrease if radiation and soot formation are included in the calculations. Hence, any improved in these predictions is to be sought in the turbulent mixing model and/or the chemistry model rather than in the modelling of radiation.

6.5 Detailed kinetics model results

The detailed chemical kinetics model, using an assumed-shape joint PDF of temperature and species mass fractions, has been successfully applied to H$_2$/air and CO/H$_2$/air flames (Bockhorn, 1987; Bockhorn, 1988). Here we apply the same modeling technique to our piloted natural-gas diffusion flames. Before doing so, some of the modeling assumptions are tested for our specific application.

Two important simplifications are used in the original model developed by Bockhorn (1989): the assumption of a joint-Gaussian PDF shape, and the approximation of the mean reaction rates by polynomial functions based on means, variances and covariances of the independent scalars. The first simplification can be checked for its validity by comparison with experiments, but these are scarce. For methane/air flames, experimental evidence obtained by Masri et al. (1990) show that a joint-Gaussian distribution is certainly not the correct PDF representation in all points of the flow. The question is still open whether an assumed PDF type which differs from the Gaussian PDF will give significantly different reaction rates and flame structure. In the present model, the assumed joint-Gaussian PDF shape has been used, because of the lack of better mathematical descriptions. The second simplification is used for numerical efficiency only. Therefore, it is important to investigate the accuracy of the polynomial representation in comparison with more time-consuming PDF integration methods. Closely related to this, is the problem of the extraction of the temperature (co)variances from the enthalpy (co)variances, using only first-order and second-order moments.

6.5.1 Numerical aspects

The original formulation used by Bockhorn to evaluate the mean reaction rates numerically was based on the notion that the influence of turbulent fluctuations of temperature and concentrations can be regarded as a perturbation with respect to the laminar reaction rates (see §3.7.2). For a given elementary reaction $k$, the mean rate $\langle \dot{\omega}_k \rangle$ therefore is expressed as the laminar rate (using mean values for $T$ and $Y_i$ only), multiplied by correction functions to account for fluctuations. In general, the influence of fluctuations is a function of the moments of the joint PDF $\tilde{f}_{TY}$ and of the parameters $\beta_k$ and $T_{A,k}$ in the Arrhenius expression for $\dot{\omega}_k$. 
Bockhorn simplified the treatment of the influence of temperature fluctuations and mass fraction fluctuations by separate correction functions $F_T$ and $F_Y$. These functions act independently. In order to account for the covariance of temperature and mass fractions, a third function $F_{TY}$ is used. Because the reaction rates depend exponentially on temperature, temperature fluctuations may increase the mean reaction rates by several orders of magnitude. For this reason, the correction functions are expressed as exponentials of polynomial functions.

Because the polynomial coefficients have been computed for several ranges of turbulent intensity $Tu_T$ and $Tu_Y$, some discontinuities may occur at the points where these ranges end ($Tu_\phi \equiv \phi''_{rms}/\bar{\phi}$). In figure 6.53 the correction function $F_Y$ for $\nu = 2$ is presented as a function of $Tu_Y$. The polynomial, although split in several ranges, exhibits a smooth behaviour. For 100% turbulent intensity of mass fraction fluctuations, the mean rate is increased by a factor of about 2 for $\nu = 2$. The same correction function is shown for stoichiometric coefficient $\nu = 3$, which will be required for the evaluation of the correlation $\langle Y \dot{\omega}_k \rangle$ appearing in the transport equation for $\dot{Y}^m$.

The temperature fluctuations have a much stronger impact on the mean reaction rates than the mass fraction fluctuations. Temperature fluctuations will change the mean reaction rates by several orders of magnitude. In addition, the polynomial function $F_T$ is more complicated than $F_Y$, because of the activation energy $T_A$. Figure 6.54 shows the correction function for an elementary reaction with zero activation temperature. Furthermore, the correction functions for the temperature ratio $T_A/\bar{T} = 5$, 10, and 20 have been given. $F_T$ depends only linearly on this ratio. From the figure, we see that the influence of activation temperature is significant. For $T_A/\bar{T} = 10$ the influence on the mean reaction rate will be one order of magnitude, for large values of $Tu_T$.

The correction function is discontinuous at the interval bounds which connect the sub-polynomials given in table 3.3. This is a serious deficiency of the used polynomial correction functions. It is very difficult to have matching polynomials for every value
of the activation temperature. A continuous function can be obtained only if a different set of terms is selected. In practical calculations, the discontinuity of $F_T$ was found to have a profound influence on the convergence behaviour of the numerical solution. On successively finer grids, numerical oscillations were observed and convergence could not be obtained. In grid points where $Tu_T$ has a value near one of the interval boundaries, a small increase in mean temperature can cause a reduction of $Tu_T$ and $T_A/\tilde{T}$, which in turn can produce a decrease of the mean reaction rate. In the next iteration, the opposite effect may occur. Even strong underrelaxation and small time steps are not sufficient to suppress this oscillatory behaviour.
The third correction function $F_{TY}$ takes into account the influence of temperature mass-fraction correlations on the mean reaction rate. By inspection of the equation for $F_{TY}$, we see that the actual correlation $T^\alpha Y''$ does not enter the formula (3.113), and neither do the mass fraction fluctuations. In other words, the function $F_{TY}$ has been reduced to a function which depends on the temperature fluctuations only, similar to the $F_T$-function. Two major differences with $F_T$ are the lack of discontinuities because the polynomial is given for one interval only, and the much higher absolute value of $10 \log F_{TY}$ compared with $10 \log F_T$.

Figure 6.55 shows the correction function for the same values of $T_A/\bar{T}$ as used in figure 6.54. Contrary to the $F_T$-function, the activation temperature does not affect the value of $F_{TY}$ much. Only for very large ratios, say $T_A/\bar{T} > 25$, or $T_A > 10000$ K, the influence of $T_A$ becomes important. In other words, the effect of $F_{TY}$ is more or less the same for every important two-body elementary reaction. However, the slow recombination reactions with high activation temperature depend stronger on $F_{TY}$.

For moderate rates of turbulent intensity $Tu_T$, say $Tu_T < 0.4$, the effect of $F_{TY}$ is fairly small. For higher turbulent intensity, the shown $F_{TY}$ correction function reduces the mean reaction rate by many orders of magnitude. Since the original formula (3.113) does not contain the covariance $Y''T''$, this behaviour seems unrealistic. If the activation temperature is positive (which is true for most of the elementary reactions relevant to CH$_4$ combustion), a temperature increase will amplify the reaction rate. In that case, a positive correlation $\rho_{TY}$ will effectively yield a higher mean reaction rate. The effect of negative correlation $\rho_{TY}$ on the mean reaction rate is not a priori clear. A positive temperature fluctuation will then be accompanied by a negative mass fraction fluctuation, but this may still produce a higher mean reaction rate, because reaction rates are more sensitive to temperature fluctuations than to mass fractions fluctuations. This behaviour is not reproduced by Bockhorn's correction formula. However, his computations of CO/air flames (Bockhorn, 1987) were not greatly affected by this, because the conditions in these flames were such that the turbulent intensity $Tu_T$ was relatively small, so $F_{TY}$ had no significant effect.

Finally, because $F_{TY}$ depends on the same quantities as $F_T$, it is interesting to see what the product function $F_T \times F_{TY}$ looks like. On a $10 \log$-scale, this implies simple addition of the graphs of figures 6.54 and 6.55. The result is shown in figure 6.56. For $Tu_T < 0.5$ and for moderate values of $T_A/\bar{T}$, equivalent with $T_A < 10000$, the combined correction function $F_T \times F_{TY}$ will affect the mean reaction rate by at most one order of magnitude. Taking into account the relatively small influence of $F_T$, we see that for flames with low turbulent intensities, the mean rates of those elementary reactions with small to moderate activation temperatures are not much amplified by the given correction functions.

### 6.5.2 Model improvements

From the discussion in the previous subsection, it is clear that the detailed-kinetics model has to be improved before it can be applied to natural gas or methane combustion. First, the jet flames studied in this thesis are characterized by fairly high levels of turbulent
6.5. Detailed kinetics model results

\[ 10 \log(F_T \times F_{TY}) \]

\[ T_A/T = 0. \]
\[ T_A/T = 5. \]
\[ T_A/T = 10. \]
\[ T_A/T = 20. \]

\( Tu_T \)

\( 0 \)
\( 0.2 \)
\( 0.4 \)
\( 0.6 \)
\( 0.8 \)
\( 1.0 \)

\( -15 \)
\( -10 \)
\( -5 \)
\( 0 \)
\( 5 \)

\textbf{Figure 6.56:} Product of polynomial correction functions \( F_T \) and \( F_{TY} \) as a function of turbulent intensity \( Tu_T \), for different ratios \( T_A/T \).

Intensities \( Tu_T \) and \( Tu_Y \). Second, the reaction mechanism for methane combustion contains several important elementary reactions with high activation temperature. Hence, model improvements are sought in the following areas:

- Better description of \( F_T \) without discontinuities.
- Taking into account the influence of the factor \( T^\beta \) in the general Arrhenius rate expression, for non-zero \( \beta \).
- Improvement of the \( F_{TY} \) function, incorporating the influence of positive and negative correlation coefficients \( p_{TY} \), and avoiding the very low values of the original \( F_{TY} \)-function for large \( Tu_T \).
- Treatment of density fluctuation effects on the mean reaction rates by writing \( \rho = \langle p \rangle \langle M \rangle / \rho^0 T \).

The best alternative for the 'old' \( F_T \)-function is to carry out the integration of the elementary reaction rates by the temperature PDF directly. If we assume that \( F_T \) represents the influence of the marginal PDF of temperature, we can employ a Gaussian temperature PDF and perform the integration directly. Contrary to the mixture fraction PDF studied before, the interval of physically allowed temperature values is not well defined. For simplicity however, we assume that the minimum achievable temperature is governed by the lowest temperature at the boundaries of the combustion chamber (295 K), and the highest achievable temperature is the adiabatic flame temperature for the fuel used (2208 K for Groningen natural gas).

For numerical convenience, we can transform the interval \([T_{\text{min}}, T_{\text{max}}]\) to the unit interval \([0, 1]\), allowing us to use exactly the same integration algorithms as described in §4.3 for the mixture fraction PDF. The mean elementary reaction rates are computed as a
function of $\bar{T}$ and $\bar{T}^{\alpha_2}$, and stored in the self-adaptive lookup-table structure discussed in Section 4.4. The tabulation of the mean reaction rates is an accurate and fast method to retrieve the mean rates for any combination of mean temperature and temperature variance (which completely govern the temperature PDF). Because the reaction rates vary with temperature over many orders of magnitude, the tabulation and lookup is performed on the $10\log$-values of the mean rates. These values behave fairly smoothly in the domain of allowed $(\bar{T}, \bar{T}^{\alpha_2})$-values.

Figure 6.57 shows the reaction rate constant $k(T)$ for the elementary reaction $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$, which has an activation temperature $T_A = 8454$ K. Because $\frac{d^2 k}{dT^2}$ is positive, fluctuations will cause an increase of the mean reaction rate. This is depicted in figure 6.58, where we show $\tilde{k}$ as a function of $\bar{T}$ and $\bar{T}^{\alpha_2}$, using the original $F_T$ correction function. Although figure 6.57 shows that $10\log k(T)$ will never exceed a value of 13, the $F_T$ correction function adds several orders of magnitude increase, giving a maximum value of 17 for the $10\log$-value of the average $\tilde{k}$.

The influence of the correction function $F_{TV}$ is presented in figure 6.59, where we used the combined correction $F_T \times F_{TV}$. The picture has changed completely. The maximum value for $10\log \tilde{k}$ has been reduced from about 17 to 13.5, which still is too high but more in line with the graph of figure 6.57. Moreover, the region in $(\bar{T}, \bar{T}^{\alpha_2})$-space where $\tilde{k}$ is high has shifted drastically. For this particular case, it appears the influence of the combined function $F_T \times F_{TV}$ is more in line with the expected theoretical behaviour than the function $F_T$ alone. For large values of $Tu_T$, however, large discrepancies may be anticipated.

The result of the direct integration of the rate constant with the temperature PDF (assumed to be truncated Gaussian) is shown in figure 6.60. The minimum and maximum value of $10\log \tilde{k}$ are in line with the theoretical limits $k(T_{\text{min}})$ and $k(T_{\text{max}})$. Furthermore,
6.5. Detailed kinetics model results

**Figure 6.58**: $\log_{10}$-value of mean reaction rate constant of $H + O_2 \rightarrow OH + O$ as a function of temperature mean and variance, using the polynomial correction function $F_T$. Contours are shown for $10\log(k) = 2 \cdots 17$ (1). Dark shading represents low $k$, white shading high $k$-values. Minimum value is 1.85, maximum is 17.0.

**Figure 6.59**: $\log_{10}$-value of mean reaction rate constant of $H + O_2 \rightarrow OH + O$ as a function of temperature mean and variance, using the correction function $F_T \times F_T$. Contours are shown for $10\log(k) = 1 \cdots 13$ (1). Minimum value is 0.27, maximum is 13.5.

we see that the value of $10\log k$ behaves smoothly in a large part of the $\bar{T} - T^{n/2}$-space, in contrast to figure 6.58 which suffers from the $F_T$-polynomial discontinuities discussed before.

The previous discussion was based on an arbitrarily chosen elementary reaction. Other reactions in the skeletal mechanism for $\text{CH}_4$-combustion behave slightly differently, but the same conclusions can be drawn. Further deviations between the polynomial
Chapter 6. Results on axisymmetric diffusion flames

\[ \frac{(T_{\text{max}} - T_{\text{min}})^2}{4} \]

\[ T^\mu/2 \]

\[ T_{\text{min}} \]

\[ T \]

\[ T_{\text{max}} \]

**Figure 6.60:** \( 10^{\log}\text{-value of mean reaction rate constant of } H + O_2 \rightarrow OH + O \text{ as a function of temperature mean and variance, using direct integration with the temperature PDF assumed to be truncated Gaussian. Contours are shown for } 10^{\log}(\tilde{k}) = 2 \ldots 12 \text{ (1). Minimum value is } 1.85, \text{ maximum is 12.6.} \)**

\[ \frac{(T_{\text{max}} - T_{\text{min}})^2}{4} \]

\[ T^\mu/2 \]

\[ T_{\text{min}} \]

\[ T \]

\[ T_{\text{max}} \]

**Figure 6.61:** \( 10^{\log}\text{-value of mean reaction rate constant of } CH_4 + (M) \rightarrow CH_3 + H + (M), \text{ as a function of temperature mean and variance, using the polynomial correction function } F_T. \text{ Contours are shown for } 10^{\log}(\tilde{k}) = -7 \ldots 7 \text{ (1). Dark shading represents low } k, \text{ white shading high } k\text{-values. Minimum value is } -38, \text{ maximum is 7.5.} \)**

representation and the direct integration are observed for those elementary reactions which have an additional temperature exponent \( b \) in the Arrhenius expression. The strongest effects are encountered for the rate of the dissociation/recombination reaction \( CH_4 + (M) \rightarrow CH_3 + H + (M) \), which contains a factor \( T^{-7} \) (see Appendix B). Because the polynomial representation disregards the influence of the factor \( T^b \), the influence of
6.5. *Detailed kinetics model results*

\[(\frac{(T_{\text{max}}-T_{\text{min}})^2}{4})^{\frac{3}{2}}\]  

**Figure 6.62:** $10^{\log}$-value of mean reaction rate constant of $\text{CH}_4 + (M) \rightarrow \text{CH}_3 + \text{H} + (M)$, as a function of temperature mean and variance, using direct integration with the temperature PDF assumed to be truncated Gaussian. Contours are shown for $10^{\log}(\bar{k}) = -7 \cdots 3$ (1). Minimum value is $-38$, maximum is $3.63$.

Temperature fluctuations on the mean reaction rate is not modeled well. Figures 6.61 and 6.62 show the averaged rate constants using the two different approaches.

Based on the previous analysis, it was decided to use the tabulated mean rate constants with direct integration, and to disregard the $F_{TY}$ correction function. Because the model does not account for covariances of mass fractions, the influence of mass fraction fluctuations on the mean rates remains limited. The tabulated mean rate constants automatically incorporate the effects of the exponential factor $T^6$.

### 6.5.3 Further numerical considerations

The standard piloted diffusion flame (flame III) was calculated with the detailed-kinetics model using several model improvements discussed in the previous section. As stated before, the basic model with polynomial correction functions did not yield convergent results, even for small time steps and relaxation factors for the reacting variables. Having implemented the evaluation of the mean rate constants $\bar{k}$ in a self-adaptive tabulation/lookup procedure, convergence was obtained.

However, the standard solution method, solving each reacting variable field completely in every iteration step before turning to the next variable gave additional problems. The standard method does not satisfy conservation of element mass fractions, which are nonreacting variables by definition. If a given reacting species' field is solved, the local values of that variable will change slightly because of net reaction rates and transport phenomena. The other species have not yet adjusted to this new situation, although basic chemistry prescribes that if a given species is produced by chemical reactions, other species have to be destroyed simultaneously by the same reactions. Thus, if the set of reacting species is
solved sequentially, the local conditions and the following order of the solution procedure will cause discrepancies in the element mass fraction fields.

For example, suppose CO₂ is formed locally by the reaction CO + OH $\leftrightarrow$ CO₂ + H. Although $Y_{CO₂}$ increases, $Y_{CO}$ is left unchanged. When evaluating the net reaction rate for CO, a too high CO₂-value is used, and consequently the reduction of CO by the reaction is underpredicted. Part of this discrepancy can be resolved if all mean reaction rates are evaluated by using the values of mean temperatures and mass fractions on the previous iteration level (or time step). Because relaxation factors and false time steps are used to solve each variable, full consistency can not be achieved if the variables are solved sequentially. Therefore, a point-by-point Newton solver was employed to solve the reacting variables. In this method, all species mass fractions are solved simultaneously, in such a way that element mass fractions are preserved. These numerical improvements were necessary to obtain consistent convergent solutions.

Of particular importance in the detailed-kinetics model is the fact that the enthalpy equation is solved rather than the temperature equation (which would involve the net heat production by reaction rates). The values of $\bar{T}$, $\bar{T}^n$ and $\bar{Y}^n\bar{T}^n$, which appear directly in the evaluation of mean reaction rates and the mean density, depend on the values of $\tilde{h}$, $\tilde{h}^n$ and $\bar{Y}^n\bar{h}^n$, for which transport equations without chemical source terms are solved. The respective dependencies are given by the algebraic relationships (3.118), (3.121) and (3.125). To investigate the influence of these approximations, we used the converged fields of the constrained-equilibrium calculation of flame III described earlier in this chapter, and we solved additional transport equations for the covariances $h^nY^n_i$, which contain no chemical source term.

As discussed before, the pilot flames constitute a three-dimensional phenomenon. The
fields of $\tilde{T}$ and $T''_{\text{rms}}$ computed with the constrained-equilibrium model are compared with the fields as derived from the algebraic expressions in terms of enthalpy variables. The differences are shown in figures 6.63 and 6.64. The two model approaches are virtually identical as far as mean temperature is concerned. Maximum differences are still less than 50 K, which is acceptable.

The rms temperature fluctuations (and the $T$-$Y$-covariances), however, show a completely different behavior. It turns out that the implicit determination of $T''_{\text{rms}}$ from the $h^{1/2}$ variance produces unrealistic results, because of the truncation of the series expansion. Furthermore, the polynomials for enthalpy as a function of $T$ are usually split into two sub-polynomials, one for $T < 1000$ K and one for $T > 1000$ K. In the algebraic expressions for $\tilde{T}$, $T''_{\text{rms}}$ etc., only the sub-polynomial valid for the current mean temperature is used. In case of strong fluctuations, this may cause unwanted effects, because the sub-polynomials have a limited range of applicability.

6.5.4 Results for the flame III case

Having established some specific numerical improvements, the standard piloted diffusion flame (flame III) is simulated with the detailed-kinetics model, without radiation. The natural gas used in the experiments is approximated by the same diluted methane as used for the previous conserved-scalar model calculations. The skeletal mechanism Smooke and Giovangigli (1991a) for methane/air flames is used since this mechanism involves relatively few species and reactions and therefore is computationally cheap. First, we used the same boundary conditions as for the constrained-equilibrium model predictions of the flame III case. In absence of pilot flame boundary conditions, the conserved-scalar
model still yields a flame which is attached to the burner rim, simply because reactions are assumed to be infinitely fast. The detailed-kinetics model, however, shows a lifted flame, which is in qualitative agreement with the experimentally observed flame lift-off when the pilot flames are switched off. In order to obtain an attached flame, the pilot flame boundary conditions are required.

As discussed before, the pilot flames constitute a three-dimensional phenomenon. The present model is not able to mimic the influence of the pilot flames with sufficient detail. Firstly, the 3D nature of the pilot flames is not reproduced by the axisymmetric geometry in combination with the \( k-\varepsilon \) turbulence model. Secondly, the ignition of the turbulent flame by the pilot flames is governed by specific ignition reactions, which are not captured well by the skeletal reaction mechanism for methane/air flames used here. Moreover, the assumption of a Gaussian joint-PDF for temperature and mass fractions is not realistic very close to the burner rim: a bimodal temperature PDF similar to the PDF shapes extracted from the conserved-scalar model may be expected. As a consequence, the correspondence between measured and computed mean temperatures is not particularly good very near the burner, as illustrated by figure 6.65. The lack of an accurate representation of the pilot flames also has an effect on the mean-temperature profiles further downstream. The reactants, which have not been ignited fast enough near the burner, will react more rapidly further away from the burner, where the turbulence causes some premixing. Hence, towards the tip of the flame, the predicted mean temperature increases significantly when compared with the constrained-equilibrium results.

Figure 6.66 shows the prediction of the mean OH number density in comparison with experiments. Again, the correspondence is not particularly good, although it is clear that the detailed-kinetics model is capable of predicting superequilibrium radical concentrations. Also, the width of the OH profiles is considerably smaller than the width
of the constrained-equilibrium profiles (see figure 6.27). On the fuel-rich side, the OH-profiles quickly drop to zero. This is related to the fact that the temperature fluctuations are not well represented by the algebraic relationship in terms of enthalpy and mass fractions, as shown earlier.

6.6 Classification of flame regime

In Chapter 3 several model approaches were presented for the description of turbulent diffusion flames. A classification of flame regimes according to Peters (see §3.2) can now be made, using the numerical results described in this chapter. The regimes depicted in figure 3.1 are governed by the parameters $\xi_{\text{rms}}/\xi_\text{st}(1 - \xi_\text{st})$ and $\tau_i/\tau_c$. These parameters are not constant for the whole flame: close to the burner the turbulence structure differs from that at the flame tip. In figure 6.67 we have plotted the combinations $(D_a, \xi_{\text{rms}}/\xi_\text{st}(1 - \xi_\text{st}))$ for the flame III case, as computed by the constrained-equilibrium model.

From this figure, we see that the current flame has features of distributed reaction zones, extinguished flamelets and the flamelet regime. The largest part of the flame, however, lies in the flamelet regime. This explains why the constrained-equilibrium model, which mimics the behavior of strained laminar flamelets as far as temperature and major species are concerned, performs fairly well for this type of flame. The distributed reaction zone regime is encountered near the nozzle, where ignition reactions play an important role, and where the shape of scalar PDFs is far from Gaussian. This explains why the detailed-kinetics model has trouble in representing this given jet flame (apart from the modeling of the pilot flames). Finally, a small part of the flame lies in the extinguishing flamelet regime. This is in agreement with the local extinction phenomena observed in the LIF experiments by De Vries (1994).

In the previous analysis, one has to bear in mind that the limits between the various
regimes are not sharp. In reality, the transition from one regime to another is more continuous. Moreover, Peters (1991) assumes a single chemical time scale for the turbulent jet diffusion flames. Clearly, it is difficult to characterize a turbulent flame involving many reactions and species, by just one chemical time scale parameter. Close to the nozzle, where temperatures are lower, chemical time scales will probably be longer, which will lead more to a distributed reaction zone regime. Further away from the nozzle, temperatures have risen and chemical time scales will be smaller, yielding a flamelet regime rather than distributed reaction zones.

6.7 Conclusions for the turbulent piloted diffusion flame

In this chapter, several models for the description of the Delft piloted diffusion flame were presented. First of all, the validity of the numerical code and the k-ε model with Launder’s round-jet correction formula was established for the prediction of round inert air jets.

Next, we applied the constrained-equilibrium model closed by a β-function PDF for mixture fraction, to the piloted diffusion flame. Comparison with experiments yielded good agreements as far as mean axial velocity and mean temperature are concerned. Turbulence properties of the piloted diffusion flame were reproduced qualitatively. The constrained-equilibrium model failed to predict the experimentally observed super-equilibrium OH concentrations. Overall, the constrained-equilibrium model was judged to be fairly accurate for this type of flame.

The influence of intermittency on the shape of the mixture fraction PDF was investigated, using the moments models of Kent and Bilger (1977) and Abou-Ellail and Salem (1990). Accounting for intermittency yielded worse agreement between model predictions and experiments. This is explained by the fact that the annular air flow destroys the coupling between scalar intermittency and intermittency of the turbulence. In the zone where the mixture fraction is mixed by the turbulence, no interface between high-vorticity
and low-vorticity regions can be identified, because the annular air and the fuel jet are both turbulent. Judged on the prediction of dependent quantities, the $\beta$-function PDF is able to represent the mixture fraction fluctuations effectively.

The analysis of predicted PDF shapes of mixture fraction, temperature and OH concentration showed that the $\beta$-function for mixture fraction predicts gives PDF shapes for the dependent quantities which do not resemble $\beta$-functions. Near the reaction zone, the computed temperature PDF shows a bimodal shape, even although the $\beta$-function itself cannot have a bimodal form. The PDFs of OH concentration showed a large peak near $c_{OH} = 0$, and a fairly flat distribution towards $c_{OH,\text{max}}$ in regions of the flow where the mean temperature is high.

The near-burner zone proved to be difficult to model because of apparent three-dimensional influences of the twelve 0.5-mm-diameter pilot flames located on a ring on the fuel-jet exit pipe. The assumption of axisymmetry breaks down close to the nozzle. In the experiments, the high-speed pilot flames act as a shield preventing the mixing of the fuel jet with the surrounding annular air flow close to the burner.

A detailed validation of various models for flame radiation in axisymmetric geometries was performed. The numerical accuracy of the Hotel zone model and the Discrete Transfer Model was established. It was shown that the Discrete Transfer Model results are sensitive to the azimuthal and polar distributions of rays, because in our axisymmetrical flame the hot region lies close to the axis and occupies a relatively small volume. A distribution of rays different from the Cartesian DTM used by Wieringa (1992) was proposed. Overall, non-luminous flame radiation was found to be of minor importance in this jet flame. Inclusion of the soot formation model of Khan and Greeves (1974) showed that near the flame tip some soot is present. The maximum temperature drop due to radiation is less than 100 K. The given flame has relatively low absorption because of its small size and because of the cold surroundings. Therefore, a simplified radiation model that neglects the absorption altogether was found to be an accurate and cheap alternative.

Finally, an analysis of the detailed-kinetics model proposed by Bockhorn (1989) was performed. Some deficiencies of the original model, based on the extensive use of polynomials, were discussed and repaired. It was shown that the influence of temperature fluctuations on mean reaction rates is not modeled well by the assumption of various polynomials as a function of activation energy and intensity of temperature fluctuations. The application of a pre-processed table of mean rates as a function of mean temperature and temperature variance proved to be efficient. Furthermore, a point-by-point Newton-method was used to solve the discretized transport equations for the reacting species. A standard sequential solution procedure was found to be numerically unstable.

The problems encountered in the description of the pilot flames were more severe for the detailed-kinetics model than for the conserved-scaler model. The ignition of the flame near the nozzle is sensitive to the hydrodynamics as well as the chemical kinetics. The present axisymmetric model is not capable of predicting the correct pilot-flame hydrodynamics, yielding a delay of ignition near the nozzle. Moreover, the assumption of a truncated joint-Gaussian distribution of temperature and mass fractions is invalid near the nozzle. Effectively, the mean reaction rates are underpredicted near the nozzle,
which contributes to the delay of ignition near the nozzle. Because of this, the detailed-kinetics model was found to yield unsatisfactory agreement with the mean temperature measurements. If the mean temperature field predicted by the conserved-scalar model is used in the evaluation of the mean reaction rates, the detailed-kinetics model yields reasonable agreement of OH concentration profiles with the experiments by De Vries (1994).

Finally, an analysis of the piloted diffusion flame in terms of the flame regimes proposed by Peters (1991) was made. This analysis largely explained the observed differences between the various models tested, and also indicated that chemical kinetic effects are important near the nozzle. In the experiments, this was evident because pilot flames were required to prevent lift-off. In the modeling, the constrained-equilibrium simply neglects this and always yields a burning flame, but the detailed-kinetics/joint-PDF model is very sensitive to this phenomenon. Further away from the nozzle, a flamelet regime seems appropriate for this kind of diffusion flame.
CHAPTER 7

Simulations of high-temperature industrial furnaces

7.1 Introduction

In previous chapters, the theory of mathematical and numerical modeling of turbulent diffusion flames has been treated, and a detailed analysis of a jet diffusion flame has been made. Here, we apply the conserved-scalar modeling concept to several large-scale furnace flows of practical interest. Important aspects of large-scale furnace flows with high temperatures are the dominant radiative heat transfer, the three-dimensionality of the geometry, and the turbulent mixing processes. In the FURNACE code, these processes are modeled by the Hottel zone method or the Discrete Transfer method for radiation, and a 3D Navier-Stokes solver for turbulent flow, using the standard $k$-$\varepsilon$ model with Favre averaged quantities. The major interest of the results discussed below is to investigate the relative influence of different conserved-scalar chemistry models and assumed PDF types on the major furnace characteristics (such as fuel burn-out, global heat balance) and the formation of thermal NO.

The furnace types simulated in this work are an industrial glass-melting furnace, extensively described by Post (1988) and Wieringa (1992), and the IFRF (International Flame Research Foundation) test furnace, described by Koster (1993). For the industrial glass-melting furnace variations of the PDF shape have been performed, without adjusting the chemistry model or the turbulence model parameters. Section 7.2 gives results for the major furnace parameters as well as the predicted NO formation. A drawback of these calculations is the lack of experimental data to validate the mathematical and numerical model.

The IFRF test furnace has been investigated thoroughly in the so-called NG6 and NG7 trials, carried out at the IFRF in IJmuiden. Despite the fact that the available experimental data may suffer from sometimes relatively large errors, they still provide valuable material for quantitative comparison with our calculations. Section 7.3 studies the effects of PDF shape and chemistry model on the prediction of the IFRF furnace characteristics, in comparison with measured data and trends.

7.2 Industrial glass-melting furnace

7.2.1 Geometry

Glass-melting furnaces can be of different type, and can be fired with different types of fuel. The industrial glass-melting furnace used for our simulations is a large-scale industrial furnace, fired with natural gas as a fuel. Natural gas is widely used in Europe and the USA as a fuel for firing glass-melting furnaces (Post, 1988) and therefore is of
great practical interest. The geometry of the industrial glass-melting furnace studied is
depicted in figure 7.1. This specific furnace is a so-called side-port-fired furnace, which
means that the flames are fired from the side walls of the furnace, perpendicular to the
flow of the glass melt. The glass enters the glass bath at the rear end of the furnace (see
figure 7.1), and is heated by the flames and radiation emitted by the furnace walls and
roof.

The burners are of the in-port firing type, meaning that the natural gas is injected in the
preheated air stream before entering the furnace. The complete furnace has many burners
placed in a row, and the exhaust gases of the flames leave the furnace at the opposite side
wall through exhaust ports identical to the burner inlet sections. The hot flue gases heat
up the solid material in the regenerator. After some time interval (e.g. 20 minutes), the
flow direction of the flames is reversed, and the exhaust ports become the burner inlets and
vice versa. Effectively, the hot regenerator causes the combustion air to be heated before
entering the furnace, thus causing a higher flame temperature and an increase of furnace
efficiency. The furnace is meant for high-quality glass manufacturing, and operates at a
high melt temperature (1700 K), which is much higher than used in the IFRF test furnace
to be described later.

In our furnace, each burner has a height of 0.8 m and a width of 1.6 m. The maximum
height of the furnace, measured from the glass surface to the roof, is 2.35 m. The roof is
slightly curved with a curvature radius of 12 m. The width of the furnace is 7.3 m, and the
total x-length of the furnace is about 20 m. Because the total furnace has many side ports,
computational costs are reduced by assuming that each flame is symmetric with respect
to its neighbour flames. By this assumption, the computational domain has an x-length
of 1.65 m, and symmetry planes exist for x = 0 m and x = 1.65 m. Typical asymmetric
effects, such as increasing glass bath temperature from the rear end of the furnace towards
the front end where the molten glass is collected (see figure 7.1), flame oscillations and
interaction of neighbouring flames are ignored. It is expected that these simplifications do
not seriously affect the validity of the prediction of furnace efficiency and NOx emission.
7.2. Industrial glass-melting furnace

7.2.2 Boundary conditions

The burner system itself produces some premixing of fuel and preheated air, as described by Post (1988). As a result, the boundary conditions at the inlet of the combustion chamber already exhibit some precombustion, implying that the mixture fraction inlet conditions are described by a smooth profile instead of the two unmixed value 0 (pure air) and 1 (pure fuel). The air is a mixture of cold primary air and preheated secondary air, such that the effective air temperature is 1325 K, whereas the fuel temperature is 298 K. In all cases, the precombustion level is taken to be 44%. Furthermore, the inlet velocity profile is nonuniform, and we simply adopted the same boundary conditions as Post (1988), with an air excess of 10%. Essential for the shape of the flame in the furnace are the inlet conditions for the turbulence quantities $\bar{k}$ and $\bar{\varepsilon}$. For the turbulent kinetic energy $\bar{k}$, a turbulent intensity $I_i$ of 0.3 was used, based on isothermal model experiments and calculations by Post:

$$\bar{k} = \frac{3}{2} I_i^2 (\bar{u}^2 + \bar{v}^2 + \bar{w}^2) \quad (7.1)$$

The inlet $\varepsilon$-profile is based on the standard formula for developed channel flow:

$$\bar{\varepsilon} = \frac{C_{\mu}^3/4 \bar{k}^{3/2}}{0.03 \ell} \quad (7.2)$$

where $\ell$ is a suitably defined macro length scale of the turbulence. For developed flow, $\ell$ is usually taken to be equal to the hydraulic diameter of the channel, but in this case the inlet flow is far from fully developed: intense mixing and combustion of fuel and air has occurred at nearby upstream locations inside the inlet section. Hence, two values of $\ell$ have been used:

- the standard value $\ell = \Delta z_{\text{inlet}}$, where $\Delta z_{\text{inlet}}$ is the height of the inlet channel. This value produces a relatively low rate of turbulent mixing near the inlet, leading to a long flame.

- the value $\ell = 10 \Delta z_{\text{inlet}}$. This value produces a relatively high rate of turbulent mixing, yielding a short flame.

Symmetry boundary conditions are used at the vertical front and back planes. At the outlet plane, the normal gradients of all variables are set to zero. Along the solid walls of the furnace, wall functions are adopted for the mean velocity components, $\bar{u}$, $\bar{v}$ and the mean enthalpy. The fluctuating quantities are set to zero at the wall. The mean mixture fraction, mean density and mean mass fractions all have homogeneous Neumann conditions at the wall.

For numerical convenience, the Hottel zone method used for the radiation calculation has been defined for a uniform Cartesian grid, which does not coincide with the curved-roof boundary. In order to handle this, especially with respect to the temperature boundary conditions, a uniform wall temperature is employed for the furnace roof, the inlet wall and the outlet wall. Hence, an averaged wall temperature is used instead of the temperature which would result from local near-wall values of enthalpy and mixture fraction.
A porosity method is used to impose the boundary conditions. This method allows the computation of flow in non-rectangular geometries, but the treatment of the wall effects is not very accurate. In our case, the near-wall flow does not have a significant influence on the flame behavior, and the porosity method works well. Figure 7.2 shows a picture of the complete furnace section, with temperature contours in three normal planes.

7.2.3 Long-flame results

The numerical results obtained by Post (1988) were used as a starting point for our simulations. Post used a simple flame-sheet model with a double-δ function PDF to account for mixture fraction fluctuations. His results were computed on a fairly coarse uniform $8 \times 21 \times 10$ grid, and he used turbulent Prandtl/Schmidt numbers of 0.9 for enthalpy, mean mixture fraction and mixture fraction variance.

In our calculations, we made some changes to the original models and boundary conditions used by Post. The thermochemical quantities were retrieved from a previously computed lookup table, which yielded only minor differences with the original encoding by Post. We extended the outlet pipe (shown at the r.h.s. of figure 7.2) to reduce the influence of Neumann boundary conditions applied at the outlet plane. Moreover, Post applied the condition $\bar{\xi}^{\nu/2} = 0$ at the outlet plane, where we used a Neumann condition instead. Forcing the turbulence intensity of mixture fraction fluctuations to zero in the outlet plane has a significant effect on the flue gas composition, except for the NO concentration which is not a direct function of mixture fraction (this is discussed later). In our computations we used turbulent Prandtl/Schmidt numbers $\sigma_{\phi}$ of 0.7 instead of 0.9 for $\bar{h}$, $\bar{\xi}$ and $\bar{\xi}^{\nu/2}$. Next, we performed grid refinement to establish grid independence. Successive doubling of the number of grid points in all three dimensions showed that a grid of $16 \times 46 \times 20$ is sufficient to have grid independence.

In order to assess the differences with Post’s calculations, table 7.1 lists some characteristic furnace properties. Results show that a longer outlet pipe with Neumann boundary
7.2. Industrial glass-melting furnace

Table 7.1: Assessment of used numerical model by comparing with results of Post, using a double-$\delta$-function PDF.

<table>
<thead>
<tr>
<th></th>
<th>Post</th>
<th>present</th>
<th>present</th>
<th>present</th>
</tr>
</thead>
<tbody>
<tr>
<td>grid</td>
<td>$8 \times 21 \times 10$</td>
<td>$8 \times 22 \times 10$</td>
<td>$8 \times 22 \times 10$</td>
<td>$16 \times 46 \times 20$</td>
</tr>
<tr>
<td>$\sigma_\phi$</td>
<td>0.9</td>
<td>0.9</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>$Q_{\text{glass}}$ (MW)</td>
<td>1.25</td>
<td>1.27</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>$T_{\text{max}}$ (K)</td>
<td>2475</td>
<td>2473</td>
<td>2472</td>
<td>2391</td>
</tr>
<tr>
<td>$T_{\text{av}}$ (K)</td>
<td>1892</td>
<td>1946</td>
<td>1954</td>
<td>1952</td>
</tr>
<tr>
<td>$T_{\infty}$ (K)</td>
<td>1849</td>
<td>1852</td>
<td>1854</td>
<td>1855</td>
</tr>
<tr>
<td>$T_{\text{flue}}$ (K)</td>
<td>1935</td>
<td>2025</td>
<td>2009</td>
<td>2017</td>
</tr>
<tr>
<td>[NO]$_{\text{flue}}$ (ppm)</td>
<td>–</td>
<td>3220</td>
<td>3132</td>
<td>3796</td>
</tr>
</tbody>
</table>

Conditions for $\bar{\xi}$ have no significant influence on the maximum temperature of the furnace, and on the used wall temperature for the Hottel zone method. Near the outlet of the furnace, however, the Neumann boundary conditions for $\bar{\xi}$ produce a higher temperature, and therefore the heat flux towards the glass bath is slightly higher. Changing $\sigma_\phi$ from 0.9 to 0.7 leads to a faster mixing of the mixture fraction field, and this better mixing gives a higher heat flux to the glass bath. The overall furnace efficiency therefore is predicted to be 50% instead of 47% according to Post. Finally, one can observe that the maximum temperature decreases if the grid is refined. This is caused by the fact that a finer grid can resolve steeper gradients. The steeper gradients of the mean mixture fraction give a higher source term for the mixture fraction variance, which in turn broadens the mixture fraction PDF. In effect, the maximum temperature is lower when using a finer grid. The effects on outlet NO concentrations is discussed later on.

Table 7.2: One-step global mechanism for glass-melting furnace; long flame. Influence of assumed PDF shape on the furnace performance.

<table>
<thead>
<tr>
<th>PDF type</th>
<th>$T_{\text{max}}$ (K)</th>
<th>$T_{\text{mean}}$ (K)</th>
<th>burn-out (%)</th>
<th>bath load (MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>single $\delta$-function</td>
<td>2604</td>
<td>1960</td>
<td>99.72</td>
<td>1.29</td>
</tr>
<tr>
<td>double $\delta$-function</td>
<td>2391</td>
<td>1952</td>
<td>96.18</td>
<td>1.32</td>
</tr>
<tr>
<td>top-hat distribution</td>
<td>2383</td>
<td>1950</td>
<td>95.40</td>
<td>1.29</td>
</tr>
<tr>
<td>$\beta$-function</td>
<td>2403</td>
<td>1955</td>
<td>96.85</td>
<td>1.29</td>
</tr>
<tr>
<td>clipped Gaussian</td>
<td>2377</td>
<td>1951</td>
<td>96.62</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Having established grid independence, we now compare the results for different types of assumed PDFs. Table 7.2 lists a number of important overall parameters which are characteristic for the furnace performance. The adiabatic flame temperature of this flame is 2628 K. In absence of mixture fraction fluctuations (single-$\delta$-function PDF), the maximum temperature in the furnace approaches this adiabatic temperature. The other PDF types
produce a lower maximum temperature as a consequence of a finite PDF width on the isopleth of stoichiometric mixture fraction. The furnace flow has a recirculation region near the roof, but the main mass flow is directed straight from the inlet plane towards the outlet pipe. This flow pattern ensures that the fresh gases that enter the furnace are mixed with combustion products.

The maximum mixture fraction variance in the furnace is about 0.005, which is equivalent to a standard deviation of 0.07 in mixture fraction space. In figure 7.4 we have depicted a random selection of local values of $\bar{\xi}$ and $\bar{\xi^{m^2}}$ for each point in the flow. Since the mixture fraction averaged over the complete furnace is equal to the averaged inlet values (about 0.055), it is not surprising that the majority of $(\bar{\xi}, \bar{\xi^{m^2}})$ combinations is found close to the stoichiometric mixture fraction, on the fuel-lean side, and with generally quite low $\bar{\xi^{m^2}}$-values. In the recirculation region of the furnace the mixture fraction gradients which drive the mixture fraction fluctuations are small, and therefore the mixture fraction variance is fairly high close to the inlet plane only.

![Figure 7.3: Burn-out rate as a function of y-distance for the long-flame case. — double-$\delta$-function PDF with $\bar{\xi^{m^2}} = 0$ in outlet; o o o double-$\delta$-function PDF with Neumann b.c. for $\bar{\xi^{m^2}}$ in outlet; \ldots single-$\delta$-function PDF (no fluctuations).](image)

Figure 7.3 compares the burn-out rate for the long-flame inlet conditions, using a single-$\delta$-function PDF (no fluctuations), and a double-$\delta$-function PDF with two types of outlet boundary conditions for $\bar{\xi^{m^2}}$. Putting $\bar{\xi^{m^2}} = 0$ at the outlet plane produces an artificial increase of fuel burn-out, since the mean mixture fraction generally is lower than $\xi_m$ in the outlet region. In absence of fluctuations, this yields zero fuel mass fraction in the outlet since $Y_{fu} = 0$ for $\xi < \xi_m$. An extension of the outlet pipe using Neumann boundary conditions for $\bar{\xi^{m^2}}$ produces a much smoother development of fuel burn-out. However, the
in-furnace results are virtually uninfluenced by the outlet boundary condition for $\bar{\xi}^{n2}$.

In the outlet pipe, some points of the flow still have mixture fraction values close to $\xi_{st}$ with a non-negligible level of turbulent fluctuations, hence a small amount of unburnt fuel leaves the furnace. As a result, the long flame does not attain complete fuel burn-out, even though 10% excess air is used. The used chemistry model (one-step global reaction) does not allow intermediate species such as CO or H$_2$ to exist. A refined chemistry model which takes into account the formation of CO, as we will discuss in Section 7.3, produces a more realistic flue gas composition. Table 7.3 shows the flue-gas composition in case of the top-hat PDF for the long flame. In addition to the calculated outlet concentrations, rescaled concentrations are given assuming 0% and 8% oxygen to be present.

In general, the double-$\delta$-function PDF is not a physically realistic description of the mixture fraction statistics. Only very close to the nozzle, where unmixed fuel and air are present, we can expect $\delta$-function PDF shapes. In our configuration with 44% precombustion, no unmixed fuel is present and a continuous PDF-shape is much more likely to occur. For the mean flow the PDF shape appears to be rather unimportant, because the density, which couples the thermochemical field to the flow field, is a weak function of mixture fraction near $\bar{\xi} = \xi_{st}$ (see figure 7.5). The mean density field is nearly independent of the PDF type, and therefore the mean mixture fraction fields are virtually the same for the different PDF types listed above. The mixture fraction variance field, which governs the intensity of turbulent fluctuations of all thermochemical quantities, is therefore also almost identical in the cases described before, except for the single-$\delta$-function PDF. Hence, the

![Figure 7.4: Local combinations of $\bar{\xi}$ and $\bar{\xi}^{n2}$ for a number of internal grid cells in the industrial furnace, for the long-flame inlet conditions.](image)
TABLE 7.3: Flue-gas composition for long-flame configuration, using a top-hat PDF. Concentrations given in mole fraction %.

<table>
<thead>
<tr>
<th>species</th>
<th>calculated</th>
<th>0% O₂</th>
<th>8% O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>72.521</td>
<td>71.562</td>
<td>74.469</td>
</tr>
<tr>
<td>O₂</td>
<td>2.638</td>
<td>0.000</td>
<td>8.000</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.287</td>
<td>0.328</td>
<td>0.202</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>0.016</td>
<td>0.019</td>
<td>0.012</td>
</tr>
<tr>
<td>C₂H₈</td>
<td>0.003</td>
<td>0.004</td>
<td>0.002</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>0.002</td>
<td>0.002</td>
<td>0.001</td>
</tr>
<tr>
<td>CO₂</td>
<td>8.496</td>
<td>9.726</td>
<td>5.996</td>
</tr>
<tr>
<td>H₂O</td>
<td>16.037</td>
<td>18.359</td>
<td>11.318</td>
</tr>
<tr>
<td>NO (ppm)</td>
<td>3795.868</td>
<td>4345.457</td>
<td>2678.865</td>
</tr>
</tbody>
</table>

differences between the PDF types mainly stem from the typical differences in PDF shape, and from different local values of $\bar{\xi}$ and $\bar{\xi}^{in2}$.

Furthermore, although the temperature is a skewed function of mixture fraction, the temperature field is relatively insensitive to the PDF shape because heat radiation has a smoothing effect. If some regions in the flow field obtain higher temperatures due to a change in PDF shape, these regions will emit more radiative energy yielding a lower temperature. Only if variances of fluctuating variables are considered, such as mass fraction variances or temperature variance, the PDF shape will have a large influence on the results. For numerical predictions of mean-flow properties of this industrial furnace, the simple double-$\delta$-function PDF can be employed with reasonable accuracy. However, since we use a precomputed table with mean values as a function of $\xi$, $\xi^{in2}$ and $\bar{h}$, there is no reason why a more reliable continuous PDF-type, such as the $\beta$-function or clipped-Gaussian PDF be used, since the CPU time does not depend on the complexity of the conserved-scalar model or the PDF model.

Table 7.4 shows the dependence of the prediction of NO emissions as a function of the assumed PDF shape. Two cases are distinguished: one case where the mean chemical source term for NO is evaluated by substituting the mean values of temperature, density and species mass fractions (note that this is not equivalent to substituting the mean mixture fraction), and one case where an assumed-shape PDF for the mixture fraction is employed to obtain the mean source term. The results show that, in line with the mean-flow data, the predicted NO emissions do not depend strongly on the PDF type. However, the closure of the source term by use of local mean values without fluctuations yields lower predictions of NO emission than the assumed-PDF closure of the source term.

Also listed in table 7.4 are the predicted NO emission levels when using a superequilibrium factor $s = 2$ for the O-atom concentrations in the computations. A higher superequilibrium factor inevitably leads to a higher NO formation rate, and it is no surprise that the predicted emissions are higher than for the $s = 1$ cases. The increase is only
about 10 to 20%, which is explained by the fact that due to the nature of the transport equation for $\bar{Y}_{\text{NO}}$ there is no linear dependence between the reaction rate and the emission level. Furthermore, as explained in Chapter 3, the NO source term decreases as a function of NO concentration, so if locally more NO is produced this is counterbalanced by the stronger reverse reaction which drives the NO concentration to its equilibrium value.

**Table 7.4:** Dependence of predicted nitric oxide emission on assumed PDF shape and super-equilibrium factor $s$, using a one-step global mechanism in the long-flame configuration. NO concentration in ppm.

<table>
<thead>
<tr>
<th>PDF type</th>
<th>[NO] without fluctuations</th>
<th>[NO] with fluctuations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$s = 1$</td>
<td>$s = 2$</td>
</tr>
<tr>
<td>single $\delta$-function</td>
<td>2973</td>
<td>3232</td>
</tr>
<tr>
<td>double $\delta$-function</td>
<td>2292</td>
<td>2987</td>
</tr>
<tr>
<td>top-hat distribution</td>
<td>2289</td>
<td>2650</td>
</tr>
<tr>
<td>$\beta$-function</td>
<td>2424</td>
<td>3100</td>
</tr>
<tr>
<td>clipped Gaussian</td>
<td>2322</td>
<td>3020</td>
</tr>
</tbody>
</table>

### 7.2.4 Short-flame results

Before discussing the short-flame results, we list the differences with the calculations of Post (1988) in table 7.5. The sensitivity of the short-flame results to grid refinements and variation of the outlet boundary condition for $\bar{\xi}^{1/2}$ is somewhat stronger than for the
TABLE 7.5: Assessment of used numerical model by comparing with results of Post, using a double-$\delta$-function PDF.

<table>
<thead>
<tr>
<th></th>
<th>Post</th>
<th>present</th>
<th>present</th>
<th>present</th>
</tr>
</thead>
<tbody>
<tr>
<td>grid</td>
<td>$8 \times 21 \times 10$</td>
<td>$8 \times 22 \times 10$</td>
<td>$8 \times 22 \times 10$</td>
<td>$16 \times 46 \times 20$</td>
</tr>
<tr>
<td>$\sigma_\phi$</td>
<td>0.9</td>
<td>0.9</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>$Q_{\text{glass}}$ (MW)</td>
<td>1.49</td>
<td>1.50</td>
<td>1.54</td>
<td>1.63</td>
</tr>
<tr>
<td>$T_{\text{max}}$ (K)</td>
<td>2398</td>
<td>2340</td>
<td>2369</td>
<td>2305</td>
</tr>
<tr>
<td>$T_{av}$ (K)</td>
<td>1915</td>
<td>1974</td>
<td>1978</td>
<td>1983</td>
</tr>
<tr>
<td>$T_w$ (K)</td>
<td>1862</td>
<td>1864</td>
<td>1866</td>
<td>1872</td>
</tr>
<tr>
<td>$T_{\text{fuel}}$ (K)</td>
<td>1876</td>
<td>1934</td>
<td>1920</td>
<td>1866</td>
</tr>
<tr>
<td>$[\text{NO}]_{\text{fuel}}$ (ppm)</td>
<td>--</td>
<td>3220</td>
<td>3132</td>
<td>1510</td>
</tr>
</tbody>
</table>

long-flame results. This is reflected by the predicted maximum temperatures, and by the fact that the heat flow to the glass bath and the furnace efficiency increases if the grid is refined. A remarkable feature is the dependence of the outlet NO concentration as a function of the grid refinement, which will be discussed in the sequel.

TABLE 7.6: Dependence of predicted mean-flow properties on assumed PDF shape using a one-step global mechanism; short flame. The fuel burn-out is 100% in all cases.

<table>
<thead>
<tr>
<th>PDF type</th>
<th>$T_{\text{max}}$ (K)</th>
<th>$T_{\text{mean}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>single $\delta$-function</td>
<td>2599</td>
<td>1985</td>
</tr>
<tr>
<td>double $\delta$-function</td>
<td>2305</td>
<td>1983</td>
</tr>
<tr>
<td>top-hat distribution</td>
<td>2298</td>
<td>1970</td>
</tr>
<tr>
<td>$\beta$-function</td>
<td>2295</td>
<td>1972</td>
</tr>
<tr>
<td>clipped Gaussian</td>
<td>2293</td>
<td>1980</td>
</tr>
</tbody>
</table>

Table 7.6 gives some important overall furnace characteristics for the short-flame configuration compared for different PDF types. The fuel burn-out (depicted in figure 7.6) is 100% for all PDF types, but the rate at which this complete burn-out is reached is different for the various models. The differences between the tested PDF shapes are not very large, which is explained again by the insensitivity of the mean density field to the PDF shape, and the strong radiation which smoothes the mean temperature field. If we compare table 7.6 with table 7.2 we see that the maximum temperatures are lower in the short flame, which is caused by the higher intensity of mixture fraction fluctuations causing a broader PDF. The averaged furnace temperature, however, differs only slightly from the long-flame results, which is not surprising since the overall energy balance of the long-flame and short-flame configurations are almost the same.

Table 7.7 lists the dependence of the predicted NO$_x$ emission on the assumed PDF shape. As we can see, there is a strong influence of turbulent fluctuations on the NO formation rate. In the one-step flame sheet model, the NO source term is zero for $\xi > \xi_u$. 


7.2. Industrial glass-melting furnace

Figure 7.6: Burn-out rate as a function of $y$-distance for the short-flame case. — single-$\delta$-function PDF (no fluctuations); ⋯ double-$\delta$-function PDF; – – clipped-Gaussian PDF.

Figure 7.7: Dependence of mean chemical formation rate of nitric oxide, as a function of mean mixture fraction and mixture fraction variance, calculated for the adiabatic, single-step reaction flame sheet using a clipped-Gaussian PDF. Contours are shown for $S_{NO} = 0.05 - 1.05 (0.10)$ s$^{-1}$. 
TABLE 7.7: Dependence of predicted NO emission on assumed PDF shape using a one-step global mechanism; short flame. NO concentration in ppm.

<table>
<thead>
<tr>
<th>PDF type</th>
<th>[NO] without fluctuations</th>
<th>[NO] with fluctuations</th>
</tr>
</thead>
<tbody>
<tr>
<td>single $\delta$-function</td>
<td>3155</td>
<td>—</td>
</tr>
<tr>
<td>double $\delta$-function</td>
<td>2100</td>
<td>1510</td>
</tr>
<tr>
<td>top-hat distribution</td>
<td>1974</td>
<td>3481</td>
</tr>
<tr>
<td>$\beta$-function</td>
<td>2053</td>
<td>3757</td>
</tr>
<tr>
<td>truncated Gaussian</td>
<td>1974</td>
<td>3896</td>
</tr>
<tr>
<td>clipped Gaussian</td>
<td>1958</td>
<td>3590</td>
</tr>
</tbody>
</table>

FIGURE 7.8: Dependence of mean chemical formation rate of nitric oxide, as a function of mean mixture fraction and mixture fraction variance, calculated for the adiabatic, single-step reaction flame sheet using a double-$\delta$-function PDF. Contours are shown for $S_{\text{NO}} = 0.05 - 1.05 (0.10) \text{ s}^{-1}$.

In the presence of turbulent fluctuations, a given point in the flow with $\widetilde{\xi} > \xi_{st}$ can still yield a significant NO formation if the local mixture fraction PDF has a tail for $\xi < \xi_{st}$. Compared to the simple case where no fluctuations are taken into account, the NO source term is positive in a larger region of the flow. However, the width of the mixture-fraction PDF is not the only factor which determines the NO emission predictions. The skewness and kurtosis are also of importance, due to small interval in mixture fraction space where the source term of NO is significant. The top-hat PDF has a larger kurtosis than the Gaussian PDFs or the $\beta$-function PDF, which means that even if the mean mixture fraction differs considerably from $\xi_{st}$, a long tail in the PDF may still cause a non-negligible contribution to the NO formation rate. That is the reason why the top-hat PDF generally produces somewhat higher predictions of NO emissions than the other PDF shapes.
Figure 7.9: Instantaneous NO source term as a function of mixture fraction for the adiabatic one-step flame sheet model, and a characteristic double-$\delta$-function PDF with $\xi < \xi_{\text{st}}$ and $\overline{\xi^2}$ fairly large.

The results in table 7.7 also show that the double-$\delta$-function PDF strongly deviates from the other PDFs. This is caused by the fact that in many points of the flow the mean mixture fraction $\bar{\xi}$ is smaller than $\xi_{\text{st}}$, but the variance $\overline{\xi^2}$ is large enough to yield one $\delta$-function at $\xi > \xi_{\text{st}}$ and of course one $\delta$-function at $\xi < \xi_{\text{st}}$ (see Figure 7.9). Since grid refinement yields an increase of mixture fraction fluctuations, a sudden drop in the predicted NO emissions is seen. For the continuous PDF types, this effect is absent.

7.3 IFRF test furnace

The full-scale industrial furnaces, like the industrial glass-melting furnace, are not well-suited for model development and validation, because detailed experiments are tedious. The IFRF test furnace at IJmuiden has been designed to provide an alternative for full-scale furnaces. In order to mimic the industrial furnaces as much as possible, preheated air is generated artificially, so that flame temperatures are comparable with the actual glass-melting furnaces. Boundary conditions (wall heat fluxes) are imposed with the same purposes, by using water-cooled segments as furnace walls. The so-called NG6 and NG7 trials, conducted at IJmuiden around 1990, have been extensively described elsewhere (Koster, 1993; Van de Kamp et al., 1989; Nakamura et al., 1991). Here, we focus upon the NG7 trial results. The objective here is not to obtain the numerically most accurate solution, but to assess the sensitivity of the simulation results to important model variations, regarding the chemistry model, PDF type and enthalpy loss model.
Chapter 7. Simulations of high-temperature industrial furnaces

![Schematic drawing of the IFRF furnace. Indicated are the burner geometries for underport (UP) and overport (OP) firing.](image)

**Figure 7.10:**

**Table 7.8:** Dimensions of IFRF test furnace for NG7 trials.

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>length</td>
<td>3750 mm</td>
</tr>
<tr>
<td>width</td>
<td>955 mm</td>
</tr>
<tr>
<td>height</td>
<td>880 mm</td>
</tr>
<tr>
<td>channel width</td>
<td>272 mm</td>
</tr>
<tr>
<td>pipe diameter</td>
<td>12 mm</td>
</tr>
<tr>
<td>air angle</td>
<td>20°</td>
</tr>
<tr>
<td>gas angle</td>
<td>12-20°</td>
</tr>
</tbody>
</table>

7.3.1 IFRF furnace geometry and boundary conditions

The geometry of the NG7 test furnace is depicted schematically in figure 7.10. Table 7.8 lists the most important furnace dimensions. Preheated air \( T = 1373 \) K is injected at a downward angle of \(-20°\), with a bulk velocity of 10 m/s. The gas \( T = 300 \) K is injected through a fuel pipe, located below (underport) or above (overport) the air inlet section, with a bulk velocity of 125 m/s. Hence, the furnace has a symmetry plane at \( y = 477.5 \) mm. The angle at which the gas is issued into the furnace is an important parameter in order to control the mixing rate of fuel and air; in the NG7 trials it was varied from \(+12°\) to \(+20°\) with the horizontal direction for the underport trials.

In the sequel, we do not attempt to repeat all of the calculations and parameter variations performed by Koster (1993). Rather, we wish to investigate how sensitive his results are with respect to chemistry model and assumed PDF shape. Of particular interest are global quantities, like maximum temperature, heat load to the furnace walls, and flue gas composition, as well as NO\(_x\) emissions.

Only one specific case is investigated here: an underport flame at an angle of \(+16°\). The gas bulk velocity was kept at 125 m/s, and preheated air at \( T = 1373 \) K was used. The air excess level was 10%, implying that effectively 10% more oxygen entered the furnace than strictly necessary to consume all fuel.

The inlet boundary conditions for the velocity and turbulence characteristics of the
TABLE 7.9: Sensitivity of predictions of IFRF test furnace to variation in assumed PDF shape, employing a constrained-equilibrium chemistry model. NO concentrations normalized for 0% O₂.

<table>
<thead>
<tr>
<th>PDF type</th>
<th>$T_{\text{max}}$ (K)</th>
<th>$T_{\text{av}}$ (K)</th>
<th>$T_{\text{flue}}$ (K)</th>
<th>bath load (kW)</th>
<th>[NO]$_{\text{out}}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>double $\delta$-function</td>
<td>2451</td>
<td>1717</td>
<td>1742</td>
<td>125.6</td>
<td>1556$^1$</td>
</tr>
<tr>
<td>top-hat</td>
<td>2427</td>
<td>1714</td>
<td>1735</td>
<td>125.3</td>
<td>1553</td>
</tr>
<tr>
<td>$\beta$-function</td>
<td>2438</td>
<td>1717</td>
<td>1732</td>
<td>124.7</td>
<td>1552</td>
</tr>
<tr>
<td>clipped-Gaussian</td>
<td>2425</td>
<td>1713</td>
<td>1734</td>
<td>124.7</td>
<td>1509</td>
</tr>
</tbody>
</table>

$^1$ A top-hat PDF was used for the closure of the NO source term.

Combustion air are critical for the prediction of the flame shape, since this is governed by the turbulent mixing. Variations of inlet profiles by Koster (1993) showed that the flue gas composition indeed is affected by the shape of the inlet velocity profile. However, like Koster, we used a uniform velocity profile of 10 m/s at an angle of $-20^\circ$ with the horizontal. The same procedure was followed for the intensity of the turbulent fluctuations in the inlet region. The turbulent kinetic energy $k$ was computed from (7.1). The numerical grid used was adopted from Koster (1993), having $16 \times 24 \times 20$ grid points. The grid is locally refined near the gas inlet. Although it can be shown that this grid does not yield fully grid independent results, the data of Koster have indicated that most trends in the predictions (like heat transfer, temperature distribution and NO$_x$ formation) are reproduced on finer grids.

7.3.2 Sensitivity on PDF shape

The investigation of the industrial glass-melting furnace of the previous section already showed the sensitivity of main-flow results on the assumed PDF shape. For the IFRF geometry we repeated this sensitivity study, using the constrained-equilibrium model for the chemistry description.

Table 7.9 summarizes the basic results of this analysis. In line with the results for the industrial glass melting furnace, the major quantities like peak temperature, heat load and NO$_x$ emissions are not sensitive to the PDF type. The average heat flow to the bottom plane (glass bath) varies only by 1%, and the NO concentration at the outlet plane differs only by 3%. Even the double-$\delta$-function PDF is acceptable as an engineering tool to obtain quick results for mean-flow properties. The NO source term, however, has to be evaluated by a continuous PDF at all times. Based on these results, we decided to use the clipped-Gaussian PDF shape for the other model variations.

7.3.3 Sensitivity on chemistry model

Using the clipped-Gaussian PDF, we simulated the IFRF furnace using three different chemistry models: the constrained-equilibrium model, the one-step Burke-Schumann


Table 7.10: Sensitivity of predictions of IFRF test furnace to variation in chemistry model, employing a clipped-Gaussian PDF closure. NO concentrations normalized for 0% O₂.

<table>
<thead>
<tr>
<th>chemistry model</th>
<th>$T_{\text{max}}$ (K)</th>
<th>$T_{\text{av}}$ (K)</th>
<th>$T_{\text{flue}}$ (K)</th>
<th>bath load (kW)</th>
<th>[NO]_{\text{out}} (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>constrained equilibrium</td>
<td>2425</td>
<td>1713</td>
<td>1734</td>
<td>124.7</td>
<td>1509</td>
</tr>
<tr>
<td>one-step flame sheet</td>
<td>2440</td>
<td>1717</td>
<td>1737</td>
<td>127.0</td>
<td>1084</td>
</tr>
<tr>
<td>two-step flame sheet</td>
<td>2343</td>
<td>1715</td>
<td>1732</td>
<td>125.0</td>
<td>1015</td>
</tr>
</tbody>
</table>

Flame sheet and the two-step Burke-Schumann flame sheet, with the reaction

$$F + \nu'O_2 \rightarrow x\left(\frac{1}{2}CO + \frac{1}{2}CO_2\right) + y\left(\frac{1}{2}H_2 + \frac{1}{2}H_2O\right)$$

as the first reaction.

The results indicate that the two-step flame sheet model produces lower temperatures and therefore lower NO formation. This is caused by the relatively high concentrations of CO and H₂ in the two-step model. The constrained-equilibrium model predicts comparable amounts of CO and H₂, but close to stoichiometry the temperature function $T(\xi)$ is slightly higher than that of the flame sheet models. Moreover, the constrained-equilibrium model predicts non-zero O-atom concentrations on the rich side of the stoichiometric isopleth, and therefore the predicted NO outlet concentration is about 50% higher compared with the two-step flame sheet model.

The measured NO concentration at the outlet, normalized for 0% O₂, was 1214 ppm. This value is not reproduced by the chemistry models used. The measured flue gas temperature was 1701 K. The predictions are not very sensitive to a variation of chemistry models, which all predict a value about 35 K higher than the measurements.

7.3.4 Sensitivity on enthalpy loss model

An important aspect of the conserved-scalars modeling of high-temperature flames with substantial radiative heat loss is the approximation used to account for heat losses. In general, the thermochemical variables have become functions of both $\xi$ and $h$, but for numerical convenience a simplification is adopted (see §3.3.7). As a standard model, we have used Megahed’s approach. To study the sensitivity of results for the enthalpy loss model, some new functions are tested, depicted in figure 7.11.

Apart from the functions suggested by Megahed (1979) and Salooja (1978), we have constructed a modified Megahed function and a parabolic fit function. All of the functions have a common reference point, defined by the local values of mean mixture fraction $\bar{\xi}$ and enthalpy $\bar{h}$. The original function of Megahed is unrealistic from several points of view. First of all, the Megahed function always has maximum enthalpy loss at the point $(\bar{\xi},\bar{h})$, which is not obvious. More realistically, one would anticipate maximum heat losses near $\xi = \xi_{st}$. Therefore, the modified Megahed function is proposed, which consists of two piecewise linear functions $h_{\text{loss}}(\xi)$, but connected at $\xi_{st}$ rather than $\bar{\xi}$. The definition
is such that this modified Megahed function always runs through the common point \((\overline{\xi}, \overline{h})\), although other variants can be defined as well. Hence, the modified Megahed function will always yield more enthalpy loss for a realization \(\phi(\xi, h)\) than the original Megahed approach.

Secondly, for small fluctuation intensity of \(\xi\), we expect a strong correlation between the instantaneous enthalpy and the instantaneous mixture fraction. This should be represented by a function \(h_{\text{loss}}(\xi)\) parallel to the adiabatic line \(h_{\text{loss}}(\xi) = 0\). The Salooja function meets this requirement. However, the Salooja function becomes unrealistic for large fluctuation intensity, where pure air or fuel is encountered. The parabolic fit function consists of two parabolas, one for \(\xi < \overline{\xi}\) and one for \(\xi > \overline{\xi}\). The parabolas are defined in a unique fashion by requiring that \(h_{\text{loss}}(0) = h_{\text{loss}} = 1\), and \(h_{\text{loss}}(\xi)\) is continuous and has zero first derivative at \(\xi = \overline{\xi}\).

In table 7.11 we have listed the most important quantities predicted by the various enthalpy loss models. The Salooja model produces the lowest mean temperatures, but the modified Megahed model yields the lowest \(NO_x\) outlet concentrations. This is explained by the fact that the modified Megahed model always has maximum heat loss near \(\xi = \xi_{\text{sat}}\), which is precisely the location in mixture fraction space where NO formation is
occuring. Comparing the results with the experimental values $T_{\text{fuel}} = 1701$ K and $[\text{NO}]_{\text{out}} = 1214$ ppm, we see that the parabolic fit function and the Salooja function yield much better agreement than the standard Megahed function.

### 7.4 Conclusions for furnace simulations

In the previous sections we have applied the FURNACE simulation code to large-scale high-temperature furnace flows. The incorporation of the self-adaptive tabulation and lookup algorithm gave a substantial reduction of computation time, which enabled the use of chemistry models and PDF functions of higher complexity than the simple flame-sheet model and double-$\delta$-PDF function used by Post (1988), Koster (1993) and Wieringa (1992) for similar flows.

Grid independent results were obtained for the industrial glass-melting furnace, studied before by Post (1988). Mean flow characteristics are not very sensitive to the assumed shape of the mixture fraction PDF, which is explained by the relatively weak coupling between the flow field and the PDF shape: the mean density field is not sensitive to the PDF type. The thermal behavior (flame radiation) is a little more sensitive to the PDF shape, because the radiative source term for emission depends on $T^4$, which is a highly non-linear function of mixture fraction near stoichiometry. However, especially the prediction of NO formation according to the Zel'dovitch mechanism is found to be very sensitive to the PDF shape. A double-$\delta$-function PDF may work well for the prediction of mean flow properties, but is inappropriate for the modeling of thermal NO formation. The continuous PDF types (top-hat, Gaussian, $\beta$-function) show slight differences, but have essentially the same behavior.

The simulation of the IFRF test furnace (NG7 trials) for the standard underport case already described in detail by Koster (1993), showed the same dependence on PDF shape as the industrial glass-melting furnace. Comparison with measurements revealed that the results are fairly insensitive to assumed PDF shape, a little bit more sensitive to the applied chemistry model, and reasonably sensitive to the model which accounts for enthalpy loss. Furthermore, the prediction of NO$_x$ formation is highly sensitive to the chemistry model as well as the enthalpy loss model. The lowest and highest predicted outlet concentration of NO varied between 883 and 1556 ppm, whereas experiments gave 1214 ppm. This shows that care has to be taken when employing this type of modeling for the prediction of pollutant formation.

Based on theoretical arguments, the variation of models, and on the validation of models for the axisymmetric diffusion flame, the present results suggest that the $\beta$-function or clipped-Gaussian PDF, combined with the constrained-equilibrium chemistry model and the parabolic fit model for enthalpy loss provide a reliable model for further application in the FURNACE code, used specifically as an engineering tool. The substantial reduction in CPU time enables further model improvements, especially with respect to advanced modeling of the turbulence mixing and local grid refinement.
CHAPTER 8

Final remarks

At the end of this Thesis, it is worthwhile reconsidering the most important conclusions drawn in the previous chapters, in the light of the aims of this study put forward in the Introduction.

In reverse order, the first aim was to study the sensitivity and validity of several reaction mechanisms for natural gas (or methane) combustion by applying them in one-dimensional laminar flame calculations. The schemes of Glarborg (1991), Kee et al. (1985), Warnatz (1993) and Smooke and Giovangigli (1991a) were tested and compared, also with respect to available experimental data. This revealed that despite its obvious simplifications, the skeletal mechanism used by Smooke and Giovangili performed reasonably well, and therefore was a first candidate for application within the detailed kinetics/joint-PDF model of Bockhorn (1989) for our turbulent flame studies. Full mechanisms, including at least C1/C2 species and reactions, will be required for the accurate prediction of natural gas combustion, if species like CO and C2H2 become important. The mechanism of Warnatz was found to be a good candidate for full detailed chemistry in the Bockhorn model.

The laminar diffusion flame computations showed that the constrained-equilibrium model, first developed by Bilger and Stärner (1981), compares well with the flamelet profiles, as far as major species and temperature are concerned. Fine tuning of the model constants in the constrained-equilibrium model can be done, in order to give marginal improvements when compared with the flamelet data. In the turbulent flame calculations, however, no change of the original model constants was made. With respect to the prediction of thermal NO formation, it was shown that the constrained-equilibrium model performs well even for radical species like OH and O, if the air stream is preheated up to 1400 K. This situation occurs frequently in glass melting furnaces where very high temperatures are wanted. Hence, the constrained-equilibrium model was found to be very useful for the large-scale furnace predictions discussed in this study, and certainly is an improvement over the often used flame sheet models or full-equilibrium models. Because departures from adiabaticity can be incorporated easily, and because it can be computed much more efficiently than laminar flamelet data, the constrained-equilibrium model was judged to be a good candidate for the prediction of turbulent natural-gas flames, at high temperatures as well as under laboratory conditions.

The second aim of this study was to construct an elliptic two-dimensional (axisymmetric) computer code, in order to validate several models for chemistry and assumed PDF shapes by comparing numerical results with the available experimental data. The experimental data have been obtained over the last five years by De Vries (1994) and Stroomer (1995), who measured the mean velocity field (by LDA), turbulent quantities, mean temperatures (by thermocouples), mean OH concentrations (by LIF) and PDF shapes of velocity as well as OH concentration. The configuration consisted of a 6-mm diameter
fuel jet in a co-current annular air jet, 45 mm in diameter. With the CARS measurements of temperature and its PDFs by Mantzaras, which have been performed and will become available as a paper shortly, this experimental program has provided very useful information on the structure and behavior of piloted jet diffusion flames. The database can be used to validate models for turbulent reacting flows, and the complexity of the flow poses some interesting modeling challenges.

The calculations showed that the typical burner used in the experiments leads to three-dimensional effects near the burner nozzle, mainly caused by the configuration of the pilot flames, which is very hard to capture by an axisymmetrical model. Despite this problem, the standard $k-\varepsilon$ model, modified for round jet development, in combination with the constrained-equilibrium model closed by a $\beta$-function PDF of mixture fraction, gives very good agreement with the measured data of mean velocity and mean temperature. The anisotropy of the turbulence in the round jet with annular air is not captured by the $k-\varepsilon$ model, but the overall turbulence level is well predicted.

The scalar mixing field is predicted well by the eddy-viscosity assumption, as can be judged from the mean-temperature results, which are very sensitive to the mean value as well as the variance of the mixture fraction. In addition, the constrained-equilibrium model was found to be applicable for this flame. Arguments based on the Peters diagram for non-premixed combustion regimes were given which corroborated these findings. Models for radiative heat exchange and soot formation were included in the computed code, but near the nozzle ($x/D < 50$), they did not influence the results.

A comparison with OH concentration measurements showed that for the laboratory flames with cold air, the constrained-equilibrium model yields far too low values, even if the experimental uncertainty of about 50% is taken into account. The shapes of the PDFs of OH, however, match the experiments in a quantitative sense, but only at locations where local flame extinction is not important.

In order to improve the prediction of radical species, the detailed-kinetics model with an assumed joint PDF of reacting scalars (Bockhorn, 1989) was tested. Originally, the model was developed and applied for H$_2$/air flames and preheated CO/air flames. These flames did not show local extinction phenomena. For the prediction of methane/air flames, a much higher computational demand is made, because more species are involved, and flame ignition and extinction is much more critical. Several improvements of submodels had to be made to enhance the numerical stability of the solution method, and finally the converged results showed that the model does not perform better than the conserved-scalar models. However, super-equilibrium levels of OH concentration were predicted, which agreed better with the experiments. Secondly, in absence of the pilot flames, the model showed a lift-off behavior in qualitative agreement with experimental observations, but for which no detailed experimental data are available. The major assumptions of the detailed-kinetics/assumed-shape joint-PDF model, however, are the Gaussian PDF shape, and the higher-order polynomials of enthalpy as a function of temperature. Further improvements along these lines will the method more feasible for the prediction of partially premixed flames and lifted flames. Moreover, the method seems well suited for post-processing of chemical reactions in a flame which do not influence the flame structure, like the formation
of NO (including 'prompt' NO).

Finally, the third aim of this Thesis was to apply more advanced and realistic models for chemistry and assumed PDF shapes to (semi-)industrial high-temperature furnaces. This should be viewed in the perspective of earlier work by Post (1988) and Koster (1993), who used a double Dirac-δ-function PDF for mixture fraction and a one-step or two-step flame sheet model for chemistry. The present results showed that the mean flow prediction is fairly insensitive to the assumption of the PDF shape and even the chemistry model, because in the flame zone, the mean density field is not a strong function of the mixture fraction field. Furthermore, radiation tends to smoothen possible differences in the temperature fields, under the prevailing thermal boundary conditions. In effect, physically unrealistic assumed PDF shapes (except for the single Dirac δ-function) can still be used with reasonable success for the prediction of some mean thermochemical quantities.

Generally speaking, however, it is important to use more reliable models for the chemistry and the PDF shape. The constrained-equilibrium model with a β-function PDF for mixture fraction fluctuations was found to be an improvement over the models used in earlier studies, because this model was validated for laboratory flames and gave a good comparison with laminar flamelet calculations. The prediction of O-atom concentrations, which is of key importance to the computation of nitric oxide formation, is more reliable than by the flame sheet models, where equilibrium of [O2]/[O] dissociation is postulated, often together with a super-equilibrium tuning factor of 2. Furthermore, highly non-linear terms like the blackbody radiative source term (∼ T⁴) are described more accurately by continuous assumed PDF shapes than the simple double Dirac δ-functions.

The development of an efficient tabulation and lookup method for the mean thermochemical properties as a function of independent variables was crucial for further application of these more advanced models for large 3D simulations. A computational speed-up of a factor 10 to 50 could thus be achieved, allowing other chemistry models, PDF shapes and variations of the enthalpy-loss model to be tested without a large increase in CPU time.

Only small changes in the prediction of the thermal behavior of the industrial glass melting furnace and the IFRF test furnace were observed when changing the mixture fraction PDF type from β-function to top-hat or (clipped) Gaussian. The same was found for the variation of the enthalpy-loss model. The prediction of thermal NO formation, however, is very sensitive to the chemistry model, the PDF shape (especially between Dirac δ-functions and continuous functions) and the enthalpy-loss model, mainly because most thermal NO is produced near the stoichiometric isopleth. Worst-case differences between the various submodels exceeded 50%. Based on the comparison with the IFRF test furnace results, the constrained-equilibrium/β-function (or clipped Gaussian)/parabolic enthalpy-loss model was found to yield accurate predictions. With the current level of modeling, improvement in furnace flow predictions will have to be sought in more advanced turbulence and radiation models and mesh refinement, rather than better assumed PDF shapes or more complex chemistry models, with an exception of CO formation and soot formation models.
APPENDIX A

Transport equations in Cartesian and cylindrical coordinates

A.1 Three-dimensional Cartesian coordinates

Instantaneous equations

The continuity equation reads:

\[
\frac{\partial \rho}{\partial t} + \frac{\partial \rho u}{\partial x} + \frac{\partial \rho v}{\partial y} + \frac{\partial \rho w}{\partial z} = 0
\]  

(A.1)

The Navier-Stokes equations for a 3D flow in Cartesian coordinates can be written in the general form:

\[
\mathcal{L}_1(u) = -\frac{\partial \rho}{\partial x} + \rho g_x + \rho S_u
\]

(A.2a)

\[
\mathcal{L}_1(v) = -\frac{\partial \rho}{\partial y} + \rho g_y + \rho S_v
\]

(A.2b)

\[
\mathcal{L}_1(w) = -\frac{\partial \rho}{\partial z} + \rho g_z + \rho S_w
\]

(A.2c)

where the general transport operator \(\mathcal{L}_1\) is defined by:

\[
\mathcal{L}_1(\phi) = \frac{\partial \rho \phi}{\partial t} + \frac{\partial \rho u \phi}{\partial x} + \frac{\partial \rho v \phi}{\partial y} + \frac{\partial \rho w \phi}{\partial z} - \frac{\partial}{\partial x} \left( \Gamma \frac{\partial \phi}{\partial x} \right) - \frac{\partial}{\partial y} \left( \Gamma \frac{\partial \phi}{\partial y} \right) - \frac{\partial}{\partial z} \left( \Gamma \frac{\partial \phi}{\partial z} \right)
\]

(A.3)

In the momentum equations, the transport coefficient \(\Gamma\) represents the dynamic molecular viscosity \(\mu\). The source terms \(\rho S_u\), \(\rho S_v\) and \(\rho S_w\) are given by:

\[
\rho S_u = \frac{\partial}{\partial x} \left( \mu \frac{\partial u}{\partial x} \right) + \frac{\partial}{\partial y} \left( \mu \frac{\partial v}{\partial y} \right) + \frac{\partial}{\partial z} \left( \mu \frac{\partial w}{\partial z} \right) - \frac{\partial}{\partial x} \left( \frac{2}{3} \mu \nabla \cdot v \right)
\]

(A.4a)

\[
\rho S_v = \frac{\partial}{\partial x} \left( \mu \frac{\partial u}{\partial y} \right) + \frac{\partial}{\partial y} \left( \mu \frac{\partial v}{\partial y} \right) + \frac{\partial}{\partial z} \left( \mu \frac{\partial w}{\partial y} \right) - \frac{\partial}{\partial y} \left( \frac{2}{3} \mu \nabla \cdot v \right)
\]

(A.4b)

\[
\rho S_w = \frac{\partial}{\partial x} \left( \mu \frac{\partial u}{\partial z} \right) + \frac{\partial}{\partial y} \left( \mu \frac{\partial v}{\partial z} \right) + \frac{\partial}{\partial z} \left( \mu \frac{\partial w}{\partial z} \right) - \frac{\partial}{\partial z} \left( \frac{2}{3} \mu \nabla \cdot v \right)
\]

(A.4c)

and the velocity gradient \(\nabla \cdot v\) is given by:

\[
\nabla \cdot v = \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}
\]

(A.5)
A.I. Three-dimensional Cartesian coordinates

In the above, we have assumed the bulk viscosity to be negligible.

The transport equation for the scalar quantity $\phi$ is written as:

$$\mathcal{L}_1(\phi) = \rho \dot{S}_\phi$$  \hspace{1cm} (A.6)

where the appropriate transport coefficient has to be substituted for $\Gamma$ in (A.3). The mathematical formula for $S_\phi$ depends on $\phi$ and may be a source term due to chemical reactions, external forces, radiation, etcetera.

Stationary Favre-averaged equations

The stationary Favre-averaged form of the 3D transport equations in Cartesian notation is easily derived by taking the ensemble average of the instantaneous equations listed previously, dropping the transient term and applying the Favre decomposition. The molecular transport term is approximated as follows:

$$\left\langle \frac{\partial}{\partial x_k} \left( \Gamma \frac{\partial \phi}{\partial x_k} \right) \right\rangle = \frac{\partial}{\partial x_k} \left( \Gamma \frac{\partial \phi}{\partial x_k} \right) = \frac{\partial}{\partial x_k} \left( \langle \Gamma \rangle \frac{\partial \tilde{\phi}}{\partial x_k} \right)$$  \hspace{1cm} (A.7)

where the correlation between fluctuations in the transport coefficient and the gradient of $\phi$ is neglected. Note that the Reynolds averaged transport coefficient is used rather than the Favre-averaged form. The continuity equation becomes:

$$\frac{\partial \langle \rho \tilde{u} \rangle}{\partial x} + \frac{\partial \langle \rho \tilde{v} \rangle}{\partial y} + \frac{\partial \langle \rho \tilde{w} \rangle}{\partial z} = 0$$  \hspace{1cm} (A.8)

The momentum equations read:

$$\mathcal{L}_2(\tilde{u}) = -\frac{\partial \langle \rho \rangle}{\partial x} + \langle \rho \rangle g_x + \langle \rho S_u \rangle$$ \hspace{1cm} (A.9a)

$$\mathcal{L}_2(\tilde{v}) = -\frac{\partial \langle \rho \rangle}{\partial y} + \langle \rho \rangle g_y + \langle \rho S_v \rangle$$ \hspace{1cm} (A.9b)

$$\mathcal{L}_2(\tilde{w}) = -\frac{\partial \langle \rho \rangle}{\partial z} + \langle \rho \rangle g_z + \langle \rho S_w \rangle$$ \hspace{1cm} (A.9c)

where the general Favre-averaged transport operator $\mathcal{L}_2$ is defined by:

$$\mathcal{L}_2(\tilde{\phi}) = \frac{\partial \langle \rho \rangle \tilde{u} \tilde{\phi}}{\partial x} + \frac{\partial \langle \rho \rangle \tilde{v} \tilde{\phi}}{\partial y} + \frac{\partial \langle \rho \rangle \tilde{w} \tilde{\phi}}{\partial z}$$

$$+ \frac{\partial \langle \rho \rangle u'' \tilde{\phi}''}{\partial x} + \frac{\partial \langle \rho \rangle v'' \tilde{\phi}''}{\partial y} + \frac{\partial \langle \rho \rangle w'' \tilde{\phi}''}{\partial z}$$

$$- \frac{\partial}{\partial x} \left( \langle \Gamma \rangle \frac{\partial \tilde{\phi}}{\partial x} \right) - \frac{\partial}{\partial y} \left( \langle \Gamma \rangle \frac{\partial \tilde{\phi}}{\partial y} \right) - \frac{\partial}{\partial z} \left( \langle \Gamma \rangle \frac{\partial \tilde{\phi}}{\partial z} \right)$$  \hspace{1cm} (A.10)
The averaged source terms read:

\[
\langle ho S_u \rangle = \frac{\partial}{\partial x} \left( \langle \mu \rangle \frac{\partial \tilde{u}}{\partial x} \right) + \frac{\partial}{\partial y} \left( \langle \mu \rangle \frac{\partial \tilde{v}}{\partial y} \right) + \frac{\partial}{\partial z} \left( \langle \mu \rangle \frac{\partial \tilde{w}}{\partial z} \right) \\
- \frac{\partial}{\partial x} \left( \frac{2}{3} \langle \mu \rangle \nabla \cdot \tilde{v} \right) \\
\langle ho S_v \rangle = \frac{\partial}{\partial x} \left( \langle \mu \rangle \frac{\partial \tilde{u}}{\partial y} \right) + \frac{\partial}{\partial y} \left( \langle \mu \rangle \frac{\partial \tilde{v}}{\partial y} \right) + \frac{\partial}{\partial z} \left( \langle \mu \rangle \frac{\partial \tilde{w}}{\partial y} \right) \\
- \frac{\partial}{\partial y} \left( \frac{2}{3} \langle \mu \rangle \nabla \cdot \tilde{v} \right) \\
\langle ho S_w \rangle = \frac{\partial}{\partial x} \left( \langle \mu \rangle \frac{\partial \tilde{u}}{\partial z} \right) + \frac{\partial}{\partial y} \left( \langle \mu \rangle \frac{\partial \tilde{v}}{\partial z} \right) + \frac{\partial}{\partial z} \left( \langle \mu \rangle \frac{\partial \tilde{w}}{\partial z} \right) \\
- \frac{\partial}{\partial z} \left( \frac{2}{3} \langle \mu \rangle \nabla \cdot \tilde{v} \right) 
\] (A.11a) (A.11b) (A.11c)

where:

\[
\nabla \cdot \tilde{v} = \frac{\partial \tilde{u}}{\partial x} + \frac{\partial \tilde{v}}{\partial y} + \frac{\partial \tilde{w}}{\partial z} 
\] (A.12)

The Favre-averaged transport equation for the scalar quantity \( \phi \) is denoted by:

\[
\mathcal{L}_2(\tilde{\phi}) = \langle \rho S_{\phi} \rangle 
\] (A.13)

where the appropriate transport coefficient has to be substituted for \( \Gamma \) in (A.10).

The correlations \( v_i^r \tilde{\phi}^r \) appearing in the operator \( \mathcal{L}_2 \) can be modeled by the Boussinesq hypothesis, thus introducing an effective transport coefficient \( \Gamma_{\text{eff}} \):

\[
\Gamma_{\text{eff}} = \Gamma + \mu_\epsilon / \sigma_\phi 
\] (A.14)

In the Favre-averaged sense, one obtains:

\[
\langle \Gamma_{\text{eff}} \rangle = \langle \Gamma \rangle + \langle \mu_\epsilon \rangle / \sigma_\phi 
\] (A.15)

where:

\[
\langle \mu_\epsilon \rangle = C_\mu \langle \rho \rangle \tilde{K}^2 / \tilde{\varepsilon} 
\] (A.16)

The Favre-averaged transport operator under the Boussinesq hypothesis is then written as:

\[
\mathcal{L}_3(\tilde{\phi}) = \frac{\partial (\rho \langle \tilde{u} \tilde{\phi} \rangle)}{\partial x} + \frac{\partial (\rho \langle \tilde{v} \tilde{\phi} \rangle)}{\partial y} + \frac{\partial (\rho \langle \tilde{w} \tilde{\phi} \rangle)}{\partial z} \\
- \frac{\partial}{\partial x} \left( \langle \Gamma_{\text{eff}} \rangle \frac{\partial \tilde{\phi}}{\partial x} \right) - \frac{\partial}{\partial y} \left( \langle \Gamma_{\text{eff}} \rangle \frac{\partial \tilde{\phi}}{\partial y} \right) - \frac{\partial}{\partial z} \left( \langle \Gamma_{\text{eff}} \rangle \frac{\partial \tilde{\phi}}{\partial z} \right) 
\] (A.17)
A.2. Two-dimensional cylindrical coordinates

It is this transport operator that has been used in the 3D furnace flow modeling. Finally, the source term expressions are altered to:

\[
\langle \rho S_u \rangle = \frac{\partial}{\partial x} \left( (\Gamma_{\text{eff}}) \frac{\partial \tilde{u}}{\partial x} \right) + \frac{\partial}{\partial y} \left( (\Gamma_{\text{eff}}) \frac{\partial \tilde{v}}{\partial x} \right) + \frac{\partial}{\partial z} \left( (\Gamma_{\text{eff}}) \frac{\partial \tilde{w}}{\partial x} \right) \\
- \frac{\partial}{\partial x} \left( \frac{2}{3} (\Gamma_{\text{eff}}) \nabla \cdot \tilde{v} \right) - \frac{\partial}{\partial x} \left( \frac{2}{3} (\rho) \tilde{k} \right) 
\]

(A.18a)

\[
\langle \rho S_v \rangle = \frac{\partial}{\partial x} \left( (\Gamma_{\text{eff}}) \frac{\partial \tilde{u}}{\partial y} \right) + \frac{\partial}{\partial y} \left( (\Gamma_{\text{eff}}) \frac{\partial \tilde{v}}{\partial y} \right) + \frac{\partial}{\partial z} \left( (\Gamma_{\text{eff}}) \frac{\partial \tilde{w}}{\partial y} \right) \\
- \frac{\partial}{\partial y} \left( \frac{2}{3} (\Gamma_{\text{eff}}) \nabla \cdot \tilde{v} \right) - \frac{\partial}{\partial y} \left( \frac{2}{3} (\rho) \tilde{k} \right) 
\]

(A.18b)

\[
\langle \rho S_w \rangle = \frac{\partial}{\partial x} \left( (\Gamma_{\text{eff}}) \frac{\partial \tilde{u}}{\partial z} \right) + \frac{\partial}{\partial y} \left( (\Gamma_{\text{eff}}) \frac{\partial \tilde{v}}{\partial z} \right) + \frac{\partial}{\partial z} \left( (\Gamma_{\text{eff}}) \frac{\partial \tilde{w}}{\partial z} \right) \\
- \frac{\partial}{\partial z} \left( \frac{2}{3} (\Gamma_{\text{eff}}) \nabla \cdot \tilde{v} \right) - \frac{\partial}{\partial z} \left( \frac{2}{3} (\rho) \tilde{k} \right) 
\]

(A.18c)

\[
- \frac{\partial}{\partial x} \left( \frac{2}{3} (\Gamma_{\text{eff}}) \nabla \cdot \tilde{v} \right) - \frac{\partial}{\partial y} \left( \frac{2}{3} (\rho) \tilde{k} \right) 
\]

(A.18d)

A.2 Two-dimensional cylindrical coordinates

Instantaneous equations

In the following it is assumed that the flow is axisymmetrical, hence the tangential gradients are zero, and furthermore gravity is supposed to work only in the axial (x-)direction. In the following, the x-coordinate is used for the axial direction and r for the radial direction. For the sake of completeness, the w-velocity is retained in the u- and v-equations. The continuity equation reads:

\[
\frac{\partial \rho}{\partial t} + \frac{\partial \rho u}{\partial x} + \frac{1}{r} \frac{\partial \rho v}{\partial r} = 0
\]

(A.19)

The Navier-Stokes equations are:

\[
\mathcal{L}_4(u) = \rho S_u - \frac{\partial p}{\partial x} + \rho g_x
\]

(A.20a)

\[
\mathcal{L}_4(v) = \rho S_v - \frac{\partial p}{\partial r}
\]

(A.20b)

where the general transport operator \( \mathcal{L}_4 \) is defined by:

\[
\mathcal{L}_4(f) = \frac{\partial f}{\partial t} + \frac{\partial u f}{\partial x} + \frac{1}{r} \frac{\partial r u f}{\partial r} - \frac{\partial}{\partial x} \left( \frac{\Gamma}{\partial x} \frac{\partial f}{\partial x} \right) - \frac{1}{r} \frac{\partial}{\partial y} \left( \frac{\Gamma f}{\partial r} \right)
\]

(A.21)

Again, as for the 3D case, the general equation for any scalar \( f \) reads:

\[
\mathcal{L}_4(f) = \rho S_f
\]

(A.22)
Appendix A. Transport equations in Cartesian and cylindrical coordinates

The source terms \( \rho S_u \) and \( \rho S_v \) are now given by:

\[
\rho S_u = \frac{\partial}{\partial x} \left( \mu \frac{\partial u}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \mu \frac{\partial u}{\partial r} \right) - \frac{\partial}{\partial x} \left( \frac{2}{3} \mu \nabla \cdot \mathbf{v} \right) \tag{A.23a}
\]

\[
\rho S_v = \frac{\partial}{\partial x} \left( \mu \frac{\partial v}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \mu \frac{\partial v}{\partial r} \right) - \frac{\partial}{\partial r} \left( \frac{2}{3} \mu \nabla \cdot \mathbf{v} \right) - 2 \frac{\mu}{r^2} \frac{v}{r} + \frac{\rho w^2}{r} \tag{A.23b}
\]

and the velocity gradient \( \nabla \cdot \mathbf{v} \) is given by:

\[
\nabla \cdot \mathbf{v} = \frac{\partial u}{\partial x} + \frac{1}{r} \frac{\partial rv}{\partial r} \tag{A.24}
\]

Note that the expressions for \( \rho S_v \) and differs considerably from the 3D case.

Stationary Favre-averaged equations

The Favre-averaged form of the 2D transport equations in cylindrical notation is derived similar to the 3D case. The averaged continuity equation is:

\[
\frac{\partial \langle \rho \rangle \tilde{u}}{\partial x} + \frac{1}{r} \frac{\partial \langle \rho \rangle \tilde{v}}{\partial r} = 0 \tag{A.25}
\]

The averaged momentum equations read:

\[
\mathcal{L}_5 (\tilde{u}) = \langle \rho S_u \rangle - \frac{\partial \langle \rho \rangle}{\partial x} + \langle \rho \rangle g_x \tag{A.26a}
\]

\[
\mathcal{L}_5 (\tilde{v}) = \langle \rho S_v \rangle - \frac{\partial \langle \rho \rangle}{\partial r} \tag{A.26b}
\]

where the general Favre-averaged transport operator \( \mathcal{L}_5 \) is defined by:

\[
\mathcal{L}_5 (\tilde{\phi}) = \frac{\partial \langle \rho \rangle \tilde{u} \tilde{\phi}}{\partial x} + \frac{1}{r} \frac{\partial \langle \rho \rangle \tilde{v} \tilde{\phi}}{\partial r} + \frac{\partial \langle \rho \rangle \tilde{u}'' \tilde{\phi}''}{\partial x} + \frac{1}{r} \frac{\partial \langle \rho \rangle \tilde{v}'' \tilde{\phi}''}{\partial r}
\]

\[= - \frac{\partial}{\partial x} \left( \langle \Gamma \rangle \frac{\partial \tilde{\phi}}{\partial x} \right) - \frac{1}{r} \frac{\partial}{\partial r} \left( \langle \Gamma \rangle \frac{\partial \tilde{\phi}}{\partial r} \right) \tag{A.27}
\]

The averaged source terms read:

\[
\langle \rho S_u \rangle = \frac{\partial}{\partial x} \left( \langle \mu \rangle \frac{\partial \tilde{u}}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \langle \mu \rangle \frac{\partial \tilde{v}}{\partial r} \right) - \frac{\partial}{\partial x} \left( \frac{2}{3} \langle \mu \rangle \nabla \cdot \mathbf{\tilde{v}} \right) \tag{A.28a}
\]

\[
\langle \rho S_v \rangle = \frac{\partial}{\partial x} \left( \langle \mu \rangle \frac{\partial \tilde{u}}{\partial r} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \langle \mu \rangle \frac{\partial \tilde{v}}{\partial r} \right) - \frac{\partial}{\partial r} \left( \frac{2}{3} \langle \mu \rangle \nabla \cdot \mathbf{\tilde{v}} \right)
\]

\[- 2 \langle \mu \rangle \frac{\tilde{v}}{r^2} + \frac{\langle \rho \rangle (\tilde{w}^2 + \tilde{w}'^2)}{r} \tag{A.28b}
\]
Note that the normal stress $\tilde{w} r^2$ appears in the $\tilde{v}$-equation even if $\tilde{w}$ is zero. The mean velocity gradient $\nabla \cdot \tilde{v}$ is given by:

$$\nabla \cdot \tilde{v} = \frac{\partial \tilde{u}}{\partial x} + \frac{1}{r} \frac{\partial r \tilde{v}}{\partial r}$$  \hspace{1cm} (A.29)

If the unknown velocity correlations are modeled by virtue of the Boussinesq hypothesis, the Favre-averaged transport operator becomes:

$$\mathcal{L}_f(\tilde{\phi}) = \frac{\partial \langle \rho \rangle \tilde{u} \tilde{\phi}}{\partial x} + \frac{1}{r} \frac{\partial r \langle \rho \rangle \tilde{v} \tilde{\phi}}{\partial r}$$

$$- \frac{\partial}{\partial x} \left( \langle \Gamma_{\text{eff}} \rangle \frac{\partial \tilde{\phi}}{\partial x} \right) - \frac{1}{r} \frac{\partial}{\partial r} \left( r \langle \Gamma_{\text{eff}} \rangle \frac{\partial \tilde{\phi}}{\partial r} \right)$$  \hspace{1cm} (A.30)

Finally, the source terms for the $\tilde{u}$- and $\tilde{v}$-equations read:

$$\langle \rho S_u \rangle = \frac{\partial}{\partial x} \left( \langle \Gamma_{\text{eff}} \rangle \frac{\partial \tilde{u}}{\partial x} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \langle \Gamma_{\text{eff}} \rangle \frac{\partial \tilde{v}}{\partial r} \right) - \frac{\partial}{\partial x} \left( \langle \rho \rangle \tilde{k} + \langle \Gamma_{\text{eff}} \rangle \nabla \cdot \tilde{v} \right)$$  \hspace{1cm} (A.31a)

$$\langle \rho S_v \rangle = \frac{\partial}{\partial x} \left( \langle \mu \rangle \frac{\partial \tilde{u}}{\partial r} \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \langle \Gamma_{\text{eff}} \rangle \frac{\partial \tilde{v}}{\partial r} \right) - \frac{\partial}{\partial r} \left( \langle \rho \rangle \tilde{k} + \langle \Gamma_{\text{eff}} \rangle \nabla \cdot \tilde{v} \right)$$

$$- 2 \langle \Gamma_{\text{eff}} \rangle \frac{\tilde{v}}{r^2}$$  \hspace{1cm} (A.31b)
APPENDIX B

Reaction mechanisms

In this appendix, the relevant chemical reaction mechanisms used for the calculation of the laminar premixed and diffusion flames are listed.

**TABLE B.1: Skeletal mechanism for methane oxidation.**

<table>
<thead>
<tr>
<th>no.</th>
<th>reaction</th>
<th>( A_k ) mole, cm(^{-3} ) s</th>
<th>( \beta_k )</th>
<th>( E_{A,k} ) cal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>1f</td>
<td>H + O(_2) → OH + O</td>
<td>2.000 ( \cdot 10^{14} )</td>
<td>0.0</td>
<td>16800.</td>
</tr>
<tr>
<td>1b</td>
<td>OH + O ( \rightarrow ) H + O(_2)</td>
<td>1.575 ( \cdot 10^{13} )</td>
<td>0.0</td>
<td>690.</td>
</tr>
<tr>
<td>2f</td>
<td>O + H(_2) → OH + H</td>
<td>1.800 ( \cdot 10^{10} )</td>
<td>1.0</td>
<td>8826.</td>
</tr>
<tr>
<td>2b</td>
<td>OH + H ( \rightarrow ) O + H(_2)</td>
<td>8.000 ( \cdot 10^{9} )</td>
<td>1.0</td>
<td>6760.</td>
</tr>
<tr>
<td>3f</td>
<td>H(_2) + OH ( \rightarrow ) H(_2)O + H</td>
<td>1.170 ( \cdot 10^{9} )</td>
<td>1.3</td>
<td>3626.</td>
</tr>
<tr>
<td>3b</td>
<td>H(_2)O + H ( \rightarrow ) H(_2) + OH</td>
<td>5.090 ( \cdot 10^{9} )</td>
<td>1.3</td>
<td>18588.</td>
</tr>
<tr>
<td>4f</td>
<td>OH + OH ( \rightarrow ) O + H(_2)O</td>
<td>6.000 ( \cdot 10^{8} )</td>
<td>1.3</td>
<td>0.0</td>
</tr>
<tr>
<td>4b</td>
<td>H(_2)O + O ( \rightarrow ) OH + OH</td>
<td>5.900 ( \cdot 10^{6} )</td>
<td>1.3</td>
<td>17029.</td>
</tr>
<tr>
<td>5</td>
<td>H + O(_2) + M ( \rightarrow ) H(_2)O + M</td>
<td>2.300 ( \cdot 10^{18} )</td>
<td>-0.8</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>H + H(_2)O ( \rightarrow ) OH + OH</td>
<td>1.500 ( \cdot 10^{14} )</td>
<td>0.0</td>
<td>1004.</td>
</tr>
<tr>
<td>7</td>
<td>H + H(_2)O ( \rightarrow ) H(_2) + O(_2)</td>
<td>2.500 ( \cdot 10^{13} )</td>
<td>0.0</td>
<td>700.</td>
</tr>
<tr>
<td>8</td>
<td>OH + H(_2)O ( \rightarrow ) H(_2)O + O(_2)</td>
<td>2.000 ( \cdot 10^{13} )</td>
<td>0.0</td>
<td>1000.</td>
</tr>
<tr>
<td>9f</td>
<td>CO + OH ( \rightarrow ) CO(_2) + H</td>
<td>1.510 ( \cdot 10^{7} )</td>
<td>1.3</td>
<td>-758.</td>
</tr>
<tr>
<td>9b</td>
<td>CO(_2) + H ( \rightarrow ) CO + OH</td>
<td>1.570 ( \cdot 10^{9} )</td>
<td>1.3</td>
<td>22337.</td>
</tr>
<tr>
<td>10f</td>
<td>CH(_4) ( \rightarrow ) CH(_3) + H</td>
<td>2.300 ( \cdot 10^{38} )</td>
<td>-7.0</td>
<td>114360.</td>
</tr>
<tr>
<td>10b</td>
<td>CH(_3) + H ( \rightarrow ) CH(_4)</td>
<td>1.900 ( \cdot 10^{36} )</td>
<td>-7.0</td>
<td>9050.</td>
</tr>
<tr>
<td>11f</td>
<td>CH(_3) + H ( \rightarrow ) CH(_2) + H(_2)</td>
<td>2.200 ( \cdot 10^{4} )</td>
<td>3.0</td>
<td>8750.</td>
</tr>
<tr>
<td>11b</td>
<td>CH(_3) + H(_2) ( \rightarrow ) CH(_4) + H</td>
<td>9.570 ( \cdot 10^{2} )</td>
<td>3.0</td>
<td>8750.</td>
</tr>
<tr>
<td>12f</td>
<td>CH(_3) + OH ( \rightarrow ) CH(_2) + H(_2)O</td>
<td>1.600 ( \cdot 10^{6} )</td>
<td>2.1</td>
<td>2460.</td>
</tr>
<tr>
<td>12b</td>
<td>CH(_3) + H(_2)O ( \rightarrow ) CH(_2) + OH</td>
<td>3.020 ( \cdot 10^{5} )</td>
<td>2.1</td>
<td>17422.</td>
</tr>
<tr>
<td>13</td>
<td>CH(_3) + O ( \rightarrow ) CH(_2)O + H</td>
<td>6.800 ( \cdot 10^{13} )</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>14</td>
<td>CH(_2)O + H ( \rightarrow ) CHO + H(_2)</td>
<td>2.500 ( \cdot 10^{13} )</td>
<td>0.0</td>
<td>3991.</td>
</tr>
<tr>
<td>15</td>
<td>CH(_2)O + OH ( \rightarrow ) CHO + H(_2)O</td>
<td>3.000 ( \cdot 10^{13} )</td>
<td>0.0</td>
<td>1195.</td>
</tr>
<tr>
<td>16</td>
<td>CHO + H ( \rightarrow ) CO + H(_2)</td>
<td>4.000 ( \cdot 10^{13} )</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>17</td>
<td>CHO + M ( \rightarrow ) CO + H + M</td>
<td>1.600 ( \cdot 10^{14} )</td>
<td>0.0</td>
<td>14700.</td>
</tr>
<tr>
<td>18</td>
<td>CH(_3) + O(_2) ( \rightarrow ) CH(_2)O + O</td>
<td>7.000 ( \cdot 10^{12} )</td>
<td>0.0</td>
<td>25652.</td>
</tr>
<tr>
<td>19</td>
<td>CH(_3)O + H ( \rightarrow ) CH(_2)O + H(_2)</td>
<td>2.000 ( \cdot 10^{13} )</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>20</td>
<td>CH(_3)O + M ( \rightarrow ) CH(_2)O + M</td>
<td>2.400 ( \cdot 10^{13} )</td>
<td>0.0</td>
<td>28812.</td>
</tr>
<tr>
<td>21</td>
<td>HO(_2) + HO(_2) ( \rightarrow ) H(_2)O(_2) + O(_2)</td>
<td>2.000 ( \cdot 10^{12} )</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>22f</td>
<td>H(_2)O(_2) + M ( \rightarrow ) OH + OH + M</td>
<td>1.300 ( \cdot 10^{17} )</td>
<td>0.0</td>
<td>45500.</td>
</tr>
<tr>
<td>22b</td>
<td>OH + OH + M ( \rightarrow ) H(_2)O(_2) + M</td>
<td>9.860 ( \cdot 10^{14} )</td>
<td>0.0</td>
<td>-5070.</td>
</tr>
<tr>
<td>23f</td>
<td>H(_2)O(_2) + OH ( \rightarrow ) H(_2)O + HO(_2)</td>
<td>1.000 ( \cdot 10^{13} )</td>
<td>0.0</td>
<td>1800.</td>
</tr>
<tr>
<td>23b</td>
<td>H(_2)O + HO(_2) ( \rightarrow ) H(_2)O(_2) + OH</td>
<td>2.860 ( \cdot 10^{13} )</td>
<td>0.0</td>
<td>32790.</td>
</tr>
<tr>
<td>24</td>
<td>OH + H + M ( \rightarrow ) H(_2)O + M</td>
<td>2.200 ( \cdot 10^{22} )</td>
<td>-2.0</td>
<td>0.0</td>
</tr>
<tr>
<td>25</td>
<td>H + H + M ( \rightarrow ) H(_2) + M</td>
<td>1.800 ( \cdot 10^{18} )</td>
<td>-1.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Third-body efficiencies are: CH\(_4\): 6.5; H\(_2\)O: 6.5; CO\(_2\): 1.5; CO: 0.75; O\(_2\): 0.4; N\(_2\): 0.4; all other species 1.
### Table B.2: Kee mechanism for hydrocarbon oxidation.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$A_k$ (mole, cm$^{-3}$ s)</th>
<th>$\beta_k$</th>
<th>$T_{A,k}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_3$ + H (+M) = CH$_4$ (+M)</td>
<td>6.000 x 10$^{16}$</td>
<td>-1.00</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>low-pressure limit</td>
<td>8.000 x 10$^{26}$</td>
<td>-3.00</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>CH$_4$ + O$_2$ = CH$_3$ + HO$_2$</td>
<td>7.900 x 10$^{13}$</td>
<td>0.00</td>
<td>28181</td>
</tr>
<tr>
<td>3</td>
<td>CH$_4$ + H = CH$_3$ + H$_2$</td>
<td>2.200 x 10$^4$</td>
<td>3.00</td>
<td>4403</td>
</tr>
<tr>
<td>4</td>
<td>CH$_4$ + O = CH$_3$ + OH</td>
<td>1.600 x 10$^6$</td>
<td>2.36</td>
<td>3724</td>
</tr>
<tr>
<td>5</td>
<td>CH$_4$ + OH = CH$_3$ + H$_2$O</td>
<td>1.600 x 10$^6$</td>
<td>2.10</td>
<td>1238</td>
</tr>
<tr>
<td>6</td>
<td>CH$_3$ + O = CH$_2$O + H</td>
<td>6.800 x 10$^{13}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>CH$_3$ + OH = CH$_2$O + H$_2$</td>
<td>1.000 x 10$^{12}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>CH$_3$ + OH = CH$_2$ + H$_2$O</td>
<td>1.500 x 10$^{13}$</td>
<td>0.00</td>
<td>2516</td>
</tr>
<tr>
<td>9</td>
<td>CH$_3$ + H = CH$_2$ + H$_2$</td>
<td>9.000 x 10$^{13}$</td>
<td>0.00</td>
<td>7599</td>
</tr>
<tr>
<td>10</td>
<td>CH$_2$ + H = CH + H$_2$</td>
<td>1.400 x 10$^{12}$</td>
<td>-2.00</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>CH$_2$ + OH = CH$_2$O + H</td>
<td>2.500 x 10$^{13}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>CH$_2$ + OH = CH + H$_2$O</td>
<td>4.500 x 10$^{13}$</td>
<td>0.00</td>
<td>1510</td>
</tr>
<tr>
<td>13</td>
<td>CH + O$_2$ = HCO + O</td>
<td>3.300 x 10$^{13}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>CH + O = CO + H</td>
<td>5.700 x 10$^{13}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>CH + OH = HCO + H</td>
<td>3.000 x 10$^{13}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>CH + CO$_2$ = HCO + CO</td>
<td>3.400 x 10$^{12}$</td>
<td>0.00</td>
<td>347</td>
</tr>
<tr>
<td>17</td>
<td>CH$_2$ + CO$_2$ = CH$_2$O + CO</td>
<td>1.100 x 10$^{11}$</td>
<td>0.00</td>
<td>503</td>
</tr>
<tr>
<td>18</td>
<td>CH$_2$ + O = CO + 2H</td>
<td>3.000 x 10$^{13}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>19</td>
<td>CH$_2$ + O = CO + H$_2$</td>
<td>5.000 x 10$^{13}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>CH$_2$ + O$_2$ = CO$_2$ + 2H</td>
<td>1.600 x 10$^{12}$</td>
<td>0.00</td>
<td>503</td>
</tr>
<tr>
<td>21</td>
<td>CH$_2$ + O$_2$ = CH$_2$O + O</td>
<td>5.000 x 10$^{13}$</td>
<td>0.00</td>
<td>4529</td>
</tr>
<tr>
<td>22</td>
<td>CH$_2$ + O$_2$ = CO$_2$ + H$_2$</td>
<td>6.900 x 10$^{11}$</td>
<td>0.00</td>
<td>252</td>
</tr>
<tr>
<td>23</td>
<td>CH$_2$ + O$_2$ = CO + H$_2$O</td>
<td>1.900 x 10$^{10}$</td>
<td>0.00</td>
<td>-503</td>
</tr>
<tr>
<td>24</td>
<td>CH$_2$ + O$_2$ = CO + OH + H</td>
<td>8.600 x 10$^{10}$</td>
<td>0.00</td>
<td>-252</td>
</tr>
<tr>
<td>25</td>
<td>CH$_2$ + O$_2$ = HCO + OH</td>
<td>4.300 x 10$^{10}$</td>
<td>0.00</td>
<td>-252</td>
</tr>
<tr>
<td>26</td>
<td>CH$_2$O + OH = HCO + H$_2$O</td>
<td>3.450 x 10$^9$</td>
<td>1.18</td>
<td>-223</td>
</tr>
<tr>
<td>27</td>
<td>CH$_2$O + H = HCO + H$_2$</td>
<td>2.190 x 10$^8$</td>
<td>1.77</td>
<td>1510</td>
</tr>
<tr>
<td>28</td>
<td>CH$_2$O + M = HCO + H + M</td>
<td>3.310 x 10$^{16}$</td>
<td>0.00</td>
<td>40762</td>
</tr>
<tr>
<td>29</td>
<td>CH$_2$O + O = HCO + OH</td>
<td>1.810 x 10$^{13}$</td>
<td>0.00</td>
<td>1551</td>
</tr>
<tr>
<td>30</td>
<td>HCO + OH = CO + H$_2$O</td>
<td>5.000 x 10$^{12}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>31</td>
<td>HCO + M + CO + H + M</td>
<td>1.600 x 10$^{14}$</td>
<td>0.00</td>
<td>7397</td>
</tr>
<tr>
<td>32</td>
<td>HCO + H = CO + H$_2$</td>
<td>4.000 x 10$^{13}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>33</td>
<td>HCO + O = CO + H$_2$</td>
<td>1.000 x 10$^{13}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>34</td>
<td>HCO + O$_2$ = CO + HO$_2$</td>
<td>3.300 x 10$^{13}$</td>
<td>-0.40</td>
<td>0</td>
</tr>
<tr>
<td>35</td>
<td>CO + O + M = CO$_2$ + M</td>
<td>3.200 x 10$^{13}$</td>
<td>0.00</td>
<td>-2114</td>
</tr>
<tr>
<td>36</td>
<td>CO + OH = CO$_2$ + H</td>
<td>1.510 x 10$^7$</td>
<td>1.30</td>
<td>-381</td>
</tr>
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<td>37</td>
<td>CO + O$_2$ = CO$_2$ + O</td>
<td>1.600 x 10$^{13}$</td>
<td>0.00</td>
<td>20632</td>
</tr>
<tr>
<td>38</td>
<td>CO + HO$_2$ = CO$_2$ + OH</td>
<td>5.800 x 10$^{13}$</td>
<td>0.00</td>
<td>11541</td>
</tr>
<tr>
<td>39</td>
<td>H$_2$ + O$_2$ = 2OH</td>
<td>1.700 x 10$^{13}$</td>
<td>0.00</td>
<td>24044</td>
</tr>
<tr>
<td>40</td>
<td>OH + H$_2$ = H$_2$O + H</td>
<td>1.170 x 10$^9$</td>
<td>1.30</td>
<td>1825</td>
</tr>
<tr>
<td>41</td>
<td>H + O$_2$ = OH + O</td>
<td>5.130 x 10$^{16}$</td>
<td>-0.82</td>
<td>8307</td>
</tr>
<tr>
<td>42</td>
<td>O + H$_2$ = OH + H</td>
<td>1.800 x 10$^{10}$</td>
<td>1.00</td>
<td>4442</td>
</tr>
<tr>
<td>43</td>
<td>H + O$_2$ = HO$_2$ + M</td>
<td>3.610 x 10$^{17}$</td>
<td>-0.72</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Efficiencies H$_2$O: 18.6; H$_2$: 2.86; N$_2$: 1.26; CO: 2.11; CO$_2$: 4.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>OH + HO$_2$ = H$_2$O + O$_2$</td>
<td>7.500 x 10$^{12}$</td>
<td>0.00</td>
<td>0</td>
</tr>
</tbody>
</table>
Appendix B. Reaction mechanisms

<table>
<thead>
<tr>
<th>no.</th>
<th>reaction</th>
<th>$A_k$ mole, cm$^{-3}$ s</th>
<th>$\beta_k$</th>
<th>$T_{A,k}$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>H + HO$_2$ $\rightarrow$ 2OH</td>
<td>$1.40 \times 10^{14}$</td>
<td>0.00</td>
<td>540.</td>
</tr>
<tr>
<td>46</td>
<td>O + HO$_2$ $\rightarrow$ O$_2$ + OH</td>
<td>$1.40 \times 10^{13}$</td>
<td>0.00</td>
<td>540.</td>
</tr>
<tr>
<td>47</td>
<td>2OH $\rightarrow$ O + H$_2$O</td>
<td>$6.00 \times 10^{9}$</td>
<td>1.30</td>
<td>0.</td>
</tr>
<tr>
<td>48</td>
<td>2H + M $\rightarrow$ H$_2$ + M</td>
<td>$1.00 \times 10^{18}$</td>
<td>-1.00</td>
<td>0.</td>
</tr>
<tr>
<td>49</td>
<td>2H + H$_2$ $\rightarrow$ 2H$_2$</td>
<td>$9.20 \times 10^{16}$</td>
<td>-0.60</td>
<td>0.</td>
</tr>
<tr>
<td>50</td>
<td>2H + H$_2$O $\rightarrow$ H$_2$ + H$_2$O</td>
<td>$6.00 \times 10^{19}$</td>
<td>-1.25</td>
<td>0.</td>
</tr>
<tr>
<td>51</td>
<td>2H + CO$_2$ $\rightarrow$ H$_2$ + CO$_2$</td>
<td>$5.49 \times 10^{20}$</td>
<td>-2.00</td>
<td>0.</td>
</tr>
<tr>
<td>52</td>
<td>H + OH + M $\rightarrow$ H$_2$O + M</td>
<td>$1.60 \times 10^{22}$</td>
<td>-2.00</td>
<td>0.</td>
</tr>
<tr>
<td>53</td>
<td>Efficiencies H$_2$O: 5.0</td>
<td>$6.20 \times 10^{16}$</td>
<td>-0.60</td>
<td>0.</td>
</tr>
<tr>
<td>54</td>
<td>H + O + M $\rightarrow$ OH + M</td>
<td>$1.25 \times 10^{13}$</td>
<td>0.00</td>
<td>0.</td>
</tr>
<tr>
<td>55</td>
<td>Efficiencies H$_2$O: 5.0</td>
<td>$2.00 \times 10^{12}$</td>
<td>0.00</td>
<td>0.</td>
</tr>
<tr>
<td>56</td>
<td>H$_2$O$_2$ + M $\rightarrow$ 2OH + M</td>
<td>$1.30 \times 10^{17}$</td>
<td>0.00</td>
<td>22897.</td>
</tr>
<tr>
<td>57</td>
<td>H$_2$O$_2$ + H $\rightarrow$ HO$_2$ + H$_2$</td>
<td>$1.60 \times 10^{12}$</td>
<td>0.00</td>
<td>1912.</td>
</tr>
<tr>
<td>58</td>
<td>H$_2$O + OH $\rightarrow$ H$_2$O + HO$_2$</td>
<td>$1.00 \times 10^{3}$</td>
<td>0.00</td>
<td>906.</td>
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</tbody>
</table>
### TABLE B.3: Warnatz mechanism for hydrocarbon oxidation.

<table>
<thead>
<tr>
<th>no.</th>
<th>reaction</th>
<th>$A_k$ mole, cm$^{-3}$ s</th>
<th>$\beta_k$</th>
<th>$T_{A,k}$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H + O$_2$ $\rightarrow$ OH + O</td>
<td>$2.00 \times 10^{24}$</td>
<td>0.00</td>
<td>8455</td>
</tr>
<tr>
<td>2</td>
<td>O + H$_2$ $\rightarrow$ OH + H</td>
<td>$5.06 \times 10^{4}$</td>
<td>2.67</td>
<td>3163</td>
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<tr>
<td>3</td>
<td>OH + H$_2$ $\rightarrow$ H$_2$O + H</td>
<td>$1.00 \times 10^{6}$</td>
<td>1.60</td>
<td>1660</td>
</tr>
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<td>4</td>
<td>2OH $\rightarrow$ H$_2$O + O</td>
<td>$1.50 \times 10^{9}$</td>
<td>1.14</td>
<td>51</td>
</tr>
<tr>
<td>5</td>
<td>2H + M $\rightarrow$ H$_2$ + M</td>
<td>$1.80 \times 10^{18}$</td>
<td>-1.00</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>2O + M $\rightarrow$ O$_2$ + M</td>
<td>$2.90 \times 10^{17}$</td>
<td>-1.00</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>H + OH + M $\rightarrow$ H$_2$O + M</td>
<td>$2.20 \times 10^{22}$</td>
<td>-2.00</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>H + O$_2$ + M $\rightarrow$ HO$_2$ + M</td>
<td>$2.30 \times 10^{18}$</td>
<td>-0.80</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>H + HO$_2$ $\rightarrow$ 2OH</td>
<td>$1.50 \times 10^{24}$</td>
<td>0.00</td>
<td>505</td>
</tr>
<tr>
<td>10</td>
<td>H + HO$_2$ $\rightarrow$ H + O$_2$</td>
<td>$2.50 \times 10^{13}$</td>
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</tr>
<tr>
<td>11</td>
<td>H + HO$_2$ $\rightarrow$ H$_2$O + O</td>
<td>$3.00 \times 10^{13}$</td>
<td>0.00</td>
<td>866</td>
</tr>
<tr>
<td>12</td>
<td>O + HO$_2$ $\rightarrow$ OH + O$_2$</td>
<td>$1.80 \times 10^{13}$</td>
<td>0.00</td>
<td>-204</td>
</tr>
<tr>
<td>13</td>
<td>OH + HO$_2$ $\rightarrow$ H$_2$O + O$_2$</td>
<td>$6.00 \times 10^{13}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>2HO$_2$ $\rightarrow$ H$_2$O + O$_2$</td>
<td>$2.50 \times 10^{11}$</td>
<td>0.00</td>
<td>-625</td>
</tr>
<tr>
<td>15</td>
<td>2OH + M $\rightarrow$ H$_2$O$_2$ + M</td>
<td>$3.25 \times 10^{22}$</td>
<td>-2.00</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>H + H$_2$O$_2$ $\rightarrow$ H + HO$_2$</td>
<td>$1.70 \times 10^{22}$</td>
<td>0.00</td>
<td>1888</td>
</tr>
<tr>
<td>17</td>
<td>H + H$_2$O$_2$ $\rightarrow$ H$_2$O + OH</td>
<td>$1.00 \times 10^{13}$</td>
<td>0.00</td>
<td>1804</td>
</tr>
<tr>
<td>18</td>
<td>O + H$_2$O$_2$ $\rightarrow$ OH + HO$_2$</td>
<td>$2.80 \times 10^{13}$</td>
<td>0.00</td>
<td>3223</td>
</tr>
<tr>
<td>19</td>
<td>OH + H$_2$O$_2$ $\rightarrow$ H$_2$O + HO$_2$</td>
<td>$5.40 \times 10^{12}$</td>
<td>0.00</td>
<td>505</td>
</tr>
<tr>
<td>20</td>
<td>CO + OH $\rightarrow$ CO$_2$ + H</td>
<td>$6.00 \times 10^{6}$</td>
<td>1.50</td>
<td>-373</td>
</tr>
<tr>
<td>21</td>
<td>CO + HO$_2$ $\rightarrow$ CO$_2$ + OH</td>
<td>$1.50 \times 10^{14}$</td>
<td>0.00</td>
<td>11871</td>
</tr>
<tr>
<td>22</td>
<td>CO + O + M $\rightarrow$ CO$_2$ + M</td>
<td>$7.10 \times 10^{13}$</td>
<td>0.00</td>
<td>-2285</td>
</tr>
<tr>
<td>23</td>
<td>CO + O$_2$ $\rightarrow$ CO$_2$ + O</td>
<td>$2.50 \times 10^{12}$</td>
<td>0.00</td>
<td>24055</td>
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<tr>
<td>24</td>
<td>CH + O $\rightarrow$ CO + H</td>
<td>$3.30 \times 10^{13}$</td>
<td>0.00</td>
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<tr>
<td>25</td>
<td>CH + O$_2$ $\rightarrow$ CHO + O</td>
<td>$3.00 \times 10^{13}$</td>
<td>0.00</td>
<td>0</td>
</tr>
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<td>26</td>
<td>CH + CO$_2$ $\rightarrow$ CHO + CO</td>
<td>$3.40 \times 10^{12}$</td>
<td>0.00</td>
<td>349</td>
</tr>
<tr>
<td>27</td>
<td>CH + H$_2$O $\rightarrow$ CH$_2$ + OH</td>
<td>$5.70 \times 10^{12}$</td>
<td>0.00</td>
<td>-385</td>
</tr>
<tr>
<td>28</td>
<td>CHO + M $\rightarrow$ CO + H + M</td>
<td>$7.10 \times 10^{14}$</td>
<td>0.00</td>
<td>8455</td>
</tr>
<tr>
<td>29</td>
<td>CHO + H $\rightarrow$ CO + H$_2$</td>
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<tr>
<td>30</td>
<td>CHO + O $\rightarrow$ CO + OH</td>
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<td>31</td>
<td>CHO + O $\rightarrow$ CO$_2$ + H</td>
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<td>32</td>
<td>CHO + OH $\rightarrow$ CO + H$_2$O</td>
<td>$1.00 \times 10^{14}$</td>
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<td>0</td>
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<td>33</td>
<td>CHO + O$_2$ $\rightarrow$ CO + O + H$_2$</td>
<td>$3.00 \times 10^{12}$</td>
<td>0.00</td>
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<tr>
<td>34</td>
<td>2CHO $\rightarrow$ CH$_2$O + CO</td>
<td>$3.00 \times 10^{13}$</td>
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<td>0</td>
</tr>
<tr>
<td>35</td>
<td>CH$_2$ + H $\rightarrow$ CH + H$_2$</td>
<td>$6.00 \times 10^{2}$</td>
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<td>-902</td>
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<tr>
<td>36</td>
<td>CH$_2$ + O $\rightarrow$ CO + 2H</td>
<td>$8.43 \times 10^{2}$</td>
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<tr>
<td>37</td>
<td>2CH$_2$ $\rightarrow$ C$_2$H$_2$ + 2H</td>
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<td>38</td>
<td>CH$_2$ + CH$_3$ $\rightarrow$ C$_2$H$_4$ + H</td>
<td>$4.20 \times 10^{13}$</td>
<td>0.00</td>
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<tr>
<td>39</td>
<td>CH$_2$ + O$_2$ $\rightarrow$ CO + OH + H</td>
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<td>40</td>
<td>CH$_2$ + O$_2$ $\rightarrow$ CO$_2$ + H$_2$</td>
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<td>746</td>
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<tr>
<td>41</td>
<td>CH$_2$($s$) + M $\rightarrow$ CH$_2$ + M</td>
<td>$1.20 \times 10^{13}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>42</td>
<td>CH$_2$($s$) + O$_2$ $\rightarrow$ CO + OH + H</td>
<td>$3.10 \times 10^{13}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>43</td>
<td>CH$_2$($s$) + H$_2$ $\rightarrow$ CH$_3$ + H</td>
<td>$7.20 \times 10^{13}$</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>44</td>
<td>CH$_2$O + M $\rightarrow$ CHO + H + M</td>
<td>$5.00 \times 10^{16}$</td>
<td>0.00</td>
<td>38488</td>
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<td>45</td>
<td>CH$_2$O + H $\rightarrow$ CHO + H$_2$</td>
<td>$2.30 \times 10^{10}$</td>
<td>1.05</td>
<td>1648</td>
</tr>
<tr>
<td>46</td>
<td>CH$_2$O + O $\rightarrow$ CHO + OH</td>
<td>$4.15 \times 10^{11}$</td>
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</tr>
<tr>
<td>no.</td>
<td>reaction</td>
<td>$A_k$</td>
<td>$\beta_k$</td>
<td>$T_{A_k}$</td>
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<tr>
<td>-----</td>
<td>----------------------------------------------</td>
<td>----------------</td>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>47</td>
<td>CH$_2$O + OH $\rightleftharpoons$ CHO + H$_2$O</td>
<td>3.400-10$^8$</td>
<td>1.20</td>
<td>-229.0</td>
</tr>
<tr>
<td>48</td>
<td>CH$_2$O + HO$_2$ $\rightleftharpoons$ CHO + H$_2$O</td>
<td>6.000-10$^8$</td>
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</tr>
<tr>
<td>49</td>
<td>CH$_2$O + CH$_3$ $\rightleftharpoons$ CHO + CH$_4$</td>
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<td>0.00</td>
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<tr>
<td>50</td>
<td>CH$_2$O + O$_2$ $\rightleftharpoons$ CHO + HO$_2$</td>
<td>6.000-10$^3$</td>
<td>0.00</td>
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</tr>
<tr>
<td>51</td>
<td>CH$_3$ + M $\rightleftharpoons$ CH$_2$ + H + M</td>
<td>1.000-10$^6$</td>
<td>0.00</td>
<td>45584.0</td>
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<tr>
<td>52</td>
<td>CH$_3$ + H $\rightleftharpoons$ CH$_2$ + H$_2$</td>
<td>6.000-10$^3$</td>
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<td>53</td>
<td>CH$_3$ + O $\rightleftharpoons$ CH$_2$O + H</td>
<td>8.430-10$^3$</td>
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<tr>
<td>54</td>
<td>CH$_3$ + H $\rightleftharpoons$ CH$_4$</td>
<td>1.930-10$^5$</td>
<td>-7.00</td>
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<td>55</td>
<td>CH$_3$ + OH $\rightleftharpoons$ CH$_2$O + H</td>
<td>2.260-10$^4$</td>
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<td>7794.0</td>
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<td>56</td>
<td>CH$_2$O + CO $\rightleftharpoons$ CH$_3$ + OH</td>
<td>4.750-10$^6$</td>
<td>-0.13</td>
<td>10584.0</td>
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<tr>
<td>57</td>
<td>CH$_3$ + O$_2$ $\rightarrow$ CH$_2$O + OOH</td>
<td>3.300-10$^{11}$</td>
<td>0.00</td>
<td>4498.0</td>
</tr>
<tr>
<td>58</td>
<td>CH$_3$ + HO$_2$ $\rightleftharpoons$ CH$_2$O + OH</td>
<td>1.800-10$^3$</td>
<td>0.00</td>
<td>0.0</td>
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<tr>
<td>59</td>
<td>CH$_3$ + HO$_2$ $\rightleftharpoons$ CH$_4$ + O$_2$</td>
<td>3.600-10$^2$</td>
<td>0.00</td>
<td>0.0</td>
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<tr>
<td>60</td>
<td>2CH$_3$ $\rightarrow$ C$_2$H$_4$ + H$_2$</td>
<td>1.000-10$^6$</td>
<td>0.00</td>
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<td>61</td>
<td>2CH$_3$ $\rightarrow$ C$_2$H$_6$</td>
<td>1.690-10$^5$</td>
<td>-12.00</td>
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<tr>
<td>62</td>
<td>CH$_3$O + M $\rightleftharpoons$ CH$_2$O + H + M</td>
<td>5.000-10$^3$</td>
<td>0.00</td>
<td>12629.0</td>
</tr>
<tr>
<td>63</td>
<td>CH$_3$O + H $\rightleftharpoons$ CH$_2$O + H$_2$</td>
<td>1.800-10$^3$</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>64</td>
<td>CH$_2$O + O$_2$ $\rightleftharpoons$ CH$_2$O + HO$_2$</td>
<td>4.000-10$^3$</td>
<td>0.00</td>
<td>1070.0</td>
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<tr>
<td>65</td>
<td>CH$_3$O + CH$_2$O $\rightarrow$ CH$_3$OH + CHO</td>
<td>6.000-10$^3$</td>
<td>0.00</td>
<td>1660.0</td>
</tr>
<tr>
<td>66</td>
<td>CH$_3$OH + CHO $\rightarrow$ CH$_2$O + CH$_2$O</td>
<td>6.500-10$^9$</td>
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<td>67</td>
<td>CH$_3$O + O $\rightleftharpoons$ O$_2$ + CH$_3$</td>
<td>1.100-10$^3$</td>
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<td>0.0</td>
</tr>
<tr>
<td>68</td>
<td>CH$_3$O + O $\rightleftharpoons$ OH + CH$_2$O</td>
<td>1.400-10$^2$</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>69</td>
<td>CH$_2$OH + M $\rightleftharpoons$ CH$_2$O + M</td>
<td>5.000-10$^3$</td>
<td>0.00</td>
<td>12629.0</td>
</tr>
<tr>
<td>70</td>
<td>CH$_2$OH + H $\rightleftharpoons$ CH$_2$O + H$_2$</td>
<td>3.000-10$^3$</td>
<td>0.00</td>
<td>0.0</td>
</tr>
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<td>71</td>
<td>CH$_2$OH + O$_2$ $\rightleftharpoons$ CH$_2$O + HO$_2$</td>
<td>1.000-10$^3$</td>
<td>0.00</td>
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<tr>
<td>72</td>
<td>CH$_4$ + H $\rightleftharpoons$ CH$_3$ + H$_2$</td>
<td>1.300-10$^6$</td>
<td>3.00</td>
<td>4041.0</td>
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<td>73</td>
<td>CH$_4$ + O $\rightleftharpoons$ CH$_3$ + OH</td>
<td>6.920-10$^6$</td>
<td>1.56</td>
<td>4270.0</td>
</tr>
<tr>
<td>74</td>
<td>CH$_4$ + OH $\rightleftharpoons$ CH$_3$ + H$_2$O</td>
<td>1.600-10$^7$</td>
<td>1.83</td>
<td>1395.0</td>
</tr>
<tr>
<td>75</td>
<td>CH$_4$ + HO$_2$ $\rightarrow$ H$_2$O + CH$_3$</td>
<td>1.100-10$^3$</td>
<td>0.00</td>
<td>12400.0</td>
</tr>
<tr>
<td>76</td>
<td>CH$_4$ + CH $\rightarrow$ C$_2$H$_4$ + H</td>
<td>3.000-10$^3$</td>
<td>0.00</td>
<td>-204.0</td>
</tr>
<tr>
<td>77</td>
<td>CH$_4$ + CH$_2$ $\rightarrow$ 2CH$_3$</td>
<td>1.300-10$^3$</td>
<td>0.00</td>
<td>4799.0</td>
</tr>
<tr>
<td>78</td>
<td>CH$_3$OH $\rightleftharpoons$ CH$_3$ + OH</td>
<td>9.510-10$^9$</td>
<td>-4.30</td>
<td>48603.0</td>
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<td>79</td>
<td>CH$_3$OH + H $\rightleftharpoons$ CH$_2$OH + H$_2$</td>
<td>4.000-10$^3$</td>
<td>0.00</td>
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<td>80</td>
<td>CH$_3$OH + O $\rightleftharpoons$ CH$_2$OH + OH</td>
<td>1.000-10$^3$</td>
<td>0.00</td>
<td>2357.0</td>
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<tr>
<td>81</td>
<td>CH$_3$OH + OH $\rightarrow$ CH$_2$OH + H$_2$O</td>
<td>1.000-10$^3$</td>
<td>0.00</td>
<td>854.0</td>
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<tr>
<td>82</td>
<td>CH$_3$OH + HO$_2$ $\rightarrow$ CH$_2$OH + H$_2$O</td>
<td>6.200-10$^{12}$</td>
<td>0.00</td>
<td>9754.0</td>
</tr>
<tr>
<td>83</td>
<td>CH$_3$OH + H$_2$O $\rightarrow$ CH$_2$OH + HO$_2$</td>
<td>1.000-10$^7$</td>
<td>1.70</td>
<td>5761.0</td>
</tr>
<tr>
<td>84</td>
<td>CH$_3$OH + CH$_3$ $\rightarrow$ CH$_4$ + CH$_2$OH</td>
<td>9.000-10$^3$</td>
<td>0.00</td>
<td>4943.0</td>
</tr>
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<td>85</td>
<td>CH$_3$O + CH$_3$OH $\rightarrow$ CH$_3$OH + CH$_3$OH</td>
<td>2.000-10$^{11}$</td>
<td>0.00</td>
<td>3524.0</td>
</tr>
<tr>
<td>86</td>
<td>CH$_3$OH + CH$_3$OH $\rightarrow$ CH$_2$OH + CH$_3$OH</td>
<td>2.200-10$^6$</td>
<td>1.70</td>
<td>5460.0</td>
</tr>
<tr>
<td>87</td>
<td>CH$_3$OH + CH$_2$O $\rightarrow$ 2CH$_3$O</td>
<td>1.500-10$^{12}$</td>
<td>0.00</td>
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<td>88</td>
<td>2CH$_3$O $\rightarrow$ CH$_2$OH + CH$_2$O</td>
<td>3.000-10$^{13}$</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>89</td>
<td>C$_2$H + O $\rightleftharpoons$ CO + CH</td>
<td>1.000-10$^{13}$</td>
<td>0.00</td>
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<tr>
<td>90</td>
<td>C$_2$H + O$_2$ $\rightarrow$ HCCO + O</td>
<td>3.000-10$^{12}$</td>
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<td>0.0</td>
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<tr>
<td>91</td>
<td>HCCO + H $\rightleftharpoons$ CH$_2$ + CO</td>
<td>1.500-10$^{14}$</td>
<td>0.00</td>
<td>0.0</td>
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<td>92</td>
<td>HCCO + O $\rightarrow$ 2CO + H</td>
<td>9.600-10$^{13}$</td>
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<td>0.0</td>
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<td>93</td>
<td>HCCO + CH$_3$ $\rightarrow$ C$_2$H + CO</td>
<td>3.000-10$^{13}$</td>
<td>0.00</td>
<td>0.0</td>
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<td>94</td>
<td>C$_2$H$_2$ + M $\rightarrow$ C$_2$H + H + M</td>
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<td>$A_k$ mole. cm$^{-3}$ s</td>
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<td>$T_{A,k}$ K</td>
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<td>----------</td>
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<td>----------</td>
<td>------------</td>
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<tr>
<td>95</td>
<td>C$_2$H$_2$ + O$_2$ = HCCO + OH</td>
<td>2.000·10$^{8}$</td>
<td>1.50</td>
<td>15155.</td>
</tr>
<tr>
<td>96</td>
<td>C$_2$H$_2$ + H = C$_2$H + H$_2$</td>
<td>1.500·10$^{14}$</td>
<td>0.00</td>
<td>9574.</td>
</tr>
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<td>97</td>
<td>C$_2$H$_2$ + O = CH$_2$ + CO</td>
<td>1.720·10$^{6}$</td>
<td>2.80</td>
<td>253.</td>
</tr>
<tr>
<td>98</td>
<td>C$_2$H$_2$ + O = HCCO + H</td>
<td>1.720·10$^{6}$</td>
<td>2.80</td>
<td>253.</td>
</tr>
<tr>
<td>99</td>
<td>C$_2$H$_2$ + OH = C$_2$H + H$_2$O</td>
<td>6.000·10$^{13}$</td>
<td>0.00</td>
<td>6519.</td>
</tr>
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<td>100</td>
<td>C$_2$H$_2$ + C$_2$H = C$_2$H$_2$ + H</td>
<td>3.000·10$^{13}$</td>
<td>0.00</td>
<td>0.</td>
</tr>
<tr>
<td>101</td>
<td>2C$_2$H$_2$ = C$_2$H$_2$ + H$_2$</td>
<td>4.000·10$^{13}$</td>
<td>0.00</td>
<td>0.</td>
</tr>
<tr>
<td>102</td>
<td>CH$_3$CO + M = CH$_2$ + CO + M</td>
<td>1.000·10$^{16}$</td>
<td>0.00</td>
<td>29828.</td>
</tr>
<tr>
<td>103</td>
<td>CH$_2$CO + H = CH$_3$ + CO</td>
<td>4.200·10$^{13}$</td>
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<td>1936.</td>
</tr>
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<td>104</td>
<td>CH$_2$CO + O = 2CHO</td>
<td>2.300·10$^{12}$</td>
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</tr>
<tr>
<td>105</td>
<td>CH$_2$CO + OH = CH$_2$O + CHO</td>
<td>1.000·10$^{13}$</td>
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<td>0.</td>
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<td>106</td>
<td>C$_2$H$_3$ = CH$_2$H + H</td>
<td>4.700·10$^{40}$</td>
<td>-8.80</td>
<td>23393.</td>
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<tr>
<td>107</td>
<td>C$_2$H$_3$ + OH = C$_2$H$_2$ + H$_2$O</td>
<td>5.000·10$^{13}$</td>
<td>0.00</td>
<td>0.</td>
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<tr>
<td>108</td>
<td>C$_2$H$_3$ + H = C$_2$H$_2$ + H$_2$</td>
<td>1.200·10$^{13}$</td>
<td>0.00</td>
<td>0.</td>
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<tr>
<td>109</td>
<td>C$_2$H$_3$ + O = C$_2$H$_2$ + OH</td>
<td>1.000·10$^{13}$</td>
<td>0.00</td>
<td>0.</td>
</tr>
<tr>
<td>110</td>
<td>C$_2$H$_3$ + O = CH$_3$ + CO</td>
<td>1.000·10$^{13}$</td>
<td>0.00</td>
<td>0.</td>
</tr>
<tr>
<td>111</td>
<td>C$_2$H$_3$ + O = CHO + CH$_2$</td>
<td>1.000·10$^{13}$</td>
<td>0.00</td>
<td>0.</td>
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<tr>
<td>112</td>
<td>C$_2$H$_3$ + O$_2$ = C$_2$H$_2$ + HO$_2$</td>
<td>5.400·10$^{12}$</td>
<td>0.00</td>
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</tr>
<tr>
<td>113</td>
<td>CH$_3$CO = CH$_2$ + CO</td>
<td>2.320·10$^{26}$</td>
<td>-5.00</td>
<td>9033.</td>
</tr>
<tr>
<td>114</td>
<td>CH$_3$CO + H = CH$_2$CO + H$_2$</td>
<td>2.000·10$^{13}$</td>
<td>0.00</td>
<td>0.</td>
</tr>
<tr>
<td>115</td>
<td>CH$_3$CO + CH$_3$ = C$_2$H$_6$ + CO</td>
<td>5.000·10$^{13}$</td>
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<td>0.</td>
</tr>
<tr>
<td>116</td>
<td>C$_2$H$_4$ + M = C$_2$H$_2$ + H$_2$ + M</td>
<td>2.500·10$^{17}$</td>
<td>0.00</td>
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</tr>
<tr>
<td>117</td>
<td>C$_2$H$_4$ + M = C$_2$H$_3$ + H + M</td>
<td>1.700·10$^{18}$</td>
<td>0.00</td>
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</tr>
<tr>
<td>118</td>
<td>C$_2$H$_4$ + H = C$_2$H$_3$ + H$_2$</td>
<td>1.700·10$^{15}$</td>
<td>0.00</td>
<td>7565.</td>
</tr>
<tr>
<td>119</td>
<td>C$_2$H$_4$ + O = CH$_2$CHO + H</td>
<td>5.200·10$^{5}$</td>
<td>2.08</td>
<td>0.</td>
</tr>
<tr>
<td>120</td>
<td>C$_2$H$_4$ + O = CHO + CH$_3$</td>
<td>1.210·10$^{6}$</td>
<td>2.08</td>
<td>0.</td>
</tr>
<tr>
<td>121</td>
<td>C$_2$H$_4$ + OH = C$_2$H$_3$ + H$_2$O</td>
<td>6.500·10$^{13}$</td>
<td>0.00</td>
<td>2995.</td>
</tr>
<tr>
<td>122</td>
<td>CH$_3$CHO + M = CH$_3$ + CHO + M</td>
<td>7.000·10$^{15}$</td>
<td>0.00</td>
<td>41230.</td>
</tr>
<tr>
<td>123</td>
<td>CH$_3$CHO + H = CH$_3$CO + H$_2$</td>
<td>2.100·10$^{9}$</td>
<td>1.16</td>
<td>1215.</td>
</tr>
<tr>
<td>124</td>
<td>CH$_3$CHO + H = CH$_2$CHO + H$_2$</td>
<td>2.000·10$^{9}$</td>
<td>1.16</td>
<td>1215.</td>
</tr>
<tr>
<td>125</td>
<td>CH$_3$CHO + O = CH$_3$CO + OH</td>
<td>5.000·10$^{12}$</td>
<td>0.00</td>
<td>914.</td>
</tr>
<tr>
<td>126</td>
<td>CH$_3$CHO + O = CH$_3$CHO + OH</td>
<td>8.000·10$^{11}$</td>
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<td>914.</td>
</tr>
<tr>
<td>127</td>
<td>CH$_3$CHO + O$_2$ = CH$_3$CO + HO$_2$</td>
<td>4.000·10$^{13}$</td>
<td>0.00</td>
<td>19761.</td>
</tr>
<tr>
<td>128</td>
<td>CH$_3$CHO + OH = CH$_3$CO + H$_2$O</td>
<td>2.300·10$^{10}$</td>
<td>0.73</td>
<td>-565.</td>
</tr>
<tr>
<td>129</td>
<td>CH$_3$CHO + HO$_2$ = CH$_3$CO + H$_2$O</td>
<td>6.000·10$^{12}$</td>
<td>0.00</td>
<td>6014.</td>
</tr>
<tr>
<td>130</td>
<td>CH$_3$CHO + CH$_2$ = CH$_3$CO + CH$_3$</td>
<td>2.500·10$^{12}$</td>
<td>0.00</td>
<td>1912.</td>
</tr>
<tr>
<td>131</td>
<td>CH$_3$CHO + CH$_3$ = CH$_3$CO + CH$_4$</td>
<td>2.000·10$^{6}$</td>
<td>5.54</td>
<td>1239.</td>
</tr>
<tr>
<td>132</td>
<td>C$_2$H$_3$ = C$_2$H$_4$ + H</td>
<td>1.020·10$^{43}$</td>
<td>-9.10</td>
<td>26965.</td>
</tr>
<tr>
<td>133</td>
<td>C$_2$H$_3$ + H = 2CH$_3$</td>
<td>3.000·10$^{13}$</td>
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<td>0.</td>
</tr>
<tr>
<td>134</td>
<td>C$_2$H$_3$ + O = CH$_3$CHO + H</td>
<td>5.000·10$^{13}$</td>
<td>0.00</td>
<td>0.</td>
</tr>
<tr>
<td>135</td>
<td>C$_2$H$_3$ + O = CH$_2$O + CH$_3$</td>
<td>1.000·10$^{13}$</td>
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<td>0.</td>
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<tr>
<td>136</td>
<td>C$_2$H$_3$ + O$_2$ = C$_2$H$_4$ + HO$_2$</td>
<td>1.100·10$^{10}$</td>
<td>0.00</td>
<td>-758.</td>
</tr>
<tr>
<td>137</td>
<td>C$_2$H$_5$ + CH$_3$ = C$_2$H$_4$ + CH$_4$</td>
<td>2.800·10$^{13}$</td>
<td>0.00</td>
<td>0.</td>
</tr>
<tr>
<td>138</td>
<td>2C$_2$H$_5$ = C$_2$H$_4$ + C$_2$H$_6$</td>
<td>1.400·10$^{12}$</td>
<td>0.00</td>
<td>0.</td>
</tr>
<tr>
<td>139</td>
<td>C$_2$H$_6$ + H = C$_2$H$_5$ + H$_2$</td>
<td>1.400·10$^{9}$</td>
<td>1.50</td>
<td>3741.</td>
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<tr>
<td>140</td>
<td>C$_2$H$_6$ + O = C$_2$H$_5$ + OH</td>
<td>1.000·10$^{9}$</td>
<td>1.50</td>
<td>2935.</td>
</tr>
<tr>
<td>141</td>
<td>C$_2$H$_6$ + OH = C$_2$H$_5$ + H$_2$O</td>
<td>7.200·10$^{6}$</td>
<td>2.00</td>
<td>433.</td>
</tr>
<tr>
<td>142</td>
<td>C$_2$H$_6$ + HO$_2$ = C$_2$H$_5$ + H$_2$O</td>
<td>1.700·10$^{13}$</td>
<td>0.00</td>
<td>10332.</td>
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### Table B.3, continued

<table>
<thead>
<tr>
<th>no.</th>
<th>reaction</th>
<th>(A_k) mole cm(^{-3}) s</th>
<th>(\beta_k)</th>
<th>(T_{A_k}) K</th>
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</thead>
<tbody>
<tr>
<td>191</td>
<td>(\text{C}_4\text{H}_6 + \text{OH} \rightleftharpoons \text{C}_2\text{H}_5 + \text{CH}_2\text{CO})</td>
<td>1.000 (\times) 10(^{-12})</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>192</td>
<td>(\text{C}_4\text{H}_6 + \text{OH} \rightleftharpoons \text{C}_2\text{H}_3 + \text{CH}_3\text{CHO})</td>
<td>5.000 (\times) 10(^{-12})</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>193</td>
<td>(\text{t-C}_4\text{H}_8 \rightleftharpoons \text{t-C}_2\text{H}_8)</td>
<td>4.000 (\times) 10(^{-11})</td>
<td>0.00</td>
<td>30189.0</td>
</tr>
<tr>
<td>194</td>
<td>(\text{t-C}_4\text{H}_8 \rightleftharpoons \text{c-C}_4\text{H}_8)</td>
<td>4.000 (\times) 10(^{-11})</td>
<td>0.00</td>
<td>30189.0</td>
</tr>
<tr>
<td>195</td>
<td>(\text{t-C}_4\text{H}_8 \rightleftharpoons \text{C}_2\text{H}_3 + \text{C}_2\text{H}_5)</td>
<td>2.000 (\times) 10(^{-18})</td>
<td>-1.00</td>
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</tr>
<tr>
<td>196</td>
<td>(\text{t-C}_4\text{H}_8 + \text{O} \rightleftharpoons \text{C}_2\text{H}_3\text{CHO} + \text{C}_2\text{H}_4)</td>
<td>2.510 (\times) 10(^{-12})</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>197</td>
<td>(\text{t-C}_4\text{H}_8 + \text{O} \rightleftharpoons \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5 + \text{CO})</td>
<td>1.630 (\times) 10(^{-13})</td>
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<td>198</td>
<td>(\text{t-C}_4\text{H}_8 + \text{O} \rightleftharpoons \text{C}_2\text{H}_6 + \text{CH}_2\text{O})</td>
<td>7.200 (\times) 10(^{5})</td>
<td>2.30</td>
<td>-529.0</td>
</tr>
<tr>
<td>199</td>
<td>(\text{t-C}_4\text{H}_8 + \text{O} \rightleftharpoons \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5)</td>
<td>1.000 (\times) 10(^{11})</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>200</td>
<td>(\text{t-C}_4\text{H}_8 + \text{O} \rightleftharpoons \text{CH}_3 + \text{C}_2\text{H}_6 + \text{CO})</td>
<td>1.000 (\times) 10(^{10})</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>201</td>
<td>(\text{t-C}_4\text{H}_8 + \text{O} \rightleftharpoons \text{n-C}_2\text{H}_7 + \text{CH}_2\text{O})</td>
<td>6.500 (\times) 10(^{-12})</td>
<td>0.00</td>
<td>0.0</td>
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<tr>
<td>202</td>
<td>(\text{t-C}_4\text{H}_8 + \text{O} \rightleftharpoons \text{C}_2\text{H}_4 + \text{CH}_3\text{CHO})</td>
<td>1.000 (\times) 10(^{-12})</td>
<td>0.00</td>
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<tr>
<td>203</td>
<td>(\text{t-C}_4\text{H}_8 + \text{O} \rightleftharpoons \text{i-C}_3\text{H}_7 + \text{CHO})</td>
<td>6.000 (\times) 10(^{-6})</td>
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<td>0.0</td>
</tr>
<tr>
<td>204</td>
<td>(\text{t-C}_4\text{H}_8 + \text{O} \rightleftharpoons \text{C}_2\text{H}_5 + \text{CH}_3\text{CHO})</td>
<td>1.510 (\times) 10(^{-13})</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>205</td>
<td>(\text{c-C}_4\text{H}_8 \rightleftharpoons \text{t-C}_4\text{H}_8)</td>
<td>1.000 (\times) 10(^{-13})</td>
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</tr>
<tr>
<td>206</td>
<td>(\text{c-C}_4\text{H}_8 \rightleftharpoons \text{c-C}_2\text{H}_6 + \text{H}_2)</td>
<td>1.000 (\times) 10(^{-13})</td>
<td>0.00</td>
<td>32967.0</td>
</tr>
<tr>
<td>207</td>
<td>(\text{c-C}_4\text{H}_8 + \text{OH} \rightleftharpoons \text{C}_2\text{H}_5 + \text{CH}_3\text{CHO})</td>
<td>1.400 (\times) 10(^{-13})</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>208</td>
<td>(\text{c-C}_4\text{H}_8 + \text{O} \rightleftharpoons \text{i-C}_3\text{H}_7 + \text{CHO})</td>
<td>6.030 (\times) 10(^{-12})</td>
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<td>0.0</td>
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<tr>
<td>209</td>
<td>(\text{c-C}_4\text{H}_8 + \text{O} \rightleftharpoons \text{i-C}_3\text{H}_7 + \text{CHO})</td>
<td>1.000 (\times) 10(^{-12})</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>210</td>
<td>(\text{p-C}_4\text{H}_9 \rightleftharpoons \text{C}_2\text{H}_4 + \text{C}_2\text{H}_3)</td>
<td>2.500 (\times) 10(^{-13})</td>
<td>0.00</td>
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</tr>
<tr>
<td>211</td>
<td>(\text{p-C}_4\text{H}_9 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H})</td>
<td>1.300 (\times) 10(^{-13})</td>
<td>0.00</td>
<td>19436.0</td>
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<tr>
<td>212</td>
<td>(\text{p-C}_4\text{H}_9 + \text{O} \rightleftharpoons \text{i-C}_4\text{H}_8 + \text{HO}_2)</td>
<td>1.000 (\times) 10(^{-12})</td>
<td>0.00</td>
<td>1010.0</td>
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<tr>
<td>213</td>
<td>(\text{s-C}_4\text{H}_9 \rightleftharpoons \text{t-C}_4\text{H}_8 + \text{H})</td>
<td>5.000 (\times) 10(^{-13})</td>
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<td>19088.0</td>
</tr>
<tr>
<td>214</td>
<td>(\text{s-C}_4\text{H}_9 \rightleftharpoons \text{c-C}_4\text{H}_8 + \text{H})</td>
<td>5.000 (\times) 10(^{-13})</td>
<td>0.00</td>
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</tr>
<tr>
<td>215</td>
<td>(\text{s-C}_4\text{H}_9 \rightleftharpoons \text{i-C}_4\text{H}_8 + \text{H})</td>
<td>2.000 (\times) 10(^{-13})</td>
<td>0.00</td>
<td>20350.0</td>
</tr>
<tr>
<td>216</td>
<td>(\text{s-C}_4\text{H}_9 \rightleftharpoons \text{C}_2\text{H}_5 + \text{CH}_3)</td>
<td>4.000 (\times) 10(^{-14})</td>
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</tr>
<tr>
<td>217</td>
<td>(\text{s-C}_4\text{H}_9 + \text{O}_2 \rightleftharpoons \text{i-C}_4\text{H}_8 + \text{HO}_2)</td>
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<tr>
<td>218</td>
<td>(\text{s-C}_4\text{H}_9 + \text{O}_2 \rightleftharpoons \text{t-C}_4\text{H}_8 + \text{HO}_2)</td>
<td>2.000 (\times) 10(^{-13})</td>
<td>0.00</td>
<td>2141.0</td>
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<tr>
<td>219</td>
<td>(\text{s-C}_4\text{H}_9 + \text{O}_2 \rightleftharpoons \text{c-C}_4\text{H}_8 + \text{HO}_2)</td>
<td>2.000 (\times) 10(^{-13})</td>
<td>0.00</td>
<td>2141.0</td>
</tr>
</tbody>
</table>

Third-body efficiencies are: \(\text{CH}_4\): 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; all other species 1.
# Appendix B. Reaction mechanisms

## Table B.4: Glarborg mechanism for hydrocarbon oxidation.

<table>
<thead>
<tr>
<th>no.</th>
<th>reaction</th>
<th>$A_k$ mole, cm$^{-3}$, s</th>
<th>$\beta_k$</th>
<th>$T_{A_k}$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O + OH $\rightleftharpoons$ H + O$_2$</td>
<td>4.000·10$^{14}$</td>
<td>-0.50</td>
<td>0.</td>
</tr>
<tr>
<td>2</td>
<td>H$_2$ + O $\rightleftharpoons$ H + OH</td>
<td>5.000·10$^{14}$</td>
<td>2.67</td>
<td>3165.</td>
</tr>
<tr>
<td>3</td>
<td>H$_2$ + OH $\rightleftharpoons$ H$_2$O + H</td>
<td>1.000·10$^{8}$</td>
<td>1.60</td>
<td>1660.</td>
</tr>
<tr>
<td>4</td>
<td>2OH $\rightleftharpoons$ H$_2$O + O</td>
<td>1.500·10$^{9}$</td>
<td>1.14</td>
<td>50.</td>
</tr>
<tr>
<td>5</td>
<td>H + OH + M $\rightleftharpoons$ H$_2$O + M</td>
<td>2.200·10$^{22}$</td>
<td>-2.00</td>
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</tr>
<tr>
<td></td>
<td>Efficiencies H$_2$O: 5.0</td>
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<td></td>
<td></td>
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<tr>
<td>6</td>
<td>2O + M $\rightleftharpoons$ O$_2$ + M</td>
<td>1.900·10$^{13}$</td>
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<td>-900.</td>
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<td>7</td>
<td>2H + M $\rightleftharpoons$ H$_2$ + M</td>
<td>1.000·10$^{18}$</td>
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<td>8</td>
<td>2H + H$_2$ $\rightleftharpoons$ 2H$_2$</td>
<td>9.200·10$^{16}$</td>
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<tr>
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<td>Efficiencies H$_2$O: 0.0; H$_2$: 0.0; CO$_2$: 0.0</td>
<td></td>
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<tr>
<td>9</td>
<td>2H + H$_2$O $\rightleftharpoons$ H$_2$ + H$_2$O</td>
<td>6.000·10$^{19}$</td>
<td>-1.25</td>
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<tr>
<td>10</td>
<td>2H + CO$_2$ $\rightleftharpoons$ H$_2$ + CO$_2$</td>
<td>5.500·10$^{20}$</td>
<td>-2.00</td>
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<tr>
<td>11</td>
<td>H$_2$ + O$_2$ $\rightleftharpoons$ 2OH</td>
<td>1.700·10$^{13}$</td>
<td>0.00</td>
<td>24000.</td>
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<tr>
<td>12</td>
<td>H + O$_2$ + M $\rightleftharpoons$ HO$_2$ + M</td>
<td>6.900·10$^{17}$</td>
<td>-0.80</td>
<td>0.</td>
</tr>
<tr>
<td></td>
<td>Efficiencies H$_2$O: 18.6; H$_2$: 3.33; N$_2$: 1.26; CO: 2.11; CO$_2$: 4.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>HO$_2$ + H $\rightleftharpoons$ H$_2$ + O$_2$</td>
<td>4.300·10$^{13}$</td>
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<td>14</td>
<td>HO$_2$ + H $\rightleftharpoons$ 2OH</td>
<td>1.700·10$^{14}$</td>
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<td>15</td>
<td>HO$_2$ + O $\rightleftharpoons$ OH + O$_2$</td>
<td>3.200·10$^{13}$</td>
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<td>0.</td>
</tr>
<tr>
<td>16</td>
<td>HO$_2$ + OH $\rightleftharpoons$ H$_2$O + O$_2$</td>
<td>2.900·10$^{13}$</td>
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<td>17</td>
<td>2HO$_2$ $\rightleftharpoons$ H$_2$O$_2$ + O$_2$</td>
<td>1.800·10$^{2}$</td>
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<td>0.</td>
</tr>
<tr>
<td>18</td>
<td>H$_2$O$_2$ + M $\rightleftharpoons$ 2OH + M</td>
<td>1.300·10$^{23}$</td>
<td>-4.86</td>
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<tr>
<td>19</td>
<td>H$_2$O$_2$ + H $\rightleftharpoons$ HO$_2$ + H$_2$</td>
<td>1.700·10$^{12}$</td>
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<td>1890.</td>
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<td>20</td>
<td>H$_2$O$_2$ + O $\rightleftharpoons$ HO$_2$ + OH</td>
<td>9.600·10$^{6}$</td>
<td>2.00</td>
<td>2000.</td>
</tr>
<tr>
<td>21</td>
<td>H$_2$O$_2$ + OH $\rightleftharpoons$ HO$_2$ + H$_2$O</td>
<td>4.600·10$^{12}$</td>
<td>0.00</td>
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<td>24</td>
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<tr>
<td>25</td>
<td>CO + HO$_2$ $\rightleftharpoons$ CO$_2$ + OH</td>
<td>5.800·10$^{3}$</td>
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<tr>
<td>26</td>
<td>CH$_3$ + H (+M) $\rightleftharpoons$ CH$_4$ (+M)</td>
<td>6.000·10$^{16}$</td>
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SRI centering: 0.45; 797., 979.

Efficiencies H$_2$O: 5.0; H$_2$: 2.0; CO: 2.0; CO$_2$: 3.0

<table>
<thead>
<tr>
<th>no.</th>
<th>reaction</th>
<th>$A_k$ mole, cm$^{-3}$, s</th>
<th>$\beta_k$</th>
<th>$T_{A_k}$ K</th>
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<tr>
<td>27</td>
<td>CH$_4$ + H $\rightleftharpoons$ CH$_3$ + H$_2$</td>
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<td>CH$_4$ + O $\rightleftharpoons$ CH$_3$ + HO</td>
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<td>CH$_4$ + OH $\rightleftharpoons$ CH$_3$ + HO$_2$</td>
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<td>CH$_3$ + O $\rightleftharpoons$ CH$_2$O + H</td>
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<td>38</td>
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### Table B.4, continued

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<th>$\beta_k$</th>
<th>$T_{A,k}$ (K)</th>
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<tr>
<td>40</td>
<td>CH$_3$ + O$_2$ $\rightarrow$ CH$_2$O + OH</td>
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<tr>
<td>42</td>
<td>CH$_3$ + CH$_2$O $\rightarrow$ CH$_4$ + HCO</td>
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<tr>
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<tr>
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<td>CH$_3$ + CH$_2$ $\rightarrow$ C$_2$H$_4$ + H</td>
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<td>46</td>
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<tr>
<td>48</td>
<td>CH$_3$O + M $\rightarrow$ CH$_2$O + H + M</td>
<td>$1.90 \times 10^{26}$</td>
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<tr>
<td>49</td>
<td>CH$_3$O + H $\rightarrow$ CH$_2$O + H$_2$</td>
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<tr>
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<td>51</td>
<td>CH$_3$O + OH $\rightarrow$ CH$_2$O + H$_2$O</td>
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<tr>
<td>52</td>
<td>CH$_3$O + O$_2$ $\rightarrow$ CH$_2$O + HO$_2$</td>
<td>$4.00 \times 10^{10}$</td>
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<tr>
<td>53</td>
<td>CH$_2$O + M $\rightarrow$ CH$_2$O + H + M</td>
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<tr>
<td>54</td>
<td>CH$_2$O + H $\rightarrow$ CH$_3$ + OH</td>
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<tr>
<td>55</td>
<td>CH$_2$O + H $\rightarrow$ CH$_2$O + H$_2$</td>
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<td>56</td>
<td>CH$_2$O + O $\rightarrow$ CH$_2$O + OH</td>
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<td>57</td>
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<tr>
<td>58</td>
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<td>59</td>
<td>CH$_2$O + M $\rightarrow$ HCO + H + M</td>
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<td>CH$_2$O + H $\rightarrow$ HCO + H$_2$</td>
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<td>CH$_2$O + O $\rightarrow$ HCO + OH</td>
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<tr>
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<td>CH$_2$O + OH $\rightarrow$ HCO + H$_2$O</td>
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<td>CH$_2$O + O$_2$ $\rightarrow$ HCO + HO$_2$</td>
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<td>$1.90 \times 10^{17}$</td>
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</table>

**Efficiencies H$_2$O: 5.0;**
**CH$_4$: 2.8; H$_2$: 1.9; CO: 1.9; CO$_2$: 3.0**

<table>
<thead>
<tr>
<th>no.</th>
<th>reaction</th>
<th>$A_k$ (mole, cm$^{-3}$, s)</th>
<th>$\beta_k$</th>
<th>$T_{A,k}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>67</td>
<td>HCO + H $\rightarrow$ CO + H$_2$</td>
<td>$7.20 \times 10^{13}$</td>
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<td>0.</td>
</tr>
<tr>
<td>68</td>
<td>HCO + O $\rightarrow$ CO + OH</td>
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</tr>
<tr>
<td>69</td>
<td>HCO + O $\rightarrow$ CO$_2$ + H</td>
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<tr>
<td>70</td>
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<tr>
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<td>CH$_2$ + OH $\rightarrow$ CH + H$_2$O</td>
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<tr>
<td>79</td>
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<tr>
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<td>750.</td>
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<td>83</td>
<td>CH$_2$ + CH $\rightarrow$ C$_2$H$_3$ + H</td>
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<tr>
<td>no.</td>
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<td>$\Delta k$ \text{ mole, cm}^{-3} \cdot \text{s}</td>
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<td>CH$_2$ + C $\rightleftharpoons$ C$_2$H + H</td>
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<td>Efficiencies H$_2$O: 3.0; C$_2$H$_2$: 4.0; H: 20.0</td>
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<tr>
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<tr>
<td>107</td>
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### Appendix B. Reaction mechanisms

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<td>mole. cm$^{-3}$ s</td>
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<td>K</td>
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<td>$1.000 \times 10^{13}$</td>
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<td>$2.000 \times 10^{13}$</td>
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<td>143</td>
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<td>0.0</td>
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<td>$\text{C}_2\text{H}_2 + \text{O}_2 \rightleftharpoons \text{HCCO} + \text{HCO}$</td>
<td>$5.000 \times 10^{13}$</td>
<td>0.00</td>
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## APPENDIX C

### Rate constants for thermal NO formation

**TABLE C.1**: Reaction rates for $\text{N}_2 + \text{O} \to \text{NO} + \text{N}$; units in $\text{m}^3 \cdot \text{k mole}^{-1} \cdot \text{s}^{-1}$.

<table>
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<th>$A$</th>
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<th>$T_A$</th>
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<th>$k_{1500}$</th>
<th>$k_{2000}$</th>
<th>$k_{2500}$</th>
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<td>Bockhorn (1990)</td>
<td>$1.80 \times 10^{11}$</td>
<td>0.</td>
<td>38367.</td>
<td>$3.91 \times 10^{-6}$</td>
<td>$1.40 \times 10^{9}$</td>
<td>$8.39 \times 10^{9}$</td>
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<td>Hanson and Salimian (1984)</td>
<td>$1.82 \times 10^{11}$</td>
<td>0.</td>
<td>38370.</td>
<td>$3.95 \times 10^{-6}$</td>
<td>$1.42 \times 10^{9}$</td>
<td>$8.47 \times 10^{9}$</td>
<td>$3.93 \times 10^{4}$</td>
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<td>Hayhurst and Vince (1980)</td>
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<td>0.</td>
<td>37890.</td>
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<td>$5.35 \times 10^{-1}$</td>
<td>$2.96 \times 10^{2}$</td>
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<td>Jensen and Jones (1978)</td>
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<td>$2.46 \times 10^{-6}$</td>
<td>$7.79 \times 10^{-1}$</td>
<td>$4.39 \times 10^{2}$</td>
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<td>Blauwens et al. (1977)</td>
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<td>0.</td>
<td>38000.</td>
<td>$1.89 \times 10^{-6}$</td>
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<td>$3.38 \times 10^{2}$</td>
<td>$1.51 \times 10^{4}$</td>
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<tr>
<td>Ay and Sichel (1976)</td>
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<td>$4.86 \times 10^{-6}$</td>
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<td>$8.25 \times 10^{2}$</td>
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<tr>
<td>Bowman (1975)</td>
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<td>Iverach et al. (1973)</td>
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<td>37943.</td>
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<tr>
<td>Fenimore (1973)</td>
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<td>$1.40 \times 10^{0}$</td>
<td>$8.39 \times 10^{2}$</td>
<td>$3.89 \times 10^{4}$</td>
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**TABLE C.2**: Reaction rates for $\text{NO} + \text{N} \to \text{N}_2 + \text{O}$

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<th>$k_{1500}$</th>
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<tr>
<td>Glarborg et al. (1986)</td>
<td>$3.30 \times 10^{9}$</td>
<td>0.3</td>
<td>0.</td>
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<td>$2.96 \times 10^{10}$</td>
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<td>Ay and Sichel (1976)</td>
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<td>$3.05 \times 10^{10}$</td>
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</tr>
<tr>
<td>Bowman (1975)</td>
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<td>0.</td>
<td>$1.60 \times 10^{10}$</td>
<td>$1.60 \times 10^{10}$</td>
<td>$1.60 \times 10^{10}$</td>
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</tr>
<tr>
<td>Fenimore (1973)</td>
<td>$1.30 \times 10^{10}$</td>
<td>0.</td>
<td>0.</td>
<td>$1.30 \times 10^{10}$</td>
<td>$1.30 \times 10^{10}$</td>
<td>$1.30 \times 10^{10}$</td>
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</tr>
<tr>
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**TABLE C.3**: Reaction rates for $\text{N} + \text{O}_2 \to \text{NO} + \text{O}$

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<th>$k_{1500}$</th>
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<td>1.</td>
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<td>$2.77 \times 10^{5}$</td>
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<td>$2.66 \times 10^{9}$</td>
<td>$4.56 \times 10^{9}$</td>
</tr>
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<td>Glarborg et al. (1986)</td>
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<td>1.</td>
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<td>$2.72 \times 10^{5}$</td>
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<td>$2.64 \times 10^{9}$</td>
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<tr>
<td>Jensen and Jones (1978)</td>
<td>$6.62 \times 10^{6}$</td>
<td>1.</td>
<td>3150.</td>
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<td>$4.69 \times 10^{9}$</td>
</tr>
<tr>
<td>Ay and Sichel (1976)</td>
<td>$6.40 \times 10^{6}$</td>
<td>1.</td>
<td>3140.</td>
<td>$2.77 \times 10^{5}$</td>
<td>$1.18 \times 10^{8}$</td>
<td>$2.66 \times 10^{9}$</td>
<td>$4.56 \times 10^{9}$</td>
</tr>
<tr>
<td>Bowman (1975)</td>
<td>$6.40 \times 10^{6}$</td>
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<td>$1.18 \times 10^{8}$</td>
<td>$2.65 \times 10^{9}$</td>
<td>$4.54 \times 10^{9}$</td>
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<tr>
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<td>$2.05 \times 10^{9}$</td>
<td>$3.06 \times 10^{9}$</td>
</tr>
<tr>
<td>present study</td>
<td>$6.40 \times 10^{6}$</td>
<td>1.</td>
<td>3139.</td>
<td>$2.77 \times 10^{5}$</td>
<td>$1.18 \times 10^{8}$</td>
<td>$2.66 \times 10^{9}$</td>
<td>$4.56 \times 10^{9}$</td>
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### TABLE C.4: Reaction rates for $\text{NO} + \text{O} \rightarrow \text{N} + \text{O}_2$

<table>
<thead>
<tr>
<th>author</th>
<th>$A$</th>
<th>$\beta$</th>
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<th>$k_{1500}$</th>
<th>$k_{2000}$</th>
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<tr>
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<td>19235</td>
<td>$6.02 \times 10^9$</td>
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<td>$1.81 \times 10^5$</td>
<td>$1.55 \times 10^6$</td>
</tr>
<tr>
<td>Hanson and Salimian (1984)</td>
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<td>20820</td>
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<tr>
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<td>$1.74 \times 10^6$</td>
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<td>Ay and Sichel (1976)</td>
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<td>1.106</td>
<td>19075</td>
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<td>$5.47 \times 10^3$</td>
<td>$1.81 \times 10^5$</td>
<td>$1.56 \times 10^6$</td>
</tr>
<tr>
<td>Bowman (1975)</td>
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<td>1.0</td>
<td>19500</td>
<td>$5.11 \times 10^9$</td>
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<td>$1.75 \times 10^5$</td>
<td>$1.54 \times 10^6$</td>
</tr>
<tr>
<td>Baulch et al. (1973)</td>
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<td>1.0</td>
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<td>$1.76 \times 10^5$</td>
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<tr>
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<td>$6.04 \times 10^9$</td>
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### TABLE C.5: Reaction rates for $\text{N} + \text{OH} \rightarrow \text{NO} + \text{H}$

<table>
<thead>
<tr>
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<th>$A$</th>
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<tr>
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<td>$3.00 \times 10^5$</td>
<td>$3.00 \times 10^6$</td>
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<tr>
<td>Glarborg et al. (1986)</td>
<td>$3.80 \times 10^6$</td>
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<td>0.0</td>
<td>$3.80 \times 10^6$</td>
<td>$3.80 \times 10^3$</td>
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</tr>
<tr>
<td>Bowman (1975)</td>
<td>$1.00 \times 10^7$</td>
<td>0.0</td>
<td>0.0</td>
<td>$1.00 \times 10^7$</td>
<td>$1.00 \times 10^3$</td>
<td>$1.00 \times 10^5$</td>
<td>$1.00 \times 10^6$</td>
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<td>0.0</td>
<td>$3.00 \times 10^6$</td>
<td>$3.00 \times 10^3$</td>
<td>$3.00 \times 10^5$</td>
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### TABLE C.6: Reaction rates for $\text{NO} + \text{H} \rightarrow \text{N} + \text{OH}$

<table>
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<th>author</th>
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<th>$\beta$</th>
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<th>$k_{1500}$</th>
<th>$k_{2000}$</th>
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<tbody>
<tr>
<td>Bockhorn (1990)</td>
<td>$8.12 \times 10^6$</td>
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<td>24125</td>
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</tr>
<tr>
<td>Bowman (1975)</td>
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<td>0.0</td>
<td>23650</td>
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<td>$2.84 \times 10^4$</td>
<td>$1.46 \times 10^6$</td>
<td>$1.56 \times 10^7$</td>
</tr>
<tr>
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<td>0.0</td>
<td>24125</td>
<td>$2.71 \times 10^9$</td>
<td>$8.41 \times 10^3$</td>
<td>$4.69 \times 10^5$</td>
<td>$5.23 \times 10^6$</td>
</tr>
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</table>

### TABLE C.7: Equilibrium constant for short Zel’dovich mechanism

<table>
<thead>
<tr>
<th>author</th>
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<tr>
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<tr>
<td>Jensen and Jones (1978)</td>
<td>$21.62$</td>
<td>0.0</td>
<td>$21780$</td>
<td>$7.51 \times 10^9$</td>
<td>$1.07 \times 10^{-5}$</td>
<td>$4.03 \times 10^{-4}$</td>
<td>$3.56 \times 10^{-3}$</td>
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<tr>
<td>Ay and Sichel (1976)</td>
<td>$19.00$</td>
<td>0.013</td>
<td>$21736$</td>
<td>$1.52 \times 10^{-8}$</td>
<td>$1.05 \times 10^{-5}$</td>
<td>$3.98 \times 10^{-4}$</td>
<td>$3.51 \times 10^{-3}$</td>
</tr>
<tr>
<td>Bowman (1975)</td>
<td>$20.27$</td>
<td>0.0</td>
<td>$21650$</td>
<td>$8.01 \times 10^{-9}$</td>
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<td>$3.50 \times 10^{-3}$</td>
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</table>

### TABLE C.8: Square root of equilibrium constant of the $\text{O}_2$ dissociation reaction

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<th>$\sqrt{K_{2000}}$</th>
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<td>$9.01 \times 10^{-9}$</td>
<td>$1.13 \times 10^{-6}$</td>
<td>$2.00 \times 10^{-5}$</td>
</tr>
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<td>Warnatz (1984)</td>
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<td>-0.5</td>
<td>$27122$</td>
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<td>$1.89 \times 10^{-8}$</td>
<td>$2.00 \times 10^{-6}$</td>
<td>$3.37 \times 10^{-5}$</td>
</tr>
<tr>
<td>Jensen and Jones (1978)</td>
<td>$153.0$</td>
<td>-0.5</td>
<td>$29790$</td>
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<td>$9.37 \times 10^{-9}$</td>
<td>$1.16 \times 10^{-6}$</td>
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<td>$3.63 \times 10^{-9}$</td>
<td>$5.59 \times 10^{-7}$</td>
<td>$1.12 \times 10^{-5}$</td>
</tr>
<tr>
<td>present study</td>
<td>$149.9$</td>
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<td>$9.11 \times 10^{-9}$</td>
<td>$1.13 \times 10^{-6}$</td>
<td>$2.00 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY


Bibliography


Bibliography


PRINCIPAL SYMBOLS

\(a_{n,i}\) polynomial coefficients in CHEMKIN tables

\(C_i\) species concentration (kmole\cdot m^{-3})

\(c_p\) specific heat (J\cdot kg^{-1}\cdot K^{-1})

\(ID\) overall molecular diffusion coefficient (m\(^2\)\cdot s^{-1})

\(ID_i\) effective species molecular diffusion coefficient (m\(^2\)\cdot s^{-1})

\(ID_{ij}\) effective species-species molecular diffusion coefficient (m\(^2\)\cdot s^{-1})

\(D_{ij}\) binary molecular diffusion coefficient (m\(^2\)\cdot s^{-1})

\(Da\) Damköhler number

\(E\) total energy per unit mass (J/kg)

\(f\) probability density function

\(g\) gravitational acceleration vector (m/s\(^2\))

\(h\) enthalpy per unit mass (J/kg)

\(H_i\) species molar enthalpy (J/kmole)

\(J\) total convective and diffusive flux

\(k\) turbulent kinetic energy per unit mass (J/kg)

\(K\) local extinction coefficient (m\(^{-1}\))

\(\ell\) length scale (m)

\(Le\) Lewis number

\(M_i\) species molar mass (kg/kmole)

\(p\) pressure (Pa)

\(Pe\) Péclet number

\(Pr\) Prandtl number

\(q\) energy flux vector (W\cdot m^{-2})

\(R^0\) universal gas constant (J\cdot kmole^{-1}\cdot K^{-1})

\(r\) radial coordinate (m)

\(r\) position vector (m)

\(Re\) Reynolds number

\(S\) source term in transport equation

\(Sc\) Schmidt number

\(t\) time (s)

\(T\) temperature (K)

\(u\) velocity component in \(x\)-direction (m/s)

\(v\) velocity component in \(y\)- or \(r\)-direction (m/s)

\(\nu\) velocity vector (m/s)

\(V\) species diffusion velocity vector (m/s)

\(w\) velocity component in \(z\)- or \(\theta\)-direction (m/s)

\(wb\) reaction rate (kg\cdot m^{-3}\cdot s^{-1})

\(x\) position vector (m)

\(x\) axial coordinate in cylindrical geometry (m)

\(x, y, z\) Cartesian coordinates (m)
Principal symbols

\( X_i \)  
\( Y_i \)  
\( Z_i \)  

species mole fraction  
species mass fraction  
element mass fraction  

Greek symbols

\( \alpha \)  
\( \beta \)  
\( \gamma \)  
\( \Gamma \)  
\( \epsilon \)  
\( \varepsilon \)  
\( \kappa \)  
\( \lambda \)  
\( \lambda \)  
\( \mu \)  
\( \nu \)  
\( \nu', \nu'' \)  
\( \xi \)  
\( \xi'' \)  
\( \zeta_{st} \)  
\( \rho \)  
\( \sigma \)  
\( \tau \)  
\( \chi \)  
\( \omega \)  
\( \Omega \)  

mixture fraction  
r.m.s. mixture fraction fluctuations at \( \tilde{\xi} = \xi_{st} \)  
density (kg m\(^{-3}\))  
Stefan-Boltzmann constant = 5.67 \( \cdot 10^{-8} \) W m\(^{-2}\) K\(^{-4}\)  
time scale (s)  
scalar dissipation rate (s\(^{-1}\))  

Subscripts

\( A \)  
\( \text{abs} \)  
\( \text{bb} \)  
\( b \)  
\( c \)  
\( \text{cl} \)  
\( \text{e,w,n,s} \)  
\( \text{E,W,N,S} \)  
\( \text{em} \)  
\( \text{ext} \)  
\( \text{f} \)  
\( i, j, k \)  
\( K \)  
\( m \)  

activation energy or temperature  
absorption part of radiation  
black body  
backward reaction  
characteristic flamelet scale  
centerline value  
est, west, north, south cell wall  
est, west, north, south neighbouring grid point  
emission part of radiation  
value at flame extinction  
forward reaction  
grid point indices  
Kolmogorov scale  
mixture-averaged property
Principal symbols

P \quad \text{grid point}
rad \quad \text{radiation}
st \quad \text{stoichiometric value}
t \quad \text{integral turbulent scale}
w \quad \text{wall value}
o \quad \text{nozzle exit value}
1/2 \quad \text{value based on jet halfwidth}

Superscripts

a \quad \text{absorption coefficient}
o \quad \text{previous time step}
s \quad \text{scattering coefficient}
- \quad \text{leaving from a surface or volume element}
+ \quad \text{arriving at a surface or volume element}
'' \quad \text{Favre fluctuation}
- \quad \text{Favre average}
' \quad \text{Reynolds fluctuation}
\quad \text{Reynolds average}
0 \quad \text{standard thermodynamic conditions}
SUMMARY

The widespread use of natural-gas in both large-scale and small-scale combustion equipment spurs an active research into the fundamental processes occurring in turbulent flames. This work aims at the development and application of reliable numerical models, to be used as predictive tools for the design of burners and combustion equipment with efficient use of fuel and minimal pollutant emissions. To achieve this, both laminar and turbulent gaseous flames are simulated and compared with available experimental data. Here, we focus on turbulent non-premixed or diffusion flames, because for safety reasons, they are commonly employed in large-scale industrial furnaces.

Laminar flames are of interest both experimentally and theoretically. The simple geometrical structure of laminar premixed and non-premixed flames allows a detailed computation of molecular transport phenomena and chemical reactions, and thus contributes to the insight in the structure of these flames. The laminar diffusion flame calculations, using detailed chemistry, can be compared with simplified chemistry models used for turbulent flames. In addition, they are used for the calibration of species concentration measurements by Laser-Induced Fluorescence.

Turbulent laboratory-scale jet flames are the next step in complexity. The boundary conditions and the geometry of these flames can be controlled to facilitate numerical simulations, e.g. by assuming axisymmetry. In the Section Heat Transfer in Delft, recent experimental studies on laboratory-scale piloted jet diffusion flames with annular air have provided a comprehensive database for model validation. Important quantities like mean velocities, turbulent fluctuations, mean temperatures and OH radical concentrations have been measured. In this thesis, numerical simulations have been performed to test several models for chemistry and probability density functions (PDFs) of scalar quantities. Both detailed chemical kinetics and conserved-scalar models for natural gas combustion have been tested.

Finally, the simulation of (semi-)industrial furnaces is of such high complexity that at present only simple models are tractable. The developed and validated conserved-scalar models and assumed PDF shapes are used to study the influence on mean flow and thermal behavior of an industrial high-temperature glass-melting furnace and the semi-industrial IFRF test furnace, with the aim of finding reliable and generally applicable models for high-temperature flames.

The first part of this work describes in detail the basic theory of turbulent gaseous combustion, with emphasis on the description of chemistry, PDFs of relevant scalar quantities and radiation. From the instationary conservation equations of mass, momentum, energy and species concentrations the averaged transport equations are described, and closed by several model assumptions. For the turbulent fluxes of momentum and scalars, the eddy-viscosity $k$-$\varepsilon$ model is applied. Favre-averaged quantities are used to avoid density correlations to be taken into account explicitly. The resulting equations are solved numerically by finite-volume discretization of which details are given.
Models for radiative heat exchange are presented, with emphasis on axisymmetrical geometries. The coupling of radiative heat transfer with soot formation is given. The Hottel zone method, the Discrete Transfer method and a simplified method are analyzed for their applicability to the axisymmetrical diffusion flame studied, where we have assumed grey-gas radiation properties. The numerical accuracy of the model implementations is investigated and established.

The treatment of chemistry models is based on a classification of turbulent non-premixed flame regimes. Laminar flames are considered to be the building blocks of a whole class of turbulent flames. The investigation of laminar flames contributes to the insight into many important combustion phenomena and chemical reaction systems. Here, the basic equations which describe both premixed and non-premixed one-dimensional laminar flames are given, and the numerical solution method is sketched.

For flames with high enough Damköhler numbers, all thermochemical variables are coupled with a single conserved scalar, the mixture fraction. The conserved-scalar approach is attractive because of the vast reduction of the number of independent thermochemical quantities. The statistics of the mixture fraction \( \xi \) are given by its local PDF. By assuming a certain PDF shape for \( \xi \), the mean field of any thermochemical variable \( \phi \) is fully determined by the mean and variance of the mixture fraction, for which modeled transport equations are given, and by the functional relationships \( \phi = \phi(\xi) \), which depend on the chemistry model chosen. Models ranging from one-step reaction, two-step reactions, constrained equilibrium to full equilibrium are described and compared. The inclusion of flame heat losses by radiation and convection, intermittency effects, and the calculation of thermal NO formation are treated in detail. Moreover, much attention is paid to the development of a numerically accurate PDF integration and an efficient tabulation and lookup procedure to speed up flame simulations.

If chemical kinetics cannot be simplified by a reduction of variables in terms of the conserved scalar, the highly non-linear chemical source terms have to be closed in a turbulent field. In this work, the method of an assumed Gaussian joint-PDF closure for the elementary reaction rates, as originally developed by Bockhorn, is outlined and applied to natural-gas flames, simplified as methane flames. Based on a careful analysis of several parts of this model, a number of modifications and improvements are suggested and employed to achieve stable numerical solutions of our laboratory-scale flame.

The second part of this work discusses the results of the numerical computations. First of all, results of laminar flame calculations are presented. Detailed comparisons with conserved-scalar models to be used for turbulent flame calculations show that the constrained-equilibrium model of Bilger and Stårner closely resembles laminar flamelet data, and therefore is superior to more simplified conserved-scalar models. The prediction of super-equilibrium radical concentrations is not possible with the (constrained) equilibrium model, but for preheated-air flames (as occurring in glass-melting furnaces) the differences with laminar flamelets are small. Premixed flames are investigated by comparing computations with experimental data, used for the calibration of Laser-Induced Fluorescence measurements.
Summary

A detailed analysis of premixed and diffusion flamelets shows the sensitivity of results on numerics and reaction mechanisms taken from literature. The skeletal mechanism for methane/air combustion yields sufficiently accurate results compared with the full mechanism of Warnatz, which is considered to be the most reliable mechanism, containing C1-, C2- and higher hydrocarbon species. For reasons of computational efficiency, the skeletal mechanism is selected to be used in the detailed kinetics/joint-PDF model calculations of the axisymmetric turbulent diffusion flame.

Secondly, the piloted jet diffusion flame of which detailed experimental data are available is studied. This particular flame consists of a central fuel jet of 21.6 m/s, surrounded by an annular air flow of 4.5 m/s. Low-speed coflowing air is used to prevent recirculation in the combustion chamber, which is about 1 m long and 0.6 m in diameter. The specific flow geometry is different from a single jet in a coflow. On the 4.5-mm wide burner rim between the fuel jet and air annulus, pilot flames are issued to stabilize the flame on the burner.

The numerical code used for the simulation of the laboratory flame is first tested by comparing with non-reacting jet data obtained in the same burner configuration. Flame computations with the constrained-equilibrium/β-function PDF model yield excellent agreement with experimental data on mean velocities, r.m.s. velocities, mean temperature and even temperature PDFs. Although the anisotropy of the turbulence is not fully captured by the eddy-viscosity model, the scalar mixing is modeled very well, judged by the comparison with measured temperatures. The inclusion of radiative heat transfer and soot formation were found to have only a small influence on the flame. The detailed-kinetics/joint-PDF model is capable of predicting qualitatively the super-equilibrium OH concentrations found in the experiments, a feature which cannot be reproduced by the constrained-equilibrium model. A detailed calibration, however, shows that the detailed-kinetics/joint-PDF model is sensitive to the stabilization mechanism of the pilot flames, and to the assumption of the Gaussian joint PDF. The successes of the different chemistry models applied to this specific laboratory-scale flame are discussed in terms of the flame regime diagram.

Thirdly, results are presented for two types of large-scale high-temperature furnaces. The sensitivity of results on thermal behavior, overall combustion characteristics and thermal NO formation is studied with respect to model variations. We tested several assumed mixture fraction PDF shapes, ranging from Dirac δ-functions to Gaussian PDFs and the β-function PDF. In addition, the chemistry model was varied from the simple one-step reaction flame sheet to the constrained-equilibrium model. Finally, some alternative models for incorporating radiative heat losses into the enthalpy model are discussed and compared. Results show that especially NO formation is sensitive to all of these submodels. The more complex model formulations like the β-function PDF and constrained equilibrium chemistry, which were already successfully applied to the laboratory flame, are found to agree well with the available experimental data, and they offer the best generality and flexibility for use in further high-temperature furnace simulations.

The major conclusions of this work are that the developed and implemented models
for flame chemistry, assumed PDF shapes and radiative heat transfer yield very good agreement with measured data on laminar flames, laboratory-scale turbulent diffusion flames and high-temperature furnace flows. Only in cases where the interaction between combustion chemistry and flow hydrodynamics is very delicate, like in the stabilization region of the piloted-jet diffusion flame or in the formation of radical species, difficulties arise in reproducing the experimental data. The development of efficient numerical tools for including more complex conserved-scalar chemistry models into CFD computations enables reliable simulations to be made, with only very limited increase in computational costs in comparison with the simplest flame sheet models.
SAMENVATTING

Het wijdverbreide gebruik van aardgas in zowel grootschalige als kleinschalige verbrandingsapparatuur stimuleert actief onderzoek naar de fundamentele processen die optreden in turbulente vlammen. Het doel van deze studie is de ontwikkeling en toepassing van betrouwbare numerieke modellen, die kunnen dienen als gereedschap bij het ontwerp van branders en verbrandingsapparatuur met efficiënt brandstofverbruik en minimale uitstoot van schadelijke stoffen. Om dit te bereiken worden zowel laminaire als turbulente vlammen gesimuleerd en vergeleken met beschikbare meetresultaten. We concentreren ons hier op turbulente niet-voorgemengde of diffusie-vlammen, omdat deze uit veiligheidsoverwegingen veelal worden toegepast in grootschalige industriële formuleren.

Zowel van experimenteel als theoretisch standpunt zijn laminaire vlammen van belang. Wegens de eenvoudige geometrie van laminaire voorgemengde en niet-voorgemengde vlammen is het mogelijk een gedetailleerde berekening te maken van moleculaire transportverschijnselen en chemische reacties, waardoor inzicht verkregen wordt in de structuur van deze vlammen. Bovendien kunnen de berekeningen aan laminaire diffusievlammen met gedetailleerde chemie, vergeleken worden met vereenvoudigde chemiemodellen voor turbulente vlammen. Daarnaast worden zij gebruikt bij de calibratie van stofconcentratiemetingen met behulp van laser-geïntroduceerde fluorescentie (LIF).


De simulatie van (semi-)industriële ovens, tenslotte, is dermate gecompliceerd dat momenteel slechts eenvoudige modellen hanteerbaar zijn. De ontwikkelde en gevalideerde behouden-scalar-modellen en aangenomen PDF-vormen zijn gebruikt om hun invloed op de gemiddelde stroming en het thermische gedrag van een industriële hoge-temperatuurglassmeltenoven en het semi-industriële testforrnis van de International Flame Research Foundation (IFRF) te bestuderen. Het uiteindelijke doel hiervan is het bepalen van betrouwbare en algemeen toepasbare modellen voor hoge-temperatuur-vlammen.

In het eerste deel van dit proefschrift wordt de theorie van turbulente gasverbranding beschreven, met accenten op de beschrijving van chemie, PDFs van relevante scalaire grootheden en straling. Uitgaande van de instationaire behoudswetten voor massa, impuls,
energie en stofconcentraties worden gemiddelde transportvergelijkingen gegeven, die gesloten worden met een aantal modelaannamen. Voor de turbulente fluxen van impuls en scalaire variabelen wordt het zogenaamde turbulente-viscositeit $k-c$-model gebruikt. Favregemiddelde grootheden worden gehanteerd om voorkomen dat dichtheids correlaties expliciet betrokken dienen te worden bij de beschrijving. De uiteindelijke vergelijkingen worden numeriek opgelost met behulp van de eindige-volume-discretisatie, welke in detail besproken wordt.

Modellen voor warmteoverdracht door straling worden gepresenteerd, met de nadruk op cylindersymmetrische geometriën. De koppeling van stralingswarmteoverdracht met roetvorming wordt gegeven. De toepasbaarheid van de Hotte-l-zonemethode, de Discrete Transfer methode en een vereenvoudigde methode worden geanalyseerd met betrekking tot de bestudeerde axisymmetrische diffusievlam, waarbij we uitgegaan zijn van grijs-gas stralingseigenschappen. De numerieke nauwkeurigheid van de implementaties van de modellen wordt nader onderzocht en vastgesteld.

De behandeling van chemimodellen is gebaseerd op een classificatie van regimes voor turbulente niet-voorgemengde vlammen. Laminaire vlammen worden gezien als de bouwstenen van een hele klasse van turbulente vlammen. De bestudering van laminaire vlammen draagt daarom bij aan het begrip van veel belangrijke verbrandingsverschijnselen en chemisch reagerende systemen. We geven hier de basisvergelijkingen die gelden voor voorgemengde en niet-voorgemengde een-dimensionale laminaire vlammen, en de numerieke oplossingsmethode wordt geschetst.

Voor vlammen met Damkohlergetallen van voldoende grootte kunnen alle thermochemische variabelen gekoppeld worden aan een enkele behouden scalar, de mengselfrac tie. De behouden-scalarenadering is aantrekkelijk voor de modellering van turbulente vlammen, omdat het aantal onafhankelijke thermochemische grootheden drastisch gereduceerd wordt. De statistische eigenschappen van de mengselfrac tie $\xi$ worden gegeven door zijn lokale PDF. Door een bepaalde vorm van de PDF voor $\xi$ te veronderstellen, wordt het gemiddelde thermomechemische veld volledig bepaald door het gemiddelde en de variantie van de mengselfrac tie, waarvoor gemodelleerde transportvergelijkingen gegeven worden, en door de functies $\phi = \phi(\xi)$, welke afhangen van het gekozen chemiemodel. Modellen die lopen van een één-stapsreactie, twee-stapsreactie, beperkt evenwicht tot volledig evenwicht worden beschreven en onderling vergeleken. Het meenemen van warmteverlies door straling en convectie, effecten van intermittentie, en de berekening van thermische NO-vorming worden in detail besproken. Daarbij is veel aandacht besteed aan de ontwikkeling van een numeriek nauwkeurige integratie van de PDF en een efficiënte tabelleringen/opzoekprocedure om de rekentijd van de simulaties te verkorten.

Indien chemische kinetiek niet vereenvoudigd kan worden door een reductie van het aantal onafhankelijke variabelen door middel van een behouden scalar, dan dienen de sterk niet-lineaire chemische brontermen gesloten te worden in de aanwezigheid van een turbulent veld. In deze dissertatie wordt de werking van de methode van een aangenomen Gaussische gezamenlijke-PDF-sluiting voor de elementaire reactiesnelheden, zoals oorspronkelijk ontwikkeld door Bockhorn, uiteengezet, en wordt deze toegepast op aardgasvlammen, vereenvoudigd als methaanvlammen. Gebaseerd op een zorgvuldige analyse van een aan-
tal onderdelen van dit model wordt een aantal aanpassingen en verbeteringen voorgesteld en toegepast, opdat stabiele numerieke oplossingen verkregen kunnen worden voor de onderzochte laboratoriumschaal vlammen.

Het tweede deel van dit werk bespreekt de resultaten van de numerieke berekeningen. Allereerst worden resultaten van laminaire-vlamberekeningen getoond. Gedetailleerde vergelijkingen met behouden-scalar-modellen voor turbulente vlammen laten zien dat het beperkt-evenwichtsmodel van Bilger en Stárner sterk lijkt op laminaire flamelet data, en daarom superieur is aan de eenvoudigere behouden-scalar-modellen. De voorspelling van boven-evenwichtsconcentraties van radicalen is niet mogelijk met het beperkte-evenwichtsmodel, maar voor vlammen met voorverwarmde lucht (die veel voorkomen in glasmeltovens) zijn de verschillen met de laminaire flamelets klein. Voorgemengde vlammen worden onderzocht door middel van een vergelijking met experimentele gegevens, die gebruikt worden bij de calibratie van LIF metingen.

Een nauwkeurige analyse van voorgemengde en niet-voorgemengde flamelets geeft een indruk van de gevoeligheid van de resultaten voor de numerieke oplosmethode en de reactiemechanismen uit de literatuur. Het basismechanisme (skeletale mechanism) voor methaan/luchtvlammen geeft voldoende nauwkeurigheid in vergelijking tot het complete mechanisme van Warnatz, wat beschouwd wordt als het meest betrouwbare mechanisme. Dit complete mechanisme omvat C_1-, C_2- en hogere koolwaterstoffen. Wegens numerieke efficiëntie wordt het skeletale mechanisme verkozen om te gebruiken in de berekeningen met het gedetailleerde-kinetiek/gezamenlijke-PDF model aan de axisymmetrische turbulente diffusievlam.

Ten tweede wordt een studie verricht naar de straaldiffusievlam waarvan uitgebreide meetgegevens beschikbaar zijn. Deze vlam bestaat een centrale brandstoffstraal van 21,6 m/s, omgeven door een annulaire luchtstroom van 4,5 m/s. Meestromende lucht (coflow) met een lage snelheid van 0,4 m/s wordt gebruikt om terugstroming te voorkomen in de verbrandingskamer, welke ongeveer 1 meter hoog en 0,6 m in diameter is. Deze specifieke geometrie is derhalve verschillend van een enkele straal in een coflow. Op de 4,5 mm brede branderrand tussen de brandstoffstraal en de annulaire lucht worden stabiliteitsvlammetjes gebruikt om de vlam te stabiliseren aan de brander.

De numerieke code die gebruikt wordt voor de simulatie van de laboratoriumvlam wordt eerst getest door middel van een vergelijking met meetgegevens aan een niet-reagerende straal, verkregen in dezelfde branderconfiguratie. Vlamberekeningen met het beperkte-evenwichtsmodel en het \( \beta \)-functie PDF-model tonen een uitstekende overeenkomst met de gemeten waarden van gemiddelde snelheden, r.m.s. snelheidsfluctuaties, gemiddelde temperatures en zelfs PDFs van temperatuur. Hoewel de anisotropie van de turbulentie niet volledig beschreven wordt door het turbulent-Viscositeitsmodel, blijkt de scalaire menging erg goed voorspeld te worden, uitgaande van de vergelijking met de gemeten temperaturen. De invloed van roetvorming en warmteoverdracht door straling bleek slechts een geringe invloed te hebben op de vlam.

Het gedetailleerde-kinetiek/gezamenlijke-PDF model is in staat om kwalitatief het optreden van boven-evenwichtsconcentraties van het OH-radiaal, zoals waargenomen in de experimenten, te voorspellen, iets wat niet mogelijk is met het beperkt-evenwichtsmodel.
Samenvatting

Een nauwkeurige calibratie laat echter zien dat het model met gedetailleerde kinetiek gevoelig is voor het stabilisatiemechanisme van de stabilisatievlammetjes, en voor de aannames van een Gaussische gezamenlijke PDF. De merites van de verschillende chemie-modellen die zijn toegepast op deze specifieke laboratoriumvlam worden besproken aan de hand van het diagram voor vlamregimes.

Ten derde worden resultaten gepresenteerd voor twee typen grootschalige hoge-temperatuur-ovens. De gevoeligheid van de resultaten betreffende thermisch gedrag, globale verbrandingskarakteristieken en vorming van thermische NO wordt bestudeerd door middel van modelvariaties. Verschillende aangenomen PDF-vormen voor de mengselfractie zijn getest, variërend van Dirac δ-functies tot Gaussische PDF's en de β-functie PDF. Bovendien werd het chemiemodel gevarieerd van het eenvoudige één-staps reactiemodel tot het beperkt-evenwichtsmodel. Tenslotte werden enkele alternatieven voor het verdisconteren van stralingsverliezen in het enthalpiemodel onderling vergeleken. De resultaten laten zien dat met name de vorming van NO gevoelig is voor al deze deelmodellen. De wat meer complexe modellen, zoals de β-functie PDF en beperkt evenwicht voor de chemie, welke al met succes werden toegepast op de laboratoriumvlam, blijken goed overeen te stemmen met de beschikbare meetgegevens. Deze modellen bieden de beste mate van algemeenheid en flexibiliteit om toegepast te kunnen worden in verdere simulaties aan hoge-temperatuur-ovens.

De belangrijkste conclusies van dit proefschrift zijn dat de ontwikkelde en geïmplementeerde modellen voor de vlamchemie, aangenomen PDF-vormen en warmteoverdracht door straling bijzonder goede overeenstemming laten zien met de experimentele gegevens voor laminaire vlammen, turbulent laboratoriumschaal diffusievlammen en hoge-temperatuur formuizer. Slechts in die gevallen waar de interactie tussen verbrandingschemie en de hydrodynamica van de stroming delicaat is, zoals in het stabilisatiegebied van de turbulente jet-diffusievlam of bij de vorming van radicalen, blijkt het problematisch te zijn om de experimentele gegevens te reproduceren. De ontwikkeling van efficiënte numerieke gereedschappen die het mogelijk maken om meer geavanceerde behouden-scalar chemiemodellen toe te passen in CFD berekeningen leiden tot betrouwbaarere simulaties, met slechts een geringe extra rekeninspanning ten opzichte van de eenvoudigste vlammodellen.
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