INAUGURAL-DISSERTATION zur Erlangung der Doktorwürde der Naturwissenschaftlich-Mathematischen Gesamtfakultät der Ruprecht-Karls-Universität Heidelberg

vorgelegt von

Diplom-Ingenieur Thomas Carraro aus: Castelfranco V.to, Italien

Tag der mündlichen Prüfung: 30.11.2005

Parameter estimation and optimal experimental design in flow reactors

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Abstract

In this work we present numerical techniques for the simulation of reactive flows in a chemical reactor as well as for the identification of the kinetic of the reactions, using measurements of observable quantities. In this context we introduce methods for the optimal design of experiments.

We present a model to simulate the detailed interplay between flow variables and those variables that describe the chemistry. We consider a model for the flow motion in the regime of low Mach number, where the velocity of the flow is much slower than the sound speed, to exploit the advantage of this phenomenology.

For the solution of the system of equations we consider the finite elements method for the discretization in space. The resulting nonlinear system of equations is time dependent and we are interested in the transitory phase during the reaction. The system has the characteristic of being stiff, this suggests the use of implicit methods for the solution in time. For the solution of the nonlinearities we use a quasi-Newton method and for the solution of the linearized equations a multi-grid method with a domain decomposition scheme as smoother. This method takes advantage of the parallelization of the finite elements code 'HiFlow', that has been used for the simulation.

As we deal with real measurements and their uncertainties, we expose a probabilistic setting of the parameter estimation problem. The natural extension of the parameter identification study, dealing with uncertainties that can be described by a given statistic distribution, is the optimal experimental design problem. For this purpose we present the theory in the context of partial differential equations and some numerical experiments.

Central role in this work is played by the simulation of a real experiment and the results from the comparison between the numerical and the experimental part. Concerning the obtained results we can state that the numerical methodology presented can be applied successfully for the study of the kinetic of reactions that take place in a laminar flow reactor at high temperature.

Zusammenfassung

In dieser Arbeit präsentieren wir numerische Methoden zur Simulation von reaktiven Strömungen in Strömunsreaktoren sowie Methoden zur Identifizierung der Reaktionskinetik mittels Messungen von erfassbaren Größen. In diesem Rahmen stellen wir Methoden für die optimale Versuchsplanung vor.

Wir präsentieren ein Model zur Simulation der detailierten Wechselwirkung zwischen

Strömung und Chemie. Im Falle niedriger Mach-Zahlen betrachten wir ein speziell auf diese Situation zugeschnittenes Stömungsmodell.

Für die Lösung der Gleichungen verwenden wir die Methode der Finiten Elemente für die Ortsdiskretisierung. Die resultierenden nichtlinearen Gleichungen sind zeitabhängig und unser besonderes Interesse gilt der Übergangsphase während der Reaktion. Die Einbindung des chemischen Teils führt zu einem steifen System, das implizite Zeitschritt-Verfahren erfordert. Zur Lösung der Nichlinearitäten verwenden wir eine Quasi-Newton-Methode und zur Lösung der linearisierten Gleichungen einen Mehrgitter Löser, kombiniert mit einer Gebietszerlegungsmethode als Glätter. Diese Methode macht sich die Parallelisierung des Finite-Elemente-Pakets 'HiFlow' zu Nutze, das für die Simulation verwendet wurde.

Da wir mit realen Messungen und deren experimentellen Unsicherheiten zu tun haben, leiten wir eine wahrscheinlichkeitstheoretische Fassung des Parameteridentifizierungsproblems her. Die natürliche Erweiterung des Parameteridentifizierungsproblems im Falle experimenteller Unsicherheiten, die durch eine bestimmte statistische Verteilung gegeben sind, ist die optimale Versuchsplanung. Wir präsentieren hierfür die Theorie im Bereich der partiellen Differentialgleichungen und einige numerische Beispiele.

Eine zentrale Rolle in dieser Arbeit spielt die Simulation eines realen Experiments und der Vergleich zwischen numerischen und experimentellen Ergebnissen. Hinsichtlich der erhaltenen Ergebnisse konstatieren wir, dass die hier vorgestellte Methode mit Erfolg auf die Untersuchung der Kinetik von Reaktionen, die in einem Strömungsreaktor bei hohen Temperaturen stattfinden, angewendet werden kann.

Table of Contents

In	trod	\mathbf{uction}	v										
1	Pro	blem formulation and experimental setup	1										
	1.1	Motivation	1										
	1.2	Experimental setup	3										
		1.2.1 Flow reactor	3										
		1.2.2 Pseudo first-order reaction approximation	6										
		1.2.3 Experimental approach to the kinetic estimation	8										
	1.3	Experimental results	10										
2	Mo	del derivation	13										
	2.1	Conservation laws	13										
	2.2	Reactive flows	16										
		2.2.1 Mass and momentum equations	16										
		2.2.2 Temperature equation	17										
		2.2.3 Transport fluxes	19										
		2.2.4 Reaction Mechanism and elementary reactions	22										
	2.3	Low Mach number model	23										
		2.3.1 Low Mach number asymptotic of the Navier-Stokes equations	24										
3	Discretization and solver												
	3.1	Finite element discretization	29										
		3.1.1 Variational formulation	29										
		3.1.2 FEM ansatz	30										
		3.1.3 Boundary conditions	31										
3	3.2	Overall solution process	32										
		3.2.1 Time step	34										
		3.2.2 Nonlinear solver	34										
		3.2.3 Linear solver	36										
	3.3	Error estimation and mesh adaptivity	39										
		3.3.1 Practical a posteriori error estimation	41										
	3.4	HiFlow	43										
	3.5	Parallel HPC	44										

4	Par	ametei	r identification and experimental design								
	4.1	4.1 Optimization methods for PDE									
	4.2	2 Parameter identification for the PDE system									
	4.3	Param	eter identification in the probabilistic setting								
		4.3.1	Statistical assumptions								
		4.3.2	Probabilistic description of the least squares method								
	4.4	A deri	vation of the covariance matrix								
	4.5	Optim	al experimental design 54								
		4.5.1	Sequential experimental design								
	4.6	Optim	al experimental design for PDE								
		4.6.1	Numerical examples: measurements								
		4.6.2	Convection-diffusion equation								
		4.6.3	Laplace with discontinuous diffusion coefficient								
		4.6.4	Reaction between two species								
	4.7	A post	teriori error estimation for optimal experimental design problems 72								
		4.7.1	Numerical example								
5	Nui	nerical	l results								
	5.1	Model	calibration								
		5.1.1	Velocity								
		5.1.2	Pressure								
		5.1.3	Mass fraction								
		5.1.4	Temperature profile 83								
	5.2	.2 Ignition									
	5.3	Measu	rements								
	5.4	Result	s of the fit $\ldots \ldots $								
		5.4.1	Case $T = 300K, 50\% H_2$								
		5.4.2	Case $T = 300K, 5\% H_2$								
		5.4.3	Case $T = 780K, 50\% H_2$ 89								
	5.5	Visual	ization of the flow $\ldots \ldots $								
C	onclu	ision									
$\mathbf{A}_{]}$	ppen	dix A									
Bi	ibliog	graphy									

Introduction

In this work we present numerical techniques for the simulation of reactive flows in a chemical reactor as well as for the identification of the kinetic of the reactions, using measurements of observable variables. In this context we introduce methods for the optimal design of experiments.

This work has been supported by the German Research Foundation (DFG) through the SFB 359 (Project B1) and is part of a co-operation with the group of prof. J. Wolfrum at the physical-chemistry institute in Heidelberg (PCI). In the framework of this project we apply the numerical techniques here described to a real case of laminar flow reactor in the high-temperature regime to determine the reaction rate of the reaction:

$$O(^{1}D) + H_{2} \rightarrow OH + H.$$

The problem of determining the reaction rate of different reaction processes is an important issue and finds its application in several areas. The study of the kinetic data is relevant with respect to the following points:

- from a practical point of view it is crucial for many applications how fast a reaction reaches a state of equilibrium,
- from a theoretical point of view it is fundamental to know how the different elementary reactions, that compose a mechanism, affect the whole process.

Complex chemical processes may lead to a huge number of elementary reactions that may take place simultaneously or sequentially (see Appendix A for the mechanism that describes the chemical process here considered). The numerical simulation offers a valuable tool for the understanding of the details of these complex processes.

The reaction studied is of interest because it is part of reactions that occur in the atmosphere in the process of reduction of ozone. Further it is relevant because it can be considered as prototype for other reactions that take place in combustion.

For experimental purposes a newly designed chemical flow reactor has been used. Typically the main part of a flow reactor is a reactive tube, where the species mix together to reach afterwards a measurements zone. In this case the reaction takes place between gas phases in a laminar flow. From the point of view of the experimental approach, laminar flows offer the necessary conditions for the experiment:

• transport of species in the measurement zone,

- mixing of the different species to create a uniform mixture,
- heat conduction to reach the temperature requested.

At this regime the mixing is mostly due to diffusion and as we will see from the numerical results the time scale of this phenomenon is small enough to permit a uniform mixture. Nevertheless the simulation of such processes has some intrinsic difficulties that has to be considered in a numerical approach: this encompasses the treatment of boundary layers, expecially in the case of high temperature (T > 500K) in concomitance with high pressure $(p \sim 1 \text{ atm})$, for which the effect of gravity creates important phenomena or the coupling between the chemistry and the flow.

In the first chapter we expose the experimental approach to the study of the kinetic of the given reaction and the related results. Here we describe the flow reactor at the PCI in Heidelberg and the experimental setup.

For the numerical study we have to solve a complete system of partial differential equations describing the flow motion in the reactor and the interaction between the flow and the chemistry.

In the second chapter we derive the mathematical model of the conservation laws, the Navier-Stokes equations, that describe the fluid motion, i.e. the mass and momentum equation and the energy equation. We extend the model to the case of multicomponent flows with transport, diffusion and reaction of different species, adding the mass conservation equation with regard to each species. Further in this chapter we introduce a low Mach number model, which is an approximation of the Navier-Stokes equations particularly adequate for the regime of flow at low velocity with respect to the sound of speed. In this case the compressibility effects are mostly due to the heat exchange. In this regime the velocity of the fluid is much slower than the pressure waves. This model takes advantage of this special phenomenology. The system of equations of the model is discretized in space by means of an adaptive finite element method.

The chapter three deals with the weak formulation of the underlying equations and the details of the time and space discretization. We expose the techniques that we have used to solve the nonlinearities of the equations and the multi-grid techniques adopted for solving the linear systems arising from the linearization of the original systems.

Chapter four presents the parameter identification problem for the estimation of the reaction rate, based on experimental data given by concentration measurements of the species. As we deal with experimental data, we introduce a formulation of the problem under statistical assumption, in order to treat the uncertainties of the data. We can derive the usual least squares method from the maximum likelihood theory in the probabilistic set of the problem. In this chapter we show how data uncertainties induce uncertainties also in the estimated values of the parameters. The way how the former maps into the latter depends also on the physical system itself, asides from the measurements' errors introduced



Figure 1: High temperature reactor at the PCI, Heidelberg

by the measurement chain. As the data are obtained by measurements on the system, the way how we choose the setup of the experiment is directly related to this issue. This leads us to introduce the optimal experimental design problem and some applications to models described by partial differential equations.

Finally the chapter five describes the so called 'calibration' of the model, in order to reproduce numerically the experimental setup. We present here some details of the numerical results and a comparison between numerical and experimental results.

In the last chapter we delineate the future work in the context of parameter estimation and optimal experimental design methods applied to systems of partial differential equations for the simulation of flow reactors.

Chapter 1

Problem formulation and experimental setup

1.1 Motivation

The experiments have been set up by the physical-chemistry group of prof. J. Wolfrum at the PCI Heidelberg. In this chapter we treat the chemistry aspects of the work and give a brief description of the experimental set up, delegating to the reading of the dissertation of A. Hanf [43] for more details. Aim of the experimental study is the investigation of the reaction:

$$O(^{1}D) + H2 \to OH + H, \tag{1.1}$$

in a large range of temperature (300K < T < 1500K). This reaction, as we have mentioned in the introduction, is important for the study of some atmospheric reactions that take part to the ozone reduction. Stratospheric ozone absorbs photons with wavelength between 200 and 300 nm:

$$O_3 + h_{\nu}(\lambda \leq 310nm) \rightarrow O(^1D) + O_2,$$

thus it works as a natural filter to the ultraviolet radiation, which is dangerous for its physiological effects. For wavelength greater than 310 nm the photolysis of ozone produces oxygen atoms in the fundamental state: $O({}^{3}P)$. Oxygen atoms react with hydrogen molecules, but the reactivity of $O({}^{3}P)$ is seven order of magnitude lower than its first exited state $O({}^{1}D)$ (reaction (1.1)). The uncertainties in the reaction rate of this reaction are one of the most important sources of error when modeling stratospheric chemistry. This reaction is of relevance also in the combustion chemistry and as a prototype for insertion-type reactions in which the barrier-less pathway leads to the formation of a H_2O complex in the deep molecular well dominating the potential energy surface (PES). Furthermore an experimental study of this reaction at a wide range of temperature offers important references for new calculations using quantum mechanical models.

Reactions which involve electronically exited species such as the reaction of metastable oxygen atoms, $O(^{1}D)$, with H_{2} can proceed via a non-adiabatic mechanism involving both the ground-state PES and one or more electronically excited PESs ([1],[54]). As outlines in [1], in case of reaction (1.1) five adiabatic surfaces correlate with the $O^1D + H_2$ reagents, two of which can be neglected in the theoretical treatment if the electronic fine structure of the reagents is not considered. The influence of the three remaining PESs, denoted as $1^{1}A'$, $2^{1}A'$ and $1^{1}A''$, on the dynamics and thermal kinetics of reaction (1.1) has been investigated in recent years in a variety of quasi-classical 'surface hopping' [12] and quantum scattering calculations ([1], [28]). These calculations revealed that the contribution state PES $1^{1}A'$, which has a deep well corresponding to the electronic ground-state of the water molecule, dominates at low collision energies. These calculations further showed that on the ground-state the reaction (1.1) proceeds via insertion of the oxygen atom into the H_2 bond leading to a highly excited H_2O^* transient reaction intermediate, which rapidly (within a few molecular vibrations) decomposes into H + OH products. Because the reaction on the ground-state proceeds without a barrier the rate coefficient of this reaction are temperature independent, which is in agreement with the results of thermal kinetics measurements performed at low temperatures (250K < T < 350K) [26]. Based on the latter measurement and an extensive evaluation of other experimental data obtained at low-temperatures a temperature-independent value of $1.1E - 10 \ [cm^3 molecule^{-1}s^{-1}]$ is recommended in the temperature range (200K < T < 350K) for the reaction rate coefficient of (1.1) [5]. However, reaction dynamics studies of reaction (1.1), in which 'hot' $O(^{1}D)$ atoms with a translational temperature of about 1200K were generated via pulsed laser photolysis, yielded a considerably high rate constant of $(2.7 \pm 0.6)E - 10 \ [cm^3 molecule^{-1}s^{-1}]$ [54], indicating a pronounced increase of the reaction rate constant with the temperature. The latter observation suggests that at higher reagent energies the chemical kinetics of the reaction is significantly influenced by the participation of at least one (or more) exited-state reaction pathway. This proposition is supported by results from a measurements of OH as described in [2], the results of which could only be reproduced if two PESs, the groundstate $PES(1^{1}A')$ and the electronically exited $PES(1^{1}A'')$, were considered in the respective quantum scattering calculations [50]. Because the electronically exited $PES(1^{1}A'')$ has a collinear transition state, the participation of this PES opens an additional abstraction pathway which exhibits a reaction barrier. This in turn could results in a thermal rate constant, which increases with temperature. In order to provide further experimental evidence for the proposed mechanism the focus of the present work on the extension of the thermal rate constant measurements of the reaction towards higher temperatures to bridge the gap between the available low-temperature thermal rate constant measurements an the 'hot' $O(^1D)$ atom studies.

There are different experimental methods that aim to study a reaction mechanism. They have usually in common the principle of measuring quantitatively the concentration of some components and from these measurements find the reaction rate. For the study of the reaction (1.1) a newly constructed high temperature flow reactor, depicted in figure 1.1 was used. The usual principle of flow reactors is the mixing of reactants upstream in a "mixing-zone", and the measurement of products of the reaction of interest in a "measurement-zone", where the flow condition is almost undisturbed laminar and stationary. This allows a better control of the thermodynamical and fluid dynamic state at which the reaction takes place



Figure 1.1: High temperature reactor at the PCI, Heidelberg

and facilitates the numerical study of the entire process. The mixing process has the two goals:

- to set the temperature of the gases at the wanted "test-temperature" in the "measurementzone"
- to mix the reactants uniformly, so that at the "measurement-zone" the concentrations are controlled by the inflow rate of the reactants at the top of the tube.

1.2 Experimental setup

1.2.1 Flow reactor

The construction and operative details of the reactor are described in the work of A. Hanf [43]. For our purpose we just give a summary description of the experimental set up and procedure, in order to introduce the numerical simulations.

A vertical ceramic alumina reaction tube (5cm i.d.) is surrounded and radiatively heated by six MoSi2 two-shank resistively heated rods inside an insulated water cooled stainless steel housing. Four ceramic alumina side arms (1.5cm i.d.), installed perpendicular to the reaction tube, provide pairwise opposing access for pump and probe laser and the possibility to monitor the intensity of both. At their end this arms are sealed by MgF2 windows, which ensure a high transmittance (λ =110nm-7,5mm) for vacuum ultraviolet laser radiation $(\lambda = 5-190 \text{ nm})$. A fifth sidearm (2cm i.d.) is installed in 45 to the reaction tube between two sidearms, whose centerline intersects the crosspoint of the two centerlines of the four sidearms. To minimize absorption and for cooling a flow of Ar through the side arm is provided. Above this ceramic tube construction is the oven which consists of a stainless steel cooling jacket in which 11 insulation rings, made of a fine porous alumina material, are fixed on top of one another with ceramic adhesive and supports the hearing rods. The MoSi2 heating rods are hanging free in a space between the ceramic reactor tube and the insulation. Because of the large mass of cooling jacket, insulation and heating rods this construction is connected over three pulleys to three counter weights, which have approximately the same mass, what enables easy changes of the oven height relatively to the optical level. The thermic expansion of the ceramic tubes is compensated by bellows at the sidearms and a spring supported disc under the reactor tube. Additionally a thermic expansion of the reaction tube can be compensated by a device connected to the reaction tube at its top, which enables to change its position vertically. The complete setup is constructed on a horizontally movable table which allows the optical alignment. The main part of the reactor consists of the ceramic tube in which is inserted a cooled movable gas inlet, installed at the top by a crimp connection, so the position can be adjusted to change the residual time in the hot zone of the gases $(N_2O \text{ and } H_2)$ that flow through. Through the outer ring between the external ceramic wall and the central gas inlet flows a buffer gas (Ar), which is heated along the ceramic wall, in the heating zone. The temperature is measured by a double shielded thermocouple, which is installed at the bottom of the reactor and can be moved vertically along the axis of symmetry of the reaction tube. The reactor was pumped by a combination of a rotary pump and an oil diffusion pump. The gases have a velocity that ensures a complete renewal of the gas mixture in the reaction volume between two laser shots, whose repetition rate is set to 6 Hz for all experiments. The gases, used in the experiments, had the following degrees of purity (as specified by the manufacturer): 99.998Vol.% for N_2O , 99.995Vol.% for H_2 and 99.998Vol.% for Ar. Mass flow controllers (Tylan FC 260), calibrated with nitrogen, are used to control the flow rates, from which partial pressures of the single gaseous components can be derived. In all experiments the H_2 partial pressure was about ten times higher than the partial pressure of N_2O , which was typically below 800mTorr. The total pressure in the reactor was measured with an absolute pressure transducer (MKS Baratron 390HA). For dissociating the N_2O precursor molecule and generate the desired $O(^{1}D)$ atoms an ArF (193nm) excimer laser (Lambda Physik, LPX 205i) is used. The VUV probe laser beam, used to detect H atoms by laser-induced fluorescence (LIF) at the corresponding Lyman- α wavelength ($\lambda_{probe} = 121.567$ nm), was generated by resonant sum-difference frequency mixing $\omega_{probe} = 2\omega_1 - \omega_2$ in a krypton/argon gas cell. The output of dye laser A (see figure 1.2) operating at a fixed wavelength of 425.1nm was frequency doubled in a BBO II crystal. Dye laser B is operated at a wavelength of $\lambda_2=845.19$ nm in order to produce the required radiation for the Lyman- α transition of H atoms. After



Figure 1.2: Schematic drawing of the experimental setup.

parallelization on a combination mirror as depicted in figure 1.2, both laser beams (λ_1, λ_2) are focused in the krypton/argon cell containing a mixture with a total pressure of 250mbar for the generation of the desired VUV radiation. The dye lasers (A: Lambda Physik FL 2002 E; B: Lambda Physik Scanmate 2E) are simultaneously pumped by a XeCl (308nm) excimer laser (Lambda Physik LPX 200i). To avoid photochemical perturbations due to the fundamental UV laser radiation, the VUV laser beams are separated from the fundamental laser beams (λ_1, λ_2) by a lense monochromator. The photolysis laser beam, with a typically intensity of $2mJ/cm^2$, is aligned perpendicular to the VUV probe laser beam for an optimal overlap in the reaction zone. The LIF signal, originating from this point is observed by a channel photomultiplier (CPM, Perkin Elmer C921P solar blind), which is equipped with a band pass filter (ARC, 122-N-1D, λ_c =122nm, fwhm=20nm). The VUV probe laser intensity is monitored by another photomultiplier (Hamamatsu R1459 solar blind). The signals of both photo-multipliers and the signal from the photodiode, which records the photolysis laser intensity behind the reaction cell, are transmitted into a three-channel boxcar system (SRS250) and transferred into an analogue to digital converter (SRS235) from which the data are transfered into a personal computer, where the LIF signal is normalized to the VUV probe and the photolysis laser intensity. Furthermore the experimental data are visualized for controlling the experimental progress and saved for evaluation. To improve the S/N ratio, the H atom signals at a given delay time are averaged over 40 laser shots. To take account for the component of the LIF signal originating from the scattered light of the photolysis laser, a shutter is used. The signals monitored at closed shutter at a given delay time are subtracted from those signals monitored with open shutter, to determine the corrected signal. A pulse generator (SRS DG 535) controls the delay times between probe and pump laser. Typically, the delay time has to be varied to cover a time of 100-1000ns with respect to the photolysis laser pulse. Delay time settings are checked using a fast oscilloscope (LeCroy 9350A, 500Mhz).

The control volume

As we have seen in the previous section, the reaction starts as soon as we have in the gas a mixture of $O({}^{1}D)$ atoms and H2 molecules. The $O({}^{1}D)$ atoms are generated by an ArF (193 mm) eximer laser that dissociates N_2O in N_2 and $O({}^{1}D)$. The reaction rate is measured by means of measurements of H atoms. The measurements are done by laser induced fluorescence (LIF) technique, where the VUV probe laser beam is perpendicular to the photolysis beam.



The control volume for the measurements is thus the intersection of the two laser, that is a cylinder of 1 mm of diameter and 5-6 mm length.

The result of the measurements is a LIF signal observed by a channel photomultiplier and normalized to the VUV probe and the photolysis laser intensity. This signal is filtered from the scattered light of the photolysis laser and is proportional to the number of atoms of H present in the control volume. The signal is a collection of measurements at different time delay from the photodissociation that starts the reaction. To improve the statistical information of the measurements for each time delay the signals are averaged over 40 laser shots. We describe later in the chapter 5 how it is possible to use this signal to perform a parameter estimation using the numerical model.

1.2.2 Pseudo first-order reaction approximation

In this section we describe the so called pseudo first-order reaction approximation, that justify the "experimental" approach to estimate the reaction rate. We consider the reaction $A + B \rightarrow C$ as being of first-order with respect to the reactant A and zero-order w.r.t. B, the differential equation describing the consumption of A is:

$$\frac{dx}{dt} = k_A(a_0 - x),$$



Figure 1.3: Pseudo first-order reaction rate

with a_0 the initial concentration of A, k_A the first-order rate constant and x the amount of A that has been consumed per unit volume.

Integration of this with boundary condition x = 0 at t = 0 yields the relation:

$$x = a_0(1 - e^{-k_a t}).$$

A semilogarithmic plot of $(a_0 - x)$ versus t gives a straight line. From the slope of this we get the rate of the reaction.

In the case of the reaction

$$O(^1D) + H_2 \to OH + H,$$

we perform the experiments with a surplus of H_2 , so that, in the relation

$$\frac{d[H]}{dt} = k_a[O(^1D)][H_2],$$

we can approximate $[H_2]$ with a constant, because the concentration of H_2 is much higher than that of $O({}^1D)$ and his change in time is negligible. This is the so called pseudo first-order model:

$$\frac{d[H]}{dt} = k_{ps}[O(^1D)]$$

where $k_{ps} = k_a[H_2]$. To calculate k_a we need several values of k_{ps} at different values of $[H_2]$. Plotting the value of k_{ps} versus $[H_2]$ we obtain a straight line, the slope of which is k_a . Some assumptions have been made in order to calculate an expression of k_{ps} :

- 1. the first is that $[H_2]$ is almost constant and this is easy to satisfy, controlling the inflow of the gases,
- 2. the secondary and tertiary reactions in the mechanism (see Appendix A) do not modify essentially the results, this assumption has to be verified. If not satisfied, we must consider the full mechanism also to get an approximation of the k_{ps} ,
- 3. the concentrations of the reactants, in the reaction zone, have to be known. Experimentally the concentrations have been calculated from the values of the calibrated mass flow controllers, from which it is possible to calculate the flow rates and consequently the partial pressures of the single gaseous components. From the partial pressures, the total pressure and the temperature, it is possible to calculate the number of particles (atoms, molecules or ions) for each species. Is is important to verify, numerically, that the mixing process from the top of the reaction tube to the "measurement-zone" give an homogeneous mixture of species at the optical level.

1.2.3 Experimental approach to the kinetic estimation

We describe here the empirical method for the estimation of the kinetics, that have been used in the work of A. Hanf [43]. A simplified reaction system was considered, together with empirical information regarding some reactions of this system, in order to estimate the reaction rate, using the pseudo first-order model:

$$O(^{1}D) + H_{2} \xrightarrow{\kappa_{H_{2}}} OH + H$$
 (1.2)

$$O(^{1}D) + N_{2}O \xrightarrow{\kappa_{N_{2}}O} \text{ products}$$
 (1.3)

$$O(^{1}D) + Ar \xrightarrow{k_{q}} O(^{3}P) + Ar$$
 (1.4)

$$H \xrightarrow{\kappa_D} \text{ diffusion}$$
 (1.5)

The variation of $O(^1D)$ is thus given by:

$$\frac{dO(^{1}D)}{dt} = k_{H_{2}}[O(^{1}D)][H_{2}] + k_{N_{2}O}[O(^{1}D)][N_{2}O] + k_{q}[O(^{1}D)][Ar] = k'[O(^{1}D)]$$
(1.6)

where

$$k' = k_{H_2}[H_2] + k_{N_2O}[N_2O] + k_q[Ar].$$

Here the different reaction rates have been derived as following:

- the rate constant k_q for the quenching of $O({}^1D)$ by collision with Ar was taken from a study of the deactivation of $O({}^1D)$ and $O({}^1\Sigma_g^+)$ by different rare gases.
- k_{N_2O} was obtained from Davidson et al. [26]
- the rate coefficient for the diffusion k_D was determined by measuring the H atoms signal at delay times of several ten microseconds. k_D was obtained as a fit parameter using the relation:

$$[H]_t = A \exp(-k_D t).$$

In the following derivation we use the symbol O^{\bullet} instead of $O(^{1}D)$ to facilitate the reading of the different passages. By separation of the variables and integration we get:

$$\int_{[O^{\bullet}]_0}^{[O^{\bullet}]_t} \frac{1}{O^{\bullet}} dO^{\bullet} = -k' \int_0^t dt$$
$$\ln \frac{[O^{\bullet}]_t}{[O^{\bullet}]_0} = -k't$$

Thus

$$[O^{\bullet}]_t = [O^{\bullet}]_0 \exp(-k't) \tag{1.7}$$

And for the concentration of H atoms, using (1.7), we obtain:

$$\frac{d[H]}{dt} = k_{H_2}[O^{\bullet}]_0[H_2] - k_D[H] = k_{ps}[O^{\bullet}]_0 \exp(-k't) - k_D[H]$$
$$\frac{d[H]}{dt} = k_{ps}[O^{\bullet}]_0 \exp(-k't) - k_D[H]$$

This is a differential equation of the form:

$$\frac{dy}{dx} = g(x) - f(x)y,$$

which solution is:

$$y(x) = \frac{1}{M(x)} \left(\int g(x) M(x) dx + C \right),$$

with $M(X) = \exp(\int f(x)dx)$. In our case $f(x) = k_D$, so

$$\int_{x_0}^x f(x)dx = \int_0^t k_D dt = k_D t$$

and $M(x) = \exp(k_D t)$. We have also $g(x) = A \exp(-k't)$, with $A = k_{ps}[O^{\bullet}]_0$. Thus

$$[H]_t = \exp(-k_D t) \left(A \frac{1}{(k_D - k')} \exp(-k' t + k_D t) + C \right)$$

for t = 0 we have $[H]_t = [H]_0$ and from

$$[H]_0 = A \frac{1}{(k_D - k')} + C$$

we determine the constant C.

Finally we obtain:

$$[H]_t = \exp(-k_D t) \left(\frac{A}{(k_D - k')} \exp(-k't + k_D t) + [H]_0 - \frac{A}{(k_D - k')}\right)$$

and substituting A we have the formula to be used for the fit with the experimental data:

$$[H]_t = \frac{k_{ps}[O^\bullet]_0}{k_D - k'} \left(\exp(-k't) - \exp(-k_D t) + [H]_0 \exp(-k_D t) \right)$$
(1.8)

After fitting [H] with the experimental data using (1.8), a RUNS test was performed to check for randomness of the scattering of the experimental data.

In the work of A. Hanf [43] is also considered an extension of this system, where the most important of the so called secondary reactions 1 is taken in account.

1.3 Experimental results

We give in this section the results of four experimental tests for four different reference temperatures at the "measurement-zone".

A detailed explanation of the results is given in the work of A. Hanf [43].

The range of temperature tested is between 370 K and 780 K.

The results are summarized in the following table:

Т	р	[Ar	\cdot][N ₂	O][H ₂]	${ m k_{ps}^{min-max}}$	k
[K]	[torr]	$[10^{15}molec/cm^3]$			$[10^6 s^{-1}]$	$[10^{-10} molec^{-1} cm^3 s^{-1}]$
300	14	350	8	18-107	1.8-11.2	0.99 ± 0.08
370	15	330	6.5	13-89	1.2-8.7	1.00 ± 0.02
580	50	700	16	33-217	2.9-24.8	1.15 ± 0.06
780	44	450	10	21-137	4.0-22.3	1.53 ± 0.15

Table 1.1: Results from the experimental approach to the determination of the kinetic. In the first column we have the test-temperature, in the second column we have the pressure inside the reactor, in the third column we have the empirically calculated concentrations of the different species, in the fourth column we have the range of values for the k_{ps} corresponding to the different values of $[H_2]$ concentration at which have been made measurements, in the last column we have the fitted value of the rate constants with the variance obtained by the RUNS tests.

As described in the section 1.1 we have expected an increased value of the reaction rate at higher temperature due to the presence of at least one exited-state reaction pathway. The value $1.53[10^{-10}molec^{-1}cm^3s^{-1}]$ at 780K shows this trend. Further, these results show that the reaction considered behaves not following the standard Arrehnius law, but the so called

¹The primary reactions are reactions that take place between the species available at time zero. The secondary reactions are reactions that take place between the species available from the beginning and the products of the primary reations.

modified Arrehnius law:

$$k(T) = A(\frac{T}{T_0})^{\beta} \exp(\frac{-E_a}{RT}),$$

where T is the temperature and $T_0 = 300K$ is a reference temperature, A is a constant, E_a is the activation energy, R is the universal gas constant and β is a constant. The modified law presents the term T^{β} and for values of β different than zero makes the

The modified law presents the term T^{β} and for values of β different than zero makes the value of the reaction rate k to dependent on the temperature in a stronger way as shown in [43].

Chapter 2

Model derivation

The mathematical model is a model of the fluid motion and of the reaction mechanism. In the reactor flows a multicomponent fluid, which motion is governed by the Navier-Stokes equations. We derive in this chapter the conservation laws governing the fluid motion. We start by the derivation of the Navier-Stokes in the more general case for a Newtonian fluid in a instationary regime. We extend the system to the case of a reacting multicomponent fluid, and then we describe the case of low Mach number regime, which is suggested by the real test conditions. We derive an asymptotic analysis of the flow, that gives the motivation of the modification to the system that we apply in this case.

2.1 Conservation laws

Given a volume \mathcal{V} of fluid, for a generic entity, which dependency on space and time is described by the function f, the conservation law is the relation between the variation in the time of this entity in the volume \mathcal{V} , the flux \mathcal{F}_f through the boundary surface $\partial \mathcal{V}$ of the volume and the source/sink term s. If n is the unity vector normal to the surface $\partial \mathcal{V}$, we have:

$$\frac{\partial}{\partial t} \int_{\mathcal{V}} f d\mathcal{V} + \oint_{\partial \mathcal{V}} \mathcal{F}_f \mathbf{n} d\mathcal{S} = \int_{\mathcal{V}} s d\mathcal{V}.$$
(2.1)

If the function f and his derivatives are continuous we can apply the Gauss theorem to obtain:

$$\frac{\partial}{\partial t} \int_{\mathcal{V}} f d\mathcal{V} + \int_{\mathcal{V}} \nabla \cdot \mathcal{F}_f d\mathcal{V} = \int_{\mathcal{V}} s d\mathcal{V}, \qquad (2.2)$$

then write the equations in differential form:

$$\frac{\partial f}{\partial t} + \nabla \cdot \mathcal{F}_f = s. \tag{2.3}$$

To describe the fluid motion we use three entities:

1. the density of the fluid ρ ,

- 2. the momentum $Q = \rho u$, where u is the velocity of the fluid,
- 3. the total energy E of the fluid.

The mass flux is simply given by:

$$\mathcal{F}_{\rho} = Q = \rho u,$$

where u is the velocity of the fluid and is a vector function of space and time. The mass conservation equation then becomes:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0, \qquad (2.4)$$

because the total mass in a closed system has no source/sink term. The momentum flux, in the case of inviscid fluid, reduces to ρuu plus a second rank isotropic tensor. Thus we can express it as:

$$\mathcal{F}_{Q_{inviscid}} = \rho u u + p(\rho, E)I,$$

where I is the unity tensor and the scalar function p is the thermodynamic pressure, dependent on the variables ρ and E. In case of viscous fluid, we have to add a term dependent on the gradient of the variables ρ , Q and E, that describes the dissipative part. By considerations on the rank of the tensors and on the operations that give a second rank tensor as result, we can deduce that the only expression allowed for the dissipative momentum flux is:

$$\mathcal{F}_Q = a\nabla\rho + b\nabla E + c\nabla Q,$$

where a and b are third rank tensors and c is a fourth rank tensor.

By other considerations on the operations, that give as result a tensor independent of the coordinate system, we reduce the dissipative momentum flux to the expression:

$$\mathcal{F}_Q = c\nabla Q = \tilde{c}\nabla u,$$

where the only operations allowed between \tilde{c} and ∇u are to take the trace and the symmetric or antisymmetric part of the tensor. We obtain:

$$\mathcal{F}_Q = -\mu' \nabla \cdot uI - \mu [\nabla u + (\nabla u)^T - \frac{2}{3} \nabla \cdot u I], \qquad (2.5)$$

where μ is the viscosity coefficient and μ' is the bulk viscosity coefficient. Finally the momentum conservation equation is:

$$\frac{\partial(\rho u)}{\partial t} + \nabla \cdot (\rho u u + pI + \mathcal{F}_Q) = \rho f, \qquad (2.6)$$

where ρf is the volume force acting on the volume \mathcal{V} . Analogously for the flux of energy we have in the case of inviscid fluid:

$$\mathcal{F}_{E_{inviscid}} = pIu + \rho Eu = pIu + \rho (e + \frac{u^2}{2})u,$$

where the total energy is divided in internal energy e and kinetic energy $\frac{u^2}{2}$.

In case of viscous fluid we add the dissipative part, which is the summation of two terms:

$$\mathcal{F}_{E_{viscous}} = \mathcal{F}_Q u + \mathcal{F}_E,$$

and for the same considerations as for the momentum flux, the term \mathcal{F}_E has the following tensor form:

$$\mathcal{F}_E = d\nabla \rho + f\nabla u + g\nabla E,$$

where d and g are second rank tensors and f is a third rank tensor. Adding the constrain that the entropy has to be positive for all the values of the variables and gradients of these, in the previous expression remains only the dependency on the energy, that usually is expressed in term of temperature:

$$\mathcal{F}_E = -k\nabla T,\tag{2.7}$$

where k is the heat conduction coefficient. Again for the second principle of the thermodynamic the three coefficients satisfy the following constraints:

$$k \ge 0,$$

$$\mu \ge 0,$$

$$\mu' \ge 0.$$

The conservation of energy equation becomes:

$$\frac{\partial}{\partial t}\rho(e+\frac{u^2}{2}) + \nabla \cdot \left[\rho(e+\frac{u^2}{2})u + pIu + \mathcal{F}_Q u - k\nabla T\right] = \rho f u, \qquad (2.8)$$

if the only external force is the gravity and we do not have radiation.

We can write now the conservation laws in the conservative formulation: mass, momentum and energy equations.

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) = 0, \qquad (2.9)$$

$$\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho u u + pI + \mathcal{F}_Q) = \rho f, \qquad (2.10)$$

$$\frac{\partial}{\partial t}(\rho e + \rho \frac{u^2}{2}) + \nabla \cdot (\rho e u + \rho \frac{u^2}{2}u + pIu + u\mathcal{F}_Q + \mathcal{F}_E) = \rho f u, \qquad (2.11)$$

with:

$$\begin{aligned} \mathcal{F}_Q &= -\mu' \nabla \cdot u \ I - \mu [\nabla u + (\nabla u)^T - \frac{2}{3} \nabla \cdot u \ I], \\ \mathcal{F}_E &= -k \nabla T. \end{aligned}$$

2.2 Reactive flows

The next step is the derivation of the conservation laws in case of reactive flows. Reactive flows are those flows of mixture fluids in which the different components can react with each-other or with the surface of the container.

2.2.1 Mass and momentum equations

In case of multicomponent fluid, to take into account the detailed composition of the mixture we have to model the conservation principles for each species. We assume that the species are mixed and the mixture can be treated as a continuum with locally changing properties, that depend on the mixing components. We introduce the species mass fractions:

$$Y_k = \frac{\rho_k}{\rho} = \frac{m_k}{m}, \quad k \in S,$$

where ρ_k is the mass density of the k species, m_k is the molar mass of the k species, m is the total mass, $m = \sum_{k \in S} m_k$, and S is the set of species indices $S = \{1, \ldots, n\}$. The ideal gas law for a mixture of gases is defined as:

$$p\bar{m} = \rho RT, \tag{2.12}$$

where \bar{m} is the mean molar mass:

$$\bar{m} = \sum_{k \in S} x_k m_k \tag{2.13}$$

and $x_k = n_k/n$ is the mole fraction, n_k the number of moles of the k species and $n = \sum_{k \in S} n_k$. For n reacting species we need n equations for the mass conservation, each including a source/sink term describing the production/destruction of the species. We denote with v_k the velocity of the k species:

$$v_k = v + V_k,$$

where $v = \sum_{k} Y_k v_k$ is the mass-weighted average velocity of the fluid mixture and V_k denote the diffusion velocity of the species k. So we can write the mass conservation for each species:

$$\frac{\partial \rho_k}{\partial t} + \nabla \cdot (\rho_k v) + \nabla \cdot (\rho_k V_k) = m_k \omega_k, \quad k \in S,$$
(2.14)

where m_k is the molar mass of the k species, ω_k is the molar production rate of the k species, a detailed description of this term is given by the laws of chemical kinetics and described later in this chapter.

We can write the conservation equation as:

$$\frac{\partial \rho Y_k}{\partial t} + \nabla \cdot (\rho Y_k v) + \nabla \cdot \mathcal{F}_k = m_k \omega_k, \quad k \in S,$$
(2.15)

where \mathcal{F}_k is the species diffusion flux and it is given in an explicit dependence on the other thermodynamical variables, in order to have an expression that can be used for the calculations.

The mass fractions satisfy the condition:

$$\sum_{k \in S} Y_k = 1 \tag{2.16}$$

and the fluxes and source terms satisfy the mass condition:

$$\sum_{k \in S} \mathcal{F}_k = 0, \tag{2.17}$$

$$\sum_{k \in S} m_k \omega_k = 0. \tag{2.18}$$

The conservation of momentum has the same form as for the homogeneous fluid but with the force term given as the sum of the force terms acting on the different species.

$$\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho u u + pI + \mathcal{F}_Q) = \sum_k \rho_k f_k.$$
(2.19)

The energy conservation can be written as follows:

$$\frac{\partial}{\partial t}(\rho e + \rho \frac{u^2}{2}) + \nabla \cdot (\rho e u + \rho \frac{u^2}{2}u + upI + u\mathcal{F}_Q + \mathcal{F}_E) = \sum_{k \in S} (\rho_k v + \mathcal{F}_k)f_k, \qquad (2.20)$$

where we have some more terms with respect to the equation derived for an homogeneous fluid. We have the term $\sum_{k \in S} \mathcal{F}_k f_k$, if the specific forces acting on the different species are different. In the case of gravity, $f_k = g$ and, for the constraint on the diffusion flux $\sum_{k \in S} \mathcal{F}_k = 0$, this term is zero. From now on we assume that the only external force is the gravity. So the energy equation becomes:

$$\frac{\partial}{\partial t}(\rho e + \rho \frac{u^2}{2}) + \nabla \cdot (\rho e u + \rho \frac{u^2}{2}u + upI + u\mathcal{F}_Q + \mathcal{F}_E) = \rho g v, \qquad (2.21)$$

where the term for the heat flux \mathcal{F}_E has to be modified to take in account the energy transfer due to species with different enthalpies and due to gradients of concentration of the different species.

In the next paragraph we derive the equation for the variable T, temperature of the fluid, which is used in the following instead of the energy equation.

2.2.2 Temperature equation

From the kinetic theory of gas mixtures we can obtain some thermodynamic relations, that we need to derive the temperature equation. This is a balance equation for the energy written in term of the thermodynamic variables temperature and density and not in term of internal energy. With this formulation we can describe the boundary conditions for the energy in term of temperature, which is normally measured in real experiments.

From the energy equation (2.21) we obtain the internal energy equation by subtracting the momentum equation (2.19) multiplied by the velocity u, which gives the kinetic energy equation:

$$\frac{\partial \rho u}{\partial t}u + \nabla \cdot (\rho u u + pI + \mathcal{F}_Q)u = \rho g u,$$

$$\frac{\partial \rho \frac{1}{2}u u}{\partial t} + \nabla \cdot (\frac{1}{2}\rho u u + p)u) + \nabla \cdot (\mathcal{F}_Q u) = p \nabla \cdot u + \mathcal{F}_Q : \nabla u + \rho g u.$$

So subtracting this to the total energy equation yields:

$$\frac{\partial \rho e}{\partial t} + \nabla \cdot (\rho e u + \mathcal{F}_E) + p \nabla \cdot u + \mathcal{F}_Q : \nabla u = 0.$$

The enthalpy per unit mass, being an intensive entity, can be expressed as the summation of the different species enthalpies, so we express the enthalpy density as the specific enthalpy times the mass density and we obtain:

$$\rho h = \sum_{k \in S} \rho_k h_k.$$

Using the definition of enthalpy:

$$h_k = h_k^0 + \int_{T_0}^T c_{p,k}(T) dT,$$

with formation enthalpy h_k^0 , standard temperature T_0 and the heat capacity at constant pressure $c_{p,k}$, and the relation:

$$\rho e = \rho h - p,$$

we can write the enthalpy equation, substituting the ρe in the equation for the internal energy:

$$\frac{\partial \rho h}{\partial t} - \frac{\partial p}{\partial t} + \nabla \cdot (\rho h u + \mathcal{F}_E) - u \nabla p + F_Q : \nabla u = 0.$$
(2.22)

Using the continuity and the conservation of species mass we have:

$$\frac{\partial \rho h}{\partial t} + \nabla \cdot (\rho h u) = \rho \frac{\partial h}{\partial t} + \rho u \nabla h$$
(2.23)

$$= \rho \sum_{k} \left\{ \frac{\partial(y_k h_k)}{\partial t} + u \nabla(y_k h_k) \right\}$$
(2.24)

$$= \rho \sum_{k} \{ y_k c_{p,k} (\frac{\partial T}{\partial t} + u \nabla T) + h_k (\partial y_k + u \nabla y_k) \}$$
(2.25)

$$= \rho c_p \{ \frac{\partial T}{\partial t} + u \nabla T \} + \sum_k h_k (m_k \omega_k - \nabla \cdot \mathcal{F}_k), \qquad (2.26)$$

thus the temperature equation is:

$$\rho c_p \frac{\partial T}{\partial t} + \rho c_p u \nabla T - \frac{\partial p}{\partial t} + \nabla \cdot \mathcal{F}_E - u \nabla p + \mathcal{F}_Q : \nabla u - \sum_{k \in S} h_k \nabla \cdot \mathcal{F}_k = -\sum_{k \in S} h_k m_k \omega_k.$$
(2.27)

We can rewrite the temperature equation using the relations:

$$\nabla \cdot \left(\sum_{k} h_k \mathcal{F}_k\right) = \sum_{k} h_k \nabla \cdot \mathcal{F}_k + \sum_{k} \mathcal{F}_k \nabla h_k,$$

and

$$\nabla h_k = c_{p,k} \nabla T,$$

yielding:

$$\rho c_p \frac{\partial T}{\partial t} + \rho c_p u \nabla T - \frac{\partial p}{\partial t} + \nabla \cdot (\mathcal{F}_E - \sum_k h_k \mathcal{F}_k) + \sum_k c_{p,k} \mathcal{F}_k \nabla T - u \nabla p + \mathcal{F}_Q : \nabla u = -\sum_{k \in S} h_k m_k \omega.$$
(2.28)

2.2.3 Transport fluxes

To complete our derivation of the equations that describe the flow we need the formulation of the two terms: the species mass flux \mathcal{F}_k , and the energy flux \mathcal{F}_E .

These are the description of different effects. The mass flux can be divided in three terms: the diffusion given by the gradient of concentration of the species, the thermal diffusion (Soret effect) and the pressure diffusion. The species flux is given by the species density ρ_k times the species diffusion velocity, which can be expressed as:

$$V_i = -\sum_{j \in S} D_{ij} (d_j - \chi_j \nabla \log T), \qquad i \in S,$$
(2.29)

with:

$$d_i = \nabla X_i + (X_i - Y_i) \frac{\nabla p}{p}, \quad i \in S,$$
(2.30)

where $D = D_{ij}$ is the diffusion matrix, d_i the diffusion driving force of the *i* species, X_i is the mole fraction of the *i* species and $\chi = \chi_i$ are the thermal diffusion ratios, a precise definition of these is given in [32].

Now we can give an explicit formulation of the heat flux including the term corresponding to the Dufour effect:

$$\mathcal{F}_E = \sum_{i \in S} h_i \mathcal{F}_i - \lambda \nabla T + p \sum_{i \in S} \chi_i V_i, \qquad (2.31)$$

with λ the thermal conductivity, h_i the enthalpy per unit mass of the i^{th} species and V_i and χ_i as previous defined. Detailed modeling of a polyatomic gas mixture requires the evaluation of the transport coefficients: $D_{ij}, d_i, \chi_i, \lambda$. These are functions of the state variables $\{p, T, Y_i, \ldots, Y_n\}$ and are not given explicitly by the kinetic theory, their evaluation requires the solution of the so called 'transport linear systems'. These are derived from a Galerkin approximation of the linearized Boltzmann equations. For the definition and solution of these systems we refer to the work of A. Ern and V. Giovangigli ([38],[33]). From the same authors is available the library Eglib [31] that implements the algorithms to solve the different coefficients with different levels of approximation. Following the work of A. Ern and V. Giovangigli we treat in the next section the transport linear system associated with the diffusion coefficients and we define the first order diffusion matrix.

Diffusion matrix

To define the diffusion matrix D we have to define the matrix $\Delta \in \mathbb{R}^{n,n}$, where n is the number of species in the mixture, by:

$$\Delta_{kk} = \sum_{l \neq k} \frac{x_k x_l}{D_{kl}^{bin}}, \qquad (2.32)$$

$$\Delta_{kl} = -\frac{x_k x_l}{D_{kl}^{bin}}, \quad k \neq l, \tag{2.33}$$

where D_{kl}^{bin} is the binary diffusion coefficient for the species pair (k, l), see [38]. The transport linear systems that define the diffusion coefficients are the *n* systems indexed by *l* and given by:

$$\Delta \alpha^l = \beta^l, \tag{2.34}$$

$$(\alpha, Y) = 0, \qquad (2.35)$$

where the symbol (\cdot, \cdot) is the scalar product in \mathbb{R}^n . The right hand side β^l is defined by:

$$\beta^l = \delta_{kl} - \frac{Y_k}{\sum_i Y_i} = \delta_{kl} - Y_k.$$
(2.36)

The matrix Δ has the following properties:

- it is symmetric and positive definite,
- $N(\Delta) = \mathbb{R}\mathcal{U},$
- $R(\Delta) = \mathcal{U}^{\perp},$
- $\beta^l \in R(\Delta),$

where $R(\cdot)$ is the range and $N(\cdot)$ is the kernel of the given matrix. The vectors α^l are the column of the diffusion matrix, thus the diffusion coefficients are given by:

$$D_{kl} = (\alpha^l, \beta^k) = (\alpha^k, \beta^l) = \alpha^l_k = \alpha^k_l.$$

$$(2.37)$$

The matrix D can be written as the solution of the following system:

$$\Delta D = I - Y \times \mathcal{U},\tag{2.38}$$

where \mathcal{U} is the vector $\{1, 1, \dots, 1\}^T \in \mathbb{R}^n$ and the symbol '×' is the tensor product between two vectors, i.e. the matrix $Y \times \mathcal{U} = (Y_i U_j)_{(i,j=1,\dots,n)}$.

It is possible to show that the diffusion matrix D is the generalized inverse of Δ , i.e. $D\Delta D = D$ and $\Delta D\Delta = \Delta$, with given range $R(D) = Y^{\perp}$ and kernel $N(D) = \mathbb{R}Y$ and has the following properties:

- it is symmetric and positive semidefinite,
- it is positive definite over \mathcal{U}^{\perp} ,
- $N(\Delta) = \mathbb{R}Y,$
- $R(\Delta) = Y^{\perp}$,
- it is irreducible.

In order to avoid matrix inversions for the calculation of D it is possible to consider an expansion of D as a convergent series and use iterative techniques to solve the system or to define analytic approximate coefficients by truncation. Considering standard iterative methods we use the decomposition of the matrix $\Delta = M - Z$, whit M not singular. The induced iteration is:

$$x_{i+1} = Tx_i + M^{-1}\beta, (2.39)$$

where $T = M^{-1}Z$. The scheme converges if $\beta \in R(\Delta)$ and if the iteration matrix T is convergent, i.e. exists the $\lim_{i\to\infty} T^i$. In the case where Δ is regular, the spectral radius of T is $\rho(T) < 1$ so the iterates converges towards $\lim_{i\to\infty} x_i = \Delta^{-1}\beta = \alpha$. When Δ is singular $\rho(T) = 1$ the limit of (2.39) depends on the initial values x_0 , in this case it has to be considered the projected version of the scheme with the projector matrix P over Y^{\perp} parallel to $\mathbb{R}\mathcal{U}$: $P = I - Y \times \mathcal{U}/(Y,\mathcal{U})$. The spectral radius of PT is strictly lower then unity and we have the series expansion [37]:

$$D = \sum_{j=0}^{\infty} (PT)^j P M^{-1} P^T.$$
 (2.40)

Truncating the summation we get different approximate diffusion matrices $D^{[i]}, i \ge 0$:

$$D^{[i]} = \sum_{j=0}^{i} (PT)^{j} P M^{-1} P^{T}, \qquad (2.41)$$

each partial sum satisfy all mathematical properties that characterize the diffusion matrix, in particular they are symmetric, conserve the mass $D^{[i]}Y = 0$ and satisfy the constraint of a positive entropy production over \mathcal{U} . Usually it is sufficient to use an approximation of the diffusion matrix and stop the expansion to the first or second term. The first order approximation is given by:

$$D^0 = P M^{-1} P^T, (2.42)$$

and this can be shown to yield the Fick's law of diffusion plus a corrector term to satisfy the mass constraint. The Fick's law is an empirical expression for the diffusion used in most practical applications.

Approximation of the transport fluxes: the Fick's law

For the evaluation of the transport fluxes, sometimes it is possible to assume some simplifications. The thermal diffusion is important only when the temperature is low, so in high temperature flows the Soret effect for species and the Dufour effect for the heat transport are negligible. Further to save computational time we can use a simplification for the species diffusion velocity, that is given by the Fick's empirical law:

$$\mathcal{F}_k = \rho Y_k V_k = -\rho D_k^M \nabla c_k = -\rho D_k^M \frac{Y_k}{x_k} \nabla x_k = -\rho D_k^M (\nabla Y_k + \frac{Y_k}{\bar{m}} \nabla \bar{m}), \qquad (2.43)$$

where c_k is the concentration of the species k and D_k^M is a mean diffusion coefficient for the species k in a mixture of the other species and is given by the following expression:

$$D_{k}^{M} = \frac{1 - Y_{k}}{\sum_{l \neq k} \frac{X_{l}}{D_{kl}^{bin}}}.$$
(2.44)

Only the second term couples all the species, thus in the case where the variation of \bar{m} is negligible we use a simplified expression of the diffusion coefficients dropping this term and obtaining a diagonal diffusion matrix. As the Fick's law doesn't ensure mass conservation, we have to add a corrector factor:

$$\tilde{\mathcal{F}}_k = \mathcal{F}_k + Y_k \mathcal{F}^{corr}, \qquad (2.45)$$

with the corrector term defined by:

$$\mathcal{F}^{corr} = -\sum_{k \in S} \mathcal{F}_k. \tag{2.46}$$

We have to define now the reactive term of the equations given a mechanism of a reaction.

2.2.4 Reaction Mechanism and elementary reactions

A mechanism is a collection of elementary steps that describes the overall reaction process. The fact that a mechanism explains the experimental results is not a proof that the mechanism is correct. A mechanism is a rationalization of a chemical reaction. An elementary reaction describes how actually molecules or ions react with each other. We write the elementary reaction equations as:

$$\sum_{k \in S} \nu_{ki}^f \mathcal{S}_k \rightleftharpoons \sum_{k \in S} \nu_{ki}^b \mathcal{S}_k, \quad i \in N_r$$
(2.47)

where S_k is the chemical symbol of k species, ν_{ki}^f and ν_{ki}^b are the stoichiometric coefficients of the k species and N_r the number of reactions. The molar production rates ω_k are given by:

$$\omega_k = \sum_i \nu_{ki} \tau_i, \tag{2.48}$$

where

$$\nu_{ki} = \nu_{ki}^b - \nu_{ki}^f, \tag{2.49}$$

and

$$\tau_{i} = k_{i}^{f} \prod_{l} c_{l}^{\nu_{li}^{f}} - k_{i}^{b} \prod_{l} c_{l}^{\nu_{li}^{b}}, \qquad (2.50)$$

where $c_k = \frac{\rho_k}{q_k}$ is the molar concentration of the k species and k_i^f and k_i^b are the forward and backward rate constants respectively. The k_i^f and k_i^b are functions of the temperature and their ratio is the equilibrium constant:

$$k_i^e(T) = \frac{k_i^f(T)}{k_i^b(T)}.$$
(2.51)

For the forward reaction we have:

$$\omega_k = \sum_i (\nu_{ki}^b - \nu_{ki}^f) k_i^f \prod_l c_l^{\nu_{li}^f}, \qquad (2.52)$$

where the forward rate constant is usually approximated by the Arrhenius empirical law:

$$k_i^f(T) = A_i T^{b_i} exp(-\frac{E_{ai}}{RT}), \qquad (2.53)$$

where E_{ai} is the activation energy of the *i* reaction. The backward reactions to be consistent have to be derived by (2.51), using an explicit form for k^e , but usually it is possible to determine the Arrenhius coefficients for the backward reaction by a least-squares fit over a certain range of temperature, although in this way consistency get lost.

2.3 Low Mach number model

When the velocity of the fluid is much slower then the sound speed, the effect of compressibility are very small. The Mach number, defined as the ratio of the fluid velocity and the sound speed, is the parameter used to measure this effect. As this parameter becomes small, the coupling between the velocity and the pressure changes in its physical meaning: the interaction between flow phenomena and acoustic waves has different scales. An asymptotic analysis gives the different orders of the terms describing the different scales. To solve the low Mach number regime we exploit the splitting of these effects to overcome the intrinsic numerical difficulties.

2.3.1 Low Mach number asymptotic of the Navier-Stokes equations

The low Mach number regime can be seen as a limit of the Navier-Stokes equations with $Ma \rightarrow 0$ and has been derived in different ways by many authors starting from the compressible formulation. Following the work of Majda [61] and [68], we show the limit starting from an asymptotic analysis as described in [62].

Non-dimensionalization

We first write the equations that we have derived in a non-dimensional form and then, assuming that the low Mach number asymptotic is a regular perturbation problem, we expand in power series of M all flow variables. We order all the terms according to the power of M and identify the different orders of the equations. We use reference quantities, marked with the subscript " ∞ ", and a typical length scale L for this flow to write the equations in a non-dimensional form. The reference quantities have to be chosen such that the nondimensional flow quantities remain of order O(1) for any low reference Mach number:

$$M_{\infty} = \frac{u_{\infty}}{\sqrt{\gamma p_{\infty}/\rho_{\infty}}},$$

where $\gamma = \frac{C_p}{C_v}$ is the ratio of specific heats. We may use:

$$\tilde{M} = \frac{u_{\infty}}{\sqrt{p_{\infty}/\rho_{\infty}}} = \sqrt{\gamma}M_{\infty}$$

to avoid the dependency on γ .

To write the non-dimensional equations we use the definition of dimensionless ratios of some coefficients:

- $Re = \frac{\rho uL}{\mu}$ is the Reynolds number and represent the ratio of inertial forces to viscous forces,
- $Fr = \frac{u}{\sqrt{gL}}$ is the Froude number, the ratio of kinetic energy to potential energy,
- $Pr = \frac{c_{p\mu}}{\kappa}$ is the Prandtl number, the ratio of momentum diffusivity to thermal diffusivity,
- $Sc = \frac{\mu}{\rho D}$ is the Schmidt number, ratio of kinetic viscosity to molecular diffusivity D,
- $Da = \frac{m\omega L}{\rho u}$ is the Damkoehler number, ratio of chemical reaction timescale to transport phenomena.

We can expand each variables in the power of \tilde{M} :

$$v(x,t,\tilde{M}) = v_0(x,t) + \tilde{M}v_1(x,t) + \tilde{M}v_2(x,t) + O(\tilde{M}^3)$$

and use this expansion in the system of equations. For the continuity equation we obtain:

$$\left[\frac{\partial\rho_0}{\partial t} + \nabla\cdot(\rho u)_0\right] + \left[\frac{\partial\rho_1}{\partial t} + \nabla\cdot(\rho u)_1\right]\tilde{M} + \left[\frac{\partial\rho_2}{\partial t} + \nabla\cdot(\rho u)_2\right]\tilde{M}^2 + O(\tilde{M}^3) = 0.$$
(2.54)
The approximation that we do is to stop the expansion at the second order term and to solve the equation with a rest term of the order $O(\tilde{M}^3)$. As the coefficients of the powers of \tilde{M} have to vanish to satisfy this equation, we have:

$$\left[\frac{\partial\rho_i}{\partial t} + \nabla \cdot (\rho u)_i\right] = 0, \quad i = 0, 1, 2.$$
(2.55)

The non-dimensional momentum equation becomes:

$$\frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho u u) + \frac{1}{\tilde{M}^2} \nabla p = \frac{1}{Re_{\infty}} \nabla \cdot \mathcal{F}_Q + \frac{1}{Fr_{\infty}^2} \rho(-e_r), \qquad (2.56)$$

(2.57)

where e_r is the unity vector in the direction of the gravity field. With the assumption that the Re and the Fr numbers remain constant and only the M number varies we can proceed and substitute the expansion of the variables and we retain only the zeroth order term, so we get:

$$\frac{\partial \rho_0 u_0}{\partial t} + \nabla \cdot (\rho_0 u_0 u_0) + \tilde{M}^{-2} \nabla p_0 + \tilde{M}^{-1} \nabla p_1 + \nabla p_2 = \frac{1}{Re_{\infty}} \nabla \cdot (\mathcal{F}_Q)_0 + \frac{1}{Fr_{\infty}^2} \rho_0(-e_r).$$
(2.58)

The first order momentum equation is thus:

$$\frac{\partial \rho_0 u_0}{\partial t} + \nabla \cdot (\rho_0 u_0 u_0) + \nabla p_2 = \frac{1}{Re_\infty} \nabla \cdot (\mathcal{F}_Q)_0 + \frac{1}{Fr_\infty^2} \rho_0(-e_r), \qquad (2.59)$$

while the two terms of pressure p_0 and p_1 must satisfy the relations:

$$\nabla p_0 = 0, \tag{2.60}$$

$$\nabla p_1 = 0. \tag{2.61}$$

From the (2.60, 2.61) we have:

$$p_0 = p_0(t), (2.62)$$

$$p_1 = p_1(t). (2.63)$$

that is, the zeroth and first order terms of the pressure are functions only of the time and constant in space.

Considering the multicomponent fluid we neglect, for simplicity, the Dufour effect and the dependency on the gradient of pressure for the diffusion of species and we adopt the Fick's law. Introducing the Schmidt number $Sc = \frac{\mu}{\rho D}$, where D is the mean diffusion coefficient in the Fick's law, and the Damkoehler number, $Da = \frac{m\omega L}{\rho u}$, we obtain the following expression for the non-dimensional temperature equation:

$$\frac{\partial \rho c_p T}{\partial t} + \nabla \cdot (\rho c_p T) = \frac{\gamma - 1}{\gamma} \frac{\partial p}{\partial t} + \frac{1}{RePr} \nabla \cdot \mathcal{F}_E - \frac{\rho}{ReSc} \sum_{i=0}^{N_{sp}} c_{p,i} V_i \nabla T - Da_i \sum_{i=0}^{N_{sp}} h_i \omega_i, \quad (2.64)$$

where N_{sp} is the number of species and V_i is the species diffusion velocity as defined in the previous chapter. In the low Mach number approximation the term due to the dissipative momentum flux:

$$\frac{\tilde{M}^2}{Re_{\infty}}\mathcal{F}_Q:\nabla u\tag{2.65}$$

is a higher order term and can be neglected. The species mass conservation equation has now to be derived and also for this equation we neglect the dependency on the temperature gradient (Soret effect) obtaining:

$$\frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho u Y_i) + \frac{1}{ReSc} \nabla \cdot \mathcal{F}_i = Da_i w_i, \qquad (2.66)$$

where we see that the form of the equation is not modified due to terms with different order w.r.t. M.

From this asymptotic analysis we can derive an approximation of the system, in the case of low Mach number regime, by considering only the zeroth order equations.

The approximation is valid only for very small Mach number because the higher order terms go to zero as $M \to 0$. The system becomes:

$$\frac{\partial \rho_0}{\partial t} + \nabla \cdot (\rho u)_0 = 0, (2.67)$$
$$\frac{\partial \rho_0 u_0}{\partial t} + \nabla \cdot (\rho_0 u_0 u_0) + \nabla p_2 - \nabla \cdot (\mathcal{F}_Q)_0 - \rho_0 g = 0, (2.68)$$

$$\frac{\partial \rho_0 c_p T_0}{\partial t} + \nabla \cdot (\rho_0 u c_p T_0) - \frac{\gamma - 1}{\gamma} \frac{\partial p_0}{\partial t} - \nabla \cdot ((\mathcal{F}_E)_0) + \sum_{i=0}^{N_{sp}} c_{p,i} \mathcal{F}_i \nabla T_0 + \sum_{i=0}^{N_{sp}} h_i m_i \omega_i = 0, (2.69)$$
$$\frac{\partial \rho_0 Y_i}{\partial t} + \nabla \cdot (\rho_0 u_0 Y_i) + \nabla \cdot \mathcal{F}_i - m_i \omega_i = 0, (2.70)$$

where the pressure is split in two terms p_0 and p_2 . The first order pressure term p_1 appear only in the first order equations and has no relevance in our formulation, if we are not interested in the acoustic effect. The zeroth order pressure p_0 constitutes the coupling between the momentum and energy equations through the equation of state $p_0 = \rho_0 RT_0$. It is constant in space while it can vary in time due to mass flux or heat transfer from the boundary and, as in the case of exothermic reactions, from heat release.

In our case we can calculate the variation in time of the pressure from the variation in time of temperature and mean molar mass and from the mass flux through the boundary. To obtain explicitly this dependency we substitute the density from the state equation (2.12) into the continuity equation (2.67) and, being p_0 constant in space, integrate over the volume. From the state equation we have:

$$o = \frac{p_0 \bar{m}}{RT},$$

substituting in the continuity equation we obtain:

$$\frac{\partial p_0}{\partial t}\frac{\bar{m}}{RT} + \frac{\partial \bar{m}}{\partial t}\frac{p_0}{RT} - \frac{1}{T^2}\frac{\partial T}{\partial t}\frac{p_0\bar{m}}{R} + \frac{p_0\bar{m}}{RT}\nabla \cdot u + u \cdot \nabla \bar{m}\frac{p_0}{RT} - \frac{1}{T^2}u \cdot \nabla T\frac{p_0\bar{m}}{R} = 0.$$

where we have used $\nabla p_0 = 0$. We can thus reformulate the continuity equation as:

$$\frac{1}{p_0}\frac{\partial p_0}{\partial t} + \frac{1}{\bar{m}}(\frac{\partial \bar{m}}{\partial t} + u \cdot \nabla \bar{m}) - \frac{1}{T}(\frac{\partial T}{\partial t} + u \cdot \nabla T) + \nabla \cdot u = 0, \qquad (2.71)$$

The thermodynamical pressure is constant in space and his variation in time can be shown to be determined by an ordinary differential equation. We can distinguish between two cases:

• flow in a closed vessel: here the variation of pressure is mostly due to heat release. The equation governing this variation is obtained by integrating over the volume:

$$\frac{\partial p_0}{\partial t} \int_{\Omega} dx = -p_0 \int_{\Omega} \left(\frac{1}{\bar{m}} (\frac{\partial \bar{m}}{\partial t} + u \cdot \nabla \bar{m}) - \frac{1}{T} (\frac{\partial T}{\partial t} + u \cdot \nabla T) + \nabla \cdot u \right) dx,$$
$$\frac{\partial p_0}{\partial t} = -\frac{p_0}{|\Omega|} \int_{\Omega} \left(\frac{1}{\bar{m}} (\frac{\partial \bar{m}}{\partial t} + u \cdot \nabla \bar{m}) - \frac{1}{T} (\frac{\partial T}{\partial t} + u \cdot \nabla T) + \int_{\partial \Omega} u \cdot n ds.$$
(2.72)

Knowing the initial conditions for the mass flow, temperature and mass composition we can integrate this ODE to calculate the variation of thermodynamic pressure.

• flow in a vessel with an open boundary: in this case the pressure is controlled from outside and the pressure can be found as the spatial mean value over the outflow boundary. The pressure is given by the following expression:

$$p_0 = \frac{1}{|\Gamma_{out}|} \int_{\Gamma_{out}} p_{out}(x, t) ds.$$
(2.73)

In our case we have an open boundary so the thermodynamic pressure is imposed from outside and constant in space and time. On the other hand the second order term p_2 corresponds to the pressure in the incompressible flow and can be considered as the constraint for the divergence of u_0 . In the case of low Mach number flow, we do not have a divergence free velocity field, but the constraint on the velocity is given by the equation (2.71).

Chapter 3

Discretization and solver

In this chapter we describe the discretization of the equations presented in the previous one. We expose also the numerical techniques we have used to solve the discretized problem. The method is based on conforming finite elements, we refer to [19, 25, 30, 51, 18] for a general introduction to FEM. First we give a variational formulation of the problem, to be used for the discretization. Then we describe the Galerkin discretization using stable elements, to fulfill the inf-sup condition (see [39, 18]), for a space discretization. Further, we present the overall solution process, describing the implicit fractional– θ method used for the time discretization, the nonlinear and linear solver. We expose an abstract formulation for a dual based a posteriori error estimation. Finally we briefly describe the HiFlow package and the HP XC6000 cluster used for the numerical simulations.

3.1 Finite element discretization

3.1.1 Variational formulation

To find a solution of a system of partial differential equations describing the flow and the chemical reactions we rewrite the entire problem in the weak formulation, that means we seek for the solution u in an appropriate space U, of an equivalent boundary value problem. Let $\Omega \in \mathbb{R}^d$ describe the computational domain, the variational formulation is obtained by multiplying the equations by the appropriate test-functions $\varphi \in U$ and integrating over the domain Ω . The diffusive terms and the pressure gradient are integrated by parts, decreasing the needed order of differentiability of the trial functions u and test functions φ .

The variables considered are the velocity, the pressure, the temperature and the n_s species: $u := \{v, p, T, Y_i\}, i = 1, \dots, n_s$. In our formulation we add the continuity equation to the momentum, energy and species mass conservation equations, in this way the system is over-determined, so for consistency with the total mass conservation we discard a species. The reduced system contains only $n_s - 1$ species. This is legitimated if a species is present in excess in the mixture, as in our case for the concentration of Ar. The system in the

weak-formulation is given by the following equations:

$$\begin{split} \langle \nabla \cdot v, \varphi_p \rangle + \langle \frac{1}{\bar{m}} (\frac{\partial \bar{m}}{\partial t} + v \cdot \nabla \bar{m}), \varphi_p \rangle - \langle \frac{1}{T} (\frac{\partial T}{\partial t} + v \cdot \nabla T), \varphi_p \rangle &= 0, \quad \forall \varphi_p \in U_p, \\ \int_{\Omega} \frac{\partial v}{\partial t} \varphi_v \ d\Omega - \langle \rho g, \varphi_v \rangle - \langle \mu \nabla v, \nabla \varphi_v \rangle - \frac{1}{3} \langle \mu \nabla \cdot v, \nabla \varphi_v \rangle + \langle p, \nabla \varphi_v \rangle - \langle \rho v \nabla v, \varphi_v \rangle &= 0, \quad \forall \varphi_v \in U_v, \\ \int_{\Omega} \frac{\rho C_p \partial T(t)}{\partial t} \varphi_T \ d\Omega - \langle \rho C_p v \nabla T, \varphi_T \rangle + \langle \sum_i C_{p_i} \mathcal{F}_i \nabla T, \varphi_T \rangle - \langle k \nabla T, \nabla \varphi_T \rangle + \\ \langle v \nabla p, \varphi_T \rangle - \langle \sum_i (h_i m_i \omega_i), \varphi_T \rangle &= 0, \quad \forall \varphi_T \in U_T \\ \int_{\Omega} \frac{\partial Y_i(t)}{\partial t} \varphi_y \ d\Omega + \langle \rho v \nabla Y_i, \varphi_y \rangle + \langle \nabla \cdot \mathcal{F}_i, \varphi_y \rangle = \langle m_i \omega_i, \varphi_y \rangle = 0, \quad \forall \varphi_y \in U_Y , \end{split}$$

where $\langle \cdot, \cdot \rangle$ is the L^2 scalar product and U_v, U_p, U_T, U_Y are appropriate Hilbert-spaces. We define thus the semi-linear form $A(\cdot, \cdot)$ given by:

$$A(u;\varphi) := \left(\frac{1}{\bar{m}}\left(\frac{\partial\bar{m}}{\partial t} + v \cdot \nabla\bar{m}\right) - \frac{1}{T}\left(\frac{\partial T}{\partial t} + v \cdot \nabla T\right) + \nabla v, \varphi_{p}\right) \\ + \left(\frac{\partial v}{\partial t} - \rho g - \rho v \nabla v, \varphi_{v}\right) + \left(\mu \nabla v - \frac{1}{3}\mu \nabla v + p, \nabla \varphi_{v}\right) \\ + \left(\frac{\rho C_{p} \partial T(t)}{\partial t} - \rho C_{p} v \nabla T + \sum_{i} C_{p_{i}} \mathcal{F}_{i} \nabla T + v \nabla p - \sum_{i} (h_{i}m_{i}\omega_{i}), \varphi_{T}\right) - \left(k \nabla T, \nabla \varphi_{T}\right) \\ + \left(\frac{\rho \partial Y_{i}(t)}{\partial t} + \rho v \nabla Y_{i} - m_{i}\omega_{i}, \varphi_{y}\right) + \left(\rho D_{i} \nabla Y_{i}, \nabla \varphi_{y}\right),$$

$$(3.1)$$

where to simplify the expression we have used the Fick's law approximation (2.43) neglecting the term with $\nabla \bar{m}$. Thus the system can be written:

$$A(u;\varphi) = 0 \quad \forall \varphi \in U. \tag{3.2}$$

3.1.2 FEM ansatz

Numerically we look for an approximation u_h of u in a finite dimensional space U_h characterized by a parameter h, that describes the discretization of U_h defining the dimension of U_h . In the finite element formulation the functions u_h are piecewise polynomials on a triangulation \mathcal{T}_h , the considered meshes are supposed to be shape regular and geometrically conforming (see [25]). These consist of, in general curvilinear, quadrilateral (or hexahedral) elements $\{K\}$ covering the domain $\hat{\Omega}$. The considered trial and test spaces $U_h \in U$ consist of continuous, piecewise polynomial vector functions (so-called Q_r elements) for all unknowns:

$$U_h := \left\{ \left\{ p_h, v_h, T_h, Y_h^i \right\} \in C(\hat{\Omega}) \mid p_{h|K}, Y_{h|K}^i \in Q_1(K), v_{h|K}, T_{h|K} \in Q_2(K) \right\}$$
(3.3)

where $Q_r(K)$ is the space of polynomials of degree r on the element K i.e.:

$$Q_r(K) := span\{x^i y^i : 0 \le i, j \le r\}.$$
(3.4)

The discretization for the flow, by using the Taylor-Hood elements with the flow velocity discretized by Q_2 elements and the pressure by Q_1 elements, satisfies the *inf-sup* condition that guarantees a stable approximation of the pressure and avoid the occurrence of spurious pressure modes (see [25]). This is important because it allows to resolve the boundary layers by properly designed anisotropic meshes.

In the work of Heuveline & Schieweck [48] it is shown that the *inf-sup* holds also for mixed hp-FEM on meshes with hanging nodes. This is an important issue if we consider local refinement allowing hanging nodes, as depicted in figure 3.1. The discretized problem holds:

$$A(u_h, \varphi_h) = 0 \quad \forall \varphi_h \in U_h, \tag{3.5}$$

where the form $A(\cdot, \cdot)$ is defined as in (3.1).



Figure 3.1: Example of a patch with two hanging nodes.

Boundary conditions 3.1.3

The system (3.2) has to be supplemented by appropriate initial and boundary conditions. The boundary of the domain Ω is decomposed into the following parts, as depicted in figure 3.2:

$$\partial \Omega = \Gamma_{in} \cup \Gamma_{opt} \cup \Gamma_{out} + \Gamma_{no-slip}. \tag{3.6}$$

At the inflow boundary, $\Gamma_{in} \cup \Gamma_{opt}$, Dirichlet conditions are prescribed for all variables with values to be experimentally determined. At the reactor walls no-slip condition is assumed for the velocity, while the temperature is fixed by the external heating elements and is determined as described in the model calibration 5.1.4, while for the species holds the Neumann condition $\frac{\partial Y_i}{\partial n} = 0$. At the outflow we have the usual 'free-stream' condition: $\mu \frac{\partial v}{\partial n} + pn = 0$, for the velocity and $\frac{\partial T}{\partial n} = 0$, $\frac{\partial Y_i}{\partial n} = 0$, for temperature and species.



Figure 3.2: Definition of the boundary. The boundary is subdivided in different parts to permit the differentiation of the boundary conditions for the solution of the system of equations.

3.2 Overall solution process

The system is a nonlinear system, the nonlinearities arise from different terms, the transport term in the momentum equation and the source terms in the energy equation and mass conservation of the species. In the system we have a coupling between the flow variables and the chemical variables through the temperature and the density and between the different species through the diffusion process and the reactive term. We are interested in the transitory solution during the reaction process, to perform the measurements, so we are not interested in the stationary solution, but we have to solve the system in time. Due to the reaction term the system is stiff and a good resolution in time can be better achieved by an implicit or semi-implicit method. The following is a scheme of the overall solution process:



Figure 3.3: Overall solution process.

3.2.1Time step

For stability issues an implicit fractional-step- θ scheme, [40, 41], was used for the discretization in time of the full system. This method is strongly A-stable and has good smoothing properties.

We consider the following system of equations:

$$\frac{\partial z}{\partial t} + A(z) + B(p) = f, \qquad (3.7)$$

$$\nabla \cdot u = g, \tag{3.8}$$

where z is the solution vector $\{u, v, p, T, Y_i\}, i = 1 \dots n_s - 1$, and the operator A(z) describes all the diffusion and transport terms in the system, the operator B(p) is the gradient of the pressure and f is the zero order term corresponding to external forces for the momentum equation or the reaction term for the energy and species equations.

In the time discretization we consider a time step $k = t^{n+1} - t^n$, and given the solution at time t^n we look for a solution at time t^{n+1} . In the fractional-step- θ -scheme each time step is subdivided in three sub-steps. Defining the following parameters $\theta = 1 - \frac{\sqrt{2}}{2}$, $\theta' = 1 - 2\theta$, $\alpha = \frac{1-2\theta}{1-\theta}$ and $\beta = 1-\alpha$, the scheme is given by the three steps:

$$[I + \alpha \theta k A(z^{n+\theta})]z^{n+\theta} + \theta k B(p^{n+\theta}) = [I - \beta \theta k A(u^n)]u^n + \theta k f^n, \qquad (3.9)$$
$$\nabla \cdot u^{n+\theta} = g^n, \qquad (3.10)$$

$$[I + \alpha \theta k A(z^{n+1-\theta})]z^{n+1-\theta} + \theta' k B(p^{n+1-\theta}) = [I - \alpha \theta' k A(u^{n+\theta})]u^{n+\theta} + \theta' k f^{n+1}(3,11)$$

$$\nabla \cdot u^{n+1-\theta} = g^{n+\theta}, \qquad (3.12)$$

$$[I + \alpha \theta k A(z^{n+1})]z^{n+1} + \theta k B(p^{n+1}) = [I - \beta \theta k A(u^{n+1-\theta})]u^{n+1-\theta} + \theta k f^{n+1-\theta}(3.13)$$

$$\nabla \cdot u^{n+1} = g^{n+1-\theta}.$$
 (3.14)

3.2.2Nonlinear solver

To solve the nonlinearities we consider a quasi-Newton method. For a Newton update we need the evaluation of the Jacobi matrix of the system, this is the most time costly step in the process solution. In the quasi-Newton method we use an approximation of the Jacobi matrix, in which we simplify some coupling terms between flow and chemistry. The residuals are computed without simplifications, so the iteration converges towards the fully coupled system. The efficiency of the nonlinear solver relies on the structure of the approximation of the Jacobi matrix. In the following we describe the structure of the Jacobi matrix in 2D. The variables are the four flow variables: u, v, p, T and $n_s - 1$ species mass fractions $Y = Y_k$, in this formulation using the continuity equation we have to discard a species to guarantee the mass constraint

$$\sum_{k=1}^{n_s} Y_k = 1,$$

the last species is calculated as:

$$Y_{last} = 1 - \sum_{k=1}^{n_s - 1} Y_k, \quad k \neq last.$$

The following structure shows the coupling between all variables. The first two equations are the two component of the momentum equation, the third is the equation for the pressure, i.e. the divergence of the velocity in the low Mach approximation with temperature dependency, the fourth is the energy equation and the last $n_s - 1$ equations are the mass conservation for the species:

$$\tilde{J} = \begin{bmatrix} U_u & U_v & U_p & U_T & 0 \\ V_u & V_v & V_p & V_T & 0 \\ P_u & P_v & 0 & P_T & 0 \\ T_u & T_v & T_p & T_T & T_Y \\ Y_u & Y_v & 0 & Y_T & Y_Y \end{bmatrix}.$$

The last row is a block $(n_s - 1) \times (n_s - 1) + 4$.

The first two equations are the two component of the momentum equation. The coupling with the temperature U_T is given by the density variation in the external force term ρg and in the transport term $\rho u \nabla u$, the latter has two contributions because is linearized as: $\rho \bar{u} \nabla u + \rho u \overline{\nabla u}$. The coupling with the species given by the density variation is neglected in our formulation, because we neglect the variation of mean molar mass \bar{m} . In the term U_u we have neglected the term of the bulk viscosity in the momentum flux: $\mu' \nabla \cdot u$.

The third equation is the divergence equation, that is the equation for the hydrodynamic part of the pressure obtained by the continuity equation. In this equation we neglect the coupling with the species due to the variation of the mean molar mass \bar{m} , while the coupling with the temperature is given by the equation (2.71).

The fourth equation is the energy equation using the temperature as variable. In the low Mach model we can neglect in the coupling with the velocity T_u the term of the dissipative momentum flux $\mathcal{F}_q : \nabla u$, because it is an higher order term, see expression (2.65). The term in the temperature equation is given by the transport term due to the flow velocity and to the diffusion flux, \mathcal{F}_k , of the species. In this formulation we have neglected the dependency of the heat diffusion on the diffusion fluxes of the species, the so called Dufour effect.

Expanding the matrix structure, we obtain in more details:

$$\tilde{J} = \begin{bmatrix} \times & \times & \times & \times & 0 & \cdots & 0 \\ \times & \times & \times & \times & 0 & \cdots & 0 \\ \times & \times & \times & 0 & 0 & \cdots & 0 \\ \times & \times & \times & \times & \times & \cdots & \times \\ \hline & \times & \times & 0 & \times & \times & \cdots & \times \\ & \times & 0 & \times & \times & \cdots & \times \\ & & & \ddots & & \cdots & & \cdots & \ddots \\ & & & & & 0 & \times & \times & \cdots & \times \end{bmatrix}$$

In the first block we can note that the temperature is the variable that couples the complete system.

In the second block we have the equations of mass conservation for all the species but one for consistency with the mass constraint. Here we have neglected the dependency of the species diffusion on the pressure gradient. This block has full structure, apart the pressure dependency, and the only simplification is given in the sub-block, $n_s - 1 \times n_s - 1$ of the coupling within the chemistry part, where we consider the diagonal diffusion matrix given by the simplified formula:

$$\mathcal{F}_k = \rho D_k^M \nabla Y_k,$$

while the coupling between the species is kept in the source term, $m_i\omega_i$, being ω_i function of the concentrations of all the species Y_j that are coupled with Y_i in all the reactions. In case the chemical mechanism contains many species, a strategy for saving memory building the Jacobi matrix, is described in the work of Braack [15]. We do not aim at saving memory changing the structure of the matrix, because we partition the variables and solve the system block-wise by means of a Block-ILU pre-conditioner applied to the decomposition as described later in this section.

3.2.3 Linear solver

The linear subproblems are solved by a GMRES method (see Saad [69]) preconditioned by a multi-grid iteration (see [78], [79], [72]). The multi-grid methods for the solution of a linear system Au = b exploit the possibility of splitting the frequency content of the residual $b - A\bar{u}$ in higher and lower parts and the characteristic of some iterative schemes to act as 'smoother', i.e. to reduce the amplitude of the part of residuals with higher frequency. The amplitude of the part of the lower frequency residuals can be reduced more efficiently on coarse meshes, where the number of un-knows is much reduced. On coarse meshes the solution can not be approximated very well if the resolution of the mesh doesn't catch the variations of the physical variables, so the algorithm has to be implemented in a recursive way, here is a scheme of the multi-grid pre-conditioner:
$$\begin{split} & \text{Multi-grid algorithm: } u_l^{m+1} = MG(l, u_l^m, b_l, \nu_1, \nu_2) \\ 1. \text{ Set discretization space: } A_l : X_{h_l} \to X_{h_l}; \\ 2. \text{ coarsest grid: if (1=0) } u_l^{m+1} = A_l^{-1}b_l; \text{ return}; \\ 3. \text{ pre-smoothing: } \bar{u}_l^m = S_l^{\nu_1}(u_m^l); \\ 4. \text{ coarse grid correction: } \\ & \text{ compute defect: } \bar{d}_l^m = b_l - A_l \bar{u}_l^m; \\ & \text{ restrict the defect in } X_{h_{l-1}}: \quad \bar{d}_{l-1}^m = R_l \bar{d}_l^m; \\ & \text{ recursion: } \hat{u}_{l-1}^m = MG(l-1, 0, \bar{d}_{l-1}^m, \nu_1, \nu_2); \\ & \text{ interpolate: } \hat{u}_l^m = P_l \hat{u}_{l+1}^{m+1}; \\ & \text{ update: } \tilde{u}_l^m = \bar{u}_l^m + \hat{u}_l^m; \\ 5. \text{ post-smoothing: } u_l^{m+1} = S_l^{\nu_2}(\tilde{u}_m^l). \end{split}$$



Figure 3.4: The mesh is partitioned in twenty subregions. A domain decomposition method is used for the smoother in the multi-grid scheme.



Figure 3.5: Grid interface.

The algorithm can be parallelized in different manner, we choose to parallelize the smoother using a domain decomposition method, where in each sub-domain we solve local linear subproblems using a *block-ILU* pre-conditioner. The conceptual scheme for the decomposition is to divide the domain for the spatial computation in sub-domains. Given a domain $\Omega \in \mathbb{R}^n$, n = 2 in our case, we divide the domain in p not overlapping sub-domains Ω_i :

$$\bar{\Omega}_i: \bigcup_{i=0}^{P} \bar{\Omega}_i = \bar{\Omega}, \quad \Omega_i \cap \Omega_j = 0 \quad j \neq i.$$
(3.15)

Each sub-domain is expanded including an additional element of the mesh belonging to the neighboring domain as illustrated in figure 3.5, the new domain $\hat{\Omega}_i$ is so defined:

$$\hat{\Omega}_i = \{ x \in \Omega \mid dist(x, \Omega_i) < h \}, \tag{3.16}$$

where h is the transversal dimension of each neighboring element (see figure 3.5). Considering the discretization of the domain Ω we have now a partition of the discretized entities like vectors and matrices. These have to be distributed between all processors to solve local problems and then recollected in a global version of the vectors and matrices. The local matrices are calculated from the global matrix using a restriction operator R_p , that restricts the matrix on a processor p, and a prolongation operator $P_p = R_p^T$:

$$A_p = R_p A R_p^T. aga{3.17}$$

The meshes are partitioned by means of the METIS graph partitioner [52], the result of the partition is depicted in the figure 3.4.

An incomplete block-LU decomposition is used to solve approximatively the restriction of the system on the sub-domains, the matrix \tilde{J}_p , that has to be inverted is decomposed into a lower and upper triangular matrix:

$$\tilde{J} = \tilde{L}\tilde{U} + R, \tag{3.18}$$

where the two matrix \tilde{L} and \tilde{U} have a given sparse pattern and the rest matrix R is not computed. The update of the solution restricted to a sub-domain is calculated applying the ILU pre-conditioner locally, considering only the diagonal blocks, the coupling is then resolved within the multi-grid step, where the matrix is the full matrix. In the multi-grid step the matrix vector multiplication is applied to a distributed version of the matrix with the coupling structure described in the previous section. To avoid numerical problems for the application of the ILU pre-conditioner the diagonal elements are increased to assure diagonal dominance, this modification of the matrix can result in a slower convergence rate, but we do not treat this point here, being outside the frame of this work.

Addressing the problem of approximating the solution with a Galerkin method, we introduce in the next section the strategy used to create local refined meshes to increase the precision of the approximation limiting the cost of the computation.

3.3 Error estimation and mesh adaptivity

We present here an abstract formulation for the mesh adaptation, based on the 'Dual-Weighted Residual (DWR) method', derived from Becker and Rannacher [10]. For this purpose we consider a differentiable semi-linear form $A(\cdot; \cdot)$ defined on a function space V, the derivative of $A(\cdot; \cdot)$ at a point v in direction δv are denoted by $A'(v; \cdot)(\delta v)$, $A''(v; \cdot)(\cdot, \delta v)$, $A'''(v; \cdot)(\cdot, \delta v)$. We assume that the variational equation:

$$A(u;\varphi) = 0 \quad \forall \varphi \in V$$

has a unique solution $u \in V$. We introduce a functional J(u) of the solution u with derivatives $J'(u; \delta v), J''(u; \delta v, \cdot), J'''(u; \delta v, \cdot, \cdot)$. We consider the case in which the goal of the computation is the evaluation of J(u), that means that the quality of the computation is measured by the numerical precision given by $J(u_h) - J(u)$, where u_h is the Galerkin approximation of u on a finite dimensional space V_h , with h a parameter related to the dimension of this space. We further assume that also the associated discrete problem:

$$A(u_h;\varphi_h) = 0 \quad \forall \varphi_h \in V_h \tag{3.19}$$

has a unique solution.

Standard error estimation techniques, based for example on the error $||u_h - u||$ in the energy norm, may be inadequate for the control of a local refinement of the mesh in this case. In many applications, using different formulation for the functional $J(\cdot)$, it has been shown that a goal oriented mesh adaptation based on the DWR method is a successful strategy for increasing the computational quality limiting the computational costs. The aim is now to derive an a posteriori estimate for the error $J(u_h) - J(u)$. For this purpose we apply the Euler-Lagrange approach. The problem of computing $J(u_h)$ from the solution of (3.19) is equivalent to the following constrained optimization problem:

$$J(u) = \{\min J(v), A(v;\varphi) = 0 \quad \forall v \in V\}.$$
(3.20)

Minima u of (3.20) correspond to stationary points $\{u, z\}$ of the Lagrangian:

$$L(u;z) = J(u) - A(u;z),$$
(3.21)

with the adjoint variable $z \in V$. Hence we seek solutions $\{u, z\} \in V \times V$ to the Euler-Langrange system:

$$A(u;\varphi) = 0 \qquad \forall \varphi \in V, \tag{3.22}$$

$$A'(u;\varphi)(z) = J'(u;\varphi) \quad \forall \varphi \in V.$$
(3.23)

The Galerkin approximation in the subspace $V_h \subset V$ reads:

$$A(u_h;\varphi_h) = 0 \qquad \forall \varphi_h \in V_h, \qquad (3.24)$$

$$A'(u_h;\varphi_h)(z_h) = J'(u_h;\varphi_h) \quad \forall \varphi_h \in V_h, \tag{3.25}$$

To the approximate solution $u_h \in V_h$ and $z_h \in V_h$ we associate the residuals:

$$\rho(u_h; \cdot) := A(u_h; \cdot), \tag{3.26}$$

$$\rho^*(z_h; \cdot) := J'(u_h; \cdot)(z_h),$$
(3.27)

defined on V. For $\varphi_h \in V_h$ we have $\rho(u_h; \varphi_h) = \rho^*(z_h; \varphi_h) = 0$, by definition. Exploiting the Galerkin orthogonality we have from Becker and Rannacher [10] the following result:

Proposition 3.1 For the Galerkin approximation (3.24, 3.25) of the saddle-point problem (3.22, 3.23), we have the a posteriori error representation:

$$J(u) - J(u_h) = \frac{1}{2}\rho(u_h; z - \psi_h) + \frac{1}{2}\rho^*(z_h; u - \varphi_h) + R_h, \qquad (3.28)$$

for arbitrary elements $\varphi_h, \psi_h \in V_h$. The remainder term R_h is given by:

$$R_h := \frac{1}{2} \int_0^1 \{ J'''(u_h + se_h; e_h, e_h, e_h) - A'''(u_h + se_h; z_h + se_h^*)(e_h, e_h, e_h) + -3A''(u_h + se_h; e_h^*)(e_h, e_h) \} s(s-1) ds,$$
(3.29)

where $e_h := u - u_h$ and $e_h^* := z - z_h$. The remainder term is of third order in e_h if A and J are three times differentiable.

For the proof see [10].

Remark 3.1 The evaluation of the error representation (3.28) requires the determination of the primal as well as the dual solution u, z. We can only determine an approximation \tilde{u}, \tilde{z} of the solution yielding an error estimation, that depends on the different techniques used for the approximation. Some of this techniques are presented below.

The error representation can be expressed also in an other useful way, that can be used for computational purposes:

Proposition 3.2 For the Galerkin approximation (3.24, 3.25) of the saddle-point problem (3.22, 3.23), we have the alternative a posteriori error representation:

$$J(u) - J(u_h) = \rho(u_h; z - \psi_h) + R_h, \qquad (3.30)$$

with the residual defined as in proposition (3.1) and the remainder term \tilde{R}_h of second order in $e_h := u - u_h$.

In this case it is sufficient to calculate only the residual of the primal problem.

3.3.1 Practical a posteriori error estimation

A practical application of the defined error representation (3.28) is the approximation of $z - \psi_h$ and $u - \varphi_h$. In the simplified version we need only an approximation $\widehat{z - \psi_h}$ of $z - \psi_h$:

$$J(u) - J(u_h) \approx \rho(u_h; \widehat{z - \psi_h}) + \tilde{R}_h, \qquad (3.31)$$

Using an approximation we do not obtain an error identity, but an estimation of the error, which quality depends on the approximation technique used. Usual techniques are those for which an estimate of the dual solution is sought in a richer finite space, than the one in which the approximation u_h is to find. Also, it can be used an approximation of the interpolation error $z - I_h z$, using an adequate interpolation operator I_h . We choose to use an approximation of z in a richer space z_h .

- One possibility is to solve the dual problem in a finer discretization \mathcal{T}_h^* , for example using a global refinement, but this can be expensive and can be in contrast with the goal of limiting the computational effort of an adaptive technique.
- An other possibility is to solve the dual problem using higher order elements. As we use for the primal solution $\{v, p\}$, for the velocity and pressure, the pair Q_2, Q_1 (Taylor-Hood ansatz), we adopt for the dual variables the pair Q_4, Q_2 . This is implemented patch-wise in 2 × 2 patches as depicted in the figure 3.6.



Figure 3.6: Example of a 2×2 patch for the hierarchical solution Q_4/Q_2 for the velocity.

Equivalent patches are considered also for the other variables using the pair Q_2/Q_1 for the pressure and the species and again Q_4/Q_2 for the temperature.

The solution is resolved only locally through an iterative defect-correction method using a fixed number of iterations N:

$$x_{k+1} = x_k - A_k^{-1} r_k, \quad k = 0, \cdots, N-1,$$

where A is the system matrix and r_k is the residual at step k. The product $A_k^{-1}r_k$ is calculated using a Block-preconditioner, where each block is a 2 × 2 patch. To obtain a local error indicator we can cell-wise integrate by parts and then use the Hölder's inequality to obtain:

$$|J(u) - J(u_h)| \le \sum_{K \in \mathcal{T}_h} \omega_K(\rho_K + \sigma_K), \qquad (3.32)$$

neglecting the remainder term R_h . Here the so called cell residuals:

$$\rho_K := h_K^{-1} \|A(u_h)\|_K,
\sigma_K := \frac{1}{2} h_K^{-\frac{1}{2}} \|[\partial_n u_h]\|_{\partial K},$$

are expressed in ρ_K in terms of the cell-wise equation residuals, while in σ_K the [·] denotes normal jumps of the discrete solution along inter-element boundaries. The weights are so defined:

$$\omega_K := max\{h_K^{-1} \| \widehat{z - \psi_h} \|_K, h_K^{-\frac{1}{2}} \| \widehat{z - \psi_h} \|_{\partial K}\}.$$

In the work of Braack [15] and Braack & Rannacher [16] is exposed in details the application of this a posteriori error estimator to reactive flows, with different techniques for the approximation of the term $z - I_h z_h$. We refer to those works and [23] for a specific formulation of the error estimator for reactive flows. In the present work have been used a hierarchy of adaptive meshes obtained using as goal-functional the integral of the H mass fraction, Y_H , over the measurement volume Ω_{meas} :

$$J(v, p, T, Y_i) = |\Omega_{meas}|^{-1} \int_{\Omega_{meas}} Y_H dx$$
(3.33)

The meshes corresponding to the level 2 and 4 are depicted in the figure 3.7.



Figure 3.7: Local refinement of the grids: level 2 (left) and 4 (right).

3.4 HiFlow

The finite elements package 'HiFlow' [45] have been used for the numerical simulation. This is a multipurpose package for scientific computing, with many features that can be exploited for the simulation in realistic contexts. The 'HiFlow Project' has been started by V. Heuveline at the end of the nineties with the scope to create a platform for the numerical treatment of different problems expecially in the field of the fluid dynamic. The package consists of a library of finite elements, that can be used for a discretization in space with different refinement strategies, both a h-strategy and a p-strategy. The former is implemented by splitting of the elements, while the latter uses a polynomial spaces with variable for the interpolation of the solution, locally on each element. Special effort has been given for the development of solvers to treat the nonlinearities of the problem and to solve with high efficiency the linear systems arising from the linearization of the equations, using multi-grid techniques and iterative solvers for parallel architectures.

The library is implemented in C++ using the object-oriented features of this programming language. A parallel version of the library is based on MPI and for the partitioning of the

meshes is used the METIS graph partitioner [52].

3.5 Parallel HPC

The computations have been done in the Scientific Supercomputing Center (SSC Karlsruhe) using a HP XC6000 Cluster based on the Intel Itanium2 processor with more than 11 TFlop/s peak performance and 7 TB main memory. The Scientific Supercomputing Center (SSC Karlsruhe) as part of the Computing Center of University Karlsruhe is embedded into the infrastructure of the High Performance Computing Competence Center Baden-Wrttemberg (hkz-bw).

Features of HP XC6000 Cluster:

- 116 2-way nodes and 12 8-way nodes with
 - 108 nodes each with 2 Intel Itanium2 processors and 12 GB main memory and 146 GB local disk space,
 - 12 nodes each with 8 Intel Itanium2 processors and 64 GB main memory and about 500 GB local disk space,
 - 8 2-way file server nodes based on Xeon processors with attached disks of the overall size of 10 TB and a
 - single rail Quadrics QsNet II Interconnect.
- The HP XC6000 Cluster is a distributed memory parallel computer with 128 nodes all in all; 108 nodes consist of 2 Intel Itanium2 processors with a frequency of 1.5 GHz and 12 nodes consist of 8 Intel Itanium2 processors with a frequency of 1.6 GHz and all nodes own local memory, locale disks and network adapters. Thus the theoretical peak performance of the system is 1.9 TFLOPS. Additionally special nodes are attached as file servers to the cluster to support a fast and scalable parallel filesystem. All nodes are connected to the Quadrics QsNet II interconnect that shows a high bandwidth of more than 800 MB/s and a low latency.
- The basic operating system on each node is HP XC Linux for High Performance Computing (HPC), a Linux implementation which is compatible to RedHat AS 3.0. On top of this operating system a set of open source as well as proprietary software components constitute the XC software environment enabling the efficient useage of the parallel computer.

As global filesystem the scalable, parallel filesystem Lustre is used within the XC cluster. By the usage of several Lustre Object Storage Target (OST) servers and Meta Data Servers (MDS) both high scalability and redundancy are reached in case of malfunction of single servers. At present 10 TB disk space is available within the global filesystem. Besides each node of the XC cluster is equipped with local disks for temporary data.

Chapter 4

Parameter identification and experimental design

4.1 Optimization methods for PDE

The parameter identification and the optimal experimental design problem are particular example of optimization problems. Within this work we treat both problems with similar techniques, because in both cases we deal with finite number of parameters. The optimization problem can be formulated in the following manner:

• an objective functional is given to be minimized over a space of (discrete) control variables of a system governed by partial differential equations.

In the system of partial differential equations, we divide the variables in state variables and control variables, we call the latter 'model parameters'. In our case the state is determined by the variables describing the flow (density, velocity, pressure and temperature), plus the variables describing the species in the fluid. While the parameters are the reaction rate coefficients, that are in our model scalar values. The functional is defined in order to give a 'distance' between measured data and values predicted by the model with a given choice of the parameters.

The functional $J(u,q) : V \times Q \times Z \to \mathbb{R}$, is function of the state $u \in V$, state space, and the parameters $q \in Q = \mathbb{R}^{n_p}$, control space. The measured data C_0 are values in $Z = \mathbb{R}^{n_m}$, observation space. We seek now the set of parameters q that satisfy the following constrained minimization problem:

Problem 4.1 (Constrained minimization) The minimum of J(u,q) is to seek in the space of the control Q,

 $\min_{q \in Q} J(u,q)$

with the state u that satisfy the following constraint:

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho u) &= 0 \quad in \quad \Omega, \\ \frac{\partial \rho u}{\partial t} + \nabla \cdot (\rho u u) + \nabla p - \nabla \cdot \mathcal{F}_Q - \rho g &= 0 \quad in \quad \Omega, \\ \frac{\partial \rho c_p T}{\partial t} + \nabla \cdot (\rho u c_p T) - \nabla \cdot \mathcal{F}_E + \sum_{i=0}^{N_{sp}} c_{p,i} \mathcal{F}_i \nabla T + \sum_{i=0}^{N_{sp}} h_i m_i \omega_i(q) &= 0 \quad in \quad \Omega, \\ \frac{\partial \rho Y_i}{\partial t} + \nabla \cdot (\rho u Y_i) + \nabla \cdot \mathcal{F}_i - m_i \omega_i(q) &= 0 \quad in \quad \Omega, \\ u(x,t) &= g \quad on \quad \Gamma_{in} \cup \Gamma_{opt}, u(x,t) = 0 \quad on \quad \Gamma_{no-slip}, \frac{\partial u(x,t)}{\partial n} &= 0 \quad on \quad \Gamma_{out}, \\ T(x,t) &= \bar{T} \quad on \quad \Gamma \setminus \Gamma_{out}, Y_i(x,t) = \bar{Y}_i \quad on \quad \Gamma_{in} \cup \Gamma_{opt}, \frac{\partial Y_i(x,t)}{\partial n} &= 0 \quad on \quad \Gamma_{no-slip} \\ \rho(x,0) &= \rho^0, u(x,0) = u^0, T(x,0) = T^0, p(x,0) = p^0, Y_i(x,0) &= Y_i^0 \quad \in \Omega \\ p\bar{m} &= \rho RT. \end{aligned}$$

The notation is the same as in (2.67-2.70), but here we have dropped all the subscript " $_0$ " and the term p is the term p_2 , because in our case the thermodynamic pressure is constant. The mean mass \bar{m} is defined as in (2.13). The boundary subdivision is depicted in the figure 3.2.

The functional to be minimized in this work is called also 'cost function' or 'objective function'. It has to be defined in a way so that it can be used in the formulation of the forward problem. For this reason we have to define a suitable norm. Restricting our framework to the Hilbert spaces, we use the L^2 Norm, this is of course not the only possible choice, but as we see in the next paragraphs, it is in agreement with the statistical description of the data we use to define the functional. In this way we can reformulate the optimization problem in a weak sense and solve it numerically. We define an observation operator $C: V \to Z$, to map the values of the state to the observation space, and obtain the objective functional, using a set of measurements $C_0 \in Z$:

$$J(u) := \frac{1}{2} \|C(u) - C_0\|_Z^2.$$
(4.1)

As shown in the chapter 3 the model for the forward problem is described by the following variational equation:

$$A(u,q;\varphi) = 0 \quad \forall \varphi \in V, \tag{4.2}$$

where $A(\cdot, \cdot; \cdot)$ is the semi-linear form (3.1). The constraint minimization problem can be formulated as stated below.

Problem 4.2 (Constraint minimization weak formulation)

$$\begin{array}{ll} minimize & J(u) \\ subject \ to \ A(u,q;\varphi) = 0 & \forall \varphi \in V, \end{array}$$

where the constraint is given by the state equation. We try to minimize the objective functional J(u) for values u, that satisfy the state equation, i.e. lie in the manifold given by the solution of (4.2). To solve the optimization problem we define a Lagrangian functional, that is the objective functional augmented with the form $A(u, q; \cdot)$ tested with the functions $\lambda \in V$:

$$L(u, q, \lambda) = J(u) - A(u, q; \lambda).$$

Remark 4.1 The functions λ are the Lagrange-multipliers in the notation of the constrained optimization. They correspond to the first variation of the objective function to a small variation of the constraint.

Theorem 4.1 (Lagrangian formulation) If the following problem

$$\inf_{u \in V} \sup_{\lambda \in V} L(u, q, \lambda) \quad u \in V, \ \lambda \in V$$

has a solution, then the solution $\{\bar{u}, \bar{\lambda}\}$ satisfy the following inequalities:

 $L(\bar{u},\lambda) \le L(\bar{u},\bar{\lambda}) \le L(u,\bar{\lambda}) \quad \forall u \in V, \lambda \in V$

and it is a saddle point of the Lagrangian. It can be shown that the solution $\{\bar{u}, \bar{\lambda}\}$ is solution of (4.2).

Proof: See [36, 42].

In the previous definition we do not need the specification of the differentiability of the functionals and the form $A(\cdot, \cdot; \cdot)$. It can be used also for not differentiable functionals. On the other side it is difficult to give a local characterization of a saddle point of the functional L, this aspect has different consequences for the numerical treatment of the minimization problem. For numerical reasons we set the problem following an other way, that allows us to define an algorithm to find iteratively the solution. We pay this step with a restriction, i.e. with the assumption of the differentiability of the functional and of the form $A(u, q; \lambda)$ at least until the first order derivatives. We can define necessary conditions for the solution $x = \{u, q, \lambda\} \in X = V \times Q \times V$ to be a solution of the minimization problem (Problem 4.2).

Theorem 4.2 (First order optimality conditions) The gradient of the Lagrangian has to vanish at a point that is a (local) minimum:

$$\nabla_x L(x)(y) = 0 \quad \forall y \in X.$$
(4.3)

Proof: We refer to [36, 42, 60] for a derivation of the first order necessary conditions and the definition of sufficient conditions, that imply a second order assumption on the Lagrangian.

We use the notation $A'(\cdot, \cdot; \cdot)(v)$ for the direction derivative of the form in direction v, which is defined as:

$$A'(u,q;\lambda)(v) = \lim_{\epsilon \to 0} \frac{A(u+\epsilon v,q;\lambda) - A(u,q;\lambda)}{\epsilon}.$$
(4.4)

With this notation the optimality conditions are given by the following system of equations:

$$\begin{cases} J'_{u}(u)(\delta u) - A'_{u}(u,q;\lambda)(\delta u) = 0 \quad \forall \delta u \in V, \\ J'_{q}(u)(\delta q) - A'_{q}(u,q;\lambda)(\delta q) = 0 \quad \forall \delta q \in Q, \\ A(u,q;\delta\lambda) = 0 \quad \forall \delta\lambda \in V. \end{cases}$$
(4.5)

We can now apply this theory to the estimation of parameters in a system of partial differential equations.

4.2 Parameter identification for the PDE system

For the study of the kinetic of the reaction we define the cost function in the form of a sum of squares, using the available experimental data $C_0 \in Z \in \mathbb{R}^m$, we can see in section 4.3 that this choice is a consequence of some statistical assumptions:

$$J(u,q) = \frac{1}{2} \|C(u) - C_0\|_Z^2,$$
(4.6)

the observation operator is defined as:

$$C(u) := |\Omega_{meas}|^{-1} \int_{\Omega_{meas}} Y_H dx, \qquad (4.7)$$

where Ω_{meas} is the measurement volume and Y_H is the mass fraction of the *H* atoms. The relation between state and parameters is given by the model:

$$A(u,q;\varphi) = 0 \quad \forall \varphi \in V, \tag{4.8}$$

as described in section (4.1). The minimization problem is the constrained problem (4.2). The discrete problem is posed in the finite element spaces $V_h \subset V$ and $Q_h \subset Q$.

Problem 4.3 (Discrete constraint minimization) Minimize the cost functional:

$$J(u_h) = \frac{1}{2} \|C(u_h) - C_0\|_Z^2$$
(4.9)

under the constraint

$$A(u_h, q_h; \varphi_h) = 0 \quad \forall \varphi_h \in V_h \tag{4.10}$$

The first order optimality conditions (4.5) give a necessary condition for the solution of the problem. This is a nonlinear system with a saddle point structure. If the form $A(\cdot, q_h; \cdot)$ is regular for any $q_h \in Q_h$, for sufficiently good approximations $V_h \subset V$, we can define the discrete solution operator $S_h : Q_h \to V_h$ and, setting $u_h := S_h(q_h)$, we obtain the following unconstrained optimization problem posed in the space $Q_h = \mathbb{R}^{n_p}$.

Problem 4.4 (Discrete unconstraint minimization) Minimize the reduced cost functional:

$$j_h(q_h) = \frac{1}{2} \|c_h(q_h) - C_0\|_Z^2, \qquad (4.11)$$

where $c_h(q_h) := C(S_h(q_h))$ is the reduced observation functional.

This problem can be solved by a Newton-like method calculating the derivative of the functional j_h with respect to the parameters q_h , we refer to [34] for a detailed description of numerical techniques for solving the problem (4.4).

The practical difficulty of solving such a problem in the instationary regime is the calculation of the derivatives with respect to the parameters as functions of the time, the dual solution is equivalent to a flow back in the time. For computing the dual solution, each step of a Newton method requires the full solution back in time. Special techniques, called checkpointing, can be used to save computational effort in calculating the dual solution (see [49]).

In the present work we have implemented a derivative free optimization method, based on the Dekker-Brent method [20], which is the most advanced of the root bracketing algorithms. This is feasible, considering the computational costs, because in the chemical mechanism we consider as parameter only the reaction rate of the reaction (1.1). This method combines the robustness of the bisection method with the increased speed of the regula falsi method. At each iteration, either a bisection or a regula falsi step is taken, depending on the behavior of the algorithm up to that point. As a result, the Dekker-Brent method converge as fast as the best case regula falsi method at its best, and as slow as the bisection method at its worst. A bracketing method in our context is suitable, because we can estimate experimentally the interval containing the optimal parameter value. As we have seen in the chapter 1 the sought parameter q in the experimental results varies between the values [0.99 - 1.53] in the range of temperature considered, we can use this estimation to compute the number of iterations necessary to converge with a given tolerance. Let's consider the bisection method, that has only a linear convergence, with an interval [a, b]where the solution q_{opt} is known to lie.

If a_n and b_n are the endpoints of the n^{th} iteration and let q^n be the n^{th} approximate solution, then the number of iterations required to obtain an error smaller then ϵ is found by noting that:

$$b_n - a_n = \frac{b-a}{2^{n-1}}$$

and that q_n is defined as:

$$q_n = \frac{1}{2}(a_n - b_n).$$

In order for the error to be smaller than ϵ ,

$$|q_n - q| \le \frac{1}{2}(a_n - b_n) = 2^{-n}(b - a) < \epsilon.$$

Taking the natural logarithm of both sides we obtain:

$$n > \frac{\ln(b-a) - \ln \epsilon}{\ln 2}.$$

Rounding the results, we get that the worst case is n = 5 for a precision $\epsilon = 0.01$ and n = 8 for a precision $\epsilon = 0.001$, with the estimated interval of 0.5.

We conclude with the choice of a derivative free method for this practical parameter estimation, considering that the precision set in the numerical experiment is $\epsilon = 0.01$ and that we are interested in only one parameter.

From the mathematical point of view it is important to define whether the optimization problem is well-posed or not, that means to define the existence, uniqueness of the solution and the continuous dependence of this on the data, we refer to [35, 60] for a seminal exposure on these issues. For many of the practical problem involving PDE this issues are not yet completely solved. In this work we do not address the well-poseness of the problem and assume that the entities that define the problem mathematically fulfill all the necessary conditions in the infinite-dimensional setting.

We give now a justification for the use of a weighted least squares functional in the case where the observation functional uses data that are measurements affected by some random errors, with specific statistics.

4.3 Parameter identification in the probabilistic setting

We consider models that describe "measurable" processes, where "measurable" means that during these processes it is possible to measure a quantity of interest. We are interested in processes as a part or as a whole of a system, where experimental data are available. Often these processes are reproduced as experiments to study the system itself.

The system can be described by a model, where we define parameters, that have to be identified by comparison with the experimental data. Aim of the parameter identification problem is the definition of methods that allow to estimate those parameters within the tolerance given by the information gathered during the experiments. Of course if the experimental data do not contain enough information for the estimation we cannot solve the problem or we can solve it only with a bad approximation.

We refer to the books of Tarantola [74], [73] and references therein for detailed derivation of the probabilistic setting of parameter estimation problem.

4.3.1 Statistical assumptions

The observed values are obtained with uncertainties, so we have to deal with the probabilistic description of the result of the measurements. That means that the result of the measurements C_0 can be represented by a probability density $\rho_Z(C_0)$ defined over the data space $C_0 \in Z$, which is the space of all the system's responses to an instrumental investigation. In the following we assume that the data have a Gaussian form. This means that they may be described using the mean value \hat{C} and the covariance operator C_D , which is a linear, symmetric positive operator, mapping Z^* (the dual of Z) into Z.

Definition 4.1 (Covariance operator) Let V be a linear space and W be a weighting operator over V, i.e. a linear, symmetric and positive definite operator mapping V into its dual V^* . Given such a weighting operator, the scalar product of two elements of V is defined via the duality product:

$$\langle u, v \rangle = \langle Wu, v \rangle.$$

The inverse of a weighting operator, $C = W^{-1}$ is called a covariance operator.

In the following we consider the usual probabilistic definition of covariance operator, which has the property described in the Definition 4.1. We refer to [66] for a precise derivation of the needed assumption. The probability density function in the data space, in the Gaussian case, is given by:

$$\rho_Z(C) = c \, \exp\left(-\frac{1}{2} \|C(u) - C_0\|_C^2\right),\tag{4.12}$$

where c is a constant and the norm in the data space is defined as follows:

$$||C(u) - C_0||_Z^2 = \langle C_D^{-1}(C(u) - C_0), (C(u) - C_0) \rangle,$$
(4.13)

the $\langle \cdot, \cdot \rangle$ is the duality product between Z and its dual Z^* , and C_D is the covariance operator defined in the data space of the measurements.

We restrict our study to finite dimensional inverse problems, where it is possible to associate to the operator C a matrix, that is the covariance matrix, and we use the same symbol C. A typical example of uncertainties are those independent of the output of the measurement process and additive to the output itself:

$$C_0 = C_{true} + \epsilon, \tag{4.14}$$

where we assume that the probability density for the error ϵ is Gaussian with zero mean (the error is not systematic) and has covariance C_D .

We assume furthermore to have an a priori information of the parameters and that this is also given in Gaussian form. The a priori information can be given by a posteriori information of a previous parameter identification problem solved with other data set, for example. We have thus the following elements for setting the parameter identification problem in a probabilistic point of view:

• the a priori information that the parameters q are described by a Gaussian probability density function in Q:

$$\rho_Q(q) = c \, \exp\{-\frac{1}{2} \|q - q_0\|_Q^2\}$$
(4.15)

where q_0 is the a priori expected value and the norm in Q is so defined:

$$||q - q_0||_Q^2 = (q - q_0)^T C_{prior}^{-1}(q - q_0)$$

where C_{prior} is the a priori covariance matrix.

• the measurements on the observable parameters C_0 , which give a data set that can be described by a Gaussian probability density function in Z with covariance C_D :

$$\rho_Z(C_0) = c \, \exp\{-\frac{1}{2} \|C(u) - C_0\|_Z^2\},\tag{4.16}$$

• the model

$$A(u,q;\varphi) = 0 \quad \forall \varphi \in V,$$

which describes the forward problem, more in detail we consider the case where A is a partial differential operator. We assume the forward problem being error free, in the sense that we do not add uncertainties in the relation between model parameters and observable variables, but it can be shown that, if these can be described using Gaussian statistics, with covariance matrix C_m , we just have to replace C_D with $C_D + C_m$, see [74].

A further assumption regards the a posteriori probability density for the parameters. We consider the a posteriori state of information as the conjunction of ρ_Z and ρ_Q :

$$\tau(q) = c \, \exp(-S(q)),\tag{4.17}$$

where the misfit function S(q) is defined as:

$$S(q) = \frac{1}{2} \|C(u) - C_0\|_Z^2 + \frac{1}{2} \|q - q_0\|_Q^2.$$
(4.18)

If the model is linear, the misfit function is quadratic and the posterior probability density $\tau(q)$ is Gaussian.

The parameter identification problem can now be formulated from the probabilistic point of view.

4.3.2 Probabilistic description of the least squares method

The vector of measurements and the parameters q are viewed as random variables with known covariance operators C_D and C_M and unknown means C_{true} and q_{true} . Then C_0 and q_0 are interpreted as two particular realizations of the random variables. The parameter identification problem can therefore be formulated as follows:

Problem 4.5 (Parameter identification) Find an estimator \hat{q} of q_{true} that is optimum in a probabilistic point of view.

An 'optimum' estimator is found at the maximum likelihood point:

Problem 4.6 (Maximum likelihood) The problem of finding an estimator for q_{true} is solved by the maximum likelihood point, i.e. the maximum of the posterior probability density (4.17) over the parameter space:

$$\hat{q} = \max_{q \in Q} \tau(q) \tag{4.19}$$

This is equivalent to finding the maximum of the logarithm of the probability density due to the monotonicity of this function, which is equivalent to minimize the misfit function defined previously (4.1).

As the a priori information and the information over the data set are Gaussian, the misfit function is a sum of squares. The problem 4.6 is thus equivalent, with the assumptions made, to the least squares problem.

Problem 4.7 (Least squares problem) The 'best' estimator of q_{true} is the point that minimizes the sum of squares defined by the misfit function (4.1):

$$\hat{q} = \min_{q \in Q} S(q)$$

When both the a priori probability density and the probability density of the measurements are Gaussian the solution of the problem is the usual least squares estimator. Furthermore if the problem is linear than the posterior probability density $\tau(q)$ is Gaussian.

Remark 4.2 We see that the assumption on the form of the probability density has lead to a particular formulation of the cost functional. From the statistical point of view the leastsquares functional is not motivated if we don't assure the Gaussian behaviour, in particular it is not adequate if there are outliers in the data set. The argument can be generalized using the so called generalized Gaussian distribution ([74]) leading to a method where the L_2 norm is substituted by an L_p norm for $1 \le p \le \infty$, but in the case $p \ne 2$ the space L_p is not an Hilbert space, for this reason we restrict the numerical formulation of the problem to the case p = 2, in order to use the techniques here described developed for this case.

A Gaussian probability density is defined by the mean value and the covariance matrix. The least squares problem is the search for the mean value, it remains to calculate the covariance of the parameters q to define completely the probability density, given the covariance of the data and the relation between the parameters and the data, defined implicitly by the first order optimality condition of the least squares problem.

4.4 A derivation of the covariance matrix

As we can deduce from (4.13) the covariance matrix of the parameters is given by the inverse of the Hessian of the cost functional. To define the covariance matrix we have to introduce some more notations. We denote G the Jacobian matrix of the observation operator C(u(q)), defined as follows:

$$G_{ij} := \frac{\partial C_i}{\partial q_j} (u(q))(w_j), \quad i = 1, \dots, m, j = 1, \dots, n_q,$$
(4.20)

where w_j is the solution of the sensitivity equation:

$$a'_{u}(u,q;\varphi)(w_{j}) + a'_{q_{j}}(u,q;\varphi)(1) = 0.$$
(4.21)

We introduce also the Hessian of the observation operator as:

$$\nabla^2 C_i(u(q)) := \frac{\partial^2 C_i(u(q))(w_j, w_k)}{\partial q_i \partial q_k}.$$
(4.22)

The inverse of the covariance matrix, using the notation above, can be written as:

$$C^{-1} = G^T C_D^{-1} G + C_0^{-1} + \sum_i \nabla^2 C_i \sum_j (C_D^{-1})_{ij} (C_j - C_{0j}).$$
(4.23)

The last term in the expression (4.23) is small if the nonlinearities of the model are small or the residuals are small. That means that close to the minimum, \hat{q} , we can neglect the last term and consider the approximation of the covariance matrix:

$$C = \left(G^T C_D^{-1} G + C_M^{-1}\right)^{-1}.$$
(4.24)

In the case where no a priori information of the parameters is available, we use the limit $C_M^{-1} \to 0$ and the covariance matrix becomes:

$$C = \left(G^T C_D^{-1} G\right)^{-1}, \tag{4.25}$$

where G is the Jacobi matrix of the model $A(u, q; \varphi)$ as defined in (4.20). Geometrically the covariance of the parameters is related to the curvature of the graph of the misfit function. In the case with one parameter it is easier to illustrate the effect of the curvature of the misfit function on the precision of the fit. In the figure 4.1 we consider a linear system with one parameter, the misfit function is then quadratic. The ordinate axis represents the misfit function values, while the abscissa represents the parameter values. The minimum of the misfit function is the estimated mean value of the parameter. In the figure we have plotted two linear models to illustrate the effect of the shape of the misfit function. A variation Δq_1 of the parameter leads to the same misfit value as a bigger variation Δq_2 , if we consider a model for which the misfit function graph has a smaller curvature. The curvature of the graph of a function is related to the inverse of the second derivative, thus the covariance is related to the inverse of the Hessian of the function S(q).

4.5 Optimal experimental design

We have seen that uncertainties in the data space infer uncertainties in the model parameters space, as described by the posterior probability density, defined in the expression (4.17). The uncertainties on the data are given by the covariance matrix C_D , while the uncertainties on the parameters q are expressed by the covariance C, (4.24), thus the matrix C contains all the information how the uncertainties in the data infer uncertainties in the model parameters space. The goal of the optimal experimental design is the minimization of the uncertainties in the model parameters q. We consider models, $A(u,q;\varphi)$, described by a function that links the observable variables of the system to some model parameters q. We consider two sets of parameters: the model parameters q, that can describe some physical properties of



Figure 4.1: Misfit function: effect of the curvature on the precision of the fit.

the system and in context of parameter identification are the parameters to be determined, and the *design parameters*. These are parameters that define the setup of the experiment or more generally the process we adopt to identify the model parameters. The design parameters could define, for example, the way how we perform the measurements or the state of the system during the experiment. The issue of the optimal experimental design is the minimization of a functional of the covariance matrix of the model parameters q over a space of design parameters $\xi \in \Pi$. The goal is to modify the system response in order to reduce the covariance matrix C, which is a function of the Jacobi matrix of the system and thus implicitly is function of the observable variables d, see (4.24). We give here a definition of the optimization of experiments and we refer to [67] and [4] for a seminal introduction to this theme.

Problem 4.8 (Optimal experimental design) Minimize a functional $\Phi(C)$ of the covariance matrix over the space of design parameters Π , under the constraint that the observable variables u are related to the parameters q through the model described by the form $A(u, q; \varphi)$.

$$\min_{\xi \in \Pi} \Phi(C(\xi)),$$

$$A(u,q;\varphi) = 0, \forall \varphi \in V, u \in V, q \in Q.$$
(4.26)

Different criteria could be chosen to minimize in some sense the covariance matrix, depending on the functional $\Phi(C)$:

- D-criterion: $\Phi(C) = det(C)$, the determinant of C,
- A-criterion: $\Phi(C) = tr(C)$, the trace,
- E-criterion: $\Phi(C) = max(\sigma(C))$, the maximum eigenvalue of the spectrum of C.

Other functionals have been defined and could be used, see [4] regarding this issue and [55] regarding this point and also an extension towards the robust design of experiment (*Worst-Case-Design*), but we restrict our tests to those here defined.

The covariance matrix has also an other geometrical interpretation. If we consider the vector

$$\chi^2 = (q - q_0)^T C^{-1} (q - q_0) \tag{4.27}$$

this is distributed as the χ^2 probability density (see [74] for a definition) with $m - n_p$ degrees of freedom, where m is the number of measurements and n_p is the dimension of Q. Gaussian random vector with mean q_0 and covariance C. Different values of χ^2 correspond to different level of uncertainties. Equation (4.27) is the equation of an ellipsoid in the space of the parameters, the values of q at the ellipsoid surface are level set values for the probability of q. The determinant of C is proportional to the volume of the ellipsoid, while the eigenvalues of C are proportional to the principal axes of the ellipsoid. The D-criterion minimize thus the volume of the ellipsoid that defines the uncertainties on the parameters, the E-criterion minimizes the maximum principal axis, that means that minimizes the covariances along the direction of maximum variance, while the A-criterion minimizes the sum of the lengths of the principal axes.

Remark 4.3 The constraint $A(u,q;\varphi) = 0$ is not given explicitly because we do not know the value of the parameters that we want to identify. In the praxis the problem 4.8 cannot be solved directly, it has to be solved iteratively.

4.5.1 Sequential experimental design

The sequential design of experiments is a procedure to iteratively configure the experiment setup gathering information on the system at each step and using the ameliorated knowledge of the system to be able to perform new measurements, that in a probabilistic sense are more informative. The sequential procedure is depicted in figure 4.2 and in the scheme underneath.



Parameters Identification

Figure 4.2: Design cycle: a sequential procedure for the identification of parameters.



4.6 Optimal experimental design for PDE

We show in this section the case in which the model A(q) is given by a system of partial differential equations, we formulate the optimization problem and we present some numerical examples. We suppose that the weak formulation of the problem is given by the following equation:

$$A(u,q;\varphi) = 0, \quad \forall \varphi \in V, \tag{4.28}$$

where u is the state variable defined in a Hilbert space V, it can be a vector function and some components of it correspond to the observable variables d of the previous formulation. The model is described by a finite number of parameters $q \in Q \subset \mathbb{R}_p^n$. To solve the parameter estimation problem we have to define an observation operator C(u) as in (4.7) and solve the least squares problem:

$$\begin{cases} \min_{q \in Q} J(u(q), q) \\ A(u, q; \varphi) = 0, \quad \forall \varphi \in V, \end{cases}$$

$$(4.29)$$

where the least squares functional is defined as follows:

$$J(u,q) = \frac{1}{2} \|C(u(q)) - C_0\|.$$
(4.30)

We have seen in the section 4.1 that this is equivalent to solve the first order optimality conditions, given by the system (4.5).

Problem 4.9 (Optimal experimental design in the context of PDE) Given a functional Φ of the covariance matrix C^{-1} of the model parameters q, we seek for the set of design parameters $\xi \in \Pi$ that minimizes this functional under the constraint that the first order optimality system is satisfied by the triple $\{u, q, \lambda\}$:

$$\begin{cases} \min_{\xi \in \Pi} \Phi(w, q, \xi) \\ J'_u(u)(\varphi_u) - A'_u(u, q; \lambda)(\varphi_u) = 0 \quad \forall \varphi_u \in V \\ J'_q(u)(\varphi_q) - A'_q(u, q; \lambda)(\varphi_q) = 0 \quad \forall \varphi_q \in Q \\ A(u, q; \varphi) = 0 \quad \forall \varphi \in V \\ A'_u(u, q; \varphi_w)(w) + A'_q(u, q; \varphi_w)(1) = 0 \quad \forall \varphi_w \in V, \end{cases}$$

$$(4.31)$$

where w is the derivative of u with respect to the model parameters q. The functional Φ is applied to the Jacobi matrix of the system, that means that it is a function of w. For this reason the sensitivity equations, that determine the derivatives of u, has to be embedded

¹Here we use the same symbol C for the covariance matrix and the observation operator C(u), but should not produce confusion, as we use the operator symbol always with the bracket to explicitly show the dependency on the state u.

in the system, as additional constraint. The functional Φ is nonlinear and not convex as we can see in the examples treated in the following section. The minimization process for the previous problem is not an easy task and is a problem of global minimization. We refer to [14, 56, 7, 55] for the definition and application of this theory in the context of system described by differential algebraic equations. We are of the advise that much effort has to be involved in future work on this topic in the context of partial differential equations.

4.6.1 Numerical examples: measurements

Scope of the numerical examples is to show how the optimal choice of the experimental set-up can improve the result of a parameter estimation problem. For this purpose we choose three different models with different parameters: the first is the convection-diffusion equation, the second is a Laplace problem with a discontinuous diffusion coefficient in the domain and the third is the system describing the reaction between two species. All the examples are 2D stationary problems.

In the first example we find the diffusion coefficient and one of the component of the transport. We have decided to consider a symmetric solution for graphic reasons.

In the second example we find the values of the two diffusion coefficients knowing a-priori how the domain is divided.

In the third example we look for the diffusion coefficient and the reaction rate for the two species. The design variables ξ are measurement points at different positions in the domain. An experiment consists of few measurements where we choose the positions ξ (three measurement points in the first two examples and two measurement points in the last) and we get the value of the state u as response of a fictive device, that measures u adding an error due to the measurement chain. We use this first information to achieve an approximation of the parameters solving a least squares problem (4.29). To improve this approximation we add one more measurement point in the experiment. The choice of the new point can be done using the theory of optimal experimental design. In the examples we compare the numerical identification of the parameters using the three criteria described in the problem 4.8 and a fourth choice taken without following a criterion. As we do not have real measurements, in our examples we have to produce artificial measurements. We do this by solving the same problem with higher precision and adding to this value an error as depicted in figure 4.3.



Figure 4.3: Artificial measurements.

The assumption for applying the theory of optimal experimental design is that the errors made during the measurements are described by a given statistic and that they are not dependent on the measurements. In order to gain statistical information of the procedure, we should repeat the experiments a number of time sufficient to have a statistic of the results, and use additive errors with a given statistic, i.e. zero mean and a given variance, to obtain the artificial measurements value.

As we have decided to use few points as first measurement cycle and to add only one measurement point, a statistic can not be made, thus we consider a fixed error in order to compare the results. In this way we can nevertheless show the optimality of the choice. At the end of the experiments we can compare the results of the parameter identification in term of mean values as shown in the tables (4.1) - (4.6) and see that the optimality criteria give better results also in term of mean value. Regarding the variance of the parameters, as we do not have a statistic, we compare the confidence regions corresponding to the different cases assuming the same variance C_D in the observable variable space, showing the mean result of the design of experiments, that is the minimization of the dimension of the confidence regions, see figures (4.5) - (4.10).

4.6.2 Convection-diffusion equation

We consider a convection-diffusion model in 2D:

$$\mu \Delta u + \beta \nabla u = f \quad in \quad \Omega,$$

where the domain Ω is the unit square $[0,1] \times [0,1]$.

The parameters are the scalar value of the viscosity coefficient, μ , and the first component of the velocity, β_0 , while the second component, β_1 , is equal to zero. As explained in the introduction we define a "true" value for the parameters to which we add a given error. The "true" value of the parameters is $\mu = 0.1$ and $\beta_0 = 1$. The force term is constant f = 1. We consider two cases for the choice of the position of the first three measurements to show that the entity of the improvement of the parameter estimation in terms of variance depends on the initial information gathered, i.e. if we have already a good level of information the gap for improvement is reduced. For the first case, "1-A", we choose the initial points for the measurements at: $\xi_1 = \{0.4, 0.5\}, \xi_2 = \{0.5, 0.5\}, \xi_3 = \{0.6, 0.5\}$. For the second case, "1-B", the initial points are the following: $\xi_1 = \{0.25, 0.5\}, \xi_2 = \{0.5, 0.5\}, \xi_3 = \{0.75, 0.5\}$. Because of the symmetries we take the measurements at the middle of the *y* coordinate. The error added at each measurement is set to 15% of the max value of the function, in this case it is 0.1.

The following tables show the results for the two cases, the column are so divided: in the first is defined the criterion, in the second the position of the measurements, in the third is given the determinant of C, in the fourth the sum of the eigenvalues of C, in the fifth the maximum eigenvalue of C, in the sixth the condition number of the covariance matrix. In the first row under this column we have the maximum and minimum condition number obtained varying the measurement position to cover the entire domain, in the last two columns we have the values of the parameters.
Criterion	Meas	Det	Sum Eig Max Eig		Cond	q1	q2
					Max Cond = 717.92		
					Min Cond = 84.881		
D	$egin{array}{c} (0.4, 0.5) \ (0.5, 0.5) \ (0.6, 0.5) \ (0.9, 0.5) \end{array}$	0.00237	0.567	0.563	133.91	0.082	0.807
А	$\begin{array}{c} (0.4, 0.5) \\ (0.5, 0.5) \\ (0.6, 0.5) \\ (0.95, 0.5) \end{array}$	0.00324	0.558	0.552	93.85	0.076	0.837
Е	$\begin{array}{c} (0.4, 0.5) \\ (0.5, 0.5) \\ (0.6, 0.5) \\ (0.95, 0.5) \end{array}$	0.00324	0.558	0.552	93.85	0.076	0.837
No Criterion	$(0.4, \overline{0.5}) \\ (0.5, 0.5) \\ (0.6, 0.5) \\ (0.1, 0.5)$	0.09346	6.144	6.128	401.882	0.12	0.474

Table 4.1: Case 1-A. In the first column is defined the criterion, in the second the position of the measurements, in the third is given the determinant of C, in the fourth the sum of the eigenvalues of C, in the fifth the maximum eigenvalue of C, in the sixth the condition number of the covariance matrix. In the first row under this column we have the maximum and minimum condition number obtained varying the measurement position to cover the entire domain, in the last two columns we have the values of the parameters.

Criterion	Meas	Det	Sum Eig	Max Eig	Cond	q1	q2
					Max Cond = 387.31 Min Cond = 150.74		
					$\operatorname{MIII}\operatorname{Cond} = 139.74$		
	(0.25, 0.5)						
D	(0.5, 0.5)	0.00282	0.833	0.830	244.46	0.084	0.778
	(0.75, 0.5)	0.000-0-	0.000	0.000	211.10	0.000-	0.110
	(0.9, 0.5)						
	(0.25, 0.5)						
A (((0.5, 0.5)	0.00245	0.787	0.783	177.476	0.070	0.821
	(0.75, 0.5)	0.00545				0.019	
	(0.95, 0.5)						
	(0.25, 0.5)						
F	(0.5, 0.5)	0.00245	0 707	0 709	177.476	0.070	0.001
E	(0.75, 0.5)	0.00345	0.787	0.783		0.079	0.821
	(0.95, 0.5)						
	(0.25, 0.5)						
No Criterion	(0.5, 0.5)	0.01499	1 799	1 795	209.106	0.000	0.629
	(0.75, 0.5)	0.01422	1.733	1.725		0.098	0.032
	(0.1, 0.5)						

Table 4.2: Case 1-B. See case 1-A for the description of the table.

Remark 4.4 The condition number is not a good criterion as the other for the design of

experiments, because it is the ratio between the largest and the shortest diameters in the ellipsoid of uncertainties in the model parameters space. It tends to reduce the correlation between the parameters and it is not assured that the uncertainties are also reduced.



Figure 4.4: From top left: solution u, determinant, trace and maximum eigenvalue of the covariance matrix.



Figure 4.5: Confidence regions: case 1-A. The ellipses with dotted line correspond to the D, A and E criteria. To the criteria A and E corresponds the same optimal position and are equivalent in this case. The abscissa corresponds to the diffusion coefficient, while the ordinate to the flow velocity.



Figure 4.6: Confidence regions: case 1-B. The ellipses with dotted line correspond to the D, A and E criteria. To the criteria A and E corresponds the same optimal position and are equivalent in this case. The abscissa corresponds to the diffusion coefficient, while the ordinate to the flow velocity.

4.6.3 Laplace with discontinuous diffusion coefficient

We consider for the second example the Laplace model defined as follows:

$$(\mu_1\chi_1 + \mu_2\chi_2)\Delta u = f \text{ in } \Omega$$

where the domain is the unit square, Ω : $[0,1] \times [0,1]$. The two parameters are the values of the diffusion coefficient: $\mu_1 = 0.1$, $\mu_2 = 0.5$. The force is constant: f = 1.

The domain is divided as follows: $\chi_1 = \begin{cases} 0. & x < 0.5 \\ 1. & x > 0.5 \end{cases}$, $\chi_2 = \begin{cases} 0. & x > 0.5 \\ 1. & x < 0.5 \end{cases}$

For the first case, "2-A", we choose the initial points for the measurements at: $\xi_1 = \{0.4, 0.5\}, \xi_2 = \{0.5, 0.5\}, \xi_3 = \{0.6, 0.5\}.$

For the second case, "2-B", the initial points are the following: $\xi_1 = \{0.25, 0.5\}, \xi_2 = \{0.5, 0.5\}, \xi_3 = \{0.75, 0.5\}.$

Also here the error added at each measurement is 0.1 (25% of the max value of the function).

The description of the values in the tables is as in the previous example, here are the results:

Criterion	Meas	Det	Sum Eig	Max Eig	Cond	q1	q2
					$\frac{\text{Max Cond} = 52.273}{\text{Min Cond} = 16.757}$		
D	$\begin{array}{c} (0.4, 0.5) \\ (0.5, 0.5) \\ (0.6, 0.5) \\ (0.75, 0.5) \end{array}$	0.00260	0.372	0.365	51.234	0.084	0.338
А	$\begin{array}{c} (0.4, 0.5) \\ (0.5, 0.5) \\ (0.6, 0.5) \\ (0.5, 0.5) \end{array}$	0.00614	0.340	0.321	16.762	0.088	0.334
Е	$\begin{array}{c} (0.4, 0.5) \\ (0.5, 0.5) \\ (0.6, 0.5) \\ (0.5, 0.5) \end{array}$	0.00614	0.340	0.321	16.762	0.088	0.334
No Criterion	$\begin{array}{c} (0.4, 0.5) \\ (0.5, 0.5) \\ (0.6, 0.5) \\ (0.1, 0.5) \end{array}$	0.00885	0.462	0.442	22.078	0.095	0.310

Table 4.3: Table case 2-A. In the first column is defined the criterion, in the second the position of the measurements, in the third is given the determinant of C, in the fourth the sum of the eigenvalues of C, in the fifth the maximum eigenvalue of C, in the sixth the condition number of the covariance matrix. In the first row under this column we have the maximum and minimum condition number obtained varying the measurement position to cover the entire domain, in the last two columns we have the values of the parameters.

Criterion	Meas	Det	Sum Eig Max Eig		Cond	q1	q2
					Max Cond = 84.434		
		1	1		$Min \ Cond = 20.817$		
	(0.25, 0.5)						
D	(0.5, 0.5)	0.00248	0.463	0.458	84.434	0.084	0.323
	(0.75, 0.5)						
	(0.9, 0.5)						_
	(0.25, 0.5)		0.202	0.281			
А	(0.5, 0.5)	0.00205			96 917	0.094	0.991
	(0.75, 0.5)	0.00295	0.292		20.817	0.004	0.551
	(0.95, 0.5)						
	(0.25, 0.5)						
E	(0.5, 0.5)	0.0000	0.000	0.001	26.8174	0.004	0.991
E	(0.75, 0.5)	0.00295	0.292	0.281		0.084	0.331
	(0.95, 0.5)						
	(0.25, 0.5)						
	(0.5, 0.5)	0.0000	0.469	0.440	40 107	0.006	0.206
no Criterion	(0.75, 0.5)	0.00885	0.402	0.442	40.197	0.086	0.306
	(0.1, 0.5)						

Table 4.4: Table case 2-B. See above for the description of the table.



Figure 4.7: Confidence regions: case 2-A. The ellipses with dotted line correspond to the D, A and E criteria. To the criteria A and E corresponds the same optimal position and are equivalent in this case. The abscissa corresponds to the diffusion coefficient, while the ordinate to the flow velocity.



Figure 4.8: Confidence regions: case 2-B. The ellipses with dotted line correspond to the D, A and E criteria. To the criteria A and E corresponds the same optimal position and are equivalent in this case. The abscissa corresponds to the diffusion coefficient, while the ordinate to the flow velocity.

4.6.4 Reaction between two species

We consider the model of a reaction between two species. The equation of mass conservation for one species is thus the model:

$$\mu(\nabla u, \nabla \varphi) + \beta(u, \nabla \varphi) = (M\omega, \varphi) \quad in \quad \Omega \\ u = 0 \qquad on \quad \partial \Omega$$

where u is the mass fraction of one species, μ is the diffusion coefficient, β is the velocity of the flow, M is the molecular mass and ω is the molar production rate of the species. The term ω is given by:

$$\omega = kc$$

where k is the reaction rate and c is the concentration of the species. k is usually given by the Arrhenius formula

$$k = AT^b \exp(-\frac{E_a}{RT}),$$

where A is the pre-exponential factor T is the temperature, E_a is the activation energy and R the gas constant. The problem is to identify given parameters of the model by means of concentration measurements of one species in given points in the domain. We assume

further that the system response to the measurements is affected by some not systematic errors. The same considerations regarding the measurements made for the previous cases have been used also here.

The parameters to identify are the rate constant k and the diffusion coefficient μ . In order to do the parameter identification we perform three point measurements of u in three positions in the domain. The domain is the unit square.

After the first two measurements, chosen without criteria, we have gathered information about the system, that can be used to perform additionally measurements. We compare different criteria for choosing the third measurement point. The first two measurement points and the added errors are the same for all the cases, so that the prior information is the same in all cases. The third measurement is chosen using different criteria. We use the three criteria above defined and in one experiment we choose a position that is not an optimal design point.

In the following table we have all the starting values. In the first column the definition of the domain, in the second the value of vector flow velocity β , in the third and fourth columns the positions of the first two measurements, while in the last column we have the added error:

Domain	β	Meas 1	Meas 2	Added Error
$(0,1)\times(0,1)$	(1.5, 0.3)	(0.4 , 0.3)	$(0.6 \ , \ 0.5)$	$10\% u_{\rm max} = 0.016$

Table 4.5: Input parameters. In the first column the definition of the domain, in the second the value of vector flow velocity β , in the third and fourth columns the positions of the first two measurements, while in the last column we have the added error.

The results are collected in the next table. In the third row we have the position of the third measurements, in the fourth and fifth rows we have the values of the identified parameters, in the sixth row the area of the ellipse (minimized by the D criterion), in the seventh and eighth the length of the minimum and maximum axes (the latter minimized by the E-criterion), in the ninth row we have the sum of axes (minimized by the A-criterion):

	no OED	D	А	Е	True Value
Meas 3	(0.9 , 0.5)	(0.12, 0.27)	(0.11 , 0.2)	(0.11 , 0.2)	-
Param 1: μ	0.236819	0.194105	0.184985	0.184985	0.2
Param 2: k	8817.56	11654.1	12215.3	12215.3	15000
Area Ellipse	1.0220e + 04	2586.0	2655.6	2655.6	-
Min Axis	0.068075	0.051487	0.054365	0.054365	-
Max Axis	4.7788e + 04	1.5988e + 04	1.5549e + 04	1.5549e + 04	-
Sum Axes	4.7788e+04	1.5988e + 04	1.5549e + 04	1.5549e + 04	-

Table 4.6: Results. In the third row we have the position of the third measurements, in the fourth and fifth rows we have the values of the identified parameters, in the sixth row the area of the ellipse (minimized by the D criterion), in the seventh and eighth the length of the minimum and maximum axes (the latter minimized by the E-criterion), in the ninth row we have the sum of axes (minimized by the A-criterion).

The least squares functional is the distance between the measured values of u_{meas} and the approximated ones by the finite element model: $F = \frac{1}{2} ||u_{meas} - u||^2$. In figures (4.11, 4.12) the least squares functionals corresponding to the case of the D-criterion and the case where no criterion has been chosen are depicted. The iso-lines represent the confidence region at different levels, these contours are the confidence regions for the model without condidering the linearization. It is possible to see that the form of the contour is close to an ellipse, as it would be in the case of a linear model. It can also be noted that the confidence region in the case of the D-criterion is smaller than the other, this again is a visualization of the optimal choice of the measurement points.



Figure 4.9: Solution with the nominal parameters.



Figure 4.10: Confidence regions.



Figure 4.11: Least squares functional for the case of the D-criterion. The iso-lines represent the confidence region at different levels. It is possible to see that the form of the contour is close to an ellipse, as it would be in the case of a linear model.



Figure 4.12: Least squares functional for the case of the position without an optimal criterion. It can be noted that the contour of the iso-lines corresponds to a larger confidence region in comparison with the figure 4.11.



Figure 4.13: Determinant of the covariance matrix.



Figure 4.14: Trace of the covariance matrix.

4.7 A posteriori error estimation for optimal experimental design problems

In this section we propose an adaptive scheme for optimal experimental design problems. We proceed following the method described in the section 3.3. We refer also to Vexler [75] for a derivation of an a posteriori error estimation for parameter estimation problems. The problem of optimal design of experiments is a natural extension of the parameter estimation problem and similar techniques can be applied, considering the peculiarity of the former problem.

In the context of design of experiments we have seen that the problem to solve is a constrained minimization, where the constraint is the system of equations corresponding to the first order optimality conditions, that originate from the parameter estimation problem. Here below we expose the derivation of the system comprehensive of the primal and the dual part necessary to define the error estimator as described in the error representation (3.28), here reported for simplicity:

$$J(u) - J(u_h) = \frac{1}{2}\rho(u_h; z - \psi_h) + \frac{1}{2}\rho^*(z_h; u - \varphi_h) + R_h,$$

where the terms are defined as in proposition 3.1.

We begin by considering the following simple model:

$$q\Delta u = f \quad in \ \Omega,$$
$$u = 0 \quad on \ \partial\Omega$$

where Ω is a 2D Lipschitz domain, $q \in Q \subset \mathbb{R}$ is a scalar parameter and f is a function in L^2 and u is the state, that we can assume to be a function defined in $V = H^1$. L^2 is the space of square integrable functions and H^1 is the Hilbert space of square integrable functions with square integrable first derivative. Aim of the parameter identification is to find the best choice for q in the set Q by means of a fit using point measurements of the state u at two distinct points $\{\xi_1, \xi_2\}$ in the domain.

After defining the observation functional C(u) as in (4.1):

$$C_i = C(u|_{\xi_i}) = u|_{\xi_i} - u_{0_i},$$

where

$$u|_{\xi_i} = \frac{1}{B(\xi_i,\epsilon)} \int_{B(\xi_i,\epsilon)} \omega(|\xi_i - \xi|) u(\xi) d\xi, \qquad (4.32)$$

we define the cost functional as the sum of squares:

$$J(u) = \frac{1}{2} (\mathcal{C}, \mathcal{C}). \tag{4.33}$$

The minimization problem is so formulated:

$$\begin{cases} \min_{q \in Q} J(u) \\ A(u,q;\varphi) = 0 \quad \forall \varphi \in V \end{cases}$$

we proceed by defining the Lagrangian:

$$L(u, q, \lambda) = J(u) - A(u, q; \lambda),$$

then we set the system corresponding to the first order optimality conditions:

$$\begin{cases} L'_{u}(u,q,\lambda)(\delta u) = (\delta u|_{\xi}, u|_{\xi} - u_{0}) - (q\nabla\delta u, \nabla\lambda) = 0 \quad \forall \delta u \in V \\ L'_{q}(u,q,\lambda)(\delta q) = -(\delta q\nabla u, \nabla\lambda) = 0 \quad \forall \delta q \in Q \\ L'_{\lambda}(u,q,\lambda)(\delta\lambda) = -(q\nabla u, \nabla\delta\lambda) + (f,\delta\lambda) = 0 \quad \forall \delta\lambda \in V, \end{cases}$$

$$(4.34)$$

where the operator $\cdot|_{\xi}$ is defined as in (4.32). Exploiting the solution of the sensitivity equation, where w is the derivative of u:

$$(q\nabla w, \nabla \varphi) = (\nabla u, \nabla \varphi),$$

$$w = -\frac{1}{q}u,$$

we can write the sum of the first two equations in (4.34) as:

$$(w|_{\xi_i}, u|_{\xi_i} - u_{0_i}) = 0,$$

or

$$\left(-\frac{1}{q}u|_{\xi_i}, u|_{\xi_i} - u_{0_i}\right) = 0,$$

we can rewrite the equation in the form:

$$\left(-u_1|_{\xi_i}, qu_1|_{\xi_i} - u_{0_i}\right) = 0,$$

with u_1 the solution of the state equation with q = 1

$$(\nabla u_1, \nabla \varphi) = (f, \varphi).$$

This says that the two vectors with components $\{-u_1|_{\xi_1}, -u_1|_{\xi_2}\}$ and $\{qu_1|_{\xi_1} - u_{0_1}, qu_1|_{\xi_2} - u_{0_2}\}$ are orthogonal.

From the orthogonality condition we get q:

$$q = \frac{u_1|_{\xi_1}u_{0_1} + u_1|_{\xi_2}u_{0_2}}{(u_1|_{\xi_1})^2 + (u_1|_{\xi_2})^2}$$

The variance of the parameter is:

$$cov_q = \frac{\Sigma}{(w|_{\xi}, w|_{\xi})}$$

where Σ is the variance of the measurements and in the following we assume $\Sigma = 1$ to simplify the notation.

In this scalar example all the functionals considered are equivalent:

$$\Phi = det(cov_q) = tr(cov_q) = \max \sigma(cov_q) = \frac{1}{(w|_{\xi}, w|_{\xi})}$$

The formulation of the optimal experimental design problem is:

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$$\begin{cases} \min_{\xi} \Phi(w,\xi) \\ L'_u(u,q,\lambda)(\delta u) = 0 \quad \forall \delta u \\ L'_q(u,q,\lambda)(\delta q) = 0 \quad \forall \delta q \\ L'_\lambda(u,q,\lambda)(\delta \lambda) = 0 \quad \forall \delta \lambda \\ (q\nabla w, \nabla \varphi) = (\nabla u, \nabla \varphi) \quad \forall \varphi, \end{cases}$$

. . .

where we have add the last equation, the sensitivity equation, that is the equation for w: the derivative of u with respect to the parameter q. The peculiarity of the experimental design problem is that the cost functional is applied to the Jacobi matrix of the system, that means that it is a function of the derivatives of the state. For this reason we have to consider the sensitivity equations in the formulation of the minimization problem. The Lagrangian reads:

$$\begin{split} L(w, u, q, \lambda, \xi, \mu, v, p, y) &= \Phi(w, \xi) - J'_u(u)(v) + A(u, q; y) \\ &+ A'_u(u, q; \lambda)(v) + A'_q(u, q; \lambda)(p) \\ &+ A'_u(u, q; \mu)(w) + A'_q(u, q; \mu)(1) \end{split}$$

The first order optimality conditions for the model considered are given by the following system:

$$\begin{cases} L'_{w}(\delta w) = -\frac{2}{D^{2}}[(\delta w, w)] + (q \nabla \delta w, \nabla \mu) = 0 \quad \forall \delta w \in V \\ L'_{\mu}(\delta \mu) = (q \nabla w, \nabla \delta \mu) + (\nabla u, \nabla \delta \mu) = 0 \quad \forall \delta \mu \in V \\ L'_{u}(\delta u) = -(v|_{\xi}, \delta u|_{\xi}) + (p \nabla \delta u, \nabla \lambda) \\ + (q \nabla \delta u, \nabla y) + (\nabla \delta u, \nabla \mu) = 0 \quad \forall \delta u \in V \\ L'_{q}(\delta q) = (\delta q \nabla v, \nabla \lambda) + (\delta q \nabla u, \nabla y) + (\delta q \nabla w, \nabla \mu) = 0 \quad \forall \delta q \in Q \\ L'_{\xi}(\delta \xi) = -\frac{2}{D^{2}}[(w'_{\xi}, w)] = 0 \\ L'_{\lambda}(\delta \lambda) = (q \nabla v, \nabla \delta \lambda) + (p \nabla u, \nabla \delta \lambda) = 0 \quad \forall \delta \lambda \in V \\ L'_{v}(\delta v) = -(\delta v|_{\xi}, u - u_{0}) + (q \nabla \delta v, \nabla \lambda) = 0 \quad \forall \delta v \in V \\ L'_{p}(\delta p) = (\delta p \nabla u, \nabla \lambda) = 0 \quad \forall \delta p \in Q \\ L'_{y}(\delta y) = (q \nabla u, \nabla \delta y) - (f, \delta y) = 0 \quad \forall \delta y \in V \end{cases}$$

$$(4.35)$$

where w'_{ξ} is the derivative of the function w with respect to the space variable ξ . In the case of optimization problems it is natural to use as goal functional for the formulation of the a posteriori error estimation the functional to be minimized. In this case the functional is Φ and the dual solution to be used for the error representation is then given by the Lagrange multipliers $\{y, p, \lambda, \mu\}$ of the system (4.35).

The system (4.35) is a linear system, it encompasses the primal and dual variables. For the error representation we use the residual of the primal system weighted with the dual solution, thus we need the solution of the complete system.

Considering the reduced formulation of the minimization problem (problem 4.4) and the reduced functional:

$$\hat{L}(q,\xi) = \Phi(w,\xi) - J'_q(u(q),q)(\delta q),$$

the first order optimality conditions become:

$$\begin{cases} \hat{L}'_q(\delta q) = \Phi'_q(w,\xi)(\delta q) - J''_{qq}(u(q),q)(\delta q,p) = 0 \quad \forall \delta q \in Q \\ \hat{L}'_{\xi}(\delta \xi) = \Phi'_{\xi}(w,\xi)(\delta \xi) = 0 \quad \forall \delta \xi \in \Pi \end{cases}$$

and applying the chain rule we obtain:

$$\begin{cases} \hat{L}'_{q}(\delta q) = \Phi'_{q}(w(q),\xi)(\delta q) - J'_{u}(u(q),\xi)(\tau(p)) - J''_{uu}(u(q),\xi)(w(p),w(1)) = 0 \quad \forall \delta q \in Q \\ \hat{L}'_{\xi}(\delta \xi) = \Phi'_{\xi}(\delta \xi) = 0 \quad \forall \delta \xi \in \Pi. \end{cases}$$
(4.36)

where w(p), the derivative of u, is the solution of the following problem under the assumption of the validity of the implicit theorem:

$$(q\nabla w, \nabla \varphi) = (p\nabla u, \nabla \varphi) \quad \forall \varphi \in V$$
(4.37)

and $\tau(p)$, the derivative of w, is the solution of the problem:

$$(q\nabla\tau,\nabla\varphi) = (p\nabla w,\nabla\varphi) \quad \forall\varphi \in V$$

which is the application of the implicit theorem to the equation (4.37), considering the function w as function of the parameter q through the same equation.

For the model considered, the first equation of the system (4.36) is:

$$-\frac{2}{(w|_{\xi}(p),w|_{\xi}(p))^{2}}(\tau|_{\xi}(p),w|_{\xi}(p)) = (w|_{\xi}(p),w|_{\xi}) + (\tau|_{\xi}(p),u|_{\xi}-u_{0}),$$

from which we obtain the dual variable p:

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$$p = -2\frac{(\tau|_{\xi}, w|_{\xi})}{(w|_{\xi}, w|_{\xi})} \frac{1}{\left[(w|_{\xi}, w|_{\xi}) + (\tau|_{\xi}, u|_{\xi} - u_0)\right]}$$

From the system (4.35) we consider the equation:

$$L'_{\lambda}(\delta\lambda) = A'_{u}(u,q;\delta\lambda)(v) + A'_{a}(u,q;\delta\lambda)(p) = 0 \quad \forall \delta\lambda \in V,$$

from which we obtain the variable v:

$$v = u \frac{p}{q},$$

and from the equation

$$L'_u(\delta u) = 0 \quad \forall \delta u \in V,$$

we obtain the dual function y.

In the next section we consider a numerical example of optimal design of experiment for which we have calculated the error representation (3.28). This is only the first step towards a systematic use of the described technique for local refinement of the mesh, the extension of this work and further investigations will be material for future work in this context.

4.7.1 Numerical example

For numerical purposes we consider a diffusion-convection model:



Figure 4.15: Solution of the diffusion-convection model with the given boundary conditions.

$$\begin{cases} -q_1 \Delta u + q_2 \nabla u = f \quad in \quad \Omega \subset R^2 \\ u = 0 \quad on \quad \partial \Omega, \end{cases}$$

where the state u is defined in an opportune Hilbert space, the external force is constant f = 1 and the two parameters considered are the viscosity coefficient and the first component of the velocity field, assuming the second component equal to zero. The experiment consists of measuring the state u at two initial positions and to use this information to find the optimal position for a third measurement using the "D-criterion". The procedure for the optimization is the same as described in section 4.31 and in the relative numerical examples. The first two measurements are performed at the points: $\xi_1 = (0.8, 0.3)$ and $\xi_2 = (0.2, 0.4)$. The true values of the parameters are: q1 = 0.1, q2 = (0.5, 0)

The result of the optimization is the optimal position for the third measurement: $\xi_{opt} = (0.42, 0.5)$.

Below we show the functional to be minimized $\Phi = Det(Cov_q)$, which is shown to be non-convex. Further we show some components of the solution of the system (4.35): the solutions of the sensitivity equations w_1 and w_2 and the three components of the dual system μ_1 , μ_2 and y.

In the table 4.7 we reproduce three values of the efficiency of the error representation for different mesh sizes.

N	$\Phi(u) - \Phi(u_h)$	Eff
100	0.011	0.99
400	0.0027	1.019
1600	0.00052	1.02

Table 4.7: Efficiency of the error representation. In the first column is reported the number of degree of freedom of the discretization, in the second column is reported the discretization error with respect to the goal functional $\Phi(u)$, that in this case is the determinant of the covariance of the two model parameters. In the third column it is reported the efficiency of the error representation (3.28).

This is the first step towards a systematic technique for the adaptivity of the mesh. In future work we want to apply the a posteriori error estimation here presented to problem involving the design of experiment.



Figure 4.16: From the top left the first picture is the functional $\Phi = Det(Cov_q)$, the second and third pictures are the dual components μ_1 , μ_2 , these are the Lagrange multipliers for the two sensitivity equations with respect to the two parameters. From the bottom left the first picture is the dual component y of the system (4.35). The second and third pictures are the solutions of the sensitivity equations w_1 and w_2 : left with respect to q_1 and right w.r.t. q_2 . The dual solution corresponds to the weighting in the error representation. These pictures show that in case of point measurements the weight is posed around those points. Regarding the solutions μ_1 and μ_2 we can see that the point measurement at ξ_1 is weighted in a different way and that the weight is related to the solutions w_1 and w_2 (see the different high of the spike). This is due to the fact that the goal functional for the error estimation is a function of the covariance matrix, which is on the other hand is a function of the Jacobi matrix of the system.

Chapter 5

Numerical results

The first step in preparing for the simulation of the reactive flow in the reactor is the determination of a complete set of initial and boundary conditions for which the model can be expected to be well-posed.

The aim of this chapter is the description of the numerical results and all the necessary preparation work, that we call 'calibration' of the model: the model calibration includes the determination of the inflow velocity for the species N_2O and H_2 from the central cooled inlet, the velocity for Ar from the external ring and from the cooling system for the optic, the determination of the pressure inside the reactor and the outflow condition at the outflowboundary, at the inflow the specification of the amount of species, in mass fraction, that is regulated by the mass controllers. Further it includes the specification of the temperature profile along the entire boundary. Then it has to be implemented the so called 'ignition', that is the procedure for starting the reaction, and, during the reaction, the numerical measurement procedure.

The following is the summary of the main items in this chapter:

- Model calibration
 - velocity profile
 - pressure in the reactor
 - inflow mass of species
 - calibration of the temperature
- Ignition
- Measurements
- Parameter estimation results
- Visualization of the flow

5.1 Model calibration

The calibration of the model is the determination of the boundary conditions necessary to prepare the simulation of a single experiment. For the simulation we get experimental data from measurements of quantities, that are indirectly related to the values we need, so the direct relation is given by the so called 'calibration'. The results of the measurements are not dependent on the calibration parameters in the same way. We have not done a complete sensitivity analysis regarding the boundary values, but during the calibration we have experienced the response of the system with respect to these values. We have observed that variations in the temperature at the measurement zone and variations in the concentrations at the ignition time, results in more variations in the results than the variations of pressure and velocity. This because, regarding the velocity, in the mixing of the species at this regime, the transport term is less important than the diffusion term. While the thermodynamic pressure is included only in the state equation and is actually a scaling factor for the density, because in our case the pressure is constant in all the volume. Only at very high external pressure (about 1 atm) the density changes are big enough to change the effect of the gravity on volumes of gases at different temperatures. This is an effect that can bring the flow in a non-stationary regime, as we can see later in this chapter.

All the needed boundary values are determined by means of measurements with different devices and some elementary calculations, except for the temperature, for which the calibration is achieved by solving a parameter estimation problem. This is a typical example of a 'real life' simulation, because in our case the temperature measurements are not available along the boundary, but for technical reasons only along the symmetry axis of the reactor.

We refer to figure 3.2 for the nomenclature of the different parts of the boundary for imposing different boundary conditions.

5.1.1 Velocity

As is described in the chapter 1 we have to determine the inlet flow of the different species. Through the central inlet of Γ_{in} flows a mixture of N_2O and H_2 and through the external ring flows Ar. We assume a parabolic profile of the velocities. The parameter describing the profile are fixed by the geometry of the inlet and by the mass flow, which is regulated by some devices. The mass controllers determine the mass flow of the species in unit of volume [*sccm*]. As the volume of gases is dependent of the temperature and pressure, the values are given with respect to a standard condition, so the values read in the devices have to be converted using the relationship

$$Q_a = Q_s(p_s/p_a)(T_a/T_s),$$

where the subscript a' indicate actual values and the subscript s' standard values. The total volume flow is equal to the volume of the solid obtained rotating the parabola around an axis, in the figure 5.1 is depicted a section of the volume and the axis of rotation is the y axis. The volume in the ring is the subtraction of the two volumes obtained by rotating the external part of the parabola from $\frac{R-r}{2}$ to R and by rotating the internal part from r to



Figure 5.1: Inflow velocity profile.

 $\frac{R-r}{2}$ around the y axis. In the local coordinate system (x, y) the parabola has the equation $y = ax^2$, the maximum of y is in $x_M = \frac{R-2}{2}$, thus $a = \frac{x_M^2}{V_{max}}$ and after integrating:

$$\int_{0}^{V_{max}} \pi \left(\left(\frac{R-r}{2} + x \right)^2 - \left(\frac{R-r}{2} + x \right)^2 \right) dy, \tag{5.1}$$

we obtain

$$V_M = F \frac{3}{8} \frac{1}{\pi} \frac{1}{r_{12}^2},$$

where F is the total flux of Ar. In this manner we can determine the profile of the inflow given a measured flow.

For the inflow at the central cooled inlet and at the lateral cooling system we calculate the velocity in a similar manner.

For the rest of the boundary we assume no-slip condition:

$$u = 0$$
 on $\Gamma \setminus \{\Gamma_{in} \cup \Gamma_{out} \cup \Gamma_{opt}\}.$

While at the outlet we impose the Neumann condition

$$\nabla v \cdot n = 0,$$

where n is the unit vector normal to the surface.

5.1.2 Pressure

As described in the chapter 2 the pressure at the boundary is given by equation (2.73):

$$p = \frac{1}{|\Gamma_{out}|} \int_{\Gamma_{out}} p_{out}(x, t) ds,$$

and in our case, as the pressure is determined by an external device, it remains constant in the volume inside the reactor except for the small fluctuations due to heat release, expecially in the reaction zone. In our formulation the pressure was split in a thermodynamic part and a hydrodynamic part. These fluctuations are accounted for in the latter component of the pressure, while the thermodynamic part is taken to be constant.

5.1.3 Mass fraction

From the flow regulators we have to define the amount of species that flows in the reactor. This could be a very important source of error for the simulation of a reaction, because experimentally we actually measure the production rate of a species (in our case H) and from this we can derive the constant rate of production if we know all the other parameters in the formula, that is, if we know the molar concentrations of all the species in this elementary reaction:

$$\omega_k = \sum_i (\nu_{ki}^b - \nu_{ki}^f) k_i^f \prod_l c_l^{\nu_{li}^J},$$

see formula (2.52) for the notation. The initial concentration in number of molecules per cm^3 is given by the partial pressure, which depend on the ratio of the flux of a species to the total flux. In the following table we show the data for the case with T=780K. The description of the content of the column is enumerated below:

- 1. Type of flow regulator,
- 2. Type of gas,
- 3. Percentage of maximum flux available,
- 4. Flux converted in [sccm],
- 5. Partial pressure of the species,
- 6. Concentration of the species in $[molec/cm^3]$.

Flow regulator	Gas	$\Phi\%$	Φ [sccm]	p[mTorr]	c $[molec/cm^3]$
500 sccm-N2	$Ar{opt}$	106.6	638	17964	$2.22E{+}17$
2000 sccm-He	Ar{buffer}	28.3	670	18863	$2.33E{+}17$
100 sccm-H2S	N2O	20	16	451	$5.59E{+}15$
660 sccm-He	H2	50	235	6620	$8.2E{+}16$

Table 5.1: Derivation of the concentrations from the fluxes for the case T=780 [K], p=43.9 [torr].

The partial pressure p_i of the i^{th} species is calculated from the relation:

$$p_i = \frac{\Phi_i}{\Phi_{tot}} p_{tot},\tag{5.2}$$

where p_{tot} is the measured pressure in the reactor (in this case p=43.9 [torr]) and Φ_{tot} is the summation of all the fluxes. From the partial pressure we can derive the number of molecules of gas per cm^3 and from this the mass fraction in the following way: the number of moles of a species n_i is given by N_i/N_A , where N_A is the number of Avogadro, the mole fraction of the i^{th} species is $x_i = n_i/n$ and the mass fraction is calculated as:

$$w_i = \frac{M_i n_i}{\sum_j M_j n_j}$$

where M_i is the molar mass of the i^{th} species and $n = \sum n_j, j \in S$, where S is the set of indexes of all the species.

5.1.4 Temperature profile

For the temperature we need the profile along the entire boundary (see Fig. 5.2).



Figure 5.2: Temperature's boundary condition.

Experimentally, due to some constraints in the construction of the reactor, we can measure



Figure 5.3: Calibration.

the temperature only along the axis of symmetry of the main duct. Thus to get the boundary values of the temperature for the numerical simulation we must perform a parameter estimation as calibration of the model with the measured temperature.

The temperature at the boundary is described by a piecewise function as shown in the figure 5.2. The values of the temperature at the positions y2 - y7 are the six parameters that we have to identify in order to set the appropriated boundary condition.

We define as functional to be minimized the distance of the measured temperatures to the simulated ones, both along the axis of symmetry:

$$F = \frac{1}{2} \|T_{meas} - T_{sim}\|^2 = \frac{1}{2} \int_{\Gamma_{sym}} |T_{meas} - T_{sim}|^2 dz.$$
(5.3)

We must calibrate the model for each set of experiments with a given temperature in the heating zone, because changing the temperature in the oven changes the distribution of the temperature in the entire reactor. Due to the nonlinearities of the model it is not possible to determine a map between the boundary values of temperature and the values at the symmetry axis without perform a new calibration, in other words it is not possible just to scale the values at the boundary to reproduce the measured ones.

The results of the calibration for the experiments with 580 K in the heating zone are plotted in the figure 5.3. The points with the '+' symbol are the measured values of temperature at different z values at the symmetry axis. The red line, piecewise linear, is the result of the calibration, that means the temperature at the boundary, while the blue one is the temperature at the symmetry axis from the simulation.

5.2 Ignition

Experimentally the reaction starts by producing an amount of $O(^{1}D)$ that combines with H_{2} . The $O(^{1}D)$ is obtained by photodissociation of $N_{2}O$. In the numerical case the pho-



Figure 5.4: Photolysis: the photodissociation in the numerical case is simulated by an ignition mechanism.

todissociation is simulated by an ignition mechanism, we define an area corresponding to the laser beam, that goes through the diameter of the reactor at the optic zone, and substitutes artificially the amount of molecules of N_2O at each degree of freedom, corresponding to the dissociated quantity, by the same amount of molecules of N_2 and of $O(^1D)$. This corresponds to an impulse of the energy of the system. At the experimental conditions the flow regime for the multicomponent fluid is stationary, while, after starting the reaction, the coupled system is not more stationary, at least until the quantity of $O(^1D)$ produced is completely consumed. The measurements are taken after the ignition time during the transient phase of the reaction, circa 400-500 ns. In the next section we describe the experimental and numerical measurements.

5.3 Measurements

In the chapter 1 we have described the setup of the experiments, here we describe the numerical approach to the determination of the kinetics of the reaction. Our approach is analogous to the experimental approach, that means that we describe the reaction by a simulation of the experiment itself. The experimental approach consists of repeating different experiments with different initial conditions, changing the ratio of the concentration of the species at the inflow: H_2 , N_2O and Ar. In all cases the concentration of H_2 can be considered in excess with respect to the others, so that during the reaction it can be regarded as almost constant for the calculation of the reaction rate. For the determination of the latter, six configurations are used, obtained by varying the inflow regulator of H_2 from 5% to 50% of the maximum flow admissible. From these six data sets a pseudo-first-order reaction rate

can be estimated and from this the "true" reaction rate, for a given temperature. With this technique the reaction rate has been "experimentally" determined.

For the numerical estimation of the reaction rate we just need one experimental curve for one of the values of initial concentration. We show this in the case of T = 300K comparing the numerical results in two extreme cases: the first with the flow regulator for H_2 at 50% of the maximum value and the second at 5%. Experimentally the reaction starts with the photodissociation of N_2O in N_2 and $O(^1D)$, produced by an ArF (193 nm) excimer laser. It is assumed that the dissociated fraction of N_2O is about 10 % of the quantity present in the measurement volume. This introduce an uncertainty in the set-up of the experiment, but we can make two considerations regarding this point. First, this uncertainty is for sure small with respect with all the measurement uncertainties in the measurement chain. Second, as we have seen in the expression for the production of the H atoms, equation (1.8), the initial concentration of $O(^{1}D)$ acts as a multiplicative constant, that means that two measurements that differ because of the different initial concentrations on $O(^{1}D)$ give two signals that differ by a multiplicative constant and this is implicitly included in the measurement procedure as described below. The detection of H atoms in the experiment is made by laser-induced fluorescence technique (LIF), the details can be found in the work of A. Hanf [43]. As described in the chapter 1 the measurements give a number of points within a time interval, that goes from the ignition time to a time sufficient for the reaction to end, this signal is proportional to the number of H atoms that are present in the measurement volume. From the numerical simulation we can obtain a 'measurement signal', that is exactly the number of atoms present in a measurement volume to be defined. This is done by numerically integrating the concentration of a species over all the elements contained in the measurement volume. The fit with the experimental data can be made only if one of the two signals is scaled by multiplying by a constant all the measurement points. Thus the uncertainty about the initial concentration of $O(^1D)$ is included in this constant and doesn't affect the result of the fit, but of course the fit procedure has to consider this additional parameter. So to compare the two signal we have to consider an additional parameter, that is the unknown scaling factor of the LIF signal. This changes the setting of the minimization problem because now we have a parameter in the definition of the cost functional, that has no physical meaning and is not included in our model. To solve this problem we have adopted an explicit technique decoupling the parameters and solving in an iterative manner the minimization problem, as following described. The functional to be minimized is the distance between the experimental data and the simulated data, each point of the latter multiplied by an unknown constant, that accounts for the 'LIF scaling':

$$F = \frac{1}{2} | [H_{meas}]_i - c [H_{sim}]_i |^2.$$
(5.4)

We present here below the scheme that describes the steps of the algorithm of minimization of this functional. We call 'model parameters' the parameters of the original parameter estimation problem and 'calibration parameters' those figuring only in the cost functional.

```
Algorithm for the minimization of the cost functional
1. use a suitable start value for the model parameters to
   calculate the initial value of the cost functional;
2. use a bisection method for the minimization of the
   cost functional with respect only to the 'calibration'
   parameter c;
3. begin loop minimization over the model parameters:
     • calculate the search direction and the step for the
       model parameters,
     • calculate the residual with updated parameters;
4. stop loop if given tolerance achieved;
5. after a number of iterations n, to be defined, stop the
   previous loop and re-calibrate the constant c using a
   bisection method;
6. calculate the new residual using the new c;
7. repeat steps 3 to 6 until convergence.
```

In our case it was enough to calibrate twice the constant. Modifying the number of iteration at the step 5, we have observed slightly different convergence rate, but the algorithm has not shown instabilities. Without the first calibration step is mostly impossible to converge, because the raw curves are scaled with a constant c of some orders of magnitude and the steps for the parameters in the point 3 would not have physical meaning.

5.4 Results of the fit

5.4.1 Case T = 300K, 50% H_2

For the numerical experiments we have used the mechanism described in the appendix A, which is composed of 50 reactions and 17 species. Here below is a table with all the species:

N_2O	$O(^1D)$	H_2	OH	0
NO	H_2O	HNO_2	N_2	O_2
HO_2	HNO	NO_2	N	Η
NH	Ar			

Table 5.2 :	Table	of s	species	of	the	full	system.
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Figure 5.5: Comparison simulation vs experiment for the case with T = 300K and 50% of H_2 . The result of the fit is the reaction rate: $k = 1.0E - 10[cm^3molec^{-1}s^{-1}]$. The other two curves, k = 0.9E - 10 and k = 1.1E - 10, are plotted to show qualitatively the sensitivity with respect to the reaction rate.

In the following list are collected the data for the experiment with the temperature at 300 K:

- P = 1866 Pa,
- Inflow mass fractions: $w_{H2} = 0.016, w_{N2O} = 0.0236,$
- Inflow velocity: main tube v = 0.86m/s, optic cooling system: v = 0.55m/s.

The result of the fit is plotted in the figure 5.5.

The blue curve, in the middle, corresponds to the $k = 1.0E - 10[cm^3molec^{-1}s^{-1}]$ and is the result of the parameter estimation. The other two curves, k = 0.9E - 10 and k = 1.1E - 10, are plotted to show qualitatively the sensitivity with respect to the reaction rate.

5.4.2 Case T = 300K, 5% H_2

In the case with less concentration of H_2 we have different initial mass fractions, but the rest of parameters is the same as the previous example:



Figure 5.6: Comparison simulation vs experiment for the case with T = 300K and 5% of H_2 . The result of the fit is the reaction rate: $k = 1.0E - 10[cm^3molec^{-1}s^{-1}]$.

- Inflow mass fractions: $w_{H2} = 0.0022, w_{N2O} = 0.0239,$
- the rest as the 50 % case.

The results are plotted in the figure 5.6. The same result, $k = 1.0E - 10[cm^3molec^{-1}s^{-1}]$, as the prevous case is found, showing that for the numerical investigation we can choose just one of the experimental curves available for the fit.

5.4.3 Case T = 780K, 50% H_2

In the case with higher temperature the set-up is slightly different, here are the given parameters:

- P = 5866 Pa,
- Inflow mass fractions: $w_{H2} = 0.02, w_{N2O} = 0.0249,$
- Inflow velocity: main tube v = 0.86m/s, optic cooling system: v = 0.55m/s.

The results of the fit are plotted in the figure 5.7. In the case of 780K the fit determines a reaction rate $k = 1.5E - 10[cm^3molec^{-1}s^{-1}]$, which shows an increment with temperature.



Figure 5.7: Comparison simulation vs experiment for the case with T = 780K. The result of the fit is the reaction rate: $k = 1.5E - 10[cm^3molec^{-1}s^{-1}]$.

5.5 Visualization of the flow

In this section we describe some details of the flow simulation, expecially the temperature diffusion and the species diffusion. The temperature diffusion is mostly given by the heat conductivity of Ar. The buffer gas flows from the external ring and transports the heat from the ceramic wall towards the center of the reaction tube. Its distribution reaches a stationary condition after 300 ms. In the picture 5.8 are depicted six states at six different time steps, it is clear that the spacial distribution follows the typical velocity profile of a flow in a tube. This simulation is made with the parameter setup described in the section 5.4.3. In this case the effect of gravity is negligible, because the pressure is too low for the volume force deriving from the gravity to overcome the transport term. In the case with higher pressure on the contrary, the gravity acts on volumes of gases with different temperatures producing a force that in the boundary layer creates a flow that goes towards the top of the reaction tube, creating vorticity and starting an instationary mixing process. The picture 5.9 shows the first phase of this phenomenon. We have not further studied this case, because we do not have yet experimental data for the case with higher pressure to compare. From the numerical point of view the instationarity of the phenomenon adds some difficulties. In the previous cases the flow is stationary until the ignition time, that means that it is possible to use a larger time step to calculate the flow until that time and to use the solution one step before ignition time as starting solution for the simulation of the reaction and for the steps of the optimization. It is also less expensive to improve the



Figure 5.8: Temperature distribution at six time steps from 50 msec to 300 msec, towards a stationary solution.

precision by local refinement of the mesh. In the instationary case the spatial discretization has to be fine enough to catch the flow pattern due to the instationary mixing (see figure 5.9) and the time step has to be decreased making the simulation much expensive.

One of the prerequisites of the flow in the reactor is the uniformity of the mixture at the measurement zone. As we have seen in the section 5.1.3, we calculate the reaction rate k from the measured production rate ω_k :

$$\omega_k = \sum_i (\nu_{ki}^b - \nu_{ki}^f) k_i^f \prod_l c_l^{\nu_{li}^f},$$

it is then important to estimate the concentration of the species c_l , that participate to this reaction, at the measurement volume, that is a small cylinder of 1 mm of diameter and 5 mm length, given by the intersection of the two lasers, at the optic zone. With the flow conditions described in the experimental setup we can assure a uniform distribution of the species in the measurement zone. The picture 5.10 shows the local distribution of mass fraction of H_2 and N_2O at the stationary solution before the ignition time, the lateral flow



Figure 5.9: Non-stationary behavior with high pressure (1 atm) and high temperature (780K). The gravity acts on volumes of gases with different temperatures producing a force that in the boundary layer creates a flow that goes towards the top of the reaction tube, creating vorticity and starting an instationary mixing process.

of Ar influences the profile of the species distribution, but at the measurement zone the distribution is uniform.



Figure 5.10: Concentrations of H_2 (left) and N_2O (right) a step before the ignition.

In the picture 5.11 is depicted the distribution of N_2O at ignition time. It is possible to see the consumption of N_2O due to the artificial dissociation. The blue zone is the zone with zero concentration of N_2O . In the central stripe, at the ignition time, starts the reaction.



Figure 5.11: The ignition mechanism starts the reaction. The concentration of N_2O is depicted at few nanoseconds after the ignition. Whithin the laser beam the molecules of N_2O are dissociated in N_2 and $O(^1D)$ atoms. The dissociation reduces the concentration of N_2O in that zone.



Figure 5.12: The two components of the velocity: x (left) and y (right).

The picture 5.13 shows a aerie of shots of the mass fraction of H atoms, during the reaction.



Figure 5.13: H production during the reaction, the first step is at 10 ns after the ignition, the other shots are taken at 100 ns of delay from each-other.

Conclusion

In this work we present numerical techniques for the study of the reaction kinetic in laminar flow reactors. These encompass the model of multicomponent flow of a reactive mixture, the finite elements method to solve the underlying system of partial differential equations (PDE) and include techniques for the identification of parameters in this context. Further we introduce methods for the optimal experimental design in the context of partial differential equations considering reactive flows.

We present a model to simulate the detailed interplay between flow variables and those variables that describe the chemistry. We consider model for the flow motion in the regime of low Mach number, where the velocity of the flow is much slower than the sound speed, to exploit the advantage of this phenomenology.

The discretization in space of the system of equations is based on the method of finite elements. The resulting nonlinear system of equations is time dependent and we are interested in the transitory phase during the reaction. The system has the characteristic of being stiff, this suggests the use of implicit methods for the solution in time. For the solution of the nonlinearities we adopt a quasi-Newton method and for the solution of the linearized equations a multi-grid method with a domain decomposition scheme as smoother. This method takes advantage of the parallelization of the finite elements code "HiFlow", that has been used for the simulation.

As we deal with real measurements and their uncertainties, we expose a probabilistic setting of the parameter estimation problem. The natural extension of the parameter identification study, dealing with uncertainties that can be described by a given statistic distribution, is the optimal experimental design problem. For this purpose we present this theory and some numerical experiments in the context of partial differential equations.

Central role in this work is played by the simulation of a real experiment and the results from the comparison between the numerical and the experimental part. The experiment consists of measuring the concentration of a species within a measurement volume in a laminar flow reactor. Making a fit using these measurements and the results from the numerical simulation, we study the kinetic of a reaction of the mechanism that describes the overall chemical system. Aim of the experiment is the study of the reaction rate in a wide range of temperature. The results here presented concern the range 300K - 780K. For the experimental approach to the study of the kinetic more measurements at a specific temperature with different initial conditions for the concentration of some species are necessary. For the numerical study we show results for the two extreme cases in the above mentioned range of temperature. For the case at 300K we show the fit with the results from two experiments using the extreme values of the initial concentration used in the experiments. In both cases we obtain the same value for the parameter showing that for the numerical approach it is sufficient to make a fit using the results from one configuration. In the chapter 5 we present the results of the simulation. Concerning the obtained results we can state that the numerical methodology presented can be applied successfully for the study of the kinetic of reactions that take place in a laminar flow reactor at high temperature. In both cases, 300K and 780K, we show the numerical results considering a small variation (around 10%of the value) of the parameter to test the response of the system. In a future work we would apply a more detailed sensitivity investigation, that includes the correlation between different reaction rates in the system. In fact the experimental approach assumes the knowledge of the values of the reaction rate for all the elementary reactions in a mechanism. In our opinion it is of interest to check which of these reactions is mostly correlated to the one that is studied to consider the effect of the uncertainties of the other reactions on the latter one.

In chapter 4 we expose the theory of optimal experimental design in the context of partial differential equations. The praxis of this theory, on the knowledge of the author, has not been yet applied to cases of complex systems of partial differential equations as the real case of experimentation in flow reactors. The present work is a first step towards this goal. Much effort has to be done in the future with regard to different aspects of this problem. The design of experiments is a step further than the parameter identification problem, it is a "minimization problem in a minimization problem". To use the usual techniques for the optimization, as described in the chapter 4, it is necessary to assume higher order differentiability of the semi-linear form $A(\cdot, \cdot; \cdot)$ that describes the model and of the cost functional $J(\cdot)$, as we need the second order derivatives to set the minimization problem, i.e. the necessary conditions for the system (4.31). This and the fact that the functional to be minimized is not convex leads to additionally difficulties with respect to the parameter identification problem.

We treat in this work problems where the parameters are scalar values, a natural extension of this class of problems is the case of parameters as functions, as for example the distribution of the temperature or other variables at the boundary.

Further areas that we underline for future work are the extension to the 3D case and the fully instationary treatment of the problems including the experimental design step.

Acknowledgement:

I'm deeply grateful to R. Rannacher and to V. Heuveline for their effort in giving me technical support as well as mathematical insight into the problem and many ideas and suggestions how to proceed towards the final results. I thanks also A. Hanf for his valuable
collaboration and for helping me to better understand the chemical phenomena treated in this work. I would like to thank the DFG that through the SFB 359 grant has supplied the financial support.

Appendix A

We refer to the work of A. Hanf [43] for the derivation and all the references for the reactions of the mechanism. The term A is the pre-factor of the modified Arrehnius law, the term β is the coefficient of the power of the temperature while the term E_a is the activation energy:

$$k = A(\frac{T}{T_0})^{\beta} \exp(\frac{E_a}{RT}).$$

For the term A in the unit we have n = 1 for the binary reactions and n = 2 for the ternary reactions.

Α

eta

 E_a

$\Big[\frac{cm^{3n}}{(molecule^n * s)}\Big]$	$\Big[\frac{cm^{3n}}{(molecule^n*s)}\Big]$	
5,000E-13	0.0	0.000
H 1,100E-10	0.0	0.000
2O 1,000E-12	0.0	0.000
NO 7,200E-11	0.0	0.000
02 4,400E-11	0.0	0.000
N2 5,730E-12	0.5	0.000
IO2 1,400E-11	0.0	41.572
- NO 1,010E-17	4.3	104.762
2O 1,550E-12	1.6	13.802
NO 1,100E-10	0.0	111.414
02 1,690E-10	0.0	117.234
H 3,440E-13	2.7	26.274
N2 2,870E-13	2.2	193.727
O 4,000E-11	0.0	0.000
2 8,50E-11	0.0	0.000
- H 1,790E-12	2.3	212.019
OH 2,190E-10	0.0	0.000
DH 1,600E-10	0.0	63.190
NO 5,030E-07	-2.2	155.481
O 5,150E-14	2.4	-8.813
4,330E-11	-0.5	0.249
	$\begin{bmatrix} cm^{3n} \\ (molecule^{n}*s) \end{bmatrix}$ $= 5,000E-13$ $= 1,100E-10$ $= 20$ $= 1,000E-12$ $= 1,000E-12$ $= 1,000E-11$ $= 1,000E-11$ $= 1,000E-11$ $= 1,000E-11$ $= 1,000E-10$ $= 1,00E-10$	$\begin{bmatrix} \frac{cm^{3n}}{(molecule^{n}*s)} \end{bmatrix}$ $= 5,000E-13 & 0.0$ $= 1,100E-10 & 0.0$ $= 0 & 1,000E-12 & 0.0$ $= 0 & 1,000E-12 & 0.0$ $= 0 & 7,200E-11 & 0.0$ $= 0 & 7,200E-11 & 0.0$ $= 0 & 7,200E-11 & 0.0$ $= 0 & 1,00E-11 & 0.0$ $= 0 & 1,010E-17 & 4.3$ $= 0 & 1,550E-12 & 1.6$ $= 0 & 1,00E-10 & 0.0$ $= 0 & 1,690E-10 & 0.0$ $= 0 & 4,000E-11 & 0.0$ $= 0 & 4,000E-10 & 0.0$ $= 0 & 0,00$ $= $

O + O + Ar	>	O2 + Ar	1,130E-34	0.0	-4.41
NO + OH	=	HNO2	2,490E-12	-0.1	3.018
NO + OH + Ar	=	HNO2 + Ar	8,630E-31	2.5	0.283
NO + O	=	N + O2	8,930E-13	1.0	162.132
NO + O	=	NO2	8,930E-13	0.3	0.000
NO + O + Ar	>	NO2 + Ar	6,700 E- 32	-1.4	0.000
NO + NO	>	N2 + O2	5,100E-12	0.5	253.591
H2O + OH	=	H2O + OH	2,310E-13	0.0	-17.460
H2O + O	>	OH + OH	1,250E-11	1.3	71.504
H + OH	>	H2O	2,690E-10	0.0	0.624
H + OH + Ar	>	H2O + Ar	2,590E-31	-2.0	0.000
H + OH	>	O + H2	6,860E-14	2.8	16.213
H + O	>	OH	4,360E-32	-1.0	0.000
H + NO	=	N + OH	3,600E-10	0.0	207.030
H + NO	=	O + NH	9,30E-10	-0.1	292.030
H + NO	=	HNO	2,440E-10	-0.4	0.000
H + NO + Ar	=	HNO + Ar	1,340E-31	-1.3	3.076
H + H2O	>	OH + H2	6,820E-12	1.6	80.817
H + H + Ar	>	H2 + Ar	6,040E-33	-1.0	0.000

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