Analysis of differential diffusion phenomena in high enthalpy flows, with application to thermal protection material testing in ICP facilities

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Summary

This thesis presents the derivation of the theory leading to the determination of the governing equations of chemically reacting flows under local thermodynamic equilibrium, which rigorously takes into account effects of elemental (de)mixing. As a result, new transport coefficients appear in the equations allowing a quantitative predictions and helping to gain deeper insight into the physics of chemically reacting flows at and near local equilibrium. These transport coefficients have been computed for both air and carbon dioxide mixtures allowing the application of this theory to both Earth and Mars entry problems in the framework of the methodology for the determination of the catalytic activity of Thermal Protections Systems (TPS) materials.

Firstly, we analyze the influence of elemental fraction variations on the computation of thermochemical equilibrium flows for both air and carbon dioxide mixtures. To this end, the equilibrium computations are compared with several chemical regimes to better analyze the influence of chemistry on wall heat flux and to observe the elemental fractions behavior along a stagnation line. The results of several computations are presented to highlight the effects of elemental demixing on the stagnation point heat flux and chemical equilibrium composition for air and carbon dioxide mixtures. Moreover, in the chemical nonequilibrium computations, the characteristic time of chemistry is artificially decreased and in the limit the chemical equilibrium regime, with variable elemental fractions, is achieved. Then, we apply the closed form of the equations governing the behavior of local thermodynamic equilibrium flows, accounting for the variation in local elemental concentrations in a rigorous manner, to simulate heat and mass transfer in CO$_2$/N$_2$ mixtures. This allows for the analysis of the boundary layer near the stagnation point of a hypersonic vehicle entering the true Martian atmosphere. The results obtained using this formulation are compared with those obtained using a previous form of the equations where the diffusive fluxes of elements are computed as a linear combination of the species diffusive fluxes. This not only validates the new formulation but also highlights its advantages with respect to the previous one: by using and analyzing the full set of equilibrium transport coefficients we arrive at a deep understanding of the mass and heat transfer for a CO$_2$/N$_2$ mixture.

Secondly, we present and analyze detailed numerical simulations of high-pressure inductively coupled air plasma flows both in the torch and in the test chamber using two different mathematical formulations: an extended chemical non-equilibrium formalism including finite rate chemistry and a form of the equations valid in the limit of local thermodynamic equilibrium and accounting for the demixing of chemical elements. Simulations at various operating pressures indicate that significant demixing of oxygen and nitrogen occurs, regardless of the degree of nonequilibrium in the plasma. As the operating pressure is increased, chemistry becomes increasingly fast and the nonequilibrium results correctly approach the results obtained assu-
ing local thermodynamic equilibrium, supporting the validity of the proposed local equilibrium formulation. A similar analysis is conducted for CO$_2$ plasma flows, showing the importance of elemental diffusion on the plasma behavior in the VKI plasmatron torch.

Thirdly, the extension of numerical tools developed at the von Karman Institute, required within the methodology for the determination of catalycity properties for thermal protection system materials, has been completed for CO$_2$ flows. Non equilibrium stagnation line computations have been performed for several outer edge conditions in order to analyze the influence of the chemical models for bulk reactions. Moreover, wall surface reactions have been examined, and the importance of several recombination processes has been discussed. This analysis has revealed the limits of the model currently used, leading to the proposal of an alternative approach for the description of the flow-surface interaction. Finally the effects of outer edge elemental fractions on the heat flux map is analyzed, showing the need to add them to the list of parameters of the methodology currently used to determine catalycity properties of thermal protection materials.
Acknowledgments

I would like to express my gratitude to my supervisor Gérard Degrez. Through these years, shared between the Institute and the University, he has been a constant reference from the scientific, didactic and personal point of view. His enthusiasm and enhanced motivating potential, represented a very powerful energy source allowing me to conduct high level research combined with an ‘intensive’ teaching activity.

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I enjoyed working with Prof. Chazot; thanks to him I experienced the ‘experimental side’ of the methodology and I was able to participate to very interesting, sometimes funny, INTAS meetings where research exchanges were very intense and of practical importance for my scientific growth. Special thanks are deserved to M. Panesi, il martire di ‘Lambdarea’, who contributed to the development of my work. Particular thanks goes to the Belgian sky . . ., far from the one I was use to look towards. Almost always grey, it helped me to feel better in my office than outside increasing considerably my performances.

Since the beginning of my work at the Institute, I benefited considerably from the research conducted by my predecessors, who devoted great efforts to create exceptional platforms for the modeling and simulation of high temperature gases. If I have achieved anything, it is by standing on the shoulders of giants. Those giants owe uncountable thanks : Barbante P., Bottin B., Magin T. and Vanden Abeele D. (in alphabetical order).

Lastly, this thesis is dedicated to my wife. Thanks to her love and support, I have been able to pass all obstacles appeared during these years.
List of principal symbols

A list of the principal symbols is provided in the following, including the SI unit of each symbol. Note however that the practical unit might differ from the standard SI. Boldface notation indicates a vector (e.g. \( \mathbf{g} \), which has a scalar intensity \( g \)).

A number of symbols are used to identify different species types within the species. These are:

- \( \mathcal{E} \) the subset containing the indexes of the core (independent) species
- \( \mathcal{R} \) the subset containing the indexes of the reaction-formed (dependent) species
- \( S \) the set containing indexes of all species

**Roman symbols**

- \( c_i \) Concentration of species \( i \) [mol/m³]
- \( D_i^T \) Elemental thermal demixing diffusion coefficient [m²/(s · K)]
- \( D_{kt} \) Elemental multicomponent diffusion coefficient [m²/s]
- \( D_{ij} \) Binary diffusion coefficient [m²/s]
- \( E \) Electric field in the absolute frame [V/m]
- \( f \) Distribution function [s³/m⁶]
- \( h \) Mixture enthalpy per unit mass [J/kg]
- \( h_s \) Enthalpy of species \( s \) [J/kg]
- \( j \) Electric current [A]
- \( J_i \) Mass diffusion flux of species \( i \) [kg/(m² · s)]
- \( J_c \) Mass diffusion flux of element \( c \) [kg/(m² · s)]
- \( k_b \) Backward reaction rate [-]
- \( k_B \) Boltzmann constant \( \text{1.380658} \times 10^{-23} \text{ J/K} \)
- \( k_f \) Forward reaction rate [-]
- \( k_T \) Thermal diffusion ratio [-]
- \( K_e \) Equilibrium constant [-]
- \( m \) Particle mass [kg]
- \( M \) Molar mass [kg/mol]
- \( M \) Generalized stoichiometric matrix [-]
- \( n \) Number density [particles/m³]
- \( N_A \) Avogadro constant \( \text{6.021367} \times 10^{23} \text{ part/mol} \)
- \( N_e \) Number of elements [-]
- \( N_{ic} \) Number of independent components [-]
- \( N_r \) Number of dependent components [-]
- \( N_{ip} \) Number of particles (or of species) [-]
$p$ Pressure \hspace{1cm} Pa
$q$ Charge \hspace{1cm} C
$q$ Heat flux \hspace{1cm} W/m$^2$
$r$ Radial coordinate \hspace{1cm} m
$R_m$ Radius of the probe hold in the test chamber \hspace{1cm} m
$R_s$ Universal gas constant \hspace{1cm} 8.31451 J/(mol · K)
$S$ Mole-specific Stefan-Maxwell matrix \hspace{1cm} m · s/mol
$t$ Time \hspace{1cm} s
$T$ Temperature \hspace{1cm} K
$u$ $z$ - component of the velocity \hspace{1cm} m/s
$v$ $r$ - component of the velocity \hspace{1cm} m/s
$V_s$ Species diffusion velocity of species $s$ \hspace{1cm} m/s
$w$ $\theta$ - component of the velocity \hspace{1cm} m/s
$W_s$ Molar flux of species $s$ \hspace{1cm} mol/(m$^2$ · s)
$x$ Physical coordinate along the body contour \hspace{1cm} m
$x_s$ Mole fraction of species $s$ \hspace{1cm} -
$X^\ell$ Volumetric fraction of element $\ell$ \hspace{1cm} -
$y$ Physical coordinate normal to the body \hspace{1cm} m
$y_s$ Mass fraction of species $s$ \hspace{1cm} -
$Y^\ell$ Elemental mass fraction of species $\ell$ \hspace{1cm} -
$Y$ Transport matrix for reactive thermal conductivity \hspace{1cm} m · s/mol
$z$ Axial coordinate \hspace{1cm} m
$Z$ Intermediate matrix in the demixing analysis \hspace{1cm} m · s/mol

**Greek symbols**

$\delta_{ij}$ Kronecker symbol (1 if $i=j$, 0 otherwise) \hspace{1cm} -
$\mu$ Coefficient of viscosity \hspace{1cm} Pa · s
$\kappa$ Electric field coefficient \hspace{1cm} C/J
$\lambda$ Coefficient of thermal conductivity \hspace{1cm} W/(m · K)
$\phi_0^s$ Formation matrix of the dependent species \hspace{1cm} -
$\psi$ Intermediate vector in demixing analysis \hspace{1cm} J/(m · s)
$\rho$ Density \hspace{1cm} kg/m$^3$
$\rho_s$ Partial density of species $s$ \hspace{1cm} kg/m$^3$
$\sigma$ Coefficient of electrical conductivity \hspace{1cm} S/m
$\xi$ First Lees-Dorodnitsyn coordinate \hspace{1cm} -
$\eta$ Second Lees-Dorodnitsyn coordinate \hspace{1cm} -
$\omega_s$ Mass production/destruction of species $s$ due to chemical reactions \hspace{1cm} kg/(m$^3$ · s)
$\nu'_{sr}$ Stoichiometric coefficient of species $s$ as a reactant in reaction $r$ \hspace{1cm} -
$\nu''_{sr}$ Stoichiometric coefficient of species $s$ as a product in reaction $r$ \hspace{1cm} -

**Subscripts**

$BB$ Butler and Brokaw model
\( D \) \hspace{1em} \text{demixing}
\( \delta \) \hspace{1em} \text{Boundary layer edge}
\( w \) \hspace{1em} \text{Wall}
Chapter 1

Introduction

During the atmospheric (re)entry phase of a space mission, spacecrafts are subjected to a very strong deceleration needed to reach the planet’s ground with the lowest possible velocity and without damages to the vehicle structure. During the descent phase into the atmosphere, a strong bow shock [Fig. 1.1] is formed around the vehicle and the kinetic energy of the vehicle is absorbed by the gas surrounding its own skin.

A rough estimation of the energy dissipated into the gas is easily made if we consider as an example the Apollo lunar return mission. For a standard altitude of 52 km, the vehicle speed was around 11 km/s leading to a specific kinetic energy \( \frac{V^2}{2} \) around 50 MJ/kg. This en-
energy is absorbed by the gas surrounding the vehicle, whose enthalpy is rapidly increased to a value \( \sim V^2/2 \). The temperature corresponding to this enthalpy depends on the model used to describe the gas thermodynamic behavior. If a calorically perfect gas model is used, then an extremely high and unrealistic temperature is found. On the contrary, if the reacting character of the flow is considered more reasonable temperatures are obtained. Indeed, under chemical equilibrium, the post-shock temperature corresponding to such an enthalpy is \( \sim 11000 \) K. The dissipation of such an amount of energy into a gas at rest, as the Earth atmosphere represented by a mixture of molecular oxygen and nitrogen, induces molecule dissociation followed by ionization leading to a complete and sudden change in the structure of the gas mixture with respect to the case where the gas is to be described by the classical thermally and calorically perfect gas model. As a consequence, a variety of 'new features' of mixtures of this kind appear, and a considerable effort has been done in the past to improve the understanding of the complex aspects of the high enthalpy flow surrounding the surface of (re)entry vehicles.

The direct consequence of the presence of a hot layer around the vehicle is the flow of a huge flux of energy which has the tendency to heat up the cooler vehicle. For this reason, the vehicle thermal protection shield is of vital importance for the success of planetary (re)entry missions. Indeed, the Thermal Protection Material (TPM), used to save the vehicle’s structure from a critical flux of energy, need to sustain mainly two kinds of heat fluxes: the conduction heat flux, related to temperature gradients; and the diffusive transport of enthalpy, which on the surface is strongly related to the influence of the surface molecular structure on the gas particles recombination. In some cases, when the gas surrounding the vehicle is sufficiently hot, the thermal radiation emitted by the gas itself may become important and an additional contribution to the heat flux, known as the radiative heat flux, should be accounted for\(^1\).

The ability of performing reliable predictions of the amount of energy dissipated during the flight into the heat shield per unit time and surface is a key aspect of the design of Thermal Protection Systems (TPS), to which a hard mission is given. They must indeed be designed to prevent, during the ‘stressful’ planetary (re)entry phase, the loss of expensive payloads, or more importantly human lives\(^2\).

Two possible approaches exist to predict the heat transfer to the vehicles surface. An ongoing theoretical investigation of the physico-chemical processes, enriching the complexity of mixtures of high enthalpy gases, lead to the definition of suitable models used to extend the cold flow Navier-Stokes equations to the enthalpy range of interest for atmospheric entry applications. This extended formalism can then be solved using up-to-date Computational Fluid Dynamics (CFD) techniques to obtain an approximate prediction of the heat transfer phenomena. This prediction is obviously affected by the range of validity of the hypotheses on which the used model are based; by the uncertainty on the ‘data’ required by these models; and finally by the accuracy of the numerical solution methods. All these aspects concur to the determination of the final confidence level of the predicted heat transfer.

A complementary approach is based on the experimental measurement of the heat transfer to the vehicle surface. Recently, the interest of the European space community has been attracted by in-flight experiments leading to the definition of the European Experimental (Re)entry Testbed (EXPERT) program [103]. This project, if successful, will allow for experimental measurements to be carried out during the entry phase making use of the instrumentation installed on the vehicle, which is designed to be a flying laboratory. The results of such a challenging mission will be of great help to the scientific community. However, the costs associated

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\(^1\)In the case of the Apollo lunar return mission, the radiative heat flux was found to be 30% of the total heat flux [3].

\(^2\)It is hard to forget the tragic loss of the Columbia crew in 2003, unfortunately related to a failure in the TPS.
with the practical realization of this kind of programs, imposed in the past a reorientation of the experimental investigation of (re)entry flow conditions towards the use of suitable ground test facilities. Unfortunately, the high enthalpy flow conditions typical of the (re)entry phase, are not yet reproducible in full scale. On the other hand, scaled tests are possible where several of the main features of real flight can be reproduced. This allows for the experimental measurement of the heat transfer to the surface of a sample of TPM used in the heat shield to be designed for a possible entry mission.

Research is still active on both the theoretico-numerical and experimental sides of the investigation of high enthalpy flows and, in many applications, the close interaction between these two approaches is of vital importance for the achievement of the prefixed objectives. However, the process of understanding of the behavior of high enthalpy gases is far from being completed and several ambitious challenges wait for the answer of the aerospace scientific community. This hopefully will drive the enthusiasm of researchers and the will of technico-political institutions towards the investment in the atmospheric (re)entry field, which plays a fundamental role in the space quest. Fortunately, a wave of optimism seems to have shaken the field recently. Indeed, the past year was rich of events showing that space and especially atmospheric entry is reaching major breakthroughs. Cassini/Huygens has opened a new era in international cooperation and planetary exploration entering the dense Titan atmosphere, down to landing and revealing picturesque landscapes and scientific data.

US shuttle return to flight demonstrated again the necessity of reliable entry systems and subsystems. Space Transportation System (STS) planned retirement no later than 2010 might impact International Space Station (ISS) completion, and also accelerate development of alternative freight transportation solutions.

US government announced its will to fly back to the moon before the end of the next decade with the objective to explore the surface, to build outposts, and to pave the way for journeys to Mars and beyond.

Major european access to space development programs are close to completion. In December 2005, the European Space Agency (ESA) ministerial council has discussed a European space vision for the next decade, including atmospheric entry initiatives both for Earth return and planetary exploration.

Russia has resumed the preparation of ambitious exploration programs and a new generation of Low Earth Orbit (LEO) vehicles. China has confirmed their ability to successfully realize LEO manned flight and return to Earth. India is definitely a member of the space club with ambitious programs. Last, but not least, 2005 private pioneer endeavors open new perspectives for access to space and return.

This selection, far from being exhaustive, shows that many countries and actors contribute to what can be considered as a common link: Mastering atmospheric entry systems and subsystems is a cornerstone of present and future space adventure.

Within this landscape, we hope that the contributions brought by this manuscript will be felt by researchers working in atmospheric (re)entry field as useful towards the improvement of TPS design.

An up-to-date review of the experimental techniques, the theoretical models, as well as the numerical simulation strategies involved in the treatment of the chemical characters of high temperatures gases is given in Ref. [161]. In this reference, aspects of both materials and high temperatures fluid sciences are discussed together, with the aim of enhancing the improvements in the understanding of the processes of heat release on solid surfaces close to reactive
gases taking place in re-usable hypersonic flight vehicles, ballistic missiles, and rockets exhaust nozzles. In addition, further details are given concerning the modeling and the experimental investigation of gas-surface interactions. This latter aspect, as previously discussed, is strongly related to the diffusive component of the heat flux experienced by a vehicle entering the atmosphere. In particular, the way in which the TPM influences the gas particle recombination on its surface has a tremendous effect on the wall heat flux. As will be shown later on, the heat flux measured in the stagnation point of a probe held in a plasma wind tunnel can simply double when materials enhancing complete recombination are used instead of inert material. Therefore, the role played by the modelling of gas/surface interactions is of fundamental importance in the understanding of heat-transfer and as a consequence in the design of TPS. When analyzing the interaction between a gas and a non ablating surface, at least two approaches can be put in evidence. A microscopic and a macroscopic approach. Recent years have seen a very important progress in the microscopic theoretical treatment of surfaces and processes on surfaces described by the so called theoretical surface science [60]. The aim of theoretical surface science is to contribute significantly to the fundamental understanding of the underlying principles governing the geometric and electronic structure of surfaces, together with the processes taking place on these surfaces such as growth of surface layers, gas-surface scattering, friction or reaction at surfaces [59]. In the framework of atmospheric (re)entry, theoretical surface science could provide a very attractive tool for the improvement of the current techniques used to estimate the catalytic activity of thermal protection materials. Some research is ongoing in this direction and published data are already available providing values of recombination probabilities of oxygen on Silica based materials computed using Molecular Dynamics techniques [113]. The main advantage of this microscopic approach is that a variety of surface properties can be described from first principles, i.e. without invoking any empirical parameters. On the other hand, this approach, based on expensive computations, has not yet been used to investigate complicated flow conditions like those typical of high enthalpy facilities. It will certainly be worth to investigate this possibility in the future.

In the field of TPS design, a macroscopic approach is more widespread, which is closely coupled with the use and the simulation of high enthalpy plasma flows produced in suitable facilities. In this manuscript, our attention is focused on this second way of analyzing gas-surface interactions. In particular, the methodology developed at the Institute for Problems in Mechanics (IPM) has been selected as a suitable instrument for the determination of the catalytic activity of TPM.

1.1 IPM Methodology to determine TPS materials catalytic activity

Within the framework of the IPM methodology, the determination of TPS materials catalytic properties rely on experimental testing on TPS materials samples in high enthalpy facilities producing flow conditions close to flight conditions. Inductively Coupled Plasma (ICP) wind tunnels are particularly suited for this purpose because they produce plasma jets of very high chemical purity, contrary to arc heated wind tunnels in which the flow is polluted by metallic impurities originating from electrode erosion, which can contaminate the TPS material sam-
1.1. IPM Methodology to determine TPS materials catalytic activity

Kolesnikov et al. [75, 70] proposed a methodology to estimate TPS materials catalytic activity. This methodology requires heat transfer and pitot pressure measurements on one hand, and numerical simulation of the flow in the testing facility and along the stagnation line in front of the heat transfer probe on the other hand. In the following, we present the main aspects of this methodology from the analysis of which the main motivations of this thesis were inspired.

The IPM methodology relies on a combination of heat transfer and pitot pressure measurements in a subsonic plasma jet produced in an ICP facility and numerical simulations of the flow. In this sense it represents a hybrid methodology which indeed builds on both experiments [35, 52, 77, 29, 9] and numerical simulation of high enthalpy flows [152, 89]. Actually, the flow conditions in the ICP facility are related to flight conditions using the Local Heat Transfer Simulation (LHTS) concept [71, 10] so that the measured heat fluxes are equivalent to the actual stagnation point heat fluxes of a certain space vehicle at a point (altitude/velocity) of its (re)entry trajectory. A detailed description of the IPM methodology is presented in Ref. [36] and hereafter we present only its main characteristics. This methodology, which is schematically represented in Fig. 1.4, is composed of the following essential building blocks:

1. An LTE with constant elemental fraction viscous flow simulation of the flow in the ICP facility heating chamber and in the downstream subsonic plasma jet. The purpose of this LTE viscous flow computation is to compute the values of the non-dimensional parameters (Π) which characterize the flow near the stagnation point of the heat flux probe in the plasma jet.

2. Experimental measurements of the stagnation point wall heat flux (q_w) and of the pitot pressure (p) on a cold wall (T_w ~ 300K) reference heat flux probe assumed to be fully catalytic

---

1For air flows the material used is copper while for CO_2 mixtures is Silver. To the question: how can we be sure...
3. Reconstruction of the plasma jet enthalpy and velocity gradient at the edge of the stagnation line using the measured stagnation point heat flux and pitot pressure.

4. Calculation of heat flux abacus (optional). Once the stagnation line edge conditions have been determined, the stagnation line solver can be run for various wall catalytic activity/temperature combinations to produce a heat flux abacus (set of $q_w, T_w$ curves at

that this material is really fully catalytic? The most common answer is: if you find a material leading to a higher heat flux, please let me know. It will be the new fully catalytic material for this particular application.

6
1.1. IPM Methodology to determine TPS materials catalytic activity

Figure 1.4: Schematic representation of the IPM methodology for the determination of the catalytic activity of TPS materials

constant catalytic activity $\gamma_w$).

5. Experimental measurement of the stagnation point heat flux to a TPS material sample and of its temperature, and determination of the material catalytic activity$^1$.

The previous list shows clearly the highly hybrid character of the methodology. A particular attention should be devoted to the third step, usually referred as the *rebuilding* of the outer edge conditions. The logic on which this process is based follows from the investigation of the parameters from which the stagnation point heat flux depends. Such investigation reveals that these parameters are as follows:

- the thermochemical state of the stagnation line outer edge. In the original version of the methodology the outer edge is supposed to be under thermochemical equilibrium conditions defined by $p_{\delta}$, $h_{\delta}$, and the elemental fraction corresponding to the ICP torch inlet.

- The radial velocity gradient $[(\partial v/\partial r)_{\delta}]$ at the stagnation line outer edge.

$^1$This can be done graphically using the heat flux abacus by identifying the $\gamma_w$ contour on which the data point $(q_w, T_w)$ lies, or alternatively numerically.
• The stagnation line finite thickness \((\delta)\) and the product of the normal (i.e. axial) velocity by the normal derivative of the radial velocity gradient at the stagnation line edge \([u_\delta\partial/\partial x(\partial v/\partial r)_{\delta}]\).

• The wall temperature \((T_w)\) and the catalytic activity of the sample surface with respect to each of the \(k^{th}\) possible recombination processes \((\gamma_w^k)\). One of the major assumption of the original version of the methodology consists in assuming all these recombination probabilities to be equal to the same effective probability \(\gamma_w\).

Among these parameters, only two are unknown: the outer edge enthalpy \((h_\delta)\) and the radial velocity gradient \([\partial v/\partial r]_\delta\). Indeed, the stagnation pressure \((p_\delta)\) and the wall temperature \((T_w)\) are known experimentally, the recombination probability \((\gamma_w^k = \gamma_w \forall k)\) is equal to one according to the assumption of a fully catalytic heat flux probe. In addition, the stagnation line thickness \((\delta)\) and \(u_\delta\partial/\partial x(\partial v/\partial r)_{\delta}\) are related to the radial velocity gradient itself and to the probe radius \(R_m\) through the non-dimensional hydrodynamic parameters obtained from the simulation of the plasma flowing in the ICP facility performed assuming thermochemical equilibrium conditions with constant elemental fraction to be established both in the torch and in the test chamber. The first two non-dimensional parameters\(^1\) read as follows:

\[
\Pi_1 = \frac{\delta}{R_m} \quad \Pi_2 = u_\delta \frac{\partial}{\partial x} \left( \frac{\partial v}{\partial r} \right)_{\delta} \frac{(\partial v)}{(\partial r)^2},
\]  \(1.1\)

so that the stagnation point heat flux can be determined from the solution of the stagnation line problem (SL) which implicitly reads

\[
q_w(h_\delta, \left(\partial v/\partial r\right)_\delta, p_\delta, \Pi_1, \Pi_2, \gamma_w, T_w).
\]  \(1.2\)

The additional equation needed to retrieve the two unknowns \((h_\delta, \left(\partial v/\partial r\right)_\delta)\) is given from the knowledge of the measured pitot pressure. This measurement is related to \(\rho_\delta\) and \(\left(\partial v/\partial r\right)_\delta\) through a third non-dimensional hydrodynamic parameter obtained from the LTE viscous flow simulation carried out assuming constant elemental fraction, i.e.

\[
\Pi_3 = \frac{\Delta p}{\rho_\delta(h_\delta, p_\delta)[R_m(\partial v/\partial r)^2]_\delta}.
\]  \(1.3\)

The two unknown flow quantities are then determined by solving the system \((1.2)-(1.3)\) by some suitable iterative scheme, relying on the fact the functional form \((1.2)\) is provided implicitly by running a non-equilibrium stagnation line solver\(^2\).

\(^1\)For the computation of the non-dimensional parameters it is necessary to define the location of the stagnation line outer edge. This position is selected to be coincident with the inflection point of the axial velocity profile along the stagnation line obtained from the inductively coupled plasma flow simulation. Further details about the theoretical background on which this choice is based are given in Ref. \([73]\), while the low sensitivity of the \(\Pi_1\) to the choice of \(\delta\) has been verified in Ref. \([144]\).

\(^2\)A slightly different approach, involving an additional dependent non-dimensional parameter, is proposed in the original version of the IPM methodology \([36]\) and implemented in the VKI-Rebuilding code \([53]\).
1.2 The contribution of this thesis

This thesis is an attempt to investigate and solve some of the issues previously described by merging and exploring some of the ideas scattered in the literature, and at the same time present and recommend new concepts. The outcome of this process consists in the proposition of a modification to the IPM methodology for the determination of the catalytic properties of TPS materials, based on the investigation of its main weak points. The determination of these weak points follows directly from the description presented in the previous section. Indeed, we notice that several conditions must be satisfied in order for the methodology to be successful:

- the plasma flowing in the ICP facility should be under thermochemical equilibrium and elemental diffusion should not affect the flow solution.
- The stagnation line flow should be under chemical non equilibrium to make the wall heat flux sensitive to variations in the surface catalytic activity.
- The recombination probability of all heterogeneous recombination processes should be the same.

The investigation of the validity of some of the assumptions/conditions previously listed represented the main motivation and objective of the present research activity and lead us to the following main contributions of our work.

- In the past, not sufficient credit has been given to the phenomenon of elemental diffusion within the atmospheric (re)entry related literature. Indeed, in a wide variety of applications, this phenomenon has been neglected. In particular, this is the case in the IPM methodology. The investigation of this aspect of high temperature flow modeling leads us to the derivation of an explicitly closed form of the governing equations of mixtures of reacting gases under LTE. This was possible reducing the equations of chemically reacting flows to an elegant system consisting of the conventional Navier-Stokes equations (mass, momentum, energy) complemented by an advection-diffusion equation for the mass fraction of each chemical element in the mixture. The obtained formalism is in closed form in the sense that diffusive fluxes are directly expressed in terms of gradients of the solution unknowns, unlike other formulations in which these fluxes are obtained in an implicit manner, by solving the full system of Stefan-Maxwell equations. The main contribution of this formalism consists in the introduction of several new LTE transport coefficients.
- The results of the derived LTE theory have been applied to extend existing models of ICP and stagnation line flows, to correctly account for elemental diffusion.
- The effects of elemental demixing in thermochemical equilibrium mixtures have been analyzed by means of stagnation line computations for both air and carbon dioxide mixtures. Furthermore, the application of the closed form of the governing equations to the description of CO$_2$/N$_2$ LTE mixtures leads to the original computation of multicomponent elemental diffusion coefficients for mixtures containing more than two elements.
Chapter 1. Introduction

- The effects of elemental diffusion on the behavior of air and CO\textsubscript{2} plasmas flowing within the VKI-Plasmatron torch has been assessed in a certain range of operating conditions.

- The hot air jet flowing into the test chamber of the VKI-Plasmatron facility has been simulated under thermochemical equilibrium both neglecting and considering elemental diffusion. In addition, chemical non equilibrium conditions have been investigated and results obtained using two finite rate chemistry models are presented. The critical analysis of the outputs of these simulations allows for the numerical characterization of the flow within the test chamber of an ICP facility. These results shows that the original version of the IPM methodology should be modified assuming, for sufficiently high operating pressures, chemical equilibrium conditions with variable elemental fraction to be established within the torch and the test chamber. As a consequence, the stagnation line outer edge elemental fractions should be added to the set of non-dimensional parameters ($\Pi_i$) needed in the rebuilding process.

- A new model for the phenomenological description of gas-surface interactions has been proposed. Analyzing the results obtained using this model we:
  - improved the understanding of the theoretical relation between a fully catalytic surface and the related equilibrium condition;
  - showed that the constant elemental fraction assumption may contradict the hypothesis of equal effective recombination probability;
  - observed that, depending on the local wall conditions, the equal recombination probability assumption may be not compatible with the surface reaction schemes under investigation.

1.3 Publications related to the thesis

The theoretical findings and the results presented in this dissertation have led to the following publications in international journals [122, 121, 128, 126]:


1.4 Structure of the manuscript

This manuscript is designed following the critical analysis of some building blocks of the methodology used at VKI for the determination of the catalytic activity of TPS materials. We hope that this results into a unique flow of concepts allowing firstly to understand the importance of new transport coefficients introduced in this thesis and secondly, to show how their knowledge improves the determination of catalytic activity. To this end we have decided to

1. Present in Chapter 2 the Theory of LTE viscous flows with variable elemental fractions. This allows for the determination of the explicitly closed form of the equations of chemically reacting flows under local thermodynamic equilibrium for mixtures of both neutral and charged components, which rigorously takes into account effects of elemental demixing. The obtained set of equations is well-suited for numerical implementations and the new transport coefficients that appear in the equations allow quantitative predictions and help to gain a depth insight into the physics of chemically reacting flows at and near local equilibrium.

2. Describe in Chapter 3 the governing equations of plasma and stagnation line flows. Firstly, we present the equations for inductively plasma flows under thermochemical equilibrium and chemical non equilibrium. Secondly, we move our attention to the description of stagnation line flows under chemical equilibrium and non equilibrium with particular emphasis on the modeling of gas/surface interactions. Thirdly, we briefly present the way followed to describe the thermodynamics and the transport processes characteristic of high temperature gases. Fourthly, we discuss the numerical methods used to discretize and solve the governing equations previously presented.

3. Present in Chapter 4 a detailed analysis of heat and mass transfer in the boundary layer near the stagnation point of a hypersonic vehicle entering the Martian and Earth atmospheres. Firstly, the results of several computations are presented to highlight the effects of elemental demixing on the stagnation point heat flux for air and carbon dioxide mixtures. Moreover, in the chemical nonequilibrium computations, the characteristic time
Chapter 1. Introduction

of chemistry is artificially decreased and, in the limit, the chemical equilibrium regime, with variable elemental fractions, is achieved. Secondly, we apply the formulation of the equations governing the behavior of local thermodynamic equilibrium flows presented in chapter 2. By using and analyzing the full set of equilibrium transport coefficients, present in the closed form of the equations, we achieve a deep understanding of the mass and heat transfer for a CO$_2$/N$_2$ mixture.

4. Describe in Chapter 5 the diffusion and chemical non equilibrium phenomena in inductively coupled plasma flows. Firstly, we present and analyze detailed numerical simulations of high-pressure inductively coupled air plasma flows using two different mathematical formulations: an extended chemical non-equilibrium formalism including finite rate chemistry and a form of the equations valid in the limit of local thermodynamic equilibrium and accounting for the demixing of chemical elements. Simulations at various operating pressures indicate that significant demixing of oxygen and nitrogen occurs, regardless of the degree of nonequilibrium in the plasma. Secondly, under local thermodynamic equilibrium we show the influence of elemental diffusion for carbon dioxide flows within the VKI plasmatron torch. Thirdly, our attention is turned to the physico-chemical characterization of the jet flowing in the test chamber for air plasmas. As a result, we show that the simulations of the jet under thermochemical equilibrium conditions are as accurate as those obtained under chemical non equilibrium for sufficiently high pressure, provided that elemental fraction variations are accounted for.

5. Discuss in Chapter 6 a practical application to TPM testing of the concepts discussed in the previous chapters. In particular, the attention is focused on the finite-rate chemistry part of the flow description. The extension of numerical tools developed at the von Karman Institute, required within the methodology for the determination of catalycity properties for thermal protection system materials, is completed for CO$_2$ flows. Non equilibrium stagnation line computations are presented for several outer edge conditions in order to analyze the influence of the finite rate chemical models for bulk reactions. Moreover, wall surface reactions are included in the simulations to assess the importance of several recombination processes. Finally the effects of outer edge elemental fractions on the heat flux map is analyzed, showing the need to add them to the list of parameters of the methodology currently used to determine catalycity properties of thermal protection materials.

6. Present in Chapter 7 the contributions brought to the modeling of stagnation line flows of reacting mixtures under strong vibrational non equilibrium, based on the so called state-to-state approach. To this end, we discuss the results of a simulation of a viscous stagnation line flow where an accurate description of the state-to-state chemistry, a consistent treatment of transport processes and a correct fluid dynamic model are fully coupled.

7. Summarize in Chapter 9 the major results of this thesis and its main achievements. Underline the current limitations of the approach proposed and show some of the research paths left open by this work together with the ones opened, suggesting some possible directions to improve and extend the work presented.

Almost every chapter is ended by a summary recalling the main theoretical findings and results presented. The contents presented in this manuscript are not organized on the basis of the
1.4. Structure of the manuscript

temporal evolution of the research conducted during this thesis. Indeed, new and old findings are interlaced to achieve a coherent presentation. At least three main building blocks can be identified in this manuscript and depending on the particular reader’s interest, each part can be read almost independently:

(a) The reader interested in the theoretical analysis of high temperature flows under thermodynamics equilibrium and under chemical non equilibrium, as well as the numerical methods used to solve the governing equations, will find all the details in Chapter 2 and Chapter 3.

(b) The reader interested in the analysis of elemental diffusion and chemical non equilibrium effects in both plasma and stagnation line flows of air and CO₂ mixtures is invited to refer to Chapter 4 and Chapter 5.

(c) The reader interested in chemical non equilibrium features of stagnation line flows including surface reactions modeling and strong vibrational non equilibrium, could skip the first two parts and jump to Chapter 6 and Chapter 7.
Chapter 2

Theory of LTE viscous flows with variable elemental fractions

2.1 Introduction

The physics of collision-dominated chemically reacting flows is described by an extended Navier-Stokes system, consisting of the following equations [135]:

- global continuity, momentum and total energy,
- a separate continuity equation for each species, including finite-rate chemistry,
- if thermal non equilibrium occurs, an energy equation for each additional mode of freedom (vibrational, rotational and electronic energies).

This formalism has several drawbacks. Firstly, the equations are costly to implement and solve numerically. Secondly, many physical parameters essential for the modeling of chemistry and energy relaxation processes are usually missing. Thirdly, even when a numerical solution is obtained, it is by no means obvious to interpret the vast amount of information obtained (e.g. concentration fields of a large number of chemical species). For these reasons, when chemistry and energy exchanges are fast, it is usually preferable to solve the more elegant and less uncertain Local Thermodynamic Equilibrium (LTE) form of the aforementioned set of equations.

A major breakthrough in the field of LTE flow modeling was made by Butler and Brokaw [22, 19], who showed that, assuming vanishing diffusive fluxes of chemical elements, the diffusive transport of species reaction enthalpies in the energy equation could be incorporated in a straightforward manner by introducing a coefficient of 'thermal reactive conductivity' \( \lambda_R \):

\[
\sum_{s=1}^{N_{sp}} W_s h_s = -\lambda_R \nabla T. \tag{2.1}
\]
Chapter 2. Theory of LTE viscous flows with variable elemental fractions

One often makes use of this result to reduce the full set of non equilibrium equations to a system formally equivalent to the ‘conventional’ Navier-Stokes equations (continuity, momentum and energy), complemented by a modified equation of state \( \rho(p, T) \) computed from statistical mechanics assuming a fixed elemental composition in the flow. For instance, Vasil’evskii et al. [156] successfully used this classical LTE formalism to simulate high-pressure air inductively coupled plasma flows, imposing a 21/79 volumetric ratio of oxygen and nitrogen elements throughout the flow field.

While appealing because of its simplicity, it is important to understand that this approach is approximate at best, since in general the elemental composition varies significantly in chemically reacting flows:

- **mixing:** consider, e.g., low-speed diffusion flames, in which fuel and air are injected through different inlets and gradually mix.

- **demixing:** consider, e.g., a thermal arc or inductive plasma torch. The kinetic theory of gases in general predicts non-zero elemental diffusion fluxes whenever the composition of the mixture varies due to chemical reactions. Thus, variations in elemental composition appear even when the inflow elemental composition is uniform [102, 128].

We know of no mixture containing more than a single element that can simultaneously satisfy the constraints of uniform elemental composition and vanishing elemental fluxes when chemical reactions occur.

Over the past four decades, several LTE formulations accounting for (de)mixing effects have been proposed:

- As pointed out by Murphy [102], a first quantitative explanation of demixing effects was presented in a series of papers by Frie and Maeccker (1961-1963), in which they classified and discussed the significance of the different processes that drive demixing [48, 49, 50, 51], and in a paper by Richter [119] (1961), who measured the degree of demixing in arcs in mixtures of argon, nitrogen, helium and hydrogen, and explained his results in a manner similar to Frie and Maeccker.

- Suslov et al. [141] (1971) presented a general theoretical description of mixtures of chemically reacting gases under chemical equilibrium where (de-)mixing is taken into account by solving a set of elemental continuity equations. Although valid for any mixture of partially ionized gases, the proposed theory does not provide any explicit relation between elemental diffusion fluxes and temperature, pressure or elemental concentration gradients and requires the solution of the Stefan-Maxwell equations [63, 47] for given concentration gradients of species in the gas mixture. This formulation, which has been further improved in two more recent papers due to G. A. Tirsky [145, 146], is in our opinion the most complete and accurate available description of LTE flows at present. While the formulation presented in this chapter is mathematically equivalent to the work of these Russian references, it has the advantage of leading to a more physically appealing explicitly closed formalism that is obtained using a considerably more straightforward mathematical derivation.
2.1. Introduction

- Vasil’evskii and Tirsky (1984) analyzed the influence of elemental separation within equilibrium air boundary layers near heat-shields of atmospheric (re)entry capsules, and observed a volumetric oxygen concentrations varying between 0.15 and 0.3 (when the far-field value is 0.23). In a successive study, Vasil’evskii (1987) investigated the influence of these effects on wall heat flux and observed variations of 3-10% depending on the wall boundary conditions.

- Kovalev et al. (1988) investigated diffusive separation of chemical elements on a catalytic surface in Ref. [78]. Using an asymptotic expansion of the solution of the boundary layer equations for a multicomponent air mixture in chemical non equilibrium for large Schmidt numbers, it was shown that an excess of a mixture element can be observed on the body under certain outer flow conditions.

- Murphy [99, 100, 102, 101] (1993-97) has investigated effects of elemental demixing in thermal arc-plasmas and points out that demixing occurs regardless of the degree of non equilibrium in the plasma. Thus, even in the LTE case, an additional continuity equation needs to be included for the mass fraction of each element in the gas mixture. He presents an LTE model which allows computation of demixing in binary mixtures of homo-nuclear gases, which do not mutually react. While rigorous, his model cannot be applied to the more general case when species composed of various nuclei appear. For instance, an air plasma, which consists of nitrogen and oxygen nuclei, will contain mixed species such as NO which cannot be described by this theory. The appearance of explicit thermodynamic derivatives in his theory is troublesome from a numerical point of view: their evaluation by means of finite differences is in general very costly, because for each finite difference the mixture composition needs to be recomputed using a Newton iterative solver. In the particular case of a mixture containing only two elements, the computational cost can be reduced by computing the thermodynamic derivatives only once and storing the data in tabular form. Then, in the framework of Computation Fluid Dynamics (CFD) codes, the tabulated coefficients can be accessed and interpolated as required. However, when the number of elements present in the mixture increases beyond 2, this approach requires multidimensional interpolations, whose cost rapidly increases with the number of elements. In spite of the limitations of his theory, Murphy should be given credit for having presented the first closed LTE formulation, and for having introduced the concept of elemental combined and thermal diffusion coefficients.

- Ern and Giovangigli [42] (1998) introduced the concept of elemental multicomponent diffusion coefficients for general non-ionized gas mixtures under LTE using two different approaches: (1) by deriving the Navier-Stokes equations directly from the LTE form of the Boltzmann equation or (2) by considering the Navier-Stokes equations for flows under chemical non equilibrium and letting chemical reactions approach equilibrium. They point out that the reduced sets of equations obtained are formally similar but contain different transport coefficients. The abstract mathematical framework underlying their theory is its strength and weakness at once: while the mathematical rigor of the model is impressive, the proposed analysis is accessible only to those with a strongly mathematical mind-set and no particular effort is made to explain the physical implications of the model. As in Murphy’s work, explicit thermodynamic derivatives remain in the final expressions. The article remains at a theoretical level and no numerical values of elemental transport coefficients are computed; rather, it is concluded that it is more advantageous to retain the species diffusion velocities in the governing equations,
which leads us back to an open formulation essentially equivalent to the one proposed by Suslov et al. [141]. We disagree with this conclusion and will argue that computing the LTE transport coefficients (Figs. 2.7-2.12) is not only more advantageous from a numerical point of view but also reveals a lot of interesting physics [see also Ch. 4].

- Van der Heijden [149] (2003) has proposed an alternative LTE model in his study of demixing in a Hg/Na/I metal halide lamp. His formulation is based upon a Fick-type diffusion model, which can only be applied when a minority species diffuses with respect to a background species, which is present in overwhelming quantities (mercury, in his case).

- In Chapter 5, we present calculations of air and carbon dioxide flows under LTE [122, 121, 128], using an open formulation similar to the one of Suslov et al. [141], valid for partially ionized gases [128]. For sufficiently high pressures, the LTE formulation is found to be as accurate as a full non equilibrium Navier-Stokes solution.

The motivation of the theory presented in this chapter is threefold.

1. The restriction to mixtures of homo-nuclear gases in Murphy’s theory strongly limits its field of application. In this contribution, this restriction is removed and a general formulation equivalent to the model of Ern and Giovangigli is provided. Contrary to their model, however, we have tried to reduce the mathematical complexity as much as possible and rely upon physical arguments where possible. The obtained formulation is well-suited for numerical implementation. In particular, the expressions for the LTE transport coefficients are readily available and do not require the computationally expensive evaluation of thermodynamic derivatives using finite differences.

2. Our closed form for the elemental diffusion fluxes allows to determine a more general expression for the LTE heat flux vector than the one proposed by Butler and Brokaw. Indeed, in this contribution a correction to \( \lambda_R \) is introduced, together with the novel concept of elemental heat transfer coefficients. The final formulation of the heat flux vector presented in this work is not formally identical to the results proposed in previous models; it will be shown that this is necessary to correctly analyze heat transfer phenomena in chemically reacting flows, in particular when interpreting measurements of thermal conductivity coefficients.

3. As will become clear from the numerical results given in this chapter, this formulation provides a useful tool to analyze diffusion phenomena in mixtures under chemical equilibrium and in those which slightly depart from that condition.

In the remaining part of the chapter we will firstly present a preliminary analysis of the influence of elemental demixing on the behavior of a mixture of reacting gases by computing the composition for a fixed pressure and several elemental compositions, in the range of temperatures [300 K,15000 K] typical of applications to TPS testing. Secondly we will present the theory of LTE viscous flows with variable elemental fractions for neutral mixtures, referring the extension to mixtures of ionized species to Sec. 2.4. Although we will focus on the particular case of air and carbon dioxide mixtures, well-suited for Earth and Mars entry applications, we
2.2 Influence of elemental fractions on thermochemical equilibrium composition

It is well known that the composition of a mixture of reacting gases under thermochemical equilibrium can be expressed as a function of pressure, temperature, and of the elemental fractions of the elements shared among the mixture species \[160, 3\]. The contents of this chapter deal mainly with the issue of elemental fraction variations in reacting flows under \(\text{LTE}\). To attract the readers’ interest, we present a preliminary analysis of the influence of elemental fraction variations on the mixture composition for both air and carbon dioxide mixtures. As a result we show that a 10% variation of oxygen elemental fraction can induce a 50% difference in the species concentration for \(\text{CO}_2\) mixtures.

2.2.1 Air mixture

Consider an air mixture composed by the following 11 species: \(\text{N}_2, \text{O}_2, \text{NO}, \text{N}, \text{O}, \text{N}_2^+, \text{O}_2^+, \text{NO}^+, \text{N}^+, \text{O}^+, \text{e}^-\).

Let us define a reference mixture characterized by elemental fractions \(X^O = 0.21, X^N = 0.79\), and two additional mixtures obtained by perturbing the oxygen fraction by an amount of \(\pm 10\%\), i.e. \(X^O = 0.231, X^N = 0.769\) and \(X^O = 0.189, X^N = 0.811\). In Figs. 2.1, 2.2, and 2.3 the composition of these mixtures is shown as a function of temperature for a fixed pressure equal to 1 atm, assuming thermochemical equilibrium conditions. From these figures appear that the
species mole fraction is little affected by the elemental fraction, whose influence is basically limited to a scaling of the various species according to the elemental fraction. The reason is because in the air mixture, there are only 2 species including both N and O atoms, i.e. NO and NO\(^+\), and in addition their concentration always remains small.

### 2.2.2 CO\(_2\) mixture

For carbon dioxide mixtures, the sensitivity of the chemical composition to elemental fraction variations is much higher than for air. Indeed, if one considers an 8 species mixture \cite{122} in chemical equilibrium composed by CO\(_2\), O\(_2\), CO, C, O, C\(^+\), O\(^+\), and e\(^-\), and computes the chemical composition as a function of tem-
Consider a reference mixture characterized by elemental fractions $X^O = \frac{2}{3}$ and $X^C = \frac{1}{3}$. Perturbing by ±10% the oxygen fraction, two new mixtures are defined: $X^O = \frac{22}{30}$, $X^C = \frac{8}{30}$ and $X^O = \frac{18}{30}$, $X^C = \frac{12}{30}$. The mole fraction evolution as a function of temperature, for a pressure of 1 atm, for these three cases is shown in Figs. 2.4, 2.5, and 2.6.

A very strong influence of the elemental fraction on the chemical composition is clearly visible. Moreover, from the analysis of the previous results, it follows that, in the case of CO$_2$ mixtures, the sensitivity to elemental fraction variation is much higher than in the case of air. This will result in an important influence of elemental demixing on heat flux in thermochemi-
Figure 2.6: Mole fractions \( X^O = \frac{22}{30}, X^C = \frac{8}{30} \).

cal equilibrium CO\(_2\) mixtures, as will be shown by the results to be presented later on in this thesis.

### Chapter 2. Theory of LTE viscous flows with variable elemental fractions

#### 2.3 Mixtures of neutral species

##### 2.3.1 Species ordering and nomenclature

To make this text more accessible, we find it useful to first introduce some important concepts and symbols. We represent mixtures of perfect gases by means of a finite set of \( N_{sp} \) species \( \tilde{S} \), amongst which we furthermore distinguish between \( N_c \) ‘independent species’ \( \tilde{E} \) consisting of pure elements (as such as in their stable form) and \( N_r \) ‘combined species’ \( \tilde{R} \), for instance:

**5-species air** \( \tilde{E} = \{O, N\}, \tilde{R} = \{O_2, N_2, NO\}, \) and \( \tilde{S} = \tilde{R} \cup \tilde{E} \),

valid for LTE mixtures at pressures above 0.01atm and for temperatures between 300 and 8000 K.

We accordingly define the three sets of indexes \( R = \{1, \ldots, N_r\}, \ E = \{N_r + 1, \ldots, N_{sp}\}, \) and \( S = R \cup E \). We characterize the chemical composition of the mixture in terms of mole fractions \( x_s = n_s/n \), where \( n_s \) and \( n \) stand for the molar densities of individual species and of the entire mixture. Alternatively, we can also characterize the mixture composition by means of the mass fraction \( y_s = \rho_s/\rho \), where \( \rho_s \) and \( \rho \) stand for the mass densities of the individual species, respectively the full mixture.

We will indicate the number of atoms of element \( e \) contained in a species \( s \) by \( \phi^e_s \), for instance,
2.3.2 Computation of composition under LTE

for NO, $\phi^3_{3} = 1$ while for O$_2$, $\phi^4_{3} = 2$. This enables us to define the mole fractions $X^e$ and mass fractions $Y^e$ of elements in the mixture as follows:

$$X^e = \frac{\sum_{s \in S} \phi^e_s x_s}{\sum_{e \in E} \sum_{s \in S} \phi^e_s x_s}; \quad Y^e = \sum_{s \in S} \phi^e_s \frac{M_e}{M_s};$$  \hspace{1cm} (2.2)

where $M_s$ is the molar mass of species $s$, related to the mixture molar mass $M = \sum_{s \in S} x_s M_s$.

We introduce the diffusion velocity $V_s$ with respect to the mass-averaged velocity of the mixture $u$. The molar and mass fluxes of species $s$ are then given by respectively $W_s = n_s V_s$ and $J_s = M_s n_s V_s$. The mole and mass fluxes of element $e$ are then given by

$$N_e = \sum_{s \in S} \phi^e_s W_s; \quad J_e = M_e N_e (e \in E).$$  \hspace{1cm} (2.3)

We use bold type fonts to indicate vectors in the physical space. With ‘bar notation’, we refer to arrays containing species, elemental or reactive properties, with respective lengths of $N_{sp}$, $N_c$ and $N_r$. For instance, the array of length $N_c$ containing the mass diffusive fluxes of elements is written

$$\bar{J} = \begin{bmatrix} J_{N_r+1} \\ J_{N_r+2} \\ \vdots \\ J_{N_r+N_c} \end{bmatrix}.$$  \hspace{1cm} (2.4)

2.3.2 Computation of composition under LTE

2.3.2.1 Species continuity equations

We consider the commonly encountered flow regime in which chemical reactions are relatively rare w.r.t. elastic collisions, such that they do not play an important role in the thermalization of species in the flow (unlike the ‘kinetic chemical equilibrium regime’ considered in the first part of Ref. [42], for which chemical reactions and elastic collisions are treated on the same level). The concentration of each species may then be determined from a respective species continuity equation [135]:

$$\partial_t (\rho y_s) + \nabla \cdot (\rho y_s u) + \nabla \cdot (M_s W_s) = \dot{\omega}_s$$  \hspace{1cm} (2.5)

where $u$ stands for the mass-averaged velocity of the mixture and $\dot{\omega}_s$ is the mass production/destruction term [160] of species $s$ due to chemical reactions. The number fluxes of species respect the mass conservation constraint

$$\sum_{s \in S} M_s W_s = 0$$  \hspace{1cm} (2.6)
Chapter 2. Theory of LTE viscous flows with variable elemental fractions

and obey the Stefan-Maxwell equations [47, 63]

\[
SW = \begin{bmatrix}
\nabla x_1 \\
\vdots \\
\nabla x_{N_{ep}}
\end{bmatrix} = \vec{d}
\] (2.7)

where

\[
S_{ij} = \frac{M}{\rho} \frac{x_i}{D_{ij}} f_{ij}(L) \quad (i \neq j),
\]

\[
S_{ij} = -\frac{M}{\rho} \sum_{k \neq i} x_k D_{ik} f_{ik}(L) \quad (i = j).
\] (2.8)

for \( i, j, k \in S \). Herein, \( \vec{d}_i = \nabla x_i \) is the \( i^{th} \) vector of driving forces. To keep the analysis as simple as possible, we have neglected effects of pressure and thermal diffusion; note however that these could be included without any particular problem as shown in Sec. 2.4. The binary diffusion coefficients \( D_{ij} \) are symmetric \( D_{ij} = D_{ji} \) and the symmetric factor \( f_{ij}(L) \) takes into account the contribution of Laguerre-Sonine polynomials [76, 47, 157, 91] of order \( L \geq 2 \) with the definition \( f_{ij}(1) = 1 \) (increasing the order \( L \) of the Laguerre-Sonine polynomials yields higher accuracy of the spectral method used to define the transport systems (2.7)).

The binary diffusion coefficients can be further expressed as

\[
D_{ij} = \frac{3}{16n} \sqrt{\frac{2\pi k_B T}{m_{ij}}} \frac{1}{\Omega_{11}^{ij}}
\] (2.9)

where \( k_B \) is Boltzmann’s constant and the reduced mass of the particle pair \( ij \) is written as \( m_{ij} = m_i m_j / (m_i + m_j) \) [in kg]. Readers eager to implement the results derived in this chapter may use the data available in MUTATION [91] or find detailed curve fits for the collision integrals \( \Omega_{11}^{ij}(T) \) of air mixtures in Ref. [17].

2.3.2.2 Stoichiometric matrix

When chemistry is sufficiently fast w.r.t. other macroscopic processes in the flow (convection, diffusion, ...), we may compute the chemical composition from statistical mechanics for given values for the pressure, temperature and elemental mass fractions [17] instead of solving Eqs. (2.5). To this end, we need to specify \( N_r \) independent reactions

\[
\sum_{s \in S} v_{rs}^f A_s = 0 \quad (r \in R)
\] (2.10)

where the stoichiometric coefficients are normalized such that \( v_{rs}^f = 1 \) and \( A_s \) is a symbolic notation for species \( s \). The mole fractions \( x_s = n_s / n \) obey the following relations

\[
\sum_{s \in S} v_s^r \ln x_s = \ln K_s^r \quad (r \in R)
\] (2.11)

where \( K_s^r(T, p) \) is the equilibrium constant in terms of mole fractions, linked to the equilibrium constant in terms of partial pressures \( K_p^r(T) \) by

\[
\ln K_s^r = \ln K_p^r - \ln p \sum_{s \in S} v_s^r.
\]
In addition, we should fix the local elemental composition

\[\sum_{s \in S} \phi^e_s \frac{M_e}{M_s} = Y^e \quad (e \in E) \quad (2.12)\]

where the mass fraction of elements \(Y^e\) is computed from the solution of a set of suitable advection-diffusion equations to be presented shortly [Eq. (2.18)].

For further mathematical convenience, we gather the \(v^r_s\) and \(\phi^e_s\) into a ‘stoichiometric matrix’ \(M:\)

\[M_{rs} = v^r_s \quad (r \in R, s \in S)\]

\[M_{es} = \phi^e_s \quad (e \in E, s \in S).\]

Following Butler and Brokaw [22], we note that \(M\) has the following structure for the chosen ordering of species

\[M = \begin{bmatrix} I & -B^T \\ B & I \end{bmatrix} \quad (2.13)\]

where

\[B_{e-N_r,r} = \phi^e_r \quad (r \in R, e \in E).\]

As an example, for a five species air mixture, \(M\) should be

<table>
<thead>
<tr>
<th></th>
<th>O₂</th>
<th>N₂</th>
<th>NO</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>0</td>
</tr>
<tr>
<td>N₂</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>-2</td>
</tr>
<tr>
<td>NO</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>N</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

(2.14)

The particular structure of the stoichiometric matrix leads to several useful results. For instance, if we multiply the upper part of \(M\) by the array of species enthalpies \(\bar{h}\), we find the array of reaction enthalpies \(\Delta h:\)

\[\begin{bmatrix} I & -B^T \end{bmatrix} \bar{h} = \Delta h \quad (2.15)\]

where \(\Delta h_r = \sum_{s \in S} v^r_s h_s\) for \(r \in R\). Moreover, by multiplying the lower part of \(M\) by the species diffusion fluxes, we obtain the array of elemental diffusion fluxes:

\[B \begin{bmatrix} I & I \end{bmatrix} \bar{W} = \bar{N}. \quad (2.16)\]

We can exploit the above result to express the array of species diffusive fluxes \(\bar{W}\) in terms of the diffusive fluxes of combined species \(\bar{W}_R\) and independent species \(\bar{N}\). By using the following trivial factorization of the identity matrix \(I\), we see that:

\[\bar{W} = \begin{bmatrix} I & \bar{W}_R \end{bmatrix} = \begin{bmatrix} I & 0 \\ -B & I \end{bmatrix} \begin{bmatrix} I & \bar{W}_R \end{bmatrix}. \quad (2.17)\]

The reader should keep in mind this relation, which will be used repeatedly in the analysis that ensues. Practical details on how to efficiently determine the equilibrium composition from Eqs. (2.10-2.11) and (2.12) can be found in an earlier publication [17].
2.3.2.3 Elemental continuity equations for neutral mixtures

As pointed out by Murphy, we need to solve additional element advection-diffusion equations to determine the elemental composition of the mixture \([100, 121]\). To obtain these equations, we multiply Eqs. (2.5) by \(\phi_e M_e/M_s\) and sum over all species. Since no elements are created in the considered chemical reactions, the mass fraction of any element \(e\) obeys the following equation:

\[
\partial_t (\rho Y_e) + \nabla \cdot (\rho \mathbf{u} Y_e) + \nabla \cdot \mathbf{J}_e = 0 \quad (e \in \mathcal{E}).
\] (2.18)

In what follows, we will show that under LTE conditions, the mass diffusion flux of elements \(\mathbf{J}_e\) can be expressed in terms of gradients of elemental mass fractions and temperature. For simplicity, we consider flows at constant pressure, consistent with the neglect of pressure diffusion in Eqs. (2.7). Once again, we remark that this does not imply any fundamental limitation and pressure diffusion could be included easily if needed [see Sec. 2.4]. The reader may note that Eqs. (2.18) are expressed in term of element mass fractions, whereas previous models were based upon mole fractions or number densities of elements. We believe this to be more advantageous for two main reasons:

1. **Mathematical elegance:**
   The element mass fraction appear in a natural manner in the right hand side of Eqs. (2.12); the mathematical analysis hence turns out to be easier if one continues to work in terms of this variable.

2. **Numerical convenience:**
   Many existing flow solvers allow to easily add advection-diffusion equations for a generic scalar quantity \(\phi\); the formalism proposed here [Eqs. (2.18)-(2.30)] fits nicely within such a numerical framework. In addition, by using the global continuity equation, Eqs. (2.18) may be cast under a non-conservative form

\[
\rho \partial_t Y_e + (\rho \mathbf{u} \cdot \nabla) Y_e + \nabla \cdot \mathbf{J}_e = 0 \quad (e \in \mathcal{E}),
\] (2.19)

which tends to be much more robust from a numerical point of view.

2.3.2.4 Elemental diffusion coefficients

**Proposition 1.** In a flow of reacting mixtures under LTE and at constant pressure, the elemental fluxes are in general non zero and can be explicitly expressed as a function of the gradients of temperature and elemental composition, i.e.

\[
\mathbf{J}_e = -\rho D_e^T (T, p, \mathbf{Y}) \nabla T - \sum_{f \in \mathcal{E}} \rho D_{ef} (T, p, \mathbf{Y}) \nabla Y_f \quad (e \in \mathcal{E}).
\] (2.20)

**Proof.** From Eqs. (2.6-2.7) the species diffusion fluxes can be expressed as a linear combination of species concentration gradients

\[
\mathbf{W} = S^{-1} \nabla \mathbf{x} = -n \nabla \mathbf{x}
\] (2.21)
where \( \tilde{D}_{sm} = \tilde{D}_{sm}(T, p, \bar{Y}) \) for \( s, m \in S \).

From Eqs. (2.10-2.11) and (2.12), since \( x_s = x_s(T, p, \bar{Y}) \), it follows that
\[
\nabla x_s = \left( \frac{\partial x_s}{\partial T} \right)_{Y, p} \nabla T + \sum_{f \in \mathcal{E}} \left( \frac{\partial x_s}{\partial Y^f} \right)_{T, p} \nabla Y^f \quad (s \in S, e \in \mathcal{E}).
\]

Therefore, from Eqs. (2.3), (2.21) and (2.22), Eq. (2.20) can be easily retrieved.

The explicit determination of the functions \( D^T_{ix} \) and \( D_{ef}^c \) requires a deeper analysis presented in the remaining part of this section and detailed in appendix A.

Considering the gradient of Eq. (2.11) written in matrix form, making use of Eqs. (2.7) and introducing Eq. (2.17), one has
\[
\begin{bmatrix} \tilde{A} & \tilde{B}^T \end{bmatrix} S \begin{bmatrix} I & 0 \\ -B & I \end{bmatrix} \begin{bmatrix} \tilde{W}_R \\ \bar{N} \end{bmatrix} = \begin{bmatrix} \nabla T \\ \frac{\Delta h_1}{R_a T^2} \\ \vdots \\ \frac{\Delta h_{N_c}}{R_a T^2} \end{bmatrix} \equiv \bar{\theta},
\]
(2.23)

where \( \tilde{A}_{ij} = \delta_{ij} / x_j \), \( \tilde{B}^T_{ij} = -B^T_{ij} / x_j \). Moreover in Eq. (2.23) we make use of van’t Hoff’s relation [160] \( d \ln K_p^r / dT = \Delta h_r / (R_a T^2) \), as suggested in Ref. [22], and we make the assumption of constant pressure, consistent with the neglect of pressure diffusion. This leads to the definition of the components of \( \bar{\theta} \) as:
\[
\bar{\theta}_r = \frac{\Delta h_r}{R_a T^2} \nabla T \quad (r \in \mathcal{R}),
\]
(2.24)

where \( \Delta h_r = \sum_{s \in S} \nu^r_r \Delta h_s \), is the enthalpy of reaction \( r \) already introduced in Eq. (2.15) and \( R_a \) is the universal gas constant. From Eq. (2.23) and after some straightforward algebra, we easily find the following expression relating the number flux of elements \( \bar{N} \) and of the combined species \( \tilde{W}_R \):
\[
\mathcal{Y} \tilde{W}_R + \mathcal{Z} \bar{N} = \bar{\theta},
\]
(2.25)

where the expressions of \( \mathcal{Y} \left( N_c \times N_r \right) \) and \( \mathcal{Z} \left( N_r \times N_c \right) \) are given in appendix A.2. Following a similar strategy for the lower part of the equilibrium system [Eq. (2.12)] we have that:
\[
\begin{bmatrix} \mathcal{B} & \mathcal{C} \end{bmatrix} S \begin{bmatrix} I & 0 \\ -B & I \end{bmatrix} \begin{bmatrix} \tilde{W}_R \\ \bar{N} \end{bmatrix} = \begin{bmatrix} \nabla Y^1 \\ \vdots \\ \nabla Y^{N_c} \end{bmatrix} \equiv \bar{\psi},
\]
(2.26)

where \( \bar{\psi}_e = \nabla Y^e \) for \( e \in \mathcal{E} \). The two matrices \( \mathcal{B} \left( N_c \times N_r \right) \) and \( \mathcal{C} \left( N_c \times N_c \right) \) are determined expressing the mass fraction gradients in terms of the species mole fraction gradients, directly related to the driving forces for diffusion phenomena (see appendix A.2). After some more straightforward algebra, we transform the above result into an additional relation between \( \tilde{W}_R \) and \( \bar{N} \):
\[
\mathcal{T} \tilde{W}_R + \mathcal{K} \bar{N} = \bar{\psi},
\]
(2.27)

where the components of \( \mathcal{T} \left( N_r \times N_r \right) \) and \( \mathcal{K} \left( N_c \times N_c \right) \) are again given in appendix A.2. Replacing \( \tilde{W}_R \) from Eq. (2.25) in Eq. (2.27), the number fluxes of elements follow from the solution of the linear system (2.28):
\[
\mathcal{J} \bar{N} = -\mathcal{T} Y^{-1} \bar{\theta} + \bar{\psi}
\]
(2.28)
where \( \mathcal{S} = (K - T \mathcal{Y}^{-1} Z) \). Eqs. (2.25) and (2.27) are still equivalent to the original singular system (2.7), but with a particular right hand side, valid only under LTE. As a consequence, the system (2.28) inherits the singular character of Eqs. (2.7) and an additional mass conservation constraint is still needed to regularize the problem:

\[
\alpha e \bar{N} = 0 \quad (2.29)
\]

where \( \alpha e = M_e \) for \( e \in E \).

The solution of the system (2.28-2.29) represents the last step for the determination of the expression of the elemental multicomponent diffusion coefficients \( D_{ef} \) and thermal demixing coefficients \( D_T^e \), for which detailed expressions may be found in appendix A.4. By inverting \( \mathcal{S} \), accounting for Eq. (2.29) [see appendix A.3], we easily find that:

\[
\mathcal{J}_e = - \sum_{j \in E} \rho D_{ej} \nabla Y^j - \rho D_T^e \nabla T. \quad (2.30)
\]

The second term in the right hand side of the above result will in general generate nonzero elemental diffusion fluxes even when the initial elemental composition is uniform.

### 2.3.3 Diffusive transport of enthalpy

In reacting flows, the diffusion of species affects the mixture energy balance through the heat flux term:

\[
q_d = \sum_{s \in S} W_s h_s. \quad (2.31)
\]

In a general non equilibrium case, to compute \( q_d \), one should determine all the \( W_s \) as a solution of Eq. (2.7) and then compute the above linear combination, as done in the methodology of Refs. [141], [42] and [121]. On the other hand, under thermochemical equilibrium, Eq. (2.31) can be cast under a particular form which avoids the computation of the \( W_s \). A first step in this direction was made by Butler and Brokaw [22], who showed that, under the assumption of vanishing elemental fluxes, the diffusive heat flux takes the form of Eq. (2.1). In this section, we extend the work of Butler and Brokaw to the more general case when elemental fluxes are nonzero.

**Proposition 2.** For a mixture of reacting gases under thermochemical equilibrium, at constant pressure, the diffusive heat flux is proportional to both temperature and elemental concentration gradients, and can be expressed as:

\[
\sum_{s \in S} W_s h_s = -(\lambda_R + \lambda_D) \nabla T - \sum_{e \in E} \lambda_{EL} \nabla Y^e. \quad (2.32)
\]
Proof. Observing that the product $\bar{W}^T h$ takes the following shape in matrix form:

\[
\bar{W}^T h = \bar{W}^T \begin{bmatrix} I & -B^T \\ 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & B^T \\ 0 & I \end{bmatrix} \bar{h} = \bar{W}^T \begin{bmatrix} I & -B^T \\ 0 & 0 \end{bmatrix} \bar{h} + \bar{W}^T \begin{bmatrix} 0 & B^T \\ 0 & I \end{bmatrix} \bar{h},
\]

the diffusive heat flux can be easily split into a contribution due to the transport of reaction enthalpies [Eq. (2.15)] by combined species and of formation enthalpies of elements [Eq. (2.16)]:

\[
\bar{W}^T \bar{h} = \bar{W}^T \bar{W} = \bar{h} + \bar{W}^T \begin{bmatrix} 0 & B^T \\ 0 & I \end{bmatrix} \bar{h},
\]

where $\bar{h}_{EL-e} = \bar{h}_e$ for $e \in \mathcal{E}$. Using Eq. (2.25), we easily find that:

\[
\bar{W}^T \bar{h} = -\lambda_R \nabla T - (\bar{\Delta h}^T \mathcal{Y}^{-1} \bar{Z} - \bar{h}_{EL}^T \bar{N}),
\]

where $\bar{\Delta h}^T \mathcal{Y}^{-1} \bar{h} = -\lambda_R \nabla T$. Next, expressing the terms proportional to $\bar{N}$ in terms of $\nabla T$ and $\nabla Y_e$ using Eqs. (2.28-2.29), we easily retrieve Eq. (2.32). Detailed expressions for $\lambda_R$, $\lambda_D$ and the $\lambda_{EL}$ may be found in appendix A.5.

We see that in an LTE flow, the diffusive heat flux vector consists of three different parts:

1. The ‘thermal reactive conductivity’ coefficient $\lambda_R$ is identical to the well-known results by Butler and Brokaw [22, 19] and takes into account diffusive transfer of species enthalpies in the absence of elemental diffusion.
2. The ‘thermal demixing conductivity’ coefficient $\lambda_D$ corrects for the additional diffusive heat transfer that occurs due to nonzero elemental diffusive fluxes when elemental mass fraction gradients are zero [see the remark below Eq. (2.30)].
3. Finally, the ‘elemental heat transfer coefficients’ $\lambda_{EL}^e$, take into account heat transfer due to elemental demixing driven by gradients in elemental composition.

At this point, it is interesting to comment on the well known thermal conductivity measurements by Asinovsky et al. [8] and Devoto et al. [39]. In their experiments, the total LTE thermal conductivity $\lambda_{tot}$ is determined from the radial energy balance in a steady, axisymmetric arc plasma of very large ratio of length over diameter. One might wonder which of the above three terms is actually being measured. Because flow velocities and axial variations in the plasma are very small, the elemental continuity equations (2.18) reduce to the simple statements that the radial fluxes of elements vanish:

\[
\frac{\partial r J^e}{\partial r} = 0 \quad \Rightarrow \quad N_e = \text{cst} = 0 \quad (e \in \mathcal{E})
\]
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since no elements go into the isolated walls of the arc. From Eq. (2.34), we then see that the measured thermal conductivity coefficient \( \lambda_{\text{Tot}} \) takes into account only the conventional thermal conductivity coefficient \( \lambda \) and the thermal reactive conductivity: \( \lambda_{\text{Tot}} = \lambda + \lambda_R \); the \( \lambda_D \) and the \( \lambda_{EL}^e \) do not play a role. Similarly, it would appear that in steady thermal boundary layers, only \( \lambda_R \) effectively contributes to the heat flux to the wall. This important physical observation has been the motivation for splitting the thermal conductivity coefficients unlike in previous LTE formulations.

2.3.4 Closed form of the governing equations for mixtures of neutral components

Thanks to the results of Secs. 2.3.2.4 and 2.3.3, the full system of the governing equations of chemically reacting gases under LTE can hence be reduced to the system (2.35) below, formally equivalent to the ‘conventional’ Navier-Stokes equations extended with a set on \( N_e \) additional advection-diffusion equations for each of the mixture elements:

\[
\partial_t (\rho e) + \nabla \cdot (\rho u e) = \nabla \cdot \left( \rho D_T e \nabla T + \sum_{f \in E} \rho D_{ef} \nabla Y^f \right) \quad (e \in E)
\]

(2.35a)

\[
\partial_t \rho + \nabla \cdot (\rho u) = 0,
\]

(2.35b)

\[
\partial_t (\rho u) + \nabla \cdot (\rho uu) + \nabla p = \nabla \hat{\tau},
\]

(2.35c)

\[
\partial_t \left[ \rho (e + u^2/2) \right] + \nabla \cdot \left[ \rho u (h + u^2/2) \right] = \nabla \cdot \left[ (\lambda + \lambda_R + \lambda_D) \nabla T + \sum_{e \in E} \lambda_{EL}^e \nabla Y^e \right] + \\
+ \nabla \cdot (u : \hat{\tau})
\]

(2.35d)

Herein, \( e \) and \( h \) are, respectively, the mixture energy and enthalpy per unit mass, \( p \) stands for the static pressure and \( \hat{\tau} \) represents the tensor of viscous stresses:

\[
\hat{\tau}_{ij} = \mu \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \delta_{ij} \nabla \cdot u \right)
\]

computed using Stokes’ hypothesis of negligible bulk viscosity effects. Practical details on how to determine the thermodynamic properties \( e, h, \rho \) and the conventional transport properties \( \mu \) and \( \lambda \) needed to solve the system (2.35), can be found in chapter 3. Expressions of the LTE transport properties \( D_T, D_{eq}, \lambda_R, \lambda_D, \lambda_{EL}^e \) may be found back in appendix A.

By writing the governing equations of chemically reacting flows under LTE as proposed in the system (2.35), the species diffusion fluxes and the enthalpy fluxes depend in an explicit manner on the solution unknowns, which is advantageous for their implementation in an implicit CFD code. Moreover, the physical effects leading to (de)mixing and its influence on the mixture energetic behavior clearly show up. The system of Eqs. (2.35) has been successfully solved in the framework of the research conducted during this thesis. The results, obtained for a mixture of hetero-nuclear components containing three elements, are presented in chapter 4.
2.3.5 An Illustrative example

To present the application of the concepts introduced in the previous sections, we select as an example, the two mixtures defined previously. The results presented below have been obtained extending the existing thermodynamics and transport library MUTATION [91].

To define a range of validity of the choice of species previously presented, we base our analysis on Figs. 2.2 and 2.5 where we plot the composition of an eleven species air mixture and an eight species carbon dioxide mixture as a function of temperature for a reference pressure and elemental composition. From the species evolution visible in the two figures and from previous studies on the influence of species choice on mixture energetic behavior [17, 122], we indicate 8000 K as the upper limit of the temperature range in which the transport properties previously introduced should be computed.

We now turn our attention to the evolution of the elemental multicomponent diffusion coefficients $D_{eq}$. For the particular case of a binary mixture, considering the expressions given in Ref. [126], the diagonal elements are seen to be both equal to a common value $D$ while the off-diagonal elements are equal to $-D$. For more general mixtures containing three or more elements, the elemental diffusion coefficient matrix will in general no longer have this elegant symmetric form. As observed by Murphy [99], for binary mixtures, the mass conservation constraint allows to collect the diagonal and off-diagonal diffusion coefficients can be collected to form only one ‘total’ elemental multicomponent coefficient for each element. Although our formulation is valid for mixtures of arbitrary number of elements, we will here use this simplification to analyze demixing in the considered air and CO2 mixtures.

Since $\nabla Y^O = -\nabla Y^N$ and $\nabla Y^O = -\nabla Y^C$ in the air, respectively CO2 mixtures, the oxygen, nitrogen and carbon diffusion fluxes read

\[
\begin{align*}
\mathcal{J}_O &= -\rho D^T_{O} \nabla Y^O - \rho D^T_O \nabla T \\
\mathcal{J}_N &= -\rho D^T_{N} \nabla Y^N - \rho D^T_N \nabla T \\
\mathcal{J}_C &= -\rho D^T_{C} \nabla Y^C - \rho D^T_C \nabla T
\end{align*}
\]

where $D^T = 2D$. The presence of negative off-diagonal diffusion coefficients does not pose problems since $D^T$ itself is positive, as shown in Fig. 2.7 for both mixtures. This result implies that the first term in the right hand side of Eq. (2.36) will tend to smooth out variations of elemental mass fractions caused by temperature gradients.

In Figs. 2.8, we show the thermal demixing coefficients, plotted as a function of temperature, for both mixtures. In both cases we observe a highly nonlinear behavior of these coefficients including the presence of a first peak just before 4000 K and a second one around 7000 K.

In the case of air, the first and second peaks correspond to the dissociation of O2 and N2, while in the case of carbon dioxide they correspond to the dissociation of carbon dioxide and the onset of CO depletion. For both mixtures, we observe that around 5500 K a change in sign takes place in $D^T_O$. This shows that, at low temperatures, oxygen will be driven in the direction opposite to the temperature gradient, while in higher temperature regions, the inverse phenomenon will take place. Figures 2.7 and 2.8 are obviously much more useful to predict and analyze diffusion phenomena in flows under LTE than the original set of Eqs. (2.5).
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Figure 2.7: Elemental total multicomponent diffusion coefficients for a 5 species air and carbon dioxide LTE mixture.

Figure 2.8: Elemental thermal demixing coefficients for a 5 species air and carbon dioxide LTE mixture.

A further step in the prediction of the effects of diffusion on the behavior of equilibrium mixtures is done by analyzing the diffusive transport of enthalpy. In the following pictures we present the thermal reactive conductivities introduced previously for both air and carbon dioxide mixtures.

To clarify the analysis and discussion of the results we introduce the following notation:
2.3.5. An Illustrative example

Figure 2.9: Thermal reactive conductivities for a 5 species air LTE mixture.

Figure 2.10: Thermal reactive conductivities for a 5 species carbon dioxide LTE mixture.

$\lambda'$ represents the sum between the thermal reactive and demixing conductivities defined as

$$\lambda' = \lambda_R + \lambda_D.$$  

$\lambda_{SM}$ represents the ratio between the diffusive heat flux computed as $\sum_{s \in S} W_s h_s$ and a unity temperature gradient, where the $W_s$ are the solution of Eq. (2.7) obtained as suggested in Ref. [91] in the absence of elemental concentration gradients.

$\lambda_{BB}$ represents the reactive conductivity computed using the formula of Ref. [19].

From Figs. 2.9 and 2.10 we see that there is a perfect match between (1) $\lambda'$ and $\lambda_{SM}$ and (2)
λ_{R} and λ_{BB} for both air and carbon dioxide. On the other hand, 20% differences between these respectively reactive conductivities due to demixing are visible. We see that the effect of demixing on the overall heat flux is stronger for carbon dioxide than for air, especially at higher temperatures where CO dissociates. In both cases, the sign of λ_{D} depends on temperature, showing that demixing may increase or decrease the heat flux depending on the local temperature in the mixture.

![Figure 2.11: Thermal demixing conductivities.](image)

λ_{D} - air
λ_{D} - CO_{2}

![Figure 2.12: Elemental total heat transfer coefficients for a 5 species air and carbon dioxide LTE mixture.](image)

λ^{\text{Tot}}_{\text{Air mixture}}
λ^{\text{Tot}}_{\text{CO}_{2} \text{ mixture}}

We now come to the last concept introduced in the previous section which deals with elemen-
2.4. Mixtures of neutral and charged components

In this section we present the extension of the theory presented in Sec. 2.3 to mixtures containing also ionized species. The purpose of such an extension is to provide the definition of the multicomponent diffusion coefficients as well as thermal demixing diffusion coefficients for mixtures commonly used in the range of temperatures where ionization occurs. This would allow the present theory to be applied to simulate high enthalpy flows produced by Arc-Jet or ICP facilities. The analysis presented hereafter relies strongly on the concepts previously introduced from which the definition of new quantities of interest is inspired. The reader is therefore invited to refer to Sec. 2.3 for further details concerning the following text.

2.4.1 Species ordering and nomenclature

As for mixtures of neutral species, we represent mixtures of perfect gases by means of three finite sets $\bar{S}$, $\bar{E}$, and $\bar{R}$, containing the mixture species, the ‘independent components’, and the ‘combined species’ respectively. For instance:

**8-species air** $\bar{E} = \{O, N, e^{-}\}$, $\bar{R} = \{O_2, N_2, NO, N^+, O^+\}$, and $\bar{S} = \bar{R} \cup \bar{E}$.

valid for LTE mixtures at pressures above 0.01atm and for temperatures between 300 and 15000 K. To these sets we again associate the three sets of indexes $S$, $E$, and $R$. In addition, we introduce the mole ($X^\ell$) and mass ($Y^\ell$) fraction of element $\ell$ following the definition of Eq. (2.2). Thanks to the previous definition, the mixture charge usually expressed as $q = \sum_{s \in S} x_s q_s$ can be assimilated to an element. Indeed $q_s = -\phi_s^N |e|$, where $e$ is the electron charge, and for example for neutral species $q_s = 0$ while for charged species like $N^+$, $q_s = -\phi_s^N = +1$ and for the electron $q_s = -\phi_s^e = -1$, $\phi_s^e$ being the atomicity coefficients. Following this notation
the charge can be measured either through the molar fraction or the mass fraction defined in Eq. (2.2) related to the mixture charge by the following equations:

\[ nq = XqN |e| \quad \text{or} \quad nq = \rho Yq \frac{|e|}{me}, \]  

(2.38)

where \( N = \sum_{\ell \in E} \sum_{s \in S} \phi_{\ell s} n_s \) is the total element number density.

We again consider the number (\( N_{\ell} \)) and mass (\( J_{\ell} \)) fluxes of element \( \ell \) as defined in Eq. (2.3) and in addition we notice that within this formalism the mixture conduction current \( j = \sum_{s \in S} j_s \), obtained from the species conduction currents \( j_s = n_s q_s V_s \), can be related to the diffusion flux of the element charge as follows

\[ j = J q |e| \frac{m e}{m_e}. \]  

(2.39)

### 2.4.2 Diffusion fluxes

As for the neutral case, under chemical non equilibrium conditions, the species concentration is to be obtained as the solution of the species continuity equations [Eqs. (2.5)]. For the solution of each of these equations, the knowledge of the species diffusion fluxes (\( J_s \)) is needed. When chemistry is sufficiently fast, we can avoid the solution of Eqs. (2.5) and compute the composition from equilibrium relations. On the other hand, the knowledge of the \( J_s \) is still required to compute the diffusive transport of enthalpy. The \( J_s \) can therefore be determined either by computing the species multicomponent diffusion coefficients [63] or alternatively as the solution of the Stefan-Maxwell equations. In the case of a mixture containing both neutral and charged species, the Stefan-Maxwell equations read [89, 92, 91]:

\[ \sum_{j \in S} x_j \rho x_j V_j \left( \frac{1}{D_{ij}} \right) = \nabla x_i + k_i E + (x_i - y_i) \nabla \ln p + k T_i \nabla \ln T \]  

(2.40)

where \( k_i = (y_i q - x_i q_i)/k_B T \) and the \( k T_i \) are the thermal diffusion ratios [146, 145, 63, 92, 91]. A fundamental difference with respect to the neutral case is the presence of the electric field \( E \), which represents an additional driving force for the diffusion of charged species. In the following we propose a compact version of Eq. (2.40) written for the number fluxes of species. These fluxes respect the mass conservation constraint

\[ \sum_{s \in S} M_s W_s = 0 \]  

(2.41)

and obey the Stefan-Maxwell equations [Eq. (2.40)]

\[ S W = S \begin{bmatrix} \bar{W}_1 \\ \vdots \\ \bar{W}_{Nsp} \end{bmatrix} = \bar{d} \]  

(2.42)

where

\[ S_{ij} = \frac{M}{\rho} \frac{x_i}{D_{ij}} \left( \frac{1}{f_{ij}} \right) \quad (i \neq j), \]

\[ S_{ij} = -\frac{M}{\rho} \sum_{k \neq i} \frac{x_k}{D_{ik}} \left( \frac{1}{f_{ik}} \right) \quad (i = j), \]  

(2.43)
for \( i, j, k \in S \). Herein, \( \overrightarrow{d}_i \) is the \( i \)th vector of driving forces given by

\[
\overrightarrow{d}_i = d_i = k_i \mathbf{E} + \nabla x_i + (x_i - y_i) \nabla \ln p + k_T \nabla \ln T.
\]

(2.44)

### 2.4.3 Stoichiometric matrix

As a result of the LTE assumption we compute the chemical composition from statistical mechanics for given values of the pressure, temperature and elemental mass fractions instead of solving Eqs. (2.5). To this end, as done in Sec. 2.3, we specify \( N_r \) independent reactions [Eq. (2.10)] and we determine the mixture composition, in terms of mole fractions, as a solution of Eqs. (2.11)-(2.12), where the mass fraction of elements \( Y^\ell \) is computed from the solution of a set of suitable advection-diffusion equations to be presented shortly [Eq. (2.46)]. As for mixtures of neutral species we introduce the concept of ‘stoichiometric matrix’ (\( \mathcal{M} \)) [Eq. (2.13)]. As an example, for a seven species air mixture, \( \mathcal{M} \) should be

\[
\begin{array}{cccccccc}
\text{O}_2 & \text{N}_2 & \text{NO} & \text{N}^+ & \text{O}^+ & \text{O} & \text{N} & \text{e}^- \\
1 & 0 & 0 & 0 & 0 & -2 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & -2 & 0 \\
0 & 0 & 1 & 0 & 0 & -1 & -1 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & -1 & 1 \\
0 & 0 & 0 & 0 & 1 & -1 & 0 & 1 \\
2 & 0 & 1 & 0 & 1 & 1 & 0 & 0 \\
0 & 2 & 1 & 1 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & -1 & -1 & 0 & 0 & 1 \\
\end{array}
\]

(2.45)

Also in the present case we find it useful to highlight that the particular structure of the stoichiometric matrix leads to several useful results. Indeed the reader can easily verify that Eqs. (2.15), (2.16), and (2.17) hold true also for mixtures containing both neutral and charged species. These relations will be used repeatedly in the analysis that ensues.

### 2.4.4 Elemental continuity equations for mixtures of ionized species

As shown in Sec. 2.3.2.3, we obtain the elemental continuity equations, multiplying Eqs. (2.5) by \( \phi_s^\ell M_s/M_r \) and summing over all species. Since no elements are created in chemical reactions, the mass fraction of any element \( \ell \) obeys the following equation:

\[
\frac{\partial}{\partial t} (\rho Y^\ell) + \nabla \cdot (\rho u Y^\ell) + \nabla \cdot \mathbf{j}^\ell = 0 \quad (\ell \in \mathcal{E}).
\]

(2.46)

Eq. (2.46) takes a particular form when the element considered corresponds to the mixture charge. Indeed, instead of considering the mass flux of electrons (\( \mathbf{j}^\ell \)), in the literature dealing with ionized mixtures of reacting gases, we usually refer to the mixture conduction current \( \mathbf{j} \) introduced in Sec. 2.4.1. Using Eq. (2.39) together with the definition of the mixture charge (\( q \)) the usual form of the plasma charge conservation equation is retrieved:

\[
\frac{\partial}{\partial t} (nq) + \nabla \cdot (nq \mathbf{v}) + \nabla \cdot \mathbf{j} = 0.
\]

(2.47)
We will now show that under LTE conditions, the mass diffusion flux of elements \( \mathbf{J}_\ell \) can be expressed in terms of the electric field and the gradients of elemental mass fractions, temperature, and pressure.

### 2.4.5 Elemental diffusion coefficients

**Proposition 3.** In a flow of reacting mixtures, of both neutral and charged species, under LTE the elemental fluxes are in general non zero and can be explicitly expressed as a function of the electric field and the gradients of temperature, pressure, and elemental composition, i.e.

\[
\mathbf{J}_\ell = \sigma_\ell \mathbf{E} - \rho D_p^T(T, p, \overline{Y}) \nabla T - \rho D_T^p(T, p, \overline{Y}) \nabla p - \sum_{k \in E} \rho D_\ell^k(T, p, \overline{Y}) \nabla Y_k \quad (\ell \in \mathcal{E}).
\]  

(2.48)

**Proof.** From Eqs. (2.41-2.42), considering Eq. (B.1), the species diffusion fluxes can be expressed as a linear combination of electric field, temperature, pressure and species concentration gradients,

\[
\bar{\mathbf{W}} = S^{-1} \mathbf{A} = -n \bar{D} \nabla x + n \bar{D} \nabla p \left[ \begin{array}{c} k_1 \\ \vdots \\ k_{N_{sp}} \end{array} \right] \mathbf{E} - n \bar{D} \left[ \begin{array}{c} x_1 - y_1 \\ \vdots \\ x_{N_{sp}} - y_{N_{sp}} \end{array} \right] \nabla p - n \bar{D} \left[ \begin{array}{c} k_{T_1} \\ \vdots \\ k_{T_{N_{sp}}} \end{array} \right] \nabla T
\]  

(2.49)

where \( \bar{D}_m = \bar{D}_m(T, p, \overline{Y}) \) for \( s, m \in \mathcal{S} \).

From Eqs. (2.10-2.11) and (2.12), since \( x_s = x_s(T, p, \overline{Y}) \), it follows that

\[
\nabla x_s = \left. \frac{\partial x_s}{\partial T} \right|_{\mathcal{Y}, \mathcal{P}} \nabla T + \left. \frac{\partial x_s}{\partial p} \right|_{T, \mathcal{P}} \nabla p + \sum_{q \in \mathcal{E}} \left. \frac{\partial x_s}{\partial Y_q} \right|_{T, \mathcal{P}} \nabla Y_q \quad (s \in \mathcal{S}, \ell \in \mathcal{E}).
\]

(2.50)

Therefore, from Eqs. (2.3), (2.49) and (2.50), Eq. (2.48) can be easily retrieved.

The explicit determination of the functions \( \sigma_\ell, D_p^T, D_T^p, \) and \( D_\ell^k \) requires a deeper analysis presented in the remaining part of this section and detailed in appendix B.

Considering the gradient of Eq. (2.11) written in matrix form, making use of Eqs. (2.42) and introducing Eq. (2.17), we have:

\[
\begin{bmatrix}
\bar{\mathbf{A}} & \mathbf{B}^T
\end{bmatrix} \begin{bmatrix}
\mathbf{S} \begin{bmatrix} I & 0 \\ -B & I \end{bmatrix} \begin{bmatrix}
\bar{\mathbf{W}}_R \\ N
\end{bmatrix} - \begin{bmatrix} k_1 \\ \vdots \\ k_{N_{sp}} \end{bmatrix} \mathbf{E} - \begin{bmatrix} x_1 - y_1 \\ \vdots \\ x_{N_{sp}} - y_{N_{sp}} \end{bmatrix} \nabla p - \begin{bmatrix} k_{T_1} \\ \vdots \\ k_{T_{N_{sp}}} \end{bmatrix} \nabla T
\end{bmatrix} = \begin{bmatrix}
\sum_{s \in \mathcal{S}} \nu_s^1 \\ \sum_{s \in \mathcal{S}} \nu_s^N
\end{bmatrix} \nabla \ln p,
\]

(2.51)
where \( \hat{A}_{ij} = \delta_{ij}/x_j \), \( \hat{B}_{ij}^T = -B_{ij}^T/x_j \). Moreover in Eq. (2.51) we make use of van’t Hoff’s relation [160] \([d\ln K_{p}^{r}/dT = \Delta h_{r}/(R_{u}T^{2})]\) [22]. From Eq. (2.51) and after some straightforward algebra, we easily find the following expression relating the number flux of elements \( \bar{N} \) and of the combined species \( \bar{W}_{R} \):

\[
\mathcal{Y} \bar{W}_{R} + \mathcal{Z} \bar{N} = \bar{\theta} + \bar{\pi} + \bar{\gamma},
\]

(2.52)

where the expressions of \( \mathcal{Y} \) \((N_r \times N_c)\) and \( \mathcal{Z} \) \((N_r \times N_c)\) have the same form of the matrixes \( \mathcal{Y} \) and \( \mathcal{Z} \) obtained for mixtures of neutral components whose expressions are given in appendix B.1. As far as the right hand side is concerned, the three new arrays introduced have the following components:

\[
\bar{\theta}_{r} = \left( \frac{\Delta h_{r}}{R_{u}T} + \sum_{s \in S} v_{r}^{s} k_{r}^{s}/x_{s} \right) \nabla \ln T,
\]

(2.53)

\[
\bar{\pi}_{r} = - \sum_{s \in S} v_{r}^{s} y_{s} \nabla \ln p,
\]

(2.54)

\[
\bar{\gamma}_{r} = \sum_{s \in S} v_{r}^{s} k_{s}^{r} E,
\]

(2.55)

for \( r \in \mathcal{R} \). From the previous equations, we notice that the components of \( \bar{\theta}, \bar{\pi} \) and \( \bar{\gamma} \) are linear function of \( \nabla T, \nabla p \) and \( E \) respectively. For what concerns \( \bar{\gamma} \) we wish to highlight that \( \bar{\gamma}_{r} = 0, \forall r \in \mathcal{R} \). Indeed, from Eq. (2.55) we notice that

\[
\bar{\gamma}_{r} = \sum_{s \in S} v_{r}^{s} k_{s}^{r} E = \frac{qE}{MKT} \sum_{s \in S} v_{r}^{s} M_{s} - \frac{E}{KT} \sum_{s \in S} v_{r}^{s} q_{s} = 0,
\]

(2.56)

since the terms present in the right hand side of the previous equations are zero because both mass and charge are conserved during chemical reactions. As a consequence, Eq. (2.52) can be simplified to

\[
\mathcal{Y} \bar{W}_{R} + \mathcal{Z} \bar{N} = \bar{\theta} + \bar{\pi}.
\]

(2.57)

From the previous equation, we observe that, if elemental fluxes vanish, the diffusive fluxes of the dependent components do not depend on the electric field. Therefore in the case where the elemental fluxes vanish and baro-thermal diffusion is neglected, the diffusive fluxes of the dependent components are obtained in the same way as in Sec. 2.3. This result is useful to understand that the formula of Butler and Brokaw [19, 22] for the computation of the reactive thermal conductivity, is valid also for mixtures of ionized gases.

Following a similar strategy for the lower part of the equilibrium system [Eq. (2.12)] we have:

\[
\begin{align*}
\begin{bmatrix} \mathcal{B} & \mathcal{C} \end{bmatrix} S \begin{bmatrix} \begin{bmatrix} I & 0 \end{bmatrix} & \begin{bmatrix} \frac{k_{1}}{x_{1}} & \frac{x_{1} - y_{1}}{x_{1}} & \frac{k_{T_{1}}}{x_{1}} \\ \vdots & \vdots & \vdots \\ \frac{k_{N_{r}}}{x_{N_{r}}} & \frac{x_{N_{r}} - y_{N_{r}}}{x_{N_{r}}} & \frac{k_{T_{N_{r}}}}{x_{N_{r}}} \end{bmatrix} \end{bmatrix} \begin{bmatrix} \nabla \ln \theta \end{bmatrix} \end{bmatrix} & = \begin{bmatrix} \nabla \ln T \end{bmatrix} \\
\nabla Y_{1} & = \bar{\psi}, \quad (2.58)
\end{align*}
\]

where \( \bar{\psi}_{\ell} = \nabla Y_{\ell} \) for \( \ell \in \mathcal{E} \). The two matrices \( \mathcal{B} \) \((N_{c} \times N_{r})\) and \( \mathcal{C} \) \((N_{c} \times N_{r})\) are determined expressing the mass fraction gradients in terms of the species mole fraction gradients, directly
related to the driving forces for diffusion phenomena (see appendix A.2). After some more straightforward algebra, we transform the above result into an additional relation between $\bar{W}_R$ and $\bar{N}$:

$$\mathcal{T}\bar{W}_R + \mathcal{K}\bar{N} = \bar{\psi} + \bar{\Theta} + \bar{\Pi} + \bar{\Gamma},$$  \hspace{1cm} (2.59)

where the components of $\mathcal{T}$ ($N_c \times N_r$) and $\mathcal{K}$ ($N_c \times N_c$) are defined in the same way as in the case of neutral mixtures and their expressions are given in appendix B.1. As far as the right hand side is concerned, the three new arrays introduced have the following components

$$\Theta_{\ell} = \left( \sum_{s \in R} B_{\ell, k_s} + \sum_{s \in E} C_{\ell, s-N_r} k_s \right) \nabla \ln T,$$  \hspace{1cm} (2.60)

$$\Pi_{\ell} = \left( \sum_{s \in R} B_{\ell, x_s - y_s} + \sum_{s \in E} C_{\ell, s-N_r} (x_s - y_s) \right) \nabla p,$$  \hspace{1cm} (2.61)

$$\Gamma_{\ell} = \left( \sum_{s \in R} B_{\ell, k_s} + \sum_{s \in E} C_{\ell, s-N_r} \right) E, $$  \hspace{1cm} (2.62)

where $\ell \in \mathcal{E}$. The analysis of the previous equations shows that the components of $\Theta$, $\Pi$ and $\Gamma$ are linear function of $\nabla T$, $\nabla p$ and $E$ respectively.

Replacing $\bar{W}_R$ from Eq. (2.57) in Eq. (2.59), the number fluxes of elements follow from the solution of the linear system (2.63):

$$\mathcal{S}\bar{N} = -\mathcal{T}^{-1}\bar{\psi} + \bar{\Theta} + \mathcal{T}^{-1}\mathcal{Y}^{-1}\mathcal{Y}\bar{\Pi} + \bar{\Gamma} + \bar{\Pi} \nabla \bar{Y}$$  \hspace{1cm} (2.63)

where $\mathcal{S} = (\mathcal{K} - \mathcal{T}^{-1} \mathcal{Z})$. Eqs. (2.57) and (2.59) are still equivalent to the original singular system (2.42), but with a particular right hand side, valid only under LTE. As a consequence, the system (2.63) inherits the singular character of Eqs. (2.42) and an additional mass conservation constraint is still needed to regularize the problem:

$$\bar{\alpha}^T \bar{N} = 0$$  \hspace{1cm} (2.64)

where $\bar{\alpha}_e = M_e$ for $e \in \mathcal{E}$.

The solution of the system (2.63-2.64) represents the last step for the determination of the expression of the elemental multicomponent diffusion coefficients $D_{\ell k}$, the thermal demixing coefficients $D^T_{\ell}$, the pressure demixing coefficients $D^P_{\ell}$, and the $\sigma_{\ell}$ for which detailed expressions may be found in appendix B.3. By inverting $\mathcal{S}$, accounting for Eq. (2.64) [see appendix A.3], we easily find that:

$$\mathcal{J}_\ell = \sigma_{\ell} E - \rho D^T_{\ell}(T, p, \bar{Y}) \nabla T - \rho D^P_{\ell}(T, p, \bar{Y}) \nabla p$$

$$- \sum_{k \in \mathcal{E}} \rho D_{\ell k}(T, p, \bar{Y}) \nabla Y^k \hspace{1cm} (\ell \in \mathcal{E}).$$  \hspace{1cm} (2.65)

The first three terms in the right hand side of the above result will in general generate nonzero elemental diffusion fluxes even when the initial elemental composition is uniform.
2.4.6 Diffusive transport of enthalpy

As in the case of mixtures of neutral species, the diffusion of species affects the mixture energy balance through the heat flux term presented in Eq. (2.31).

Under thermochemical equilibrium, Eq. (2.31) can be cast under a particular form which avoids the computation of the $W_i$. In this section, we extend the work of Butler and Brokaw to the more general case when elemental fluxes are nonzero for mixtures containing both neutral and charged species, including the effects of thermal and pressure diffusion.

**Proposition 4.** For a mixture of reacting gases, of both neutral and charged species, under thermochemical equilibrium the diffusive heat flux is proportional to the electric field and to the pressure, temperature, and elemental concentration gradients, and can be expressed as:

$$\sum_{s \in S} W_s h_s = -\lambda_R E - \lambda_p \nabla p - (\lambda_R + \lambda_D + \lambda_T) \nabla T - \sum_{\ell \in E} \lambda'_E \nabla Y^\ell. \quad (2.66)$$

**Proof.** Observing that the product $\bar{W}^T \bar{h}$ takes the following shape in matrix form:

$$\bar{W}^T \bar{h} = \bar{W}^T \left( \begin{bmatrix} I & -B^T \\ 0 & 0 \end{bmatrix} + \begin{bmatrix} 0 & B^T \\ 0 & I \end{bmatrix} \right) \bar{h}$$

we easily split the diffusive heat flux into contributions due to the transport of reaction enthalpies [Eq. (2.15)] by combined species and of formation enthalpies of elements [Eq. (2.16)]:

$$\bar{W}^T \bar{h} = \bar{h}^T \bar{W} = \bar{h}^T \bar{W}_R + \bar{h}^T \bar{W}_E + \bar{h}^T \bar{W}_Y.$$

Using Eq. (2.57), we easily find that:

$$\bar{W}^T \bar{h} = -(\Delta h^T Y^{-1} \bar{Z} - \bar{h}^T_{EL} \bar{N}) \bar{N} + \Delta h^T Y^{-1} \bar{N} + \Delta h^T Y^{-1} \bar{\pi}, \quad (2.68)$$

where $\bar{\pi} \propto \nabla T$ and $\bar{\pi} \propto \nabla p$. Next, expressing the terms proportional to $\bar{N}$ in terms of $\nabla T$, $\nabla p$, $E$ and $\nabla Y^\ell$ using Eqs. (2.63-2.64), we easily retrieve Eq. (2.66). Detailed expressions for $\lambda_R$, $\lambda_D$, $\lambda_p$, $\lambda_E$ and the $\lambda'_E$ may be found in appendix B.5.

We see that in an LTE flow, the heat flux vector consists of six different parts:

1. The ‘thermal reactive conductivity’ coefficient $\lambda_R$ is identical to the well-known results by Butler and Brokaw [22, 19] and takes into account diffusive transfer of species enthalpies in the absence of baro-thermal and elemental diffusion.
(2) The ‘thermal demixing conductivity’ coefficient $\lambda_D$ corrects for the additional diffusive heat transfer that occurs due to nonzero elemental diffusive fluxes when elemental mass fraction and pressure gradients are zero and thermal diffusion is neglected.

(3) The ‘thermal diffusion conductivity’ coefficients $\lambda_T$ accounts for the effects of thermal diffusion on the diffusive transport of enthalpy.

(4) The ‘pressure heat transfer coefficient’ $\lambda_p$ accounts for the heat transfer due to the presence of a pressure gradient.

(5) The ‘electric field heat transfer coefficient’ is a measure of how the diffusive transport of energy is affected by the electric field $E$.

(6) Finally, the ‘elemental heat transfer coefficients’ $\lambda_{EL}$ account for the heat transfer due to elemental demixing driven by gradients in elemental composition.

2.4.7 Quasi neutral and current free plasmas

As already noticed at the beginning of this section, the major difference between the case of mixtures of neutral components and mixtures of both charged and neutral species, is the presence of the electric field in the second case. To provide an accurate and consistent formulation we are therefore faced to the problem of determining $E$ in order to compute the species diffusion fluxes from Eq. (2.40). In this section we focus on a specific condition widely diffused in the literature on partially ionized plasmas. The definition of this condition is based on two major assumptions.

- Firstly we assume quasi neutrality to be established in the whole flowfield, i.e.

$$\sum_{s \in S} q_s x_s = 0 \quad \text{or} \quad \sum_{s \in S} q_s \nabla x_s = 0. \quad (2.69)$$

- Secondly we assume the mixture current to vanish everywhere in the flow, i.e.

$$\mathbf{j} = 0. \quad (2.70)$$

At this point it is important to notice that the condition $\mathbf{j} = 0$ forces the mixture charge to be constant along a stream line [Eq. (2.47)] and everywhere if the inlet of the domain is neutral. Therefore the assumption of vanishing current, is consistent with the quasi neutrality of the plasma. On the other hand it represents a stronger hypothesis then what really needed. Indeed, any solenoidal current field is in agreement with quasi neutrality, i.e. any $\mathbf{j}$ such that:

$$\nabla \cdot \mathbf{j} = 0. \quad (2.71)$$

Eq. (2.71) admit the solution $\mathbf{j} = 0$, provided that this is in agreement with the boundary conditions, which is not the case in Arc-Jets. On the other hand, this assumption ($\mathbf{j} = 0$) is widely used in the simulation of inductive plasma torches [153] for what concerns the symmetry plane.
2.4.7. Quasi neutral and current free plasmas

of the torch. The first practical consequence of the current free assumption consists in the possibility to eliminate the electric field from the set of unknowns. Indeed the electric field that satisfies the constraint $j = 0$ is such that [Eq. (2.65)]:

$$
E = \frac{\rho D_T^q(T, p, \overline{Y})}{\sigma_q} \nabla T + \frac{\rho D_p^q(T, p, \overline{Y})}{\sigma_q} \nabla p + \sum_{k \in \mathcal{E}} \frac{\rho D_{qk}(T, p, \overline{Y})}{\sigma_q} \nabla Y_k. \quad (2.72)
$$

The so determined electric field is known as ambipolar electric field, the knowledge of which is sufficient to compute the species diffusion fluxes from Eq. (2.40). In the more general, but more complex, case where the condition (2.71) is considered, the electric field should be found as the solution of the following partial differential equation:

$$
\nabla \cdot \left( \sigma_q E \right) = \nabla \cdot \left( \frac{\rho D_T^q(T, p, \overline{Y})}{\sigma_q} \nabla T + \frac{\rho D_p^q(T, p, \overline{Y})}{\sigma_q} \nabla p + \sum_{k \in \mathcal{E}} \frac{\rho D_{qk}(T, p, \overline{Y})}{\sigma_q} \nabla Y_k \right), \quad (2.73)
$$

complemented by the adequate set of boundary conditions to be specified depending on the characteristics of the case under investigation. In the following sections we focus on the most spread assumption of current free flows [Eq. (2.70)] for sake of simplicity. On the other hand we wish to highlight that the theory presented in Secs. 2.4.5-2.4.6 allows for the determination of the transport coefficients needed to solve the partial differential equation (2.73), which can be easily added to the system of Navier-Stokes equations describing the flow motion.

As will be shown shortly, if Eq. (2.70) is used, then the ambipolar electric field determined from Eq. (2.72), together with the quasi neutrality assumption [Eq. (2.69)], allows for the determination of a simplified form of the transport properties previously introduced.

2.4.7.1 Elemental mass diffusive fluxes

The influence of the choice of the ambipolar electric field on the diffusion coefficients can be easily determined substituting Eq. (2.72) into Eq. (2.65). This leads to the following form of the element mass diffusive fluxes:

$$
\mathcal{F}_\ell = -\rho D_T^\ell(T, p, \overline{Y}) \nabla T - \rho D_p^\ell(T, p, \overline{Y}) \nabla p - \sum_{k \in \mathcal{E}} \rho D_{\ell k}^q(T, p, \overline{Y}) \nabla Y_k \quad (\ell \in \mathcal{E} \setminus \{q\}) \quad (2.74a)
$$

$$
\mathcal{F}_q = M_e N_q = j \frac{m_e}{|e|} = 0 \quad (2.74b)
$$

where

$$
\rho D_{\ell k}^q = \rho D_{\ell k} - \rho D_{qk}^q \frac{\sigma_k}{\sigma_q} \quad (2.75a)
$$

$$
\rho D_T^\ell = \rho D_T^\ell - \rho D_T^q \frac{\sigma_T}{\sigma_q} \quad (2.75b)
$$

$$
\rho D_p^\ell = \rho D_p^\ell - \rho D_p^q \frac{\sigma_p}{\sigma_q} \quad (2.75c)
$$

for $\ell \in \mathcal{E} \setminus \{q\}$.
2.4.7.2 Enthalpy diffusive flux

As previously shown the ambipolar electric field has an influence on the elemental diffusive fluxes and therefore [Eq. (2.77)] on those of the dependent components. Indeed from Eq. (2.67) we have:

$$\sum_{s \in S} \mathbf{W}_s h_s = \Delta h^T W_R + \Delta h^T N = \Delta h^T Y^{-1} \theta + \Delta h^T Y^{-1} \pi + \beta^T N \tag{2.76}$$

where $\beta^T = \Delta h^T - \Delta h^T Y^{-1} \tilde{Z}$. The third term of the right hand side takes the following form [Eq.(2.63)]

$$\beta^T N = -\beta^T D_p T T^{-1} \theta + \beta^T D_p \Theta + -\beta^T D_p T T^{-1} \pi + \beta^T D_p \Pi + \beta^T \sigma \mathbf{E} \tag{2.77}$$

where

$$\sigma = D_p \Gamma = D_p \begin{bmatrix} k_1 & \ldots & k_{N_p} \end{bmatrix} \tag{2.78}$$

and $D_p$ is the inverse of $\mathcal{J}$ [Eq. (2.4.4)] determined as shown in appendix B. Substituting the form of the ambipolar electric field Eq. (2.72) into Eq. (2.77), the enthalpy diffusive flux reads:

$$\sum_{s \in S} \mathbf{W}_s h_s = \frac{\Delta h^T \theta + \beta^T D_p \Theta + \beta^T \sigma D_q^R \nabla T}{\sigma \nabla T} + \frac{\Delta h^T \pi + \beta^T D_p \Pi + \beta^T \sigma D_q^R \nabla p}{\sigma \nabla p} + \frac{\beta^T D_p \tilde{\psi} + \beta^T \sigma \sum_{k \in E} \rho D_q \nabla Y^k}{\sigma \nabla Y^k} \tag{2.79}$$

where $\Delta h^T = \Delta h^T Y^{-1} - \beta^T D_p T Y^{-1}$. Eq. (2.79) allows for the definition of several transport properties of interest for the description of quasi neutral and current free plasmas. Indeed the previous equation can be further simplified to

$$\sum_{s \in S} \mathbf{W}_s h_s = -(\lambda_R + \lambda_D + \lambda_T) \nabla T - \lambda_p \nabla p - \sum_{k \in E} \lambda_{E_k} \nabla Y^k \tag{2.80}$$

Comparing the previous equation with Eq. (2.66) we notice the absence of the coefficient $\lambda_E$, in Eq. (2.80). This is indeed the result of the assumption (2.72) which allows to express $\mathbf{E}$ as a function of $\nabla T$, $\nabla p$, and $\nabla Y^k$. The explicit determination of the transport coefficients present in Eq. (2.80) requires a deeper analysis illustrated in appendix B, together with detailed expressions for $\lambda_R$, $\lambda_D$, $\lambda_T$, $\lambda_p$, and $\lambda_{E_k}$. 

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2.4.8 Air and carbon dioxide quasi neutral and current free plasmas

In this section we present the evolution of the transport properties presented in Sec. 2.4.7.1 and 2.4.7.2 for both air and carbon dioxide mixtures. The purpose of this analysis is threefold:

- Firstly we wish to highlight that the formulation proposed for mixtures of neutral and charged components reproduces the results obtained for neutral mixtures following the formulation presented in Sec. 2.3 for sufficiently low temperatures.
- Secondly, observing the evolution of the thermal reactive conductivity we will validate the proposed formulation against the direct solution of the Stefan-Maxwell equations [Eq. (2.40)] as proposed for example in Ref. [92].
- Thirdly, by analyzing the evolution as a function of temperature of the new transport properties introduced in Sec. 2.3, we will emphasize the main advantages of the proposed formulation in terms of physical understanding of the flow behavior.

To simplify the analysis that ensues we neglect in the following both baro and thermal diffusion, referring the description of the importance of these terms to a further study. In addition we make use of both the quasi neutrality [Eq. (2.69)] and the current free [Eq. (2.70)] assumptions. Therefore the transport properties to be presented shortly are those corresponding to the theory presented in Sec. 2.4.7.

We start our analysis recalling the definition of two mixtures of interest for both Earth and Mars entry applications:

11-species air $\tilde{E} = \{N, O, e^-\}, \tilde{R} = \{O_2, N_2, NO^+, N_2^+, O_2^+, N^+, O^+\}$, and $\tilde{S} = \tilde{R} \cup \tilde{E}$.

8-species CO$_2$ $\tilde{E} = \{C, O, e^-\}, \tilde{R} = \{CO_2, CO, O_2, C^+, O^+\}$, and $\tilde{S} = \tilde{R} \cup \tilde{E}$.

As observed for neutral mixtures, if charge neutrality is assumed, then it is possible, for mixtures containing two elements, to define a total multicomponent diffusion coefficient. Indeed from Eq. (2.74a) we have for the air mixture

\begin{align}
\mathbf{J}_N &= -\rho D_{NN}^{\text{Tot}} \nabla Y^N - \rho D_{NO}^{\text{Tot}} \nabla Y^O - \rho D_{Nq}^{\text{Tot}} \nabla Y^q - \rho D_{NT}^{\text{Tot}} \nabla T, \\
\mathbf{J}_O &= -\rho D_{ON}^{\text{Tot}} \nabla Y^N - \rho D_{OO}^{\text{Tot}} \nabla Y^O - \rho D_{Oq}^{\text{Tot}} \nabla Y^q - \rho D_{OT}^{\text{Tot}} \nabla T, \\
\mathbf{J}_q &= 0.
\end{align}

(2.81a, 2.81b, 2.81c)

In addition we notice that $\nabla Y^O = -\nabla Y^N$, since $\nabla Y^q = 0$. Therefore Eqs. (2.81) simplifies to

\begin{align}
\mathbf{J}_N &= -\rho D_N^{\text{Tot}} \nabla Y^N - \rho D_T^{\text{Tot}} \nabla T, \\
\mathbf{J}_O &= -\rho D_O^{\text{Tot}} \nabla Y^O - \rho D_T^{\text{Tot}} \nabla T, \\
\mathbf{J}_q &= 0.
\end{align}

(2.82a, 2.82b, 2.82c)

where $D_N^{\text{Tot}} = D_N^{NN} - D_N^{NO}, D_O^{\text{Tot}} = D_O^{OO} - D_O^{ON}, D_T^{\text{Tot}} = D_T^{NN} = D_T^{OT}$, and $D_T^N = -D_T^O$. A similar analysis can be conducted for carbon dioxide leading to expressions of the diffusive fluxes...
similar to those presented in Eq. (2.82), where the total multicomponent coefficient will be defined for oxygen \((D_{O}^{Tot})\) and carbon \((D_{C}^{Tot})\). From Eq. (2.82) we suddenly realize that the multicomponent diffusion of elements reduces to a Fick’s law and the knowledge of only one total multicomponent diffusion coefficient is required to properly describe the mixing term \(\sum \rho D_{k} \nabla Y_{k}\).

In Fig. 2.13 we present the evolution of the total multicomponent diffusion coefficient as a function of temperature for a pressure of 1 atm and for both air and carbon dioxide mixtures. From the analysis of this picture we realize how the formulation proposed for ionized mixtures reproduces the neutral results for temperatures lower than \(\sim 8000 \text{ K}\) for air and \(\sim 10000 \text{ K}\) for carbon dioxide. As temperature rises above 10000 K we notice a decreasing behavior of the \(D_{O}^{Tot}\) for the case of the CO\(_2\) mixtures while for air we notice the presence of a second peak around 12000 K followed by a successive decrease. In addition we wish to stress that even in the case where ionization is correctly taken into account, the total multicomponent diffusion coefficients do not change sign and stay always positive providing therefore a mixing term \((-\sum \rho D_{k} \nabla Y_{k})\) which tends to smooth out gradients in elemental concentrations.

In Fig. 2.14 we present the evolution of the thermal demixing diffusion coefficients. As for the multicomponent diffusion coefficients we remark that the formulation proposed for ionized mixtures reproduces the results previously obtained for neutral mixtures. An important conclusion concerning the elemental thermal demixing diffusion coefficients can be drawn from the analysis of the plots presented in Fig. 2.14. Indeed we observe that the thermal demixing coefficients change their sign only once in the temperature range of interest around 5000 K for both air and CO\(_2\) mixtures. This will of course affect the behavior of the demixing term \((-D_{T}^{Q} \nabla T\)). This term will indeed change sign depending on the local temperature in the flow even if the sign of the temperature gradient does not, as for example along the stagnation line.

Figure 2.13: Elemental multicomponent diffusion coefficients for air mixtures \([p=1 \text{ atm}, X^{O} = 0.21, X^{N} = 0.79\) for air and \(X^{O} = 1/3, X^{C} = 2/3\) for CO\(_2\), \(D_{N}^{Tot} = D_{O}^{Tot}, D_{C}^{Tot} = D_{O}^{Tot}\).]
in front of a probe placed in a plasma wind tunnel [see Ch. 4]. Starting from zero at low temperatures, the thermal demixing coefficients increase as soon as the $\delta x_s/\delta T|_{p,Y}$ differ from zero and for both air and CO$_2$ mixtures these coefficients present two local extrema in the first half of the temperature range under investigation. The values assumed by the first two extrema are almost identical for CO$_2$, while for air the first extreme is much higher than the second. In the ionization zone we notice for both air and CO$_2$ an increase of the $\rho D'_T\ell$ followed by a local maximum for CO$_2$, while for air a monotone increasing behavior is observed until 15000 K. A major difference between the results obtained for air and CO$_2$ mixtures consists in the fact that the maximum value of $\rho D'_T\ell$ for air is observed in the neutral region ($T \sim 3000$ K) while for CO$_2$ the maximum value is reached in the ionized region around 12500 K. Therefore for a given temperature gradient for air the demixing term $(\rho D'_T\ell \nabla T)$ will be maximum at low temperatures while for CO$_2$ flows demixing will be more enhanced at higher temperatures.

We now move to the analysis of the transport coefficients introduced to express the diffusive transport of enthalpy as a function of $\nabla T$ and $\nabla Y^\ell$. Firstly we analyze the part of this heat flux contribution proportional to the temperature gradient. As for neutral species we consider $\lambda = \lambda_R + \lambda_D$, $\lambda_{BB}$ computed with the formula of Ref. [22] and $\lambda_{SM}$ representing the ratio between $\sum W_s h_s$ and a unity temperature gradient, where the $W_s$ are computed as solution of Eq. (2.40) where the electric field is ambipolar and absence of both baro-thermal diffusion and elemental concentration gradients is assumed.

The analysis of Figs. 2.15-2.16 reveals several important results.

- $\lambda_R$ computed with Eq. (B.28) matches the results obtained with the Butler and Brokaw formula [22]. This clearly shows that the formula of Butler and Brokaw is valid also for
mixtures containing both neutral and charged species, even though originally derived for neutral mixtures.

- As expected, $\lambda'$ is equal to $\lambda_{SM}$ in the whole temperature range. This validates the for-
2.4.8. Air and carbon dioxide quasi neutral and current free plasmas

Simulation presented in Sec. 2.4 for ionized mixtures against the direct solution of the Stefan-Maxwell equations [Eq. (2.40)], obtained using for example the algorithms presented in Ref. [91].

- In the ionization region the difference between $\lambda_{BB}$ and $\lambda'$ is rather important and increases as temperature rises. This shows that assuming vanishing elemental fluxes, and therefore using $\lambda_{BB}$, leads to maximum relative error in the estimation of the thermal conductivity of the order of $\sim 30\%$ for CO$_2$ and $\sim 20\%$ for air.

The latter observation is confirmed by the profiles presented in Fig. 2.17 where we plot $\lambda_D$ for both air and CO$_2$ mixtures.

We now move to the investigation of the elemental heat transfer coefficients needed to compute the term $\sum_{k} \lambda_{EL}^{k} \nabla Y^{k}$. As observed for neutral mixtures, we can introduce a total elemental heat transfer coefficient. Indeed for both the air and the carbon dioxide mixtures previously introduced we have:

$$- \sum_{\ell \in E} \lambda_{EL}^{\ell} \nabla Y^{\ell} = - \lambda_{EL}^{O} \nabla Y^{O} - \lambda_{EL}^{N} \nabla Y^{N} = - \lambda_{EL}^{Tot} \nabla Y^{O}$$

where $\lambda_{EL}^{Tot} = \lambda_{EL}^{O} - \lambda_{EL}^{N}$ and $\lambda_{EL}^{Tot} = \lambda_{EL}^{O} - \lambda_{EL}^{C}$ for air and CO$_2$ mixtures respectively.

In Fig. 2.18 we present the evolution of $\lambda_{EL}^{Tot}$ for both air and CO$_2$ mixtures. From the analysis of the lines plotted in Fig. 2.18 we easily notice how the $\lambda_{EL}^{Tot}$ change sign only once in the temperature range of interest as the thermal demixing coefficients. In addition we observe a second extremum for the $\lambda_{EL}^{Tot}$ of CO$_2$ mixtures around 12500 K corresponding to the one of the thermal elemental demixing coefficients [Fig. 2.14]. For what concerns the air mixture, the evolution of the $\lambda_{EL}^{Tot}$ is monotone between 5000 K and 15000 K where we start observ-
Chapter 2. Theory of LTE viscous flows with variable elemental fractions

Figure 2.18: Elemental heat transfer coefficients for air mixtures \([p=1 \text{ atm}, X^O = 0.21, X^N = 0.79 \text{ for air and } X^O = 1/3, X^C = 2/3 \text{ for } \text{CO}_2]\).

ing a decrease in slope as already observed for the thermal demixing diffusion coefficients
[Fig. 2.14].

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2.5 Summary

In this chapter, we have presented the transport coefficients for both air and CO₂ mixtures that under conditions of LTE, allows to reduce the equations of chemically reacting flows to an elegant system consisting of the conventional Navier-Stokes equations (mass, momentum, energy) complemented by an advection-diffusion equation for the mass fraction of each chemical element in the mixture. Two formulations have been presented: one for the treatment of mixtures of neutral components and the other to describe mixtures of both neutral and charged species. The results obtained using the formalism derived for mixtures of both neutral and charged components reproduces those coming from the application of the formalism derived for mixtures of neutral species for sufficiently low temperature. The obtained formalisms are in closed form in the sense that diffusive fluxes are directly expressed in terms of gradients of the solution unknowns, unlike other formulations in which these fluxes are obtained in an implicit manner, by solving the full system of Stefan-Maxwell equations. Several new LTE transport coefficients appear:

- The elemental advection-diffusion equations contain \( N_c^2 \) elemental multicomponent and \( N_c \) thermal demixing coefficients. While the matrix of elemental multicomponent diffusion coefficients takes a particularly simple form for the binary mixtures considered in the application, it is in general non symmetric.

- In the energy equation, the well-known thermal reactive conductivity coefficient (due to Butler and Brokaw) takes into account diffusive transport of species enthalpies in the absence of elemental demixing. An additional demixing thermal conductivity coefficient and a set of \( N_c \) elemental heat transfer coefficients correct for the additional flow of heat due to elemental demixing caused by temperature respectively elemental fraction gradients when baro-thermal diffusion is neglected.

- When baro diffusion is taken into account, and additional pressure heat transfer coefficient \( (\lambda_p) \) is to be computed to account for the contribution to diffusive transport of enthalpy due to pressure gradients. The same apply to the case where thermal diffusion is consider. We have shown that an additional thermal diffusion heat transfer coefficient \( (\lambda_T) \) allows for the computation of an additional contribution to the enthalpy diffusive flux.

From a physical point of view, the derived transport coefficients provide a useful tool for the qualitative and quantitative understanding of diffusive phenomena in chemically reacting flows at and near LTE. For instance,

- graphs such as those presented in this article can be used to make an estimate of the degree of demixing to be expected in a chemically reacting flow prior to a numerical calculation. Based upon this knowledge, one may then decide whether or not to include the effect of demixing in the calculation.

- full non equilibrium calculations tend to yield excessively large amounts of information. If the flow is not too far from LTE, then graphs of LTE transport properties may be used to obtain a qualitative understanding of the computed species and temperature fields.
Chapter 3

Governing Equations

As mentioned in the introduction, the von Karman Institute is actively involved in the determination of catalytic properties of thermal protection materials since several years. The methodology used for this purpose requires both the simulation of inductively coupled plasma and stagnation line flows. Among all the assumptions on which the methodology is based, one of the most criticized consists in assuming LTE conditions, with constant elemental fractions, to be established in the torch and in the chamber of the facility. For what concerns the stagnation line problem, the outer edge conditions are determined assuming LTE and using the inlet elemental fraction as representative of the zone close to the probe. In order to investigate the validity of this assumption, the original version of the ICP code [152, 89] has been upgraded to solve the equations of plasma flows under chemical equilibrium with variable elemental fraction and under chemical non equilibrium both in the torch and in the test chamber. In the purpose of helping the description of the results presented in chapter 5 we present in Secs. 3.1.1-3.2 the governing equations of plasma flows under thermochemical equilibrium and chemical non equilibrium, inspired by the formulation proposed by Rini et. al. in Ref. [128]. In Sec. 3.1.2, the attention is turned to the stagnation line problem. Several numerical experiments have been performed in the framework of the research conducted during this thesis in order to improve the physical understanding of diffusion phenomena and gas-surface interaction mechanisms for both Earth and Mars entry applications. To this end the VKI boundary layer code has been upgraded to solve the equations of mixtures of reacting flows under thermochemical equilibrium with variable elemental fraction. To help the description of the results presented in chapters 4 and 6, we present in Sec. 3.1.2 the stagnation line equations for both chemical equilibrium and non equilibrium conditions inspired by the formulation presented by Rini and Degrez in Ref. [121]. In addition, to describe how gas-surface interactions have been modeled in the framework of this thesis, we present the model for the description of gas-surface interaction presented by Rini et al. in Ref. [122]. To close the system of the presented governing equations, further information should be provided on the computation of the thermodynamics and transport properties of the reacting mixtures for which the conservation equations have been written. To this end we present in Sec. 3.4 the models used to compute the thermodynamics properties of mixtures of thermally perfect and calorically imperfect gases for temperatures between 300 K and 15000 K, while in Sec. 3.5
we discuss the milestones of the transport kinetic theory used to compute the transport properties of such mixtures. Finally, in Sec. 3.6 we present the numerical methods used to discretize and solve the governing equations of inductively coupled plasmas and stagnation line flows. The discussion presented in Sec. 3.4, 3.5, and 3.6 is based on several references already available in the literature when this thesis was started [97, 160, 3, 94, 14, 11, 152, 89]. The reason why we present this material is to increase the readability of this manuscript providing a self-contained structure where all the needed information and citations are organized in a coherent way.

3.1 Hydrodynamic equations for mixtures of reacting gases

In this section we firstly present the governing equations for a mixture of reacting gases specialized for steady and axisymmetric conditions in presence of external electromagnetic fields [Sec. 3.1.1]. Then we discuss a particular case described by this set of equations in the absence of external fields, consisting in the stagnation line flow [Sec. 3.1.2] of a reacting mixture impinging on a solid wall. In Sec. 3.2 expressions for the source terms present in the governing equations, related to external fields, will be provided for the particular case of an ICP torch using a quasi-steady formulation.

3.1.1 General case

In this section we present the governing equations for mixtures of reacting gases containing both neutral and charged species. We represent air plasmas by a mixture of eleven chemical components, suited for Earth (re)entry applications [61]:

- neutral species: O$_2$, N$_2$, O, N, NO,
- charged species: NO$^+$, O$^+$, N$^+$, O$_2^+$, N$_2^+$, e$^-$,

and carbon dioxide plasmas by a mixture of eight species suited for Mars entry applications [90, 124]:

- neutral species: CO$_2$, CO, O$_2$, C, O,

Thanks to the presence of non uniform concentration fields of charged species, currents may be generated in the flow. Therefore the dynamics of mixtures of this kind will be influenced by the presence of external electromagnetic fields. To correctly account for this phenomena we include in our derivation the presence of the Lorentz force as well as Joule heating. The form of these terms depends on the particular type of electromagnetic coupling and, in the framework
of this thesis, we present their definition for the special case of an inductively coupled radio-
frequency plasma facility in Sec. 3.2.
A wide variety of plasmas exists in nature and our interest is limited to the particular case of
weakly ionized plasmas [89]. Several observations and assumptions are needed to derive the
governing equations of this kind of plasmas, which are recalled hereafter [152]:

- the plasma is strongly collision-dominated and may be described with a Navier-Stokes
type fluid model;
- magnetic fields are relatively weak, such that the gyroradii of charged particles exceed
their mean free paths by one or more orders of magnitude. The plasma transport proper-
ties are then isotropic and Hall-currents may be neglected;
- the Debye length is small compared to the flow characteristic length\(^1\); the plasma may
therefore be considered quasi-neutral;
- the plasma frequency by far exceeds the frequency of any external applied electromag-
netic fields\(^2\); a magneto-hydrodynamic (MHD) description of the plasma is then justi-
fied.

3.1.1.1 Governing equations

To establish the governing equations of the mixtures of reacting gases described in the previ-
ous section, we need to express the conservation of mass, momentum and energy. Moreover,
depending on the chemical regime under investigation, a suitable way to determine the mixture
composition should be defined. Additional assumptions are made to simplify the hydrodynamic aspects of the final formal-
ism to be presented shortly. Indeed, we simplify the flowfield description on the basis of the
following considerations [152]:

- as Reynolds numbers are low (Re \(\sim\) 500), we consider the flow to be laminar; hence no
turbulence modeling terms need to be included.
- For the considered operating pressures (< 1 atm), radiative effects may be neglected [153].
- The flow conditions are supposed to be steady and axisymmetric; an orthogonal cylindri-
cal coordinate system \((r, \theta, z)\) is therefore selected as the best suited for a straight forward
derivation of the hydrodynamic equations.

While we incorporate general chemical non equilibrium effects, we make the working as-
sumption that the plasma is under thermal equilibrium. Although this is rarely the case at low
operating pressures in ICPs torches [153], the inclusion of thermal non equilibrium would not

\(^1\)In the particular case of an ICP facility, the Debye length is small compared to the torch dimensions
\(^2\)In the particular case of an ICP facility the plasma frequency is supposed to be much higher than the operating
frequency of the torch.
add anything to the discussion presented in the remaining part of this thesis, in particular in chapter 5. Indeed we will address exclusively issues of chemical non equilibrium and the conclusions drawn on the basis of the results presented in chapter 5 would be the same if thermal non equilibrium would be included in the non equilibrium simulations. Under these assumptions, indicating the $z$, $r$- and $\theta$-components of the velocity by $u = (u, v, w)$, the governing equations of a mixture of reacting gases are:

- **continuity**

\[
\frac{\partial \rho u}{\partial z} + \frac{\partial \rho v}{\partial r} = 0, \tag{3.1}
\]

- **$z$-momentum**

\[
\frac{\partial (\rho u^2 + p)}{\partial z} + \frac{\partial \rho u v}{\partial r} = \frac{\partial r\tau_{zz}}{\partial z} + \frac{\partial r\tau_{zr}}{\partial r} + r F_L^z. \tag{3.2}
\]

- **$r$-momentum**

\[
\frac{\partial \rho u v}{\partial z} + \frac{\partial (\rho v^2 + p)}{\partial r} = \frac{\partial r\tau_{zr}}{\partial z} + \frac{\partial r\tau_{rr}}{\partial r} + p + \rho w^2 - \tau_{\theta\theta} + r F_L^r. \tag{3.3}
\]

- **$\theta$-momentum**

\[
\frac{\partial \rho u w}{\partial z} + \frac{\partial \rho v w}{\partial r} = \frac{\partial r\tau_{\theta\theta}}{\partial z} + \frac{\partial r\tau_{r\theta}}{\partial r} - \rho w^2 + \tau_{\theta\theta}, \tag{3.4}
\]

- **energy**

\[
\frac{\partial \rho u H}{\partial z} + \frac{\partial \rho v H}{\partial r} = \frac{\partial}{\partial z} [r(u\tau_{zz} + v\tau_{zr} + w\tau_{\theta\theta} - q_z)] + \frac{\partial}{\partial r} [r(u\tau_{rz} + v\tau_{rr} + w\tau_{r\theta} - q_r)] + r P, \tag{3.5}
\]
3.1.1. General case

where \( H = h + ||u||^2/2 \). The shear stress components \( \tau_{ij} \) take the form:

\[
\tau_{zz} = 2\mu \frac{\partial u}{\partial z} - \frac{2}{3}\mu \left( \frac{\partial u}{\partial z} + \frac{\partial v}{\partial r} + \frac{v}{r} \right),
\]

\[
\tau_{zr} = \tau_{rz} = \mu \left( \frac{\partial u}{\partial r} + \frac{\partial v}{\partial z} \right),
\]

\[
\tau_{rr} = 2\mu \frac{\partial v}{\partial r} - \frac{2}{3}\mu \left( \frac{\partial u}{\partial z} + \frac{\partial v}{\partial r} + \frac{v}{r} \right),
\]

\[
\tau_{z\theta} = \mu \frac{\partial w}{\partial z},
\]

\[
\tau_{r\theta} = \mu \left( \frac{\partial w}{\partial r} - \frac{w}{r} \right),
\]

\[
\tau_{\theta\theta} = -\frac{2}{3}\mu \left( \frac{\partial u}{\partial z} + \frac{\partial v}{\partial r} - 2\frac{v}{r} \right).
\]

Indicating the components of the mass diffusion flux of species \( s \) by \( J_s = (J_z^s, J_r^s, J_\theta^s) \), the heat flux components are written:

\[
q_z = -\sum_{s=1}^{N_{sp}} J_z^s h_s + \lambda \frac{\partial T}{\partial z},
\]

\[
q_r = -\sum_{s=1}^{N_{sp}} J_r^s h_s + \lambda \frac{\partial T}{\partial r},
\]

where \( \lambda \) accounts for all non-reactive [22] contributions to the thermal conductivity under thermal equilibrium (heavy particles, electron translational, rotational, vibrational and electronic thermal conductivities) and it is computed as specified in Sec. 3.5.

### 3.1.1.2 Chemical composition

Chemical Nonequilibrium (CNEQ)

Under chemical non equilibrium conditions, the mixture composition is obtained from partial differential equations describing the advection, diffusion and chemical processes that make the species concentrations vary within the flowfield. These equations read, for a species \( s \):

\[
\frac{\partial \rho \nu y_s}{\partial z} + \frac{\partial \rho v y_s}{\partial r} = -\frac{\partial J_z^s}{\partial z} - \frac{\partial J_r^s}{\partial r} + \dot{r} \omega_s.
\]

Note that the index \( s \) runs over heavy particles only. Indeed, when charged species are to be considered, we obtain the electron mole fraction by explicitly imposing quasi-neutrality:

\[
x_e - \sum_{s \text{ions}} x_s = 0.
\]

For a given set of \( N_r \) chemical processes of the type:

\[
\sum_{s=a}^{N_{sp}} \nu_{s,a} A_{s,a} = \sum_{s=a}^{N_{sp}} \nu_{s,a} A_{s,a},
\]

\[
\sum_{s=a}^{N_{sp}} \nu_{s,a} A_{s,a} = \sum_{s=a}^{N_{sp}} \nu_{s,a} A_{s,a},
\]

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the mass production terms $\dot{\omega}_s$, present in the above species continuity equations, are computed using the law of mass-action [160]:

$$
\dot{\omega}_s = \sum_{r=1}^{N_s} \omega_{sr},
$$

(3.9)

where

$$
\omega_{sr} = M_s (v_{s'r'} - v_{s'r}) k_{f,r} \left\{ \prod_{k=1}^{Nsp} \left( \frac{\rho_k}{M_k} \right)^{\nu_k'} - \frac{1}{\nu_k} \prod_{k=1}^{Nsp} \left( \frac{\rho_k}{M_k} \right)^{\nu_k} \right\},
$$

and $k_{b,r} = k_{f,r}/K_{c,r}$, $K_{c,r}$ being the equilibrium constant of reaction $r$ computed from statistical mechanics [160]. The use of Eq. (3.9) for the description of chemical reactions requires the knowledge of the forward reaction rates. The results presented in the remaining part of this thesis have been obtained using several finite rate chemistry models specified each time non equilibrium results are presented. Eqs. (3.8) describe a wide variety of physical phenomena and in particular allow for demixing of elements in the plasma [see Eq. (3.10) below]. The boundary condition on solid surfaces, needed for Eqs. (3.8), is presented in Sec. 3.1.1.3.

**Chemical Equilibrium**

It is well known [160] that the composition of a mixture of thermally perfect gases under thermochemical equilibrium can be obtained as a function of two independent thermodynamic variables for given fractions of elements in the mixture (e.g. oxygen and nitrogen for air mixture or oxygen and carbon for a CO$_2$ mixture). This topic has been addressed at the beginning of this thesis and we invite the reader to refer to chapter 2 for further details.

(1) **LTE, Variable Elemental Fraction (LTE-VEF)**

To correctly account for the fact that elemental fractions vary, as shown in chapter 2, we should solve a set of elemental continuity equations which can be obtained as a linear combination of the species continuity equations. Multiplying Eqs. (3.8) by $\phi_c^z M_c/M_s$, and summing over all species, one obtains:

$$
\frac{\partial r pu Y_c}{\partial z} + \frac{\partial r pv Y_c}{\partial r} = - \frac{\partial r J_c^z}{\partial z} - \frac{\partial r J_c^r}{\partial r},
$$

(3.10)

where the index $c$ runs over the $N_{el}$ elements contained in each species of the mixture (N and O or C and O for Earth and Mars entry applications respectively). The previous set of equations, valid regardless of the degree of chemical non equilibrium, can be solved with respect to the element mass fractions $Y_c$ introduced in Eq. (2.2).

From an analysis of Eq. (3.10) one clearly observes that diffusion of species results in elemental diffusion by means of element mass diffusion fluxes defined in Eq. (2.3). When considering the flow in an ICP facility, this will in general induce variations of elemental concentrations, even when the elemental composition of the injected gas mixture is uniform. It is interesting to notice that this phenomenon is independent from the degree of chemical non equilibrium [122, 121] owing to the absence of chemical source terms in Eqs. (3.10). Within the previous formalism the $J_c$ have been computed as a linear combination of the species diffusion fluxes computed as a solution of the Stefan-Maxwell equations.
3.1. General case

In chapter 2 the elemental mass diffusion fluxes are expressed as linear combination of temperature and elemental mass fraction gradients at constant pressure and under thermochemical equilibrium conditions. Following this approach, $\mathcal{J}_c$ for oxygen and nitrogen read:

$$\mathcal{J}_O = -\rho D^T_D O \nabla T - \rho D^{tot}_D O \nabla Y_O,$$

(3.11a)

$$\mathcal{J}_N = -\rho D^T_D N \nabla T - \rho D^{tot}_D N \nabla Y_N.$$

(3.11b)

Detailed expressions for the elemental thermal demixing and elemental diffusion coefficients $D^T_D$ and $D^{tot}_D$ are given in chapter 2. Since under thermochemical equilibrium and at constant pressure

$$\nabla x_s = \left. \frac{\partial x_s}{\partial T} \right|_{Y_f, p} \nabla T + \sum_{f=1}^{N_d} \left. \frac{\partial x_s}{\partial Y_f} \right|_{T, p} \nabla Y_f,$$

(3.12)

the thermal demixing diffusion coefficients are proportional to $\left. \frac{\partial x_s}{\partial Y_f} \right|_{T, p}$ while the total mixing diffusion coefficients depend linearly on $\left. \frac{\partial x_s}{\partial T} \right|_{Y_f, p}$. These observations will be helpful to justify the boundary condition used on solid surfaces for Eq. (3.10).

(2) **LTE, Constant Elemental Fraction (LTE-CEF)**

If elemental diffusion is neglected, the elemental fractions are supposed to be constant in the flow field. For this particular case, the condition $\mathcal{J}_c = 0$ corresponding to vanishing elemental fluxes \cite{22} and conduction current \cite{17}, allows for the diffusive transport of enthalpy to be reduced to the Fourier-type heat flux term shown in Eq. (2.1) \cite{17}, where $\lambda_R$ is the thermal reactive conductivity.

(3) **Species concentration**

Within both the LTE-CEF and LTE-VEF formalisms, a suitable way to compute the mixture species concentration should be defined. In chapter 2 we already addressed this issue from a theoretical point of view and here we provide more details concerning the way followed to practically compute the mixture composition. We start considering the LTE-CEF case where for a set of $N_{sp}$ species, amongst which $N_{ic}$ independent and $N_r$ dependent components can be identified, the mixture composition can be found as the solution of the following non linear system \( (3.13) \) \cite{14}. Firstly, we introduce equilibrium relations for a set of $N_r$ independent chemical reactions:

$$\sum_{s=1}^{N_{sp}} \nu^r_s \ln x_s = \ln K^r_s \quad (r = 1, \ldots, N_r).$$

(3.13a)

Secondly, we impose mass conservation:

$$\sum_{s=1}^{N_{sp}} \phi^c_s x_s = \varphi \sum_{s=1}^{N_{sp}} \phi^c_s x_s_{ref} = \frac{\xi_c}{\rho_c |M_c|} = \frac{\xi_c}{p} R_c T \quad (c = 1, \ldots, N_{ic}),$$

(3.13b)

where $\nu^r_c$ are the stoichiometric coefficients normalized such that $\nu^r_c = 1$, $K^r_c$ is the equilibrium constant for reaction $r$ based on species mole fractions \cite{160} and $R_c$ is the universal gas
constant. \(x_{s,\text{ref}}\) are the mole fractions of the species in a mixture at reference pressure \((p_{\text{ref}})\) and temperature \((T_{\text{ref}})\), which has the same elemental fractions as the mixture for which the composition should be computed, i.e. \(X_{\text{ref}}^c = X^c\). The factor \(\varphi\), given by:

\[
\varphi = \frac{p_{\text{ref}}\xi_c T}{p\xi_{c,\text{ref}} T_{\text{ref}}},
\]

is unknown a priori for a given thermodynamic state within the LTE-CEF formalism\(^1\). For this reason an additional compatibility condition is needed, which is expressed by the following equation:

\[
\sum_{s=1}^{N_{\text{sp}}} x_s = 1.
\]  

(3.13c)

In the definition of \(\varphi\), \(\xi_c\) is the number of molar density of element \(c\) (moles/V), defined as:

\[
\xi_c = \sum_{s=1}^{N_{\text{sp}}} \phi_c \frac{p_s}{M_s}.
\]  

(3.14)

and related to the element mass fraction by a simple relation \(\xi_c = \rho Y^c/M_c\). When the LTE-VEF formalism is used, in each cell of the computational domain, temperature and pressure are found as the solution of respective the energy and global continuity equation, while the elemental mass fractions follow from the elemental continuity equations (3.10). As an example, for the 11 species mixture defined at the beginning of this chapter we identify 8 dependent components \(\text{(N}_2, \text{O}_2, \text{NO, NO}^+, \text{O}^+, \text{N}^+, \text{O}_2^+, \text{N}_2^+)\) and 3 elements \(\text{(oxygen and nitrogen plus the mixture charge)}\), while for the eight species carbon dioxide mixture we have five dependent components \(\text{(CO}_2, \text{CO, O}_2, \text{C, O)}\) and three elements \(\text{(oxygen and carbon plus the mixture charge)}\). The mass fraction of charge is set to zero everywhere, inline with the quasi-neutrality assumption. Hence only demixing of 2 elements \(\text{(O and N or O and C)}\) need to be considered in the end. In this case, since the factor \(\varphi\) is equal to 1, there is no need to add the equation (3.13c) to the system (3.13).

\(^1\)The factor \(\varphi\) can be interpreted as follows. From its definition we have

\[
\varphi = \frac{p_{\text{ref}}\xi_c T}{p\xi_{c,\text{ref}} T_{\text{ref}}} = \frac{p_{\text{ref}}X^c \sum_{j \in E} \xi_j T}{p\xi_{c,\text{ref}} \sum_{j \in E} \xi_{j,\text{ref}} T_{\text{ref}}}.
\]

To further simplify this equation we observe that \(X_{\text{ref}}^c = X^c\) and \(N^c = N^c_{\text{ref}}\), where with \(N^c\) we indicate the total number of moles of element \(c\). As a consequence, observing that \(\sum_{j \in E} \xi_j = N/V\), we have

\[
\varphi = \frac{p_{\text{ref}}V_{\text{ref}} T}{pV T_{\text{ref}}} = \frac{N_{\text{ref}}}{N},
\]

where \(N_{\text{ref}}\) is the number of moles of the reference mixture, while \(N\) represents the number of moles of the mixture at local conditions. Within the LTE-CEF formalism chemical reactions induce variations in \(N\) leading to a factor \(\varphi\) different from one and changing with temperature. On the other hand, within the LTE-VEF formalism, \(\varphi = 1\) since \(p_{\text{ref}} = p\) and \(T_{\text{ref}} = T\).
3.1.1.3 Gas surface interactions

In the case of non equilibrium flow conditions, the recombination phenomenon happening at the solid surface can be represented by a set of \( N_r \) heterogeneous reactions. The modeling of the way in which the species involved in these reactions exchange atoms aims to express the mass production term \( \dot{\omega}_{i,\text{cat}} \) as a function of known quantities. Scott [137] proposes a model of the boundary conditions for the species equations based on the following expression for the net mass flux of species \( i \) at the surface

\[
\dot{\omega}_{i,\text{cat}} = M_i \dot{\omega}_i = M_i \sum_{r=1}^{N_r} \nu_{ri} \gamma^r - \sum_{r=1}^{N_r} \sum_{j=1}^{N_{sp}} \mu_{ijr} \gamma^r M_j \dot{\omega}_j, \tag{3.15}
\]

where \( \gamma^r \) is the reaction probability of the \( r \)th reaction, \( M_i \) the molar mass of the \( i \)th species, and \( M_i \dot{\omega}_i \) is the thermal agitation flux of \( i \)-particles towards the surface. The matrix \( \nu_{ri} \) indicates which \( i \)th reactants collide upon the surface in the \( r \)th reaction, while the matrices \( \mu_{ijr} \) define the \( j \)th incident reactants producing the \( i \)th products for the \( r \)th reaction. Within the methodology followed for the determination of catalytic properties of TPS materials, the reaction probability \( \gamma^r \) is supposed to be independent from the reaction and equal to an effective recombination probability \( \gamma_w \).

Therefore, the expression for the impinging flux \( M_i \dot{\omega}_i \), if the Chapman-Enskog perturbation term is considered, reads

\[
M_i \dot{\omega}_i = \frac{2}{2 - \gamma_i} n_i \sqrt{\frac{kT_w}{2\pi M_i}}. \tag{3.16}
\]

This formulation ensures a zero net total mass flux at the wall but does not satisfy in general the element conservation, indeed, considering a catalytic surface model constituted by the two reactions \( O + O \rightarrow O_2 \) and \( CO + O \rightarrow CO_2 \), one notices a coupling between the two chemical processes. This in some way establishes a link between the reaction probabilities of the two reactions which is not specified in the previous formulation.

Elaborating further on this consideration, an alternative approach is proposed. Let us define a rate of reaction per unit surface and unit time for the wall reaction \( \chi_r \), which represents the frequency at which reactions take place on the surface.

With this in mind, a formalism similar to the one used for bulk reactions is followed. The number of moles produced per unit surface and unit time are given by

\[
\frac{\dot{\omega}_i}{M_i} = \sum_{r=1}^{N_r} \left( \nu_{iir} - \nu_{ii} \right) \chi_r \tag{3.16}
\]

where, for \( \nu_{iir} \neq 0 \)

\[
\chi_r = \frac{\gamma^r}{\nu_{iir}}. \tag{3.17}
\]

The surface reaction rate \( \chi_r \) is therefore related to the recombination probability of species \( i \) involved in the \( r \)th reaction \( \gamma^r_i \) by the relation (3.17). As the reaction rate \( \chi_r \) has to be independent of the species \( i \), it results that the species reaction probabilities \( \gamma^r_i \) are linked by the constraints \( \gamma^r_i / \nu_{iir} = \text{constant} = \chi_r \), for all species such that \( \nu_{iir} \neq 0 \).

In this case, the flux of particle \( M_i \dot{\omega}_i \) is given by \( M_i \dot{\omega}_i = 2/(2 - \gamma_i) n_i \sqrt{kT_w/(2\pi M_i)} \), while
\[ \gamma_i = \sum_{r=1}^{N_r} \gamma_i^r \] represents the recombination probability of species \( i \). The computation of the boundary condition for the species continuity equations will therefore consist of firstly calculating \( \chi_r \) and then evaluating the production term by means of Eq. (3.16). The purpose of this alternative formulation is not to better describe the physical phenomenon of heterogeneous catalyticity, which is hidden in the definition of the different recombination probabilities. But at least, it provides a model which is consistent with both the global mass and element conservation at the wall, as will be demonstrated by numerical experiments. The latter property comes directly from the form of Eq. (3.16), which is similar to the one of Eq. (3.9). Moreover, it should be noticed that the quantity \( \chi_r \) depends only on the reaction considered and not on the species involved in it, which represents another similitude with the bulk reaction mechanism.

### 3.1.2 Stagnation Line Problem

In Fig. 3.1 we present a sketch describing the typical geometric configuration of standard tests/simulations conducted in the framework of the application of the methodology used at VKI for the determination of the catalytic properties of thermal protection materials.

![Figure 3.1: Geometrical configuration.](image)

The simulation of the flow in the torch and in the chamber is done assuming LTE conditions and the results of this simulation are used to define the stagnation line differential problem. This is made thanks to the computation of a set of non-dimensional parameters used as inputs to rebuild the outer edge conditions in order to match the experimental heat flux. This iterative rebuilding process relies upon the simulation of the stagnation line flow of a mixture of reacting gases under chemical non equilibrium assuming complete recombination at the wall. For the considered torch operating conditions, the ions concentrations rapidly decay after the
torch outlet allowing the description of the flow close to the probe by means of neutral species and hence, in the absence of electromagnetic coupling. After the outer edge conditions are rebuilt \[36\], a set of stagnation line non equilibrium computations are performed to compute the wall heat flux as a function of wall temperature for several effective recombination probabilities.

### 3.1.2.1 Stagnation line equations

In this section, the governing equations of a mixture of reacting gases for the stagnation line flow are recalled \[11, 3, 73\]. The stagnation line flow represents a particular case of the general description presented in Sec. 3.1.1.1. Indeed, in a classical ICP facility, the material to be tested is held by a probe immersed in a low subsonic axisymmetric high temperature jet. The heat flux is measured in the probe stagnation region. To determine the catalytic activity, it is necessary to solve the governing equations in the layer surrounding the stagnation region of the probe. If one focuses the interest only on the stagnation line, the Boundary Layer and the Navier-Stokes equations become equivalent and moreover there exists a self similar solution of the latter along the stagnation line. Therefore Eqs. (3.1)-(3.5), complemented by Eqs. (3.8) under non equilibrium, could still be applied to describe the stagnation line flow impinging on the probe. In addition, because of the absence of electromagnetic coupling, the Lorentz forces and Joule heating terms vanish. As a consequence, the previous equations can be further simplified setting \(F_r = F_z = 0\) and \(P_J = 0\).

Due to the combined effects of low Mach number, high temperature, high viscosity, and relatively small probe diameter, the flow Reynolds number is of the order of 100. In the classical boundary layer theory \((R_e \gg 1)\), the pressure gradient in the momentum and energy equations is computed by extrapolating the external inviscid solution to the wall.

In our case, the self-similar stagnation line flow is matched with a Local Thermal Equilibrium (LTE) Navier-Stokes solution at some distance \(\delta\) representative of the diffusion boundary layer thickness. Now, the pressure gradient at this location is

\[
\frac{\partial p}{\partial x} = -\rho_\delta \left[ u_\delta \frac{\partial u_\delta}{\partial x} + v_\delta \frac{\partial u_\delta}{\partial y} \right].
\]

(3.18)

In classical boundary layer theory, the second term is zero because \(v_\delta \approx 0\). For the present low-Reynolds number flows, it is non-zero and obtained from the LTE Navier-Stokes solution \[36\]. To derive the stagnation line equations we could either start from the Navier-Stokes equations presented in Sec. 3.1.1.1 or from the boundary layer equations written with respect to a local Cartesian reference system [Fig. 3.1] having the \(x\) axis lying on the body surface and the \(y\) axis normal to it and apply the Lees-Dorodnitsyn transformation. In the following the Lees-Dorodnitsyn transformation is applied to the axisymmetric boundary layer equations, defining

\[
\xi(x) = \int_0^x \rho_\delta \mu_\delta u_\delta r^2 ds \quad \text{and} \quad \hat{\eta} = \mathcal{K} \eta = \mathcal{K} \frac{u_\delta r}{\sqrt{2\xi}} \int_0^\eta \rho \, dt,
\]

where \(\mathcal{K} = \frac{1}{\delta} \frac{\sqrt{2\xi}}{u_\delta r} \int_0^{\delta_{\text{sec}}} \frac{1}{\rho} \, d\hat{\eta}\).

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Three new dependent variables are introduced as

\[ F = \frac{u}{u_0}, \quad g = \frac{h}{h_0}, \quad \text{and} \quad \tilde{V} = \mathcal{K} \frac{2\xi}{\delta} \left( F \frac{\partial \eta}{\partial x} + \frac{\rho v r}{\sqrt{2\xi}} \right) \]

Therefore, the stagnation line equations read

- **Continuity**
  \[ \frac{\partial \tilde{V}}{\partial \tilde{\eta}} + F = 0 \quad (3.19) \]

- **Species concentration** (see Sec. 3.1.2.2)

- **Momentum**
  \[ \tilde{V} \frac{\partial F}{\partial \tilde{\eta}} = \frac{1}{2} \frac{\rho_0}{\rho} \left[ 1 + \left( \frac{\delta u}{\delta x} \right)^2 \right] - \frac{F^2}{2} + \frac{\partial}{\partial \tilde{\eta}} \left( \mathcal{K}^2 l_0 \frac{\partial F}{\partial \tilde{\eta}} \right) \quad (3.20) \]

- **Energy**
  \[ \tilde{V} \frac{\partial g}{\partial \tilde{\eta}} = \frac{\partial}{\partial \tilde{\eta}} \left( \mathcal{K}^2 l_0 \frac{\partial g}{\partial \tilde{\eta}} \right) - \frac{\delta}{\partial \tilde{\eta}} \left( \mathcal{K} \sum_{i=1}^{N_s} \tilde{J}^i \frac{h_i}{h_0} \right) \quad (3.21) \]

where the dimensionless diffusion flux \( \tilde{J}^i \) is defined as

\[ \tilde{J}^i = \frac{J^i}{\sqrt{2\rho_0 \mu_0 \delta u_0 \delta x}} \quad (3.22) \]

The boundary conditions for the transformed variables are as follows. At the wall \( F = 0 \) and \( g = h_{\infty}/h_0 \), while at the outer edge \( F = 1 \) and \( g = 1 \). On the other hand, the boundary conditions for the physical variable are at the wall \( u = 0, v = 0, h = h[T_w(x)], \) and \( J_{w,i}^i = \dot{\omega}_{i,cat} \), while at the outer edge \( u = u_0(x), h = h_0(x), y_i = y_{\infty,i}(x) \).

### 3.1.2.2 Mixture composition

In this section we present the various formalisms applied to close the set of Eqs. 3.19-3.21 specifying the procedure followed to compute the mixture composition. As in Sec. 3.1.1.2,
three chemical regimes have been considered: chemical non equilibrium (CNEQ) and chem-
cical equilibrium with constant (LTE-CEF) and variable elemental fraction (LTE-VEF). The
equations to be solved in these three conditions have already been described in Sec. 3.1.1.2. In
the following those equations are specialized for the particular case of the stagnation line flow,
after the application of the Lees-Dorodnitsyn transformation.

Chemical non equilibrium composition

Under chemical non equilibrium conditions the species concentration field is obtained as the
solution from Eqs. (3.23), which, after the application of the Lees-Dorodnitsyn transformation
read:

$$\hat{V} \frac{\partial y_i}{\partial \hat{\eta}} + \mathcal{K} \frac{\partial \hat{J}}{\partial \hat{\eta}} = \dot{W}_i. \quad (3.23)$$

The bulk reactions give a contribution to $\dot{\omega}_i$ computed as specified in Eq. (3.9) and related to
the dimensionless mass production rate

$$\hat{W}_i = \frac{\dot{\omega}_i}{2 \rho \frac{\partial u}{\partial x}}. \quad (3.24)$$

As far as the gas-solid interaction is concerned, the surface reactions define the boundary
conditions for the species continuity equations. Indeed, the amount of species $i$ produced or
consumed by the surface reactions has to be balanced by the diffusion flux of species $i$ itself.
Therefore the boundary condition is $\mathbf{J}_{w,i} \cdot \mathbf{n} = \dot{\omega}_{i,\text{cat}}$. Sec. 3.1.1.3 is focused on the modeling of
the term $\dot{\omega}_{i,\text{cat}}$.

Chemical equilibrium composition

In order to analyze the influence of demixing on the computation of the composition for a mix-
ture along a stagnation line, two approaches have been followed to obtain the results presented
in chapter 4. First constant elemental fractions, equal to the outer edge values, have been im-
posed along the stagnation line. Later this constraint has been removed allowing for elemental
fractions to vary, by solving suitable advection diffusion equations.

(1) LTE Constant Elemental Fraction (LTE-CEF)

Assuming the absence of elemental demixing along the stagnation line leads to constant ele-
mental fractions of the elements present in the mixture.
In this case there is no need for solving additional continuity equations for each mixture ele-
ment. Indeed, the mixture composition is computed along the stagnation line using the local
value of temperature together with the outer edge elemental composition and pressure. This is
practically done, as explained in Sec. 3.1.1.2, solving Eqs. (3.13) using for each value of $\hat{\eta}$:
$T(\hat{\eta})$, $p_0$, and $X^e_\delta \forall e \in \mathcal{E}$. 

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(2) LTE Variable Elemental Fraction (LTE-VEF)

In presence of demixing, the elemental fractions will vary within the boundary layer according to the conservation equations introduced in Sec. 2.3.2.3 and recalled in Sec. 3.1.1.2 for a cylindrical coordinate system. During the investigation of stagnation line flows conducted in the framework of this thesis, we have considered two forms of the elemental conservation equations presented hereafter: the molar \[122\] and mass \[127\] formulations.

Molar formulation

Consider the species continuity equations for a multicomponent steady gas

\[ \text{div} (\rho_i u + J_i) = \dot{\omega}_i \]

where \(\rho_i\) is the partial density, and \(J_i\) the diffusion flux of the \(i\)th species. After multiplication by \(\phi_i\) and summation among all the species, the previous equation reads

\[
\text{div} \left( \sum_{i=1}^{N_{sp}} \phi_i c_i u + \sum_{i=1}^{N_{sp}} \phi_i \frac{J_i}{M_i} \right) = \sum_{i=1}^{N_{sp}} \phi_i \dot{\omega}_i M_i. \tag{3.25}
\]

Since the right hand side of the previous equation is zero, the driving mechanisms for the atoms present in the mixture are explained by the following equation

\[ \text{div} (\xi_c u + N_c) = 0, \]

where \(N_c\) is the number flux of the element \(c\) defined by Eq. (2.3).

Applying the Lees-Dorodnitsyn transformation one finally reaches the non dimensional form of the elements conservation equations, which read

\[
\tilde{V} \frac{\partial \xi_c}{\rho \partial \tilde{\eta}} - \frac{\bar{V}}{\rho^2} \frac{\partial \rho}{\partial \tilde{\eta}} \xi_c + K \frac{\partial}{\partial \tilde{\eta}} \left( \sum_{i=1}^{N_{sp}} \phi_i \frac{\tilde{J}^h_i}{M_i} \right) = 0. \tag{3.25}
\]

Two boundary conditions are required for this equation, at the wall and at the outer edge. In the latter case the chemical composition is fixed, and from it follows the number of moles per unit volume \(\xi_c|_{\delta}\). On the other hand, at the wall both the chemical composition and the elemental fractions are unknown; nevertheless, the wall boundary condition can be expressed in terms of the number fluxes of the elements. Indeed at the wall the value of \(N_c\) must be zero for each element, ablation being neglected in the current application. The wall boundary condition has therefore been imposed in the form

\[ N_c = 0 \quad (c \in \mathcal{E}). \tag{3.26} \]

The solution of the elemental conservation equations allows for the determination of the moles of the mixture elements \(\xi_c\), and therefore of the elemental fractions at any point within the boundary layer. The knowledge of the elemental fractions allows for the determination of the mixture composition as the solution of Eqs. (3.13).
3.1.2. Stagnation Line Problem

Mass formulation

- Direct solution of the Stefan-Maxwell equations

A similar formulation can be easily derived focusing on the mass fraction of elements $Y^e$, as done to retrieve Eq. (3.10). Indeed, after application of the Lees-Dorodnitsyn transformation to the elemental continuity equations we have

$$
\tilde{V} \frac{\partial Y^c}{\partial \hat{\eta}} = \frac{-K}{\sqrt{2 \rho \mu \rho \delta}} \frac{\partial J^c}{\partial \hat{\eta}} \quad (c \in E),
$$

(3.27)

Solving for Eq. (3.27) allows for the determination of the $Y^c$ to be used as input for the system (2.11)-(2.12) needed to obtain the mixture composition. Within this formalism the $J^c$ are obtained as a linear combination of the species diffusive fluxes solution of the Stefan-Maxwell equations [Eq. (2.7)] written for a mixture of neutral species.

- Closed form of the equations

With respect to previous formulations [121], the new formalism introduced in this thesis will affect the form of the element continuity and energy equations. Indeed from Eq. (2.30), the diffusive fluxes of carbon, nitrogen, and oxygen read:

$$
J^c = -\rho D_{CC} \nabla Y^C - \rho D_{CN} \nabla Y^N - \rho D_{CO} \nabla Y^O - \rho D^T \nabla T, \quad (3.28a)
$$

$$
J^N = -\rho D_{NC} \nabla Y^C - \rho D_{NN} \nabla Y^N - \rho D_{NO} \nabla Y^O - \rho D^T \nabla T, \quad (3.28b)
$$

$$
J^O = -\rho D_{OC} \nabla Y^C - \rho D_{ON} \nabla Y^N - \rho D_{OO} \nabla Y^O - \rho D^T \nabla T. \quad (3.28c)
$$

The direct consequence of these expressions is reflected on the heat flux vector which, in the absence of thermal and pressure diffusion, reads as follows

$$
q = -(\lambda + \lambda_R + \lambda_D)\nabla T - \lambda_{EL}^C \nabla Y^C - \lambda_{EL}^N \nabla Y^N - \lambda_{EL}^O \nabla Y^O.
$$

(3.29)

Using Eq. (2.30), we obtain the following form of the elemental continuity equation

$$
\rho^2 D_{cc} \frac{\partial^2 Y^c}{\partial \hat{\eta}^2} = \left( \tilde{V} - \frac{\partial \rho^2 D_{cc}}{\partial \hat{\eta}} \right) \frac{\partial Y^c}{\partial \hat{\eta}} - \frac{\hat{\eta}}{\partial \hat{\eta}} \left( \rho^2 D^T \frac{\partial T}{\partial \hat{\eta}} \right) - \frac{\hat{\eta}}{\partial \hat{\eta}} \left\{ \rho^2 \sum_{q \neq c} D_{cq} \frac{\partial Y^q}{\partial \hat{\eta}} \right\}
$$

(3.30)

where the parameter $\chi = K^2/(\mu \rho \delta)$ is the result of the finite thickness assumption. As far as the energy equation is concerned, introducing the variable $\theta = T/T_\delta$, we have

$$
\tilde{V} \frac{\partial \theta}{\partial \hat{\eta}} = \frac{\tilde{V}}{h_{fr}} \tilde{h} \frac{\partial y_i}{\partial \hat{\eta}} + \frac{h_{fr}}{h_i} \frac{\partial}{\partial \hat{\eta}} \left[ \frac{K^2 \ell_0 h_{fr}}{Pr} \frac{h_{fr}}{\lambda} (\lambda + \lambda_R + \lambda_D) \frac{\partial \theta}{\partial \hat{\eta}} \right] + \frac{h_{fr}}{h_i} \frac{\partial}{\partial \hat{\eta}} \left[ \frac{K^2 \ell_0 h_{fr}}{Pr} \frac{h_{fr}}{\lambda T_\delta} \sum_{q \neq c} \lambda_{EL}^q \frac{\partial Y^q}{\partial \hat{\eta}} \right]
$$

(3.31)
where \( \ell_0 = \rho \mu / (\partial \mu / \partial T) \), \( Pr = \mu C_p f / \lambda \), \( C_p f = \sum_{i \in S} y_i \partial h_i / \partial T \), and \( h f = C_p f T \). The boundary conditions at the wall for the non-dimensional temperature is \( \theta = T_{w} / T_{\delta} \), while at the outer edge \( \theta = 1 \). The boundary condition for elements at the wall follows directly from mass conservation, i.e. \( J_e = 0 \) for \( e \in E \), since no new elements are generated in the surface chemistry (non-ablative wall). From Eqs. (3.28), we see that for each element, the straightforward expressions for the diffusive fluxes are well suited for the numerical implementation of this boundary conditions. Indeed for each element, the mass conservation at the surface reads:

\[
\rho D_{cc} \frac{\partial Y_c}{\partial \hat{\eta}} \bigg|_{w} = \rho D_{c} \frac{\partial T}{\partial \hat{\eta}} \bigg|_{w} - \rho \sum_{q \neq c} D_{cq} \frac{\partial Y_q}{\partial \hat{\eta}} \bigg|_{w} \quad (c \in E). \tag{3.32}
\]

It is important to notice how advantageous [128] the use of Eq. (3.32) is from a numerical point of view. The implementation of this boundary condition is substantially more difficult if the element diffusive fluxes were to be computed as a linear combination of the solutions of Eqs. (2.7) as done in Eq. (3.26): in general, inner iterations are then needed to impose the boundary condition.

### 3.2 Electromagnetic field equations for inductively plasma flows

We now turn our attention to the description of plasma flows flowing into an Inductively Coupled Plasma facility. From the flow modeling point of view, at least two main parts of the facility can be put in evidence. The torch, used to produce the plasma, and the test chamber where a hot jet impinging on a probe, is used for TPM testing.

An ICP torch is a device which allows to heat the gases at pressures greater than 1000 Pa to temperatures of \( \sim 10,000 \) K in an electrodeless manner. The gas is injected into a quartz tube surrounded by a copper inductor (see Fig. 3.2).

![Figure 3.2: VKI Minitorch torch facility (argon, 0.1 atm, 3 kW, 27.6 MHz).](image)

A radio-frequency electrical current runs through the inductor and induces a secondary current through the gas inside the quartz tube, which heats up by means of Ohmic dissipation.
High-pressure ICPs are rather close to equilibrium, in contrast with low-pressure inductive discharges, in which non equilibrium (NEQ) processes play a dominant role [21].

The VKI Plasmatron-torch geometry used in the simulations presented in chapter 5, is shown in Fig. 3.3. The torch is modeled by a fully axisymmetric configuration by approximating the (solenoidal) inductor by a series of \( n \) parallel, current-carrying rings. For simplicity, we assume the rings to be infinitely thin current loops, located at the innermost part of the true coil rings, where most of the electric current is known to run [153].

![Figure 3.3: VKI plasmatron torch geometry.](image)

**External current density**

For the radio frequencies typically used in ICPs, it is reasonable to assume that a single current with amplitude \( I_c \) and frequency \( f \) oscillates at phase-angle zero through each coil ring [67]. The external current density amplitude \( J_V \) then reads:

\[
J_V = -I_c \sum_{i=1}^{n_c} \delta(r - r_i),
\]

(3.33)

where the Dirac-distribution \( \delta(r - r_i) \) takes care of the singular current density in the \( i \)-th loop.

**Assumption of vanishing poloidal electrical current**

Inside the plasma, powerful induced currents oscillate in the toroidal (\( \theta \)) direction. In the poloidal (\( r-z \)) plane, on the contrary, we make the reasonable assumption that electrical currents vanish [156, 153] [Eq. (2.70)].

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MHD induction equation

The induced electric field \( E \) is purely toroidal and consists of a single Fourier mode at the torch operating frequency:

\[
E = E \exp(i2\pi ft) e_\theta.
\] (3.34)

As the magnetic Reynolds number is small, the electric field satisfies the following Helmholtz-type MHD induction equation, both inside the torch and on a far field domain covering the space around the torch [96]:

\[
\frac{\partial^2 E}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial E}{\partial r} \right) - \frac{1}{r^2} E - i\mu_02\pi f\sigma E = i\mu_02\pi f J_V,
\] (3.35)

where \( \mu_0 \) represents the magnetic permeability of free space. To take into account phase differences inside the torch, \( E \) stands for a complex variable.

The electric field amplitude should be zero far from the torch:

\[
E(z,0) = 0; \quad E(z, +\infty) = 0; \quad E(\pm\infty, r) = 0.
\] (3.36)

Quasi-steady formulation

The radio-frequency electro-magnetic field generates small oscillating perturbations on all flow field quantities. By averaging the flow equations in time, a quasi-steady flow formulation similar to the steady Navier-Stokes equations is obtained. In the momentum equation, a time-averaged Lorentz force \( F_L \) appears, while in the energy equation a time averaged Joule heating source term \( P_J \) must be taken into account. In this sense the governing equations of mixtures of partially ionized gases, presented in Sec. 3.1.1.1, can be applied to describe the plasma flowing into an ICP facility [153, 97].

Indicating the real and complex part of the electric field amplitude by \( E_R \) and \( E_I \), the time-averaged Lorentz forces \( F^c_L \) and \( F^r_L \) are written:

\[
F^c_L = \frac{\sigma}{4\pi f} \left( \frac{E_R}{r} \frac{\partial rE_I}{\partial z} - \frac{E_I}{r} \frac{\partial rE_R}{\partial z} \right),
\] (3.37)

\[
F^r_L = \frac{\sigma}{4\pi f} \left( \frac{E_R}{r} \frac{\partial rE_I}{\partial r} - \frac{E_I}{r} \frac{\partial rE_R}{\partial r} \right).
\]

The time-averaged Joule heating source term is given by:

\[
P_J = \frac{\sigma}{2} (E^2_R + E^2_I).
\] (3.38)

3.3 Flow and composition boundary conditions

In this section we present the set of boundary conditions used to well pose the differential problem previously presented to analyze the flow in an inductively coupled plasma facility re-
alized following a standard design. To simulate tests of TPS samples held in the test chamber we should ideally consider the plasma flow behavior in the torch and in the whole chamber simultaneously [90].

![Boundary conditions and the computational domain](image)

Figure 3.4: Boundary conditions and the computational domain

In order to reduce the computation time, Magin [89] suggested to consider a sub-domain of the chamber containing the hot-jet impinging on a probe, instead of extending the computational domain until the chamber outer walls. This simplifies considerably the solution of the problem still conserving the importance of the obtained results, since the region richest in physics corresponds to the hot jet and certainly not to the cold recirculation zone present at higher radius. In the framework of the research conducted during this thesis we just performed analysis of the hot jet without the presence of a probe referring to the geometrical configuration presented in Fig. 3.4. By analyzing fig. 3.4 we notice the need to define a boundary condition for the axis of symmetry (AF), the Eastern boundary (EF) in the chamber, the quartz tube wall (BC) and a part of the chamber wall (CD), the torch inlet (AB), and the outer boundary in the chamber (DE). In the case where only the torch is simulated, the torch outlet (CF') condition will coincide with the Eastern boundary in the chamber to be presented shortly. In the following we present the details of each of the boundary conditions previously cited, referring to ambient conditions using the index A.

**Axis of symmetry**

At the torch axis, we impose symmetry:

\[
\begin{align*}
\frac{\partial p}{\partial r} &= 0; \quad \frac{\partial \rho u}{\partial r} = 0; \quad \rho v = 0; \quad \frac{\partial \rho w}{\partial r} = 0; \quad \frac{\partial T}{\partial r} = 0; \\
\text{CNEQ:} \quad \frac{\partial x_s}{\partial r} &= 0; \quad \text{LTE-VEF:} \quad \frac{\partial Y_c}{\partial r} = 0.
\end{align*}
\]
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Torch outlet

We take the torch outlet corresponding to a discharge in ambient space:

\[ p = p_A ; \quad \frac{\partial p}{\partial z} = 0 ; \quad \frac{\partial T}{\partial z} = 0 ; \]

CNEQ : \( \frac{\partial \chi_s}{\partial z} = 0 ; \)

LTE-VEF : \( \frac{\partial Y_e}{\partial z} = 0 , \)

where \( p_A \) stands for the ambient pressure in the outlet vessel.

Quartz tube wall

On the quartz tube inner surface, no-slip boundary conditions are imposed:

\[ \frac{\partial p}{\partial r} = 0 ; \quad \rho u = 0 ; \quad T = T_{\text{wall}}. \]

The species concentrations are extrapolated imposing homogeneous Neumann boundary conditions corresponding to a non-catalytic surface :

\[ \text{CNEQ} : \quad \frac{\partial \chi_s}{\partial r} = 0. \quad (3.39) \]

When using the variable elemental fraction LTE model, we use the following boundary condition instead :

\[ \text{LTE-VEF} : \quad \frac{\partial Y_e}{\partial r} = 0. \quad (3.40) \]

The reader may remark that the conditions \((3.39)\) and \((3.40)\) are not necessarily equivalent when LTE conditions are reached. The mole fractions depend not only on the elemental concentrations but also on temperature (and to a lesser extent, pressure). Therefore, if a temperature gradient exists, non-zero mole fraction gradients may be obtained even when gradients of elemental fractions vanish. In high pressures ICPs, however, temperatures near the wall \(\sim 300 \text{ K} \) are too low to cause chemical reactions. Within this low-temperature zone (where \( \chi_s / (\partial T |_{Y_e, p} = 0, \)), gradients of temperature do not induce concentration gradients such that the boundary conditions \((3.39)\) and \((3.40)\) become fully equivalent in the LTE limit.

Torch inlet

The flow is injected through a thin ring near the torch wall. The axial inlet momentum \( Q \) is to be calculated from a given total mass injection rate. The model allows for an azimuthal inlet momentum component, which is taken to be a ‘swirl’ number \( S \) times the axial inlet momentum. This translates into the following inlet boundary condition:

\[ \frac{\partial p}{\partial z} = 0 ; \quad \rho u = Q ; \quad \rho v = 0 ; \quad \rho w = S \times Q ; \quad T = T_A ; \]
3.3. Flow and composition boundary conditions

CNEQ: \( x = x_A \); LTE-VEF: \( Y_c = Y_{A,c} \),
where the temperature, the composition and the elemental concentrations of the (cold) ambient
gas fed to the torch are written, respectively, \( T_A, x_A, \) and \( Y_{A,c} \).

In the ICP torches for TPM-testing simulated here, the central inlet is generally removed and
replaced by a solid wall (see Fig. 3.3); there, we impose an adiabatic no-slip condition:
\[
\frac{\partial p}{\partial z} = 0; \quad \rho u = 0; \quad \frac{\partial T}{\partial z} = 0; \\
CNEQ: \quad \frac{\partial x_s}{\partial z} = 0; \quad \text{LTE-VEF:} \quad \frac{\partial Y_c}{\partial z} = 0.
\]
Observe that in this case the boundary condition \( \frac{\partial Y_c}{\partial z} = 0 \) is valid, not because temperature
is low, but because the temperature gradient \( \frac{\partial T}{\partial z} = 0 \).

Outer boundary in the chamber

It is well known that for subsonic flow conditions, the pressure in the test chamber of ICP
facilities is almost constant [66, 90], especially when no probe is placed in it. For this reason
we build the mesh cutting in the chamber at a certain radius without including the outer wall
in the domain discretization. This introduces an additional boundary on which we impose the
following conditions. The value of the state variables, except pressure and species concentra-
tions in case of CNEQ (or elemental fraction in case of LTE-VEF), is extrapolated from the
inner field. The pressure on the other hand is imposed and it is supposed to be constant along
all the boundary. The species concentration (in case of CNEQ or the elemental composition in
case LTE-VEF) is fixed and it is equivalent to the LTE-CEF composition 79\%\(N_2\) and 21\%\(O_2\)
(or 79\%\(N\) and 21\%\(O\) for LTE-VEF). this leads to the imposition of the following boundary
condition :
\[
\frac{\partial \rho u}{\partial n} = 0; \quad \frac{\partial T}{\partial n} = 0; \quad \rho = p_A \;
CNEQ: \quad x_{N_2} = 0.79; \quad x_{O_2} = 0.21 \quad \text{LTE-VEF:} \quad X_{N_2} = 0.79; \quad X_{O_2} = 0.21
\]
where \( p_A \) stands for the ambient pressure in the chamber.

Eastern boundary in the chamber

This boundary condition is a consequence of the implicit assumption that the area of the cham-
ber behind the sample has a negligible influence on the test area and can therefore be excluded
from the numerical simulation. This is done imposing:
\[
\frac{\partial p}{\partial n} = 0; \quad \frac{\partial \rho u}{\partial n} = 0; \quad \frac{\partial T}{\partial n} = 0 \\
CNEQ: \quad \frac{\partial x_s}{\partial z} = 0; \quad \text{LTE-VEF:} \quad \frac{\partial Y_c}{\partial z} = 0.
\]
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3.4 Thermodynamic properties

In this section we present the main thermodynamic properties of a mixture of thermally perfect and calorically imperfect gases. Each species is assumed to behave as a thermally perfect gas: a gas where interparticle forces are negligible. For most problems in aerothermodynamics this is a reasonable assumption. Conditions that require consideration of interparticle forces are very high pressure or low temperature, both of which in general far from the conditions described in this manuscript.

3.4.1 Thermally perfect gases

In this work we consider mixtures of thermally perfect gases. Each species $i$ contained in the mixtures therefore obeys the thermally perfect gas equation of state [3]:

$$p_i = \rho_i R_i T,$$  \hspace{1cm} (3.41)

where $p_i$ is the partial pressure of $i^{th}$ species, $\rho_i$ the partial density, $R_i$ the specific gas constant and $T$ the temperature.

The specific gas constant may also be expressed as:

$$R_i = \frac{R_u}{M_i},$$  \hspace{1cm} (3.42)

where $R_u$ is the universal gas constant and $M_i$ is the species molar mass. Dalton’s law for perfect gases states that the mixture pressure $p$ is equal to the sum of the species partial pressures $p_i$:

$$p = \sum_{i=1}^{N_s} p_i,$$  \hspace{1cm} (3.43)

The same law is valid for the partial densities:

$$\rho = \sum_{i=1}^{N_s} \rho_i,$$  \hspace{1cm} (3.44)

which correspond to the mixture density definition.

3.4.2 Calorically imperfect gases: energy modes and Boltzmann distribution

While we consider mixtures of thermally perfect gases, to compute the mixture energy (and enthalpy) we abandon the simple model of calorically perfect gas based on the linear relation between energy and temperature. Indeed, it is well known that such a model fails to describe the highly non linear features of mixtures of reacting gases. Therefore an approach based on quantum physics is followed.
Quantum physics [3] [94], shows that atoms and molecules have different modes to store energy and that each mode is quantized, i.e. the energy of a molecule or an atom can take only discrete values.

In an atom there are two energy modes:

1. Translational energy mode: associated with the motion of center of mass.
2. Electronic energy mode: associated with the electrons orbit around the nucleus.

For a molecule two additional energy modes should be considered:

3. Rotational energy mode: associated with the rotation of the molecule around the center of mass.
4. Vibrational energy mode: associated with the vibration of the atoms with respect to the equilibrium position within the molecule.

Every energy mode can assume an ensemble of different discrete values (energy levels or states). Each level, in its turn, may manifest itself in a number of different ways, which result in degeneracy of the level.

In a ‘real’ molecule the internal energy modes (rotational, vibrational and electronic) are not truly independent of each other, i.e. the content of an internal energy mode is affected by the state of the other internal modes. However, in the present work we use a simple molecule model, i.e. rotational, vibrational, and electronic energy modes are considered to be decoupled.

Comparing the numerical results derived from this assumption with experimental results [14], in the range of temperatures considered in this work, the error committed is not too large.

Under the previous assumptions, the energy of a particle belonging to the mixture, can be expressed as the sum of the independent contributions of different energy modes:

\[
\hat{\epsilon} = \epsilon^\text{tr} + \epsilon^\text{rot} + \epsilon^\text{vib} + \epsilon^\text{el} + \epsilon^0,
\]  

(3.45)

where superscript (\text{tr}) refers to translational mode, (\text{rot}) to rotational, (\text{vib}) to vibrational and (\text{el}) to electronic. It is customary to express the energies of energy modes with respect to the value they assume at absolute zero (also called the zero-point energy). Therefore, to compute the energy of a particle it is necessary to add the contribution due to the zero-point energy \(\epsilon^0\).

This allows for the introduction of the sensible energy (measured from absolute zero) defined as:

\[
\epsilon = \epsilon^\text{tr} + \epsilon^\text{rot} + \epsilon^\text{vib} + \epsilon^\text{el}.
\]  

(3.46)

The particle’s energies \(\epsilon^\text{tr}, \epsilon^\text{rot}, \epsilon^\text{vib}, \epsilon^\text{el}\) are provided by quantum mechanics and, as stated before, they can assume only a set of discrete values. Obviously, for an atom \(\epsilon^\text{rot} = \epsilon^\text{vib} = 0\).

Consider now a gas containing a certain number of identical particles with number density \(n\). If the internal energy modes are considered uncoupled, the internal energy per unit mass of the gas is expressed as the sum of different contributions:

\[
e = n \epsilon^\text{tr} + n \epsilon^\text{rot} + n \epsilon^\text{vib} + n \epsilon^\text{el} + n \epsilon^0.
\]  

(3.47)
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As already mentioned, \( e^\text{rot} = e^\text{vib} = 0 \) if the particles of the gas are atoms.

If the gas is in thermal equilibrium, statistical mechanics provides a simple expression for the internal energy per unit mass. This occurs because, by definition of thermal equilibrium, the most probable distribution of particles among energy levels (macrostate) is the Boltzmann distribution:

\[
n_j = n \frac{g_j \exp \left( -\epsilon_j / k_B T \right)}{Q}.
\]  

(3.48)

Here \( n_j \) is the number density of the particles with energy \( \epsilon_j \), \( g_j \) is the degeneracy of the \( j \)th energy level, \( k_B \) is Boltzmann’s constant and \( Q \) is the partition function defined as:

\[
Q = \sum_j g_j \exp \left( -\epsilon_j / k_B T \right).
\]

(3.49)

The Boltzmann distribution is uniquely defined if the temperature of the system is known. Since the Boltzmann distribution requires only one parameter to be defined (under thermal equilibrium conditions), it is possible to use the temperature to specify uniquely the particles energy distribution and, as consequence, the internal energy of the system.

If the internal energy modes are decoupled, four contributions to the molecule energy should be accounted for \((\epsilon^\text{tr}_\alpha, \epsilon^\text{rot}_\beta, \epsilon^\text{vib}_\gamma, \epsilon^\text{el}_\delta)\), to which four degeneracies will be associated \((g^\text{tr}_\alpha, g^\text{rot}_\beta, g^\text{vib}_\gamma, g^\text{el}_\delta)\), leading to the following simple form of the partition function:

\[
Q = \sum_\alpha \sum_\beta \sum_\gamma \sum_\delta g^\text{tr}_\alpha g^\text{rot}_\beta g^\text{vib}_\gamma g^\text{el}_\delta \exp \left[ -(\epsilon^\text{tr}_\alpha + \epsilon^\text{rot}_\beta + \epsilon^\text{vib}_\gamma + \epsilon^\text{el}_\delta)/kT \right] = Q^\text{tr} Q^\text{rot} Q^\text{vib} Q^\text{el}.
\]

(3.50)

As an example, if we consider the vibrational levels (identified with the index \( \beta \)) of a gas made by molecules, the number density \( n_\beta \) of molecules with vibrational energy equal to \( \epsilon^\text{vib}_\beta \) is:

\[
n_\beta = n \frac{g^\text{vib}_\beta \exp \left( -\epsilon^\text{vib}_\beta / kT \right)}{Q^\text{vib}}.
\]

(3.51)

The vibrational partition function is expressed as:

\[
Q^\text{vib} = \sum_{\beta=1}^{N_v} g^\text{vib}_\beta \exp \left( -\epsilon^\text{vib}_\beta / kT \right),
\]

(3.52)

where \( N_v \) is the number of vibrational levels. The main practical interest of the definition of the partition function is that from its knowledge, the thermodynamics properties of the system can be computed.

### 3.4.3 Internal energy, enthalpy, specific heat

The translational internal energy is the same for both atoms and molecules and its value per unit mass is:

\[
\epsilon^\text{tr}_i = \frac{3}{2} R_i T.
\]

(3.53)
For linear molecules behaving as a rigid rotator, the rotational internal energy per unit mass can be written as:

\[ e_{rot}^i = R_i T \left( 1 - \frac{\theta_{rot}^i}{\theta_{rot}^i + 3T} \right), \]  

(3.54)

where \( \theta_{rot}^i \) is the rotational characteristic temperature.

As far as the vibrational energy is concerned, diatomic molecules (\( \text{O}_2, \text{N}_2, \text{NO}, \text{CO} \)) possess only a single vibrational mode. On the other hand molecules like \( \text{CO}_2 \), which is a linear triatomic molecule, several vibrational modes can be observed. Three vibrational modes are considered: two stretching modes vibrate parallel to the molecule axis, one symmetric and the other antisymmetric, and in addition a doubly degenerate bending mode vibrates in two planes at right angles, perpendicular to the molecule axis. Therefore indicating with \( m \) the vibrational mode, the vibrational energy per unit mass reads:

\[ e_{vib}^i = \sum_m \frac{R_i \theta_{vib}^i m}{\exp \left( \frac{\theta_{vib}^i m}{T} \right) - 1}, \]  

(3.55)

where \( \theta_{vib}^i m \) is the vibrational characteristic temperature of the mode \( m \) of the species \( i \).

The electronic internal energy per unit mass reads:

\[ e_{el}^i = R_i \sum_{h=1}^{\infty} \frac{g_{el}^i h^i \theta_{el}^{i h}}{\exp \left( \frac{\theta_{el}^{i h}}{T} \right) - 1}, \]  

(3.56)

where \( g_{el}^i h \) is the degeneracy for electronic level \( h \) and \( \theta_{el}^{i h} \) is its characteristic electronic temperature. The series in Eq. (3.56) diverges and has to be truncated. The criteria used here is to take into account the strictly necessary minimum number of electronic levels that produces a non negligible change of energy in the temperature range of interest \([14, 89]\).

The zero-point energy \([11]\) of species \( i \) is computed from the heat of formation of such species at absolute zero (\( \Delta h_0^F, i \)), easily available in the literature.

The enthalpy of the species \( i \) is by definition \( h_i = e_i + p_i / \rho_i \) that using equation of state reads:

\[ h_i = e_i + R_i T. \]  

(3.57)

The mixture energy and enthalpy per unit mass are:

\[ e = \sum_{i=0}^{N_s} y_i e_i \quad \text{and} \quad h = \sum_{i=0}^{N_s} y_i h_i = e + \frac{P}{\rho} = e + R_i T. \]  

(3.58)

The single species constant pressure specific heats is, by definition:

\[ c_{p,i} = \frac{\partial h_i}{\partial T} \bigg|_p, \]  

(3.59)

function of temperature only, as it is the case of internal energy and enthalpy. In a mixture under chemical non equilibrium conditions, the composition is function not only of two thermodynamic variables \((p, T)\) as in the case of an equilibrium mixture, but also of the previous system history. The same happens for the mixture enthalpy that by Eq. (3.58) depends on the composition. For this reason a definition of mixture constant pressure specific heat does not
make sense. Instead of it, we can define a frozen constant pressure specific heat considering the mixture as if the composition is fixed:

\[ c_{p,fr} = \left( \frac{\partial h}{\partial T} \right)_{p,y} = \sum_{i=0}^{N_s} y_i \left( \frac{\partial h_i}{\partial T} \right)_{p} = \sum_{i=0}^{N_s} y_i c_{p,i}. \]  

(3.60)

The constant volume specific heat \( (c_v) \) follows from analogous arguments.

### 3.5 Transport properties

Transport fluxes, i.e. the diffusion fluxes \( J_i \), the stress tensor \( \hat{\tau} \), the heat flux \( q \) and the related transport coefficients, are computed by the kinetic theory of gases [47] [27] [63]. Diffusion is the transport of mass from one region to another, viscous stresses are the transport of momentum through the gas and conduction heat flux is the transport of thermal energy.

In the following we remind to the reader the main aspects of kinetic theory in order to simplify the presentation of the transport coefficients used to obtain the results presented in chapter 4, 5 and 6. Our derivation represents a summary of a much wider field described in detail in classical text books and recent publications to which the interest reader is referred for more details [63, 47, 164, 89, 11, 152].

#### 3.5.1 Molecular description

The starting point of the kinetic theory is the Boltzmann equation which describes a mixture from a molecular point of view. The exact representation of the mixture dynamical state is impossible in practice, because it requires the knowledge of velocity, position and internal state of every particle in the mixture. Henceforth, following a continuum description of the system, we prefer to use a statistical approach that gives the average behavior of the system under investigation.

Consider a particle belonging to species \( i \): its state is completely characterized by its position \( r \), its velocity \( c_i \) and its internal quantum state \( \ell \) (each species having a certain number of internal states). In the present work the internal states of the particles are not taken into account, which consists in neglecting the internal energy of atoms and molecules present in the mixture to which the results of the present theory should be applied. In general conditions, both elastic and inelastic collisions may take place involving the mixture particles. During elastic collisions the internal degrees of freedom remain unchanged, resulting in a passive transport of internal energy. On the other hand, during inelastic collisions variations in the internal degrees of freedom are induced by the particles impact. The influence of inelastic collision on transport phenomena is investigated in Refs. [41, 47, 105, 164], where a rigorous treatment including internal energies is presented leading to collision integrals difficult to estimate with sufficient accuracy in high-temperature regions. Therefore in the following we consider only elastic encounters between particles without accounting for their internal degrees of freedom. Once the transport coefficient determined, the influence of internal energy will be accounted for using the Eucken correction [61, 27, 47, 63].
3.5.1. Molecular description

Under this assumption, the state of particle $i$ is completely characterized by its position $\mathbf{r}$ and its velocity $\mathbf{c}_i$. The six-dimensional space having as components the three components of $\mathbf{r}$ and the three components of $\mathbf{c}_i$ is called the phase space. Inspired by the philosophy of the continuum description, we introduce a distribution function $f_i(\mathbf{r}, \mathbf{c}_i, t)$ that gives the expected amount of $i$ species particles in an elementary volume $d\mathbf{r}d\mathbf{c}_i$ of the phase space. In other words, $f_i(\mathbf{r}, \mathbf{c}_i, t)d\mathbf{r}d\mathbf{c}_i$ is the expected number of $i$ species particles in the volume element $d\mathbf{r}$ located at $\mathbf{r}$, whose velocities lies in the interval $d\mathbf{c}_i$ about velocity $\mathbf{c}_i$ at the time $t$.

Integration with respect to $\mathbf{c}_i$ gives the total number of $i$ species particles in the volume $d\mathbf{r}$; to obtain the number density $n_i$ of $i$ species we need to divide this number by $d\mathbf{r}$:

$$n_i(\mathbf{r}, t) = \int f_i(\mathbf{r}, \mathbf{c}_i, t)d\mathbf{c}_i. \quad (3.61)$$

The partial density is $\rho_i = m_in_i$ where $m_i$ is the mass of the $i$ species particle, while the global density follows from Eq. (3.44).

If $\phi_i(\mathbf{r}, \mathbf{c}_i, t)$ is a generic property for species $i$, function of the particle velocity and position, its average value is:

$$\overline{\phi_i}(\mathbf{r}, t) = \frac{1}{n_i(\mathbf{r}, t)} \int \phi_i(\mathbf{r}, \mathbf{c}_i, t)f_i(\mathbf{r}, \mathbf{c}_i, t)d\mathbf{c}_i. \quad (3.62)$$

The $i$ species average velocity is ($\phi_i = \mathbf{c}_i$):

$$\mathbf{u}_i(\mathbf{r}, t) = \frac{1}{n_i(\mathbf{r}, t)} \int \mathbf{c}_i f_i(\mathbf{r}, \mathbf{c}_i, t)d\mathbf{c}_i. \quad (3.63)$$

The mixture average velocity is defined as:

$$\mathbf{u}(\mathbf{r}, t) = \frac{1}{\rho(\mathbf{r}, t)} \sum_{i=1}^{N_i} \rho_i(\mathbf{r}, t)\mathbf{u}_i(\mathbf{r}, t). \quad (3.64)$$

The difference between the $i$ species particle velocity and the mixture average velocity is the peculiar velocity: $\mathbf{C}_i = \mathbf{c}_i - \mathbf{u}$, which is linked to the thermal motion of the molecules. The translational temperature $T_i$ of the species $i$ is a measure of its translational internal energy and is defined as ($\phi_i = 1/2m_iC_i^2$):

$$\frac{3}{2}k_B T_i(\mathbf{r}, t) = \frac{1}{n_i(\mathbf{r}, t)} \int \frac{1}{2}m_iC_i^2 f_i(\mathbf{r}, \mathbf{c}_i, t)d\mathbf{c}_i. \quad (3.65)$$

Under general non equilibrium conditions, the temperature of different species may assume different values. On the other hand, under translational thermal equilibrium, thanks to the short relaxation time of translational energy exchanges through collisions, the translational temperature of different species assumes the same value. In this work we assume a unique translational temperature for all the species: $T_i = T \forall i$.

---

1If the internal degrees of freedom of colliding particles would have been considered, a different distribution function should have been defined. Indeed, in this case we would have need to known the expected number of $i$ species particles in the quantum state $i$ in the volume element $d\mathbf{r}$ located at $\mathbf{r}$, whose velocities lies in the interval $d\mathbf{c}_i$ about velocity $\mathbf{c}_i$ at the time $t$, given by $f_i(\mathbf{r}, \mathbf{c}_i, t)d\mathbf{r}d\mathbf{c}_i$. 

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3.5.2 Transport fluxes definition

In a gas under general conditions, gradients exist in one or more of the macroscopic physical properties of the system: composition, velocity, temperature. The gradients of these properties result in the molecular transport of mass, momentum and energy through the mixture. The flux vector associated with the transport of a generic property \( \varphi_i(r, c_i, t) \) is:

\[
\varphi_i(r, t) = \int \varphi_i(r, c_i, t) C_i f_i(r, c_i, t) dc_i.
\] (3.66)

We wish to highlight that the velocity with which \( \varphi_i \) is transported is the peculiar velocity \( C_i \) of \( i \) species particles because we consider the transport of \( \varphi_i \) with respect to a reference frame moving with the mixture average velocity \( u \).

For instance, the transport of mass of the \( i \)th species is obtained by setting \( \varphi_i = m_i \) and is given by:

\[
J_i(r, t) = \int m_i C_i f_i(r, c_i, t) dc_i.
\] (3.67)

The transport of momentum is obtained by setting \( \varphi_i = m_i C_i \) and reads:

\[
\hat{P}_i(r, t) = \int m_i C_i C_i f_i(r, c_i, t) dc_i.
\] (3.68)

The quantity \( \hat{P}_i \) is the \( i \) species pressure tensor. It is a symmetric tensor and it is the sum of the normal stresses and the shear stresses. The arithmetic mean value of the tensor trace is the thermodynamic pressure of species \( i \). The pressure tensor for the whole mixture is the sum of the species pressure tensors.

The transport of the \( i \) species energy is obtained by setting \( \varphi_i = \frac{1}{2} m_i C_i^2 \) and reads:

\[
q_i(r, t) = \int \frac{1}{2} m_i C_i^2 C_i f_i(r, c_i, t) dc_i.
\] (3.69)

The sum over all the species gives the mixture heat flux vector.

3.5.3 Boltzmann equation

In the previous section we introduced the transport fluxes of particles mass, momentum and energy leading to the definition of the species diffusive fluxes [Eq. (3.67)], the species pressure tensor [Eq. (3.68)] and the species heat flux [Eq. (3.69)]. The expressions provided for the computation of these quantities depend on the distribution functions \( f_i(r, c_i, t) \), which still need to be determined. To supply this need, Boltzmann derived the governing equation for the distribution function, which may be written as:

\[
\frac{\partial f_i}{\partial t} + c_i \cdot \nabla_r f_i + F_i \cdot \nabla_c f_i = \sum_{j=1}^{N_s} J(f_i, f_j).
\] (3.70)

The left hand side is the streaming operator and gives the change of the distribution function due to convection and to the effect of the body forces \( F_i \); the right hand side is the collisional
operator and gives the change in the distribution function due to the processes of collision happening into the flow. The collisional operator generally takes into account elastic collisions, inelastic collisions (collisions that change the internal state of the involved particles) and reactive collisions (collisions that change the chemical nature of the involved particles). As previously discussed, in the present work only elastic collisions are taken into account in the collisional operator.

Since the Boltzmann equation describes the evolution of the distribution function, multiplying both sides of such equation by \( \varphi_i \) and integrating with respect to \( c_i \), we obtain an equation describing the evolution of \( \varphi_i(r, t) \).

\[
\int \varphi_i(r, c_i, t) \left( \frac{\partial f_i}{\partial t} + c_i \cdot \nabla_r f_i + F_i \cdot \nabla_c f_i \right) dc_i = \int \varphi_i(r, c_i, t) \sum_{j=1}^{N_x} J(f_i, f_j) dc_i.
\] (3.71)

The equation of change for the mixture property \( \varphi(r, t) \) is obtained by summing up over all the species. The mixture governing equations (Sec. 3.1.1.1) can be retrieved following this procedure. For instance, identifying \( \varphi_i \) with the mass \( m_i \) of species \( i \), we obtain the species continuity equation. Summing over all the species we retrieve the global continuity equation. Furthermore, identifying \( \varphi_i \) with the momentum \( m_i c_i \) and summing over all the species, the mixture momentum equation is recovered. Finally identifying \( \varphi_i \) with the internal energy \( \frac{1}{2} m_i C_i^2 \) and summing over the species, the mixture energy equation is recovered. We remark that in retrieving the global continuity equation, the momentum equation and the energy equation, the collisional operator plays no role because mass, momentum and energy are conserved in collisions (collisional invariants). This is not true for species continuity equations if there are reactive collisions.

At this point the logic behind the use of kinetic theory in the framework of this thesis should appear more clear. Indeed, starting from a molecular description [Sec. 3.5.1] of a mixture of reacting gases we have defined a way to compute the transport fluxes [Sec. 3.5.2] of quantities of interest in fluid dynamics like mass, momentum and energy. Furthermore, thanks to the Boltzmann equation, we observed the possibility, starting from a molecular description, to retrieve the macroscopic governing equations of mixtures of reacting gases. On the other hand, in Sec. 3.1.1.1 we based the derivation of the Navier-Stokes equations following a macroscopic approach based on local balances made on a suitable control volume. In this way we retrieved a system of equations in which transport coefficients appears as the result of a suitable choice of the form of transport fluxes, expressed as linear functions of the macroscopic variable gradients [Eqs. (3.6)-(3.7)]. By comparing these sets of equations and after identification of the transport coefficients, kinetic theory provides a way to close the system of equations obtained following the macroscopic control volume approach\(^1\). The final expressions of transport coefficients depend on the knowledge of the distribution function \( [f_i(r, c_i, t)] \) obtained as the solution of the Boltzmann equation following the Chapman-Enskog method recalled in the following section.

\(^1\)To be more precise, the so obtained form of the transport coefficients is not sufficient to practically close the set of Navier-Stokes equations. Indeed, the transport properties depends on the dynamics of the interaction between particles described by the particle interaction potential. As a consequence, even if kinetic theory provides a way to compute transport properties, their practical calculation depends on the knowledge of the interaction potentials which are not always easy to find.
3.5.4 Chapman-Enskog solution

Consider a gas at equilibrium, where there are no gradients in composition, velocity and temperature, then the distribution function $f_i$ reduces to the Maxwellian distribution:

$$f_i^M = n_i \left( \frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left( -\frac{1}{2} \frac{m_i C_i^2}{k_B T} \right). \quad (3.72)$$

At equilibrium, $f_i^M$ is independent of time and this constitutes a state of overall balance in the collision processes: the number of molecules of species $i$ in a particular velocity range which are lost due to collisions is exactly compensated by the number created by the collisional processes.

Usually we are interested in the investigation of gases which are under conditions only slightly different from equilibrium. In such a case the Chapman-Enskog method for the solution of the Boltzmann equation allows to compute the distribution function $f_i(r, c, t)$ and consequently gives the possibility to compute the transport fluxes (3.67), (3.68), and (3.69) as linear functions of the macroscopic variables gradients through some proportionality scalar quantities, i.e. the transport coefficients.

In non equilibrium conditions, the distribution function is developed in a series. Stopping the expansion to the first order we have:

$$f_i = f_i^M (1 + \phi_i), \quad (3.73)$$

where the expression of $\phi_i$ can be found in several classical references [47, 63] or more recent publications [152, 89, 92]. The approximate solution of the Boltzmann equation [47, 63] is obtained by inserting the series expansion into Eq. (3.70).

If the Maxwell distribution is used into the derivation of the mixture governing equations using Eqs. (3.71), they reduce to the Euler equations which are characterized by the absence of the transport fluxes, i.e. Eqs. (3.67), (3.69) are identically zero and Eq. (3.68) is equal to the thermodynamic pressure tensor $p I$.

If the approximate solution $f_i = f_i^M (1 + \phi_i)$ is inserted into Eqs. (3.71), they reduce to the Navier-Stokes equations. The diffusion flux, the pressure viscous tensor and the heat flux are obtained by computing the transport fluxes (3.67), (3.68), and (3.69) with the approximate value of the distribution function.

3.5.5 Viscous stress tensor and heat flux

The viscous stress tensor in the Chapman-Enskog approximation is computed by means of Eq. (3.68) summing up over all the species and reads:

$$\dot{\tau} = \mu \left( \nabla u + (\nabla u)^T \right) + \left( \kappa - \frac{2}{3} \mu \right) (\nabla \cdot u) I, \quad (3.74)$$

where $\mu$ is the coefficient of shear viscosity and $\kappa$ is the coefficient of bulk viscosity. The contribution to the viscous stress tensor proportional to the bulk viscosity $[\kappa (\nabla \cdot u)]$ is neglected in all the computations presented in this work, following the Stokes hypothesis. The viscosity
3.5.5. Viscous stress tensor and heat flux

\( \mu \) is computed with the mixture rules of Yos [163], as listed by Gupta et al. [61]. The heat flux vector is computed by means of Eq. (3.69) neglecting pressure diffusion and summing up over all the species:

\[
q = -\lambda \nabla T + \sum_{i=1}^{N_{s}} h_i J_i - p \sum_{i=1}^{N_{s}} D_i^T d_i, \tag{3.75}
\]

where the \( D_i^T \) accounts for thermal diffusion. In the results presented in the remaining part of the manuscript we neglect the contribution to the heat flux due to the thermal diffusion obtaining the following expression:

\[
q = -\lambda \nabla T + \sum_{i=1}^{N_{s}} h_i J_i. \tag{3.76}
\]

Here \( \lambda \) is the coefficient of thermal conductivity and it is computed as the result of the following sum

\[
\lambda = \lambda_h + \lambda_{el} + \lambda_{rot} + \lambda_{vib} + \lambda_E. \tag{3.77}
\]

The heavy particles thermal conductivity (\( \lambda_h \)) is evaluated by means of the Yos mixture rule [163]. The electron thermal conductivity \( \lambda_E \) is computed with the formulas due to Devoto [38], where two non-vanishing Sonine polynomial contributions were found to yield accurate results [17]. The rotational, vibrational and electronic thermal conductivities \( \lambda_{rot}, \lambda_{vib} \) and \( \lambda_{el} \) are modeled by means of the Eucken approximation [61, 27, 47, 63].

### 3.5.5.1 Diffusion fluxes

A detailed description of diffusion phenomena has been given in chapter 3 for mixtures of both neutral and charged components under thermochemical non equilibrium. In this section we consider also the case of chemical non equilibrium and we briefly recall how the expressions of the species mass transport fluxes [Eq. (3.67)] have been computed both in the case of a plasma flowing in an ICP facility and for a mixture of neutral species along a stagnation line.

#### Inductively coupled plasma flow

In the computational model presented in Sec. 3.2, diffusion fluxes are evaluated using the full Stefan-Maxwell equations introduced in Sec. 2.4, which are mathematically equivalent to the Chapman-Enskog multi-component diffusion expressions [63] resulting from the analysis presented in Sec. 3.5.4. Neglecting pressure and thermal diffusion as well as the effect of the magnetic field [153], from Eq. (2.40) we have

\[
\frac{M}{p} \sum_{i=1}^{N_{s}} \left( x_i M_i J_x - x_t M_t J_x \right) = \nabla x_x + \frac{\rho y x q_t}{p} E_{amb}, \tag{3.78}
\]

where \( M_s \) are the species molar masses, \( M \) the mixture molar mass, \( x_s \) the molar fractions, and \( q_t \) the species charge per unit mass. The binary diffusion coefficients \( D_{st} \) can be further
expressed as a function of the collision integrals [Eq. (2.9)]. Readers eager to reproduce the results obtained in chapter 5 may find detailed curve fits for the collision integrals of air mixtures in Ref. [14].

As said, we assume that no net electric current flows in the poloidal \((r, z)\) plane under conditions of LTE [153]. The ambipolar electric field \(E_{\text{amb}}\) is then determined by imposing the current free assumption [Eq. (2.70)]. Eqs. (3.78–2.70) represent a linear system (one in each coordinate direction) in \(N_{sp} + 1\) unknowns, the diffusion fluxes and the ambipolar electric field, which are solved using an iterative method proposed in Ref. [142], adapted to the case of diffusion in ionized mixtures.

Different physics takes place in the azimuthal direction \((\theta)\), where strong electric currents act. Diffusion is driven by the azimuthal induced electric field [Eq. (3.34)] instead of the poloidal ambipolar field [Eq. (2.70)] and Eqs. (3.78) can be reduced to Ohm’s law in its simplest form

\[
q_e J_e = \sigma E,
\]

which has been used to derive Eq. (3.35). More details about the numerical method used to solve the previous system of equations can be found in Refs. [153] and [37]. As for the electron thermal conductivity, the electrical conductivity \(\sigma\) is computed with the formulas due to Devoto [38], where two non-vanishing Sonine polynomial contributions were found to yield accurate results [17]. Under chemical non equilibrium conditions the gradient of species molar fractions \((\nabla x_s)\) are computed using the solution of Eqs. (3.8).

**Stagnation line flow**

As already discussed in Sec. 3.1.2, the species diffusion fluxes have been computed as the solution of the Stefan-Maxwell equations [Eq. (2.7)] neglecting baro-thermal diffusion. Under thermochemical equilibrium the elemental diffusive fluxes have been computed both as a linear combination of the species ones and using the formulation [Eq. (2.20)] presented in chapter 2.

### 3.6 Numerical methods

In this section we briefly present the numerical techniques used to solve the governing equations presented in Sec. 3.1 and 3.2. The purpose of this part of the manuscript is to remind the reader of the main aspects of the numerical solution strategies adopted, referring the interested reader to already published works [152, 89, 11] for more details.

#### 3.6.1 Inductively coupled plasmas

In Sec. 3.1.1.1 and 3.2 we have presented the full set of governing equations describing the inductively coupled plasma flow model used in this work. In the following we present the numerical techniques used to:

- discretize the governing equations;
3.6.1 Inductively coupled plasmas

Figure 3.5: (a) Multiblock grid used for the discretization of the hydrodynamics equations; (b) Cell-centered finite-volume discretization; (c) stencil for the diffusive fluxes; (d) stencil for the source terms.

- reach a converged solution of the discretized equations through an implicit iterative procedure starting from an arbitrary initial guess.

3.6.1.1 Discretization of the governing equations

As repeatedly said in the previous sections and chapters we wish to solve the governing equations of an inductively coupled plasma flow both in the torch and in the test chamber [Fig. 3.5]. To this end we use a finite volume technique, on a multiblock structured mesh, developed by Magin [89] on the basis of the work performed by Vanden Abeele [152]. In this thesis the approach followed by Magin has been extended including additional elemental continuity equations under LTE and species continuity equations to describe chemical non equilibrium conditions. For this latter improvement, we acknowledge Panesi for his efforts during his Diploma Course project at VKI [109].

Hydrodynamics

We start rewriting the governing equations of ICP flows under a suitable form. From Eqs. (3.1), (3.2), (3.3), (3.4), (3.5), (3.8), and (3.10) we obtain the following conservative axisymmetric form:

$$
\frac{\partial}{\partial t} (rQ) + \frac{\partial}{\partial z} (rF_z^r) + \frac{\partial}{\partial r} (rF_r^r) = \frac{\partial}{\partial z} (rF_z^s) + \frac{\partial}{\partial r} (rF_r^s) + r\Sigma, \quad (3.80)
$$
where $Q$ contains the conservative variables, $F^c_{_c}$ and $F^r_{_c}$ the convective fluxes, $F^d_{_c}$ and $F^r_{_d}$ the diffusive fluxes, and finally $\Sigma$ the source terms$^1$. Their expressions depend on the chemical regime under consideration and read as follows:

**LTE with Constant Elemental Fraction**

\[
Q = \left[ \rho, \rho u, \rho v, \rho w, \rho \left( e + \frac{|v|^2}{2} \right) \right], \quad (3.81a)
\]

\[
F^c_{_c} = \left[ \rho u, \rho u^2 + p, \rho uv, \rho vw, \rho uH \right], \quad (3.81b)
\]

\[
F^c_{_d} = \left[ \rho v, \rho v^2 + p, \rho uv, \rho vw, \rho vH \right], \quad (3.81c)
\]

\[
F^d_{_c} = \left[ 0, \tau_{zz}, \tau_{zr}, \tau_{z\theta}, ur_{zz} + vtr_{zr} + wt_{z\theta} - q_z \right], \quad (3.81d)
\]

\[
F^d_{_d} = \left[ 0, \tau_{rr}, \tau_{r\theta}, ur_{rr} + vtr_{r\theta} + wt_{r\theta} - q_r \right], \quad (3.81e)
\]

\[
\Sigma = \left[ 0, F^L_{_c}, \frac{1}{r} \left( p + \rho w^2 - \tau_{\theta\theta} \right) + F^L_{_d}, \frac{1}{r} (-\rho vw + \tau_{r\theta}) \right], \quad (3.81f)
\]

**LTE with Variable Elemental Fraction**

\[
Q = \left[ \rho Y, \rho u, \rho v, \rho w, \rho \left( e + \frac{|v|^2}{2} \right) \right], \quad (3.82a)
\]

\[
F^c_{_c} = \left[ \rho uY, \rho u^2 + p, \rho uv, \rho uw, \rho uH \right], \quad (3.82b)
\]

\[
F^c_{_d} = \left[ \rho vY, \rho v^2 + p, \rho uv, \rho vw, \rho vH \right], \quad (3.82c)
\]

\[
F^d_{_c} = \left[ -J^c_r, 0, \tau_{zz}, \tau_{zr}, \tau_{z\theta}, ur_{zz} + vtr_{zr} + wt_{z\theta} - q_z \right], \quad (3.82d)
\]

\[
F^d_{_d} = \left[ -J^d_r, 0, \tau_{rr}, \tau_{r\theta}, ur_{rr} + vtr_{r\theta} + wt_{r\theta} - q_r \right], \quad (3.82e)
\]

\[
\Sigma = \left[ 0, 0, F^L_{_c}, \frac{1}{r} \left( p + \rho w^2 - \tau_{\theta\theta} \right) + F^L_{_d}, \frac{1}{r} (-\rho vw + \tau_{r\theta}) \right], \quad (3.82f)
\]

**Chemical Non Equilibrium**

\[
Q = \left[ \rho Y_s, \rho u, \rho v, \rho w, \rho \left( e + \frac{|v|^2}{2} \right) \right], \quad (3.83a)
\]

\[
F^c_{_c} = \left[ \rho uY_s, \rho u^2 + p, \rho uv, \rho uw, \rho uH \right], \quad (3.83b)
\]

\[
F^c_{_d} = \left[ \rho vY_s, \rho v^2 + p, \rho uv, \rho vw, \rho vH \right], \quad (3.83c)
\]

\[
F^d_{_c} = \left[ -J^c_r, 0, \tau_{zz}, \tau_{zr}, \tau_{z\theta}, ur_{zz} + vtr_{zr} + wt_{z\theta} - q_z \right], \quad (3.83d)
\]

\[
F^d_{_d} = \left[ -J^d_r, 0, \tau_{rr}, \tau_{r\theta}, ur_{rr} + vtr_{r\theta} + wt_{r\theta} - q_r \right], \quad (3.83e)
\]

\[
\Sigma = \left[ \dot{\omega}_s, 0, F^L_{_c}, \frac{1}{r} \left( p + \rho w^2 - \tau_{\theta\theta} \right) + F^L_{_d}, \frac{1}{r} (-\rho vw + \tau_{r\theta}) \right], \quad (3.83f)
\]

where $c \in E$ and $s \in S$.

Consider the integral of Eq. (3.80) over a control volume $\Omega$. Using the Gauss’ theorem we obtain

\[
\frac{\partial}{\partial t} \int_{\Omega} rQ \, d\Omega + \oint_{S=\partial\Omega} rF^c \, dS = \oint_{S=\partial\Omega} rF^d \, dS + \int_{\Omega} r\Sigma \, d\Omega, \quad (3.84)
\]

$^1$In Eq. (3.80) we have introduced a time dependent term $(\partial rQ/\partial t)$ which is not present in the governing equations presented in Sec. 3.1.1.1. The reason for this is that, even though we search for the steady solution of Eq. (3.80), we will use a time marching technique which mimics the temporal evolution of the solution of Eq. (3.80), through a transient phase and towards a steady state.
where $S$ is the border of $\Omega$, which in a two dimensional case corresponds to a polygon with four sides ($\Omega$ being a surface element). In Eq. (3.84), $F^c = F^c_r n_r + F^c_z n_z$ and $F^d = F^d_r n_r + F^d_z n_z$, $n$ being the local unit vector normal to each side of $S$, defined by its components as follows: $n \equiv (n_z, n_r, 0)$. The next step towards the discretization of the governing equations (3.80) consists in spatially discretizing the integral equation (3.84) by means of a cell-centered finite-volume method on the quadrilateral cells of the structured mesh presented in Fig. 3.5. This leads to the following form

$$\Omega_i \frac{\partial Q_i}{\partial t} + \sum_{j=1}^{n_{side}} \ell_{ij} r_{ij} F^c_{ij} = \sum_{j=1}^{n_{side}} \ell_{ij} r_{ij} F^d_{ij} + \Omega_i r_i \Sigma_i, \quad (3.85)$$

where $n_{side} = 4$ and the index $i$ runs over all the cells of the multiblock mesh used for the solution of the hydrodynamic equations. To obtain the previous equation we have considered that the volume $\Omega$ is fixed in time and in addition we have implicitly replaced the local value of $rQ$ and $r\Sigma$ by their averages on the volume $\Omega_i$, defined as follows

$$r_i Q_i = \frac{1}{\Omega_i} \int_\Omega rQ \, d\Omega, \quad (3.86)$$

$$r_i \Sigma_i = \frac{1}{\Omega_i} \int_\Omega r\Sigma \, d\Omega. \quad (3.87)$$

For what concern the integrals on $S$, we have firstly decomposed the integral in four contributions on each of the quadrilateral side. Secondly, we have replaced the local values of $rF^c$ and $rF^d$ by their average values as follows

$$\oint_{S_i = \partial \Omega_i} rF^c \, dS = \sum_{j=1}^{n_{side}} \ell_{ij} \int_{\ell_i} rF^c \, d\ell = \sum_{j=1}^{n_{side}} \ell_{ij} r_{ij} F^c_{ij}, \quad (3.88)$$

The final result of the discretization procedure is to provide a form of the discretized equations which fits within the formalism of a suited numerical technique allowing for the determination of the steady state approximate solution of Eq. (3.80). To this end we collect the diffusive terms ($F^c$ and $F^d$) together with the source terms ($\Sigma$) in a single term known as ‘residual’ and indicated in the present case with the symbol $R_H$ to highlight its relation with the hydrodynamic description of the plasma. Eq. (3.85) is therefore simplified to

$$\frac{\partial Q_i}{\partial t} = -R_{H_i}. \quad (3.89)$$

Obviously, when a steady state is reached, the condition $\partial / \partial t = 0$ implies $R_{H_i} = 0$. As will be shown in Sec. 3.6.1.2, the implicit time marching solution technique, used to obtain the approximate steady solution of Eq. (3.80), is based on this simple observation.

To determine $R_H$ we need to compute the diffusive and convective fluxes at the cell interfaces as well as the source terms in the center of the cell. Each of these contributions requires an appropriate discretization technique. Hereafter we present the main aspects of the discretization techniques adopted in this work.
Chapter 3. Governing Equations

Convective fluxes discretization

The convective fluxes are the most difficult to discretize. In the case of reacting flows, their intrinsic nonlinearity combined with the need of sufficient accuracy in the resolution of boundary layers, impose strong requirements for the construction of suitable schemes. There exists a vast literature concerning a variety of schemes proposed by several authors for the discretization of convective fluxes. A detail description of the theory proposed in these contributions is out of the scopes of the present manuscript and we refer the interested reader to classical textbooks [2, 147, 159] or more recent publications [11, 152, 89].

During the research activity performed in the framework of this thesis we have used at least two schemes for the discretization of the convective fluxes: the pressure stabilized solver presented by Vanden Abeele and Degrez [153] and an AUSM scheme presented by Magin [89] adapted to low speed regimes [148]. The latter scheme has been used to investigate some supersonic flow conditions not presented in this manuscript, but also to perform several low subsonic computations. To investigate conditions under chemical non equilibrium and chemical equilibrium with variable elemental fraction, we have extended the AUSM scheme with viscous preconditioning, presented in Ref. [89]. This easy extension [11] is simply done by modifying the convected quantity $\Psi$, including either the species mass fractions ($y_s$) or element mass fractions ($Y_c$).

The discretized fluxes are expressed in terms of variables reconstructed to the left and right of the cell interface. Variables are reconstructed using a second-order Total Variation Diminishing (TVD) discretization formula [152, 89].

Diffusive fluxes discretization

The diffusive fluxes evaluated at the cell interfaces are discretized in a centered manner. Using Gauss’ theorem to compute the divergence of $q_e$ and $q_r$ on the dual surface indicated in Fig. 3.6, we easily obtain a discretization of the derivatives ($\partial/\partial z$ and $\partial/\partial r$) of a scalar quantity $q$ as follows

$$\frac{\partial q}{\partial z} = \frac{1}{A} \left[ q_w (r_4 - r_1) + q_s (r_3 - r_4) + q_e (r_2 - r_3) + q_n (r_1 - r_2) \right], \quad (3.90a)$$

$$\frac{\partial q}{\partial r} = -\frac{1}{A} \left[ q_w (z_4 - z_1) + q_s (z_3 - z_4) + q_e (z_2 - z_3) + q_n (z_1 - z_2) \right], \quad (3.90b)$$

where $q_n$ and $q_s$ are evaluated by the following averages

$$q_n = \frac{1}{4} (q_{nw} + q_{ne} + q_e + q_{sw}) \quad \text{and} \quad q_s = \frac{1}{4} (q_w + q_e + q_{se} + q_{sw})$$

and the coordinates of the corner points of the dual cell are obtained as an average of the related cell centers, i.e.

$$r_1 = \frac{1}{2} (r_{nw} + r_w), \quad r_2 = \frac{1}{2} (r_{ne} + r_e), \quad r_3 = \frac{1}{2} (r_e + r_{se}), \quad \text{and} \quad r_4 = \frac{1}{2} (r_{sw} + r_n).$$

A similar strategy is followed for the star topology arising when the flow around the probe held in the test chamber is analyzed [89].
3.6.1. Inductively coupled plasmas

**Source term discretization**

The average value of the source terms, to be calculated in each cell, is retrieved by computing the source term with the cell centers values. For those source terms involving gradients, we again used the discretization formulae presented in Eqs. (3.90) but applied on a different stencil [Fig. 3.6].

**Electromagnetics**

The mesh used to discretize the electromagnetic field equations is made by a single block and covers a space including the torch and its close neighborhood as shown in Fig. 3.6.

![Figure 3.6: Electromagnetic far-field computational domain.](image)

This mesh consists in quadrilaterals cells and within the torch it overlaps the first block of the flowfield mesh shown in Fig. 3.6. The main reason for this choice [152] is that the extension of the outer boundary of the computational domain is chosen to be sufficiently far from the coils region, in such a way that the electromagnetic field may be supposed to be vanishing at that location. In this sense the boundary of the computational domain can be considered as belonging to a sort of 'far-field'. As a consequence, this model leads to the so called far field approach.

The practical computation of the electric field \( E \), solution of Eq. (3.35) proceeds as follows. Firstly, the Electric field is split into two contributions related to the electric field induced by the coils \( E_C \) and the one induced by the plasma \( E_p \), i.e.

\[
E = E_c + E_p. \tag{3.91}
\]

Then, the part related to the coils \( E_C \) is obtained summing the contributions of every coil. Each coil is considered as being an infinitely thin current loop [Sec. 3.2] producing an electric field which has an analytical expression derived from the Biot-Savart law. Then, the part related to the plasma \( E_p \) is obtained as the solution of the following equation, obtained substituting Eq. (3.91) into Eq. (3.35)

\[
\frac{\partial^2 E_p}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial E_p}{\partial r} \right) - \frac{1}{r^2} E_p - i\mu_0 2\pi f \sigma (E_c + E_p) = 0, \tag{3.92}
\]
where, inline with the far field approach previously described, \( E_p \) is set to zero on the mesh outer boundaries. The previous equation is discretized on the mesh presented in Fig. 3.6 using a cell-centered finite volume method in a similar way as done for the hydrodynamic equations in the previous section. As a consequence, the discretized equation can be written under a residual form collecting the discretizations of each term present in Eq. (3.92) into a single cell residual \( R_{E_i} \). Then the discretized form of Eq. (3.92) can be written as

\[
R_{E_i} = 0 \quad (3.93)
\]
in each cell \((i)\) of the electromagnetic computational domain.

### 3.6.1.2 Solution of the discretized equations

A strategy must be selected to solve the discretized equations presented in the previous two sections for both the hydrodynamic and electromagnetic fields. Usual solution techniques in CFD mimic the unsteady nature of the flow governing equations. Indeed, starting from an arbitrary initial guess, a marching procedure is used to reach, after a reasonable number of iterative steps, a steady converged approximate solution of the flow equations. In the present case, the governing equations are characterized by a highly nonlinear character coupled with the high computational cost of the evaluation of thermodynamic and transport properties. Henceforth, the selected technique should minimize the number of iterative steps required to end the marching procedure to reduce the solution computational time to a limited acceptable value. To this end we have opted for an implicit time marching technique for both the hydrodynamic and electromagnetic field recalled hereafter.

**Hydrodynamics**

The discretized Navier-Stokes equations are solved using a time marching technique applied to a modified form of Eq. (3.89). Indeed a useful change of variable

\[
dQ = (\frac{\partial Q}{\partial U})dU
\]

is introduced. The variables contained in the array \( U \) are more suitable for the computation of the transport and thermodynamics properties of reacting flows and are selected depending on the chemical regime as follows :

- **LTE Constant Elemental Fraction** : \( U^T = (\Delta p, \rho u, \rho v, \rho w, T) \),
- **LTE Variable Elemental Fraction** : \( U^T = (Y^c, \Delta p, \rho u, \rho v, \rho w, T) \),
- **Chemical Non Equilibrium** : \( U^T = (Y_s, \Delta p, \rho u, \rho v, \rho w, T) \),

where the use of \( \Delta p = p - p_{\text{ref}} \), \( p_{\text{ref}} \) being a reference pressure, allows to avoid round-off errors when pressure variations are small, as in the low Mach number regime. The form of the transformation matrix\(^1\) \((\frac{\partial Q}{\partial U})\) depends on the chemical regime and in each case reads as follows:

\(^1\)The transformation matrix \((\frac{\partial Q}{\partial U})\) is computed by finite differences when needed.
### 3.6.1. Inductively coupled plasmas

**LTE Constant Elemental Fraction**

\[
\frac{\partial Q}{\partial U} = \begin{bmatrix}
\frac{\partial \rho}{\partial \rho} & 0 & 0 & 0 & \frac{\partial \rho}{\partial \rho} \\
0 & 1 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 \\
\frac{\partial}{\partial \rho} [\rho (e + \frac{\|u\|^2}{2})] & u & v & w & \frac{\partial}{\partial \rho} [\rho (e + \frac{\|u\|^2}{2})]
\end{bmatrix}.
\] (3.94)

**LTE Variable Elemental Fraction**

\[
\frac{\partial Q}{\partial U} = \begin{bmatrix}
\frac{\partial \rho Y_c}{\partial \rho Y_c} & \frac{\partial \rho Y_c}{\partial Y_c} & 0 & 0 & 0 & \frac{\partial \rho Y_c}{\partial \rho} \\
\frac{\partial \rho Y_c}{\partial Y_c} & \frac{\partial \rho Y_c}{\partial \rho Y_c} & 0 & 0 & 0 & \frac{\partial \rho Y_c}{\partial \rho} \\
0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 \\
\frac{\partial}{\partial \rho} [\rho (e + \frac{\|u\|^2}{2})] & \frac{\partial}{\partial \rho} [\rho (e + \frac{\|u\|^2}{2})] & u & v & w & \frac{\partial}{\partial \rho} [\rho (e + \frac{\|u\|^2}{2})]
\end{bmatrix}.
\] (3.95)

**Chemical Non Equilibrium**

\[
\frac{\partial Q}{\partial U} = \begin{bmatrix}
\frac{\partial \rho_\gamma}{\partial \rho_\gamma} & \frac{\partial \rho_\gamma}{\partial \rho_\gamma} & 0 & 0 & 0 & \frac{\partial \rho_\gamma}{\partial \rho} \\
\frac{\partial \rho_\gamma}{\partial \rho_\gamma} & \frac{\partial \rho_\gamma}{\partial \rho_\gamma} & 0 & 0 & 0 & \frac{\partial \rho_\gamma}{\partial \rho} \\
0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 \\
\frac{\partial}{\partial \rho} [\rho (e + \frac{\|u\|^2}{2})] & \frac{\partial}{\partial \rho} [\rho (e + \frac{\|u\|^2}{2})] & u & v & w & \frac{\partial}{\partial \rho} [\rho (e + \frac{\|u\|^2}{2})]
\end{bmatrix}.
\] (3.96)

Then a backward Euler time discretization is applied to Eq. (3.89) resulting in the following implicit time discretization

\[
\frac{\partial Q}{\partial U} \bigg| \frac{U^{n+1} - U^n}{\Delta t} = -R_{Hi}^{n+1},
\] (3.97)

which is then linearized and a certain under-relaxation (\(\alpha\)) is applied to the system

\[
\sum_j \left( \frac{1}{\Delta t} \frac{\partial Q}{\partial U} \bigg| \delta_{ij} + \frac{\partial R_{Hi}}{\partial U_j} \right) \delta U_j = -R_{Hi}^n,
\] (3.98a)

\[
U_i^{n+1} = U_i^n + \alpha \delta U_i,
\] (3.98b)

where the indexes \(i\) and \(j\) run over the centers of all the flowfield cells, except the ghost cells which are updated after each iteration.

To obtain a converged solution we have observed that in the first iterations a small value of \(\alpha\) is required together with a small time step \(\Delta t\). These values can then be increased as the main flow features start to establish.
Chapter 3. Governing Equations

Electromagnetics

The electromagnetic field equations [Eq. (3.93)] and the discretized Navier-Stokes equations [Eq. (3.89)] are solved in a loosely coupled way. Starting from an initial coil current ($I_C$): firstly, we update the electric field applying a Newton method to the Eq. (3.93) as follows

$$\sum_j \frac{\partial R_E}{\partial E_j} \delta E_i = -R_{E,i},$$  

(3.99a)

and we calculate the dissipated power into the plasma ($P_t$); secondly, we multiply [18] both the electric field ($E$) and the coil current ($I_C$) by a factor $\sqrt{P_t/P_p}$, where $P_p$ is the fixed power we want to be dissipated into the plasma. Only thereafter, the Lorentz forces [Eqs. (3.37)] and the Joule heating [Eq. (3.38)] are computed in each cell and used to update the source terms in the momentum and energy equations. This procedure, based on the linearity of $E$ in $I_C$, ensures the required power dissipation in the plasma by Joule heating.

Linear system solution

The implicit technique previously described leads, at each iteration, to the solution of a linear system for the hydrodynamic [Eq. (3.98)] and electromagnetic equations [Eq. (3.99)]. There the jacobian matrices ($\partial R_E/\partial E$ and $\partial R_H/\partial U$) are computed by finite differences using for each cell only the four nearest neighbors cells. The Generalized Minimum RESidual (GMRES) [133] method implemented in the Aztec library [65] has been used to solve the two linear systems at each step of the iterative time marching procedure. To improve the convergence of the GMRES method, the Block Incomplete LU preconditioner with graph fill $\text{BILU}(p \geq 0)$ was used in the code [134].

3.6.2 Stagnation line flows

Under the assumptions made in Sec. 3.1.2, the set of boundary layer governing equations, after the Lees-Dorodnitsyn transformation, is presented in Sec 3.1.2.1. In the transformed coordinates, along the stagnation line of an axisymmetric body, we deal with ordinary differential equations. These equations, including the continuity equations expressing the conservation of the mass of each species [Eq. (3.23)] or element [Eq. (3.25), or (3.27), or (3.30)], can be written in the general form:

$$a \frac{\partial^2 w}{\partial \eta^2} + b \frac{\partial w}{\partial \eta} + cw = d$$  

(3.100)

with the boundary conditions:

$$\hat{\eta} = 0 \quad \frac{\partial w}{\partial \hat{\eta}} + gw = h$$  

(3.101)

$$\hat{\eta} = \hat{\eta}_\delta \quad w = w_\delta$$  

(3.102)
3.6.2 Stagnation line flows

The above equations are nonlinear because the coefficients \(a, b, \ldots, h\) depend in general from \(w, \partial w/\partial \hat{\eta}, \partial^2 w/\partial \hat{\eta}^2\), besides the transformed coordinate \(\hat{\eta}\).

Special care must be taken to solve the species continuity equations (3.23) and the elemental continuity equations under the form (3.25) and (3.27).

The diffusion fluxes of species are computed from the Stefan-Maxwell equations [Eq. (2.7)] using the solution at the \((k - 1)^{th}\) iteration and from their knowledge the elemental diffusive fluxes are retrieved. If the diffusion fluxes of either species or elements are considered to be a known data, the species [Eqs. (3.23)] and the elements [Eqs. (3.25)-(3.27)] continuity equations reduce to first order equations in their respective unknowns: the species mass fractions \(y_s\), the elements concentrations \(\xi_c\), and the element mass fractions \(Y^c\). In theory it is possible to couple the species equations and the Stefan-Maxwell equations in order to obtain second order equations. In practice it is not feasible because the resulting structure of the discretized equations is not easily reducible to the tridiagonal form. To overcome the problem a fictitious diffusion term is added to the diffusion fluxes into each equation; such term vanishes when convergence is reached. This procedure ensures that the species and element equations are second order differential equations in \(y_s\) and \(\xi_c\) or \(Y^c\). This technique is not required when the elemental continuity equations are written under the form of Eq. (3.30), obtained using the theory presented in chapter 2. Indeed, in this case, the second derivative of the element mass fraction is automatically present in the elements continuity equations.

3.6.2.1 Hermitian discretization

In the Eqs. (3.100) the nonlinearity is removed by evaluating the coefficients \(a, b, \ldots, h\) by means of a simple iterative procedure. The coefficients at the \(k^{th}\) iteration are evaluated by using the solution at the \((k - 1)^{th}\) iteration. The procedure is stopped when the difference between the solution \(w\) at the \(k^{th}\) iteration and the one at the \((k - 1)^{th}\) iteration is less than a fixed tolerance.

A constant step \(\Delta \hat{\eta}\) in the discretization along the \(\hat{\eta}\) direction is used. The unknown quantity \(w(\hat{\eta})\) is discretized by means of a Hermitian polynomial of 4th order:

\[
w(\hat{\eta}) = \frac{1}{2}w_{n+1}(r^2 + t) + w_n(1 - r^2) + \frac{1}{2}w_{n-1}(r^2 - t) + \alpha t (1 - r^2) + \beta r^2 (1 - r^2) \tag{3.103} \]

Here \(w_{n+1}, w_n, w_{n-1}\) are the values taken by \(w(\hat{\eta})\) at the locations \(\hat{\eta}_{n+1}, \hat{\eta}_n, \hat{\eta}_{n-1}\) respectively. The variable \(t\) is defined as: \(t = (\hat{\eta} - \hat{\eta}_n)/\Delta \hat{\eta}\); for \(t = 1, t = 0\) and \(t = -1\), the test function (3.103) equals \(w_{m,n+1}, w_{m,n}\) and \(w_{m,n-1}\) respectively. The two parameters \(\alpha\) and \(\beta\) can be freely chosen.

The first and second derivative of (3.103) are:

\[
\frac{\partial w}{\partial \hat{\eta}} = \left[\frac{1}{2}w_{n+1}(2t + 1) - 2w_n t + \frac{1}{2}w_{n-1}(2t - 1), + \alpha(1 - 3t^2) + 2t\beta(1 - 2t^2)\right]/\Delta \hat{\eta} \tag{3.104}
\]

\[
\frac{\partial^2 w}{\partial \hat{\eta}^2} = \left[w_{n+1} - 2w_n + w_{n-1} - 6\alpha t + 2\beta(1 - 6t^2)\right]/\Delta \hat{\eta}^2. \tag{3.105}
\]
Chapter 3. Governing Equations

The polynomial should be equal to the exact solution of the differential equation in several, in general arbitrary points. To eliminate the free parameters $\alpha$ and $\beta$ we need to equal the polynomial and the exact solution in 3 collocation points. It is useful and logical to choose the collocation points at the levels $n+1$, $n$, and $n-1$. Then the parameter $t$ equals $1$, $0$ and $-1$. The quantities $w$, $dw/d\hat{\eta}$, $d^2w/d\hat{\eta}^2$ are evaluated from Eqs. (3.103), (3.104), and (3.105) and substituted in Eq. (3.100). The system of three equations in five unknowns ($w_{n+1}$, $w_n$, $w_{n-1}$, $\alpha$, $\beta$), arising from the substitution can be reduced to a unique equation in three unknowns by eliminating the free parameters $\alpha$ and $\beta$. The final result is a single equation linking the unknown values:

$$C_n w_{n-1} + B_n w_n + A_n w_{n+1} = D_n.$$  \hspace{1cm} (3.106)

Eq. (3.106) is the discrete implicit representation of the differential equation for $n = 2, 3, \ldots, N-1$, where $N$ is the total number of grid points. For $n = N$ all the variables are given from the outer flow. For $n = 1$ the boundary condition (3.101) should be taken into account. This is made by setting $n = 2$ in Eqs. (3.103), (3.104), and (3.105) and substituting the quantities evaluated for $t = 0$ and $t = 1$ into Eq. (3.100). The quantities evaluated for $t = -1$ are substituted into Eq. (3.101). This leads to a system of three equations in the five unknowns $w_1, w_2, w_3, \alpha, \beta$, which again, can be reduced to a single equation:

$$R_1 w_1 + R_2 w_2 + R_3 w_3 = R.$$  \hspace{1cm} (3.107)

Collecting all the equations a linear system is obtained. The structure, written in matrix form, is:

$$
\begin{bmatrix}
R_1 & R_2 & R_3 \\
C_2 & B_2 & A_2 \\
C_3 & B_3 & A_3 \\
\vdots & \vdots & \vdots \\
C_{N-2} & B_{N-2} & A_{N-2} \\
C_{N-1} & B_{N-1} & A_{N-1}
\end{bmatrix}
\begin{bmatrix}
w_1 \\
w_2 \\
w_3 \\
\vdots \\
w_{N-2} \\
w_{N-1}
\end{bmatrix}
= 
\begin{bmatrix}
R \\
D_2 \\
D_3 \\
\vdots \\
D_{N-2} \\
D_{N-1} - A_{N-1} w_N
\end{bmatrix}
$$

It is possible to obtain a tridiagonal system as follows: multiply the first equation by $A_2$ and the second one by $R_3$; then subtract the second equation from the first. This results in:

$$(R_1 A_2 - C_2 R_3) w_1 + (R_2 A_2 - B_2 R_3) w_2 = R A_2 - D_2 R_3$$  \hspace{1cm} (3.108)

The dependence of the first equation from $w_3$ has been eliminated, resulting in a tridiagonal system, which can then be solved with the Thomas’ algorithm [62].

The procedure is fourth order accurate in step size across the boundary layer, but leads to a tridiagonal algebraic system as second order methods do.

In principle all the governing equation could be solved together. In practice, the system is split and not all the equations are solved at the same time. Continuity, momentum and energy equations are solved individually. The species and elements governing equations are solved together.

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Chapter 4

Diffusion phenomena in reacting mixtures : applications to stagnation line flows

In this chapter we present a detailed analysis of diffusion phenomena in flows of reacting mixtures along a stagnation line present in front of a probe placed in the test chamber of an inductively coupled plasma facility [Fig. 3.1]. Three mixtures have been selected as representative of Earth and Mars entry:

**Air-5 species**: \( E = \{N, O\}, R = \{N_2, O_2, NO\} \),

**CO\(_2\)-5 species**: \( E = \{C, O\}, R = \{CO_2, CO, O_2\} \),

**Mars-8 species**: \( E = \{C, N, O\}, R = \{CO_2, CO, O_2, N_2, NO\} \).

The first two mixtures are characterized by the presence of heteronuclear molecules but they contain only two elements (N and O or C and O). On the other hand, the third mixture contains three elements (C, N, and O). The investigation of the Air-5 and the CO\(_2\)-5 mixtures will be presented in the first two sections using the LTE formulation where the elemental fluxes are computed as a linear combination of the species ones obtained as the solution of the Stefan-Maxwell equations [Eq. (2.7)]. This analysis, based on the results presented by Rini and Degrez in Ref. [121], will allow for the assessment of the importance of demixing in the framework of stagnation line flows. In addition, we will show that results of computations carried out under chemical non equilibrium tend toward those obtained assuming LTE when chemistry is sufficiently fast, provided that demixing is correctly taken into account. The computations carried out using the Mars-8 mixture represent a direct application of the theory presented in Sec. 2.3. This represents the first attempt to simulate mixtures of heteronuclear molecules with more than two elements using the closed form of the equations presented in...
Chapter 4. Diffusion phenomena in reacting mixtures: applications to stagnation line flows

Sec. 2.3. The use of the theory presented in Sec. 2.3, will moreover allow to show the improvements brought by the theory itself in terms of physical understanding of the flow behavior. As far as the accuracy of the results obtained is concerned, all the computations presented in the following are converged for a 100 points discretization of the stagnation line. After a grid convergence study presented in Ref. [122] and recalled in Sec. 6.1.1, the chosen number of points showed to be enough to obtain reliable heating predictions.

4.1 Air stagnation line

An analysis of elemental demixing is presented by considering the solution of the stagnation line flow equations introduced in Sec. 3.1.2. For Earth (re)entry applications, the 5 species air model previously presented has been selected. The flow conditions considered [53], characteristic of Earth (re)entry, are presented in Tab. 4.1.

Table 4.1: Flow parameters and outer edge conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{wall}}$</td>
<td>300 K</td>
</tr>
<tr>
<td>$h_0$</td>
<td>14 MJ/Kg</td>
</tr>
<tr>
<td>$p_0$</td>
<td>0.1 atm</td>
</tr>
<tr>
<td>$R_m$ [mm]</td>
<td>25</td>
</tr>
<tr>
<td>$\delta$ [mm]</td>
<td>9.3</td>
</tr>
<tr>
<td>$v_0\partial/\partial y (\partial u_0/\partial x)/ (\partial u_0/\partial x)^2$ [-]</td>
<td>2.90</td>
</tr>
<tr>
<td>$\partial u_0/\partial x$ [s$^{-1}$]</td>
<td>1102</td>
</tr>
</tbody>
</table>

Three different chemical regimes have been analyzed.

**LTE - CEF** The flow is in thermochemical equilibrium and the composition is computed as a function of pressure, temperature, and elemental fractions, where the latter ones are supposed to be constant and equal to the outer edge values.

**LTE - VEF** The flow is in thermochemical equilibrium and the composition is computed as a function of pressure, temperature, and elemental fractions, obtained from the solution of Eq. (3.25).

**CNEQ-FCW** The flow is in chemical non equilibrium (CNEQ) and the composition is computed as the solution of a set of species continuity equations with a fully catalytic wall (FCW) boundary condition.

In the chemical non equilibrium computations the Dunn-Kang model, as listed by Gnoffo et al. [58], has been used. The wall has been considered to be fully catalytic with respect to oxygen and nitrogen recombination, and the wall reactions chosen are

$$O + (O - s) \rightarrow O_2 \quad N + (N - s) \rightarrow N_2.$$
4.1. Air stagnation line

The wall reaction model of Ref. [137] has been used, where the mass production term is computed as in Eq. (3.15). The results for an air mixture shown in Fig. 4.1 are presented in terms of mass fractions, in order to analyze the evolution of the chemical composition along the stagnation line.

![Figure 4.1: Mass fraction and nondimensional temperature along the stagnation line.](image)

Thanks to the choice of the previous wall reactions, a fully catalytic surface will promote the formation of O$_2$ and N$_2$ molecules. Since the equilibrium composition of a 5-species air mixture at the wall temperature of 300K is characterized mainly by the presence of only O$_2$ and N$_2$, one should expect the non equilibrium fully catalytic wall chemical composition to tend toward the equilibrium one. This happens only if we allow for elemental separation within the boundary layer as shown in Fig. 4.1. Indeed if one neglects the demixing effect, the wall chemical equilibrium composition is far from the non equilibrium fully catalytic one because of the wrong value of the elemental fractions used in the computation.

The analysis of the temperature profiles in Fig. 4.1 reveals the presence of non equilibrium phenomena. Indeed, the two LTE profiles differ from the CNEQ especially as we approach the wall, where the gradients are higher for the LTE solutions. On the other hand the wall species concentrations gradients are higher in the case of chemical non equilibrium, the LTE composition being almost constant until a dissociation temperature is reached, in agreement with the results shown in Sec. 2.2.

From the previous considerations one should expect the conductive part of the heat flux to be higher and the diffusive one to be lower in the LTE cases. These effects on the wall heat flux are mainly balanced and the values of heat flux for the three chemical regimes are listed in Tab. 4.2.

It is interesting to notice that in the chemical equilibrium case, neglecting the demixing effect leads to a slightly underestimated wall heat flux.

A further investigation of the elemental fraction behavior can be done by considering the elemental balance around the stagnation line. Let us now consider the global elemental balance over the control volume consisting of a cylinder of height $\delta$ and radius $x$ around the stagnation...
Table 4.2: Wall heat flux for three chemical regimes [$h_d = 14\text{MJ/kg}, T_w = 300\text{K}$].

<table>
<thead>
<tr>
<th>Chemical regime</th>
<th>$q_w [\text{MW/m}^2]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTE - VEF</td>
<td>0.660</td>
</tr>
<tr>
<td>LTE - CEF</td>
<td>0.658</td>
</tr>
<tr>
<td>CNEQ - FCW</td>
<td>0.656</td>
</tr>
</tbody>
</table>

Figure 4.2: Control volume for the determination of the global elemental balance Eq. (4.1).

line (Fig. 4.2). Taking the integral of Eq. (3.25) over this cylindrical control volume surrounding the stagnation line we obtain the following integral balance [122] for the element $c$:

\[
\begin{align*}
\xi_{j0} V_\delta + & \sum_{i=1}^{N_{ip}} \lambda_{ij} \frac{J_{yi}}{M_i} + \sum_{i=1}^{N_{ip}} \lambda_{ij} \frac{J_{yi}}{M_i} \\
& + 2 \frac{\partial \mu_{i0}}{\partial x} \frac{\delta}{\eta_{\text{max}}} \int_0^{\eta_{\text{max}}} \xi_j \frac{F(\hat{\eta})}{\rho} d\hat{\eta} = 0, \\
\end{align*}
\]

where ① and ④ are the elemental convection fluxes through the top surface (boundary layer edge) and through the lateral surface respectively, and ② and ③ are the elemental diffusion fluxes through the top (boundary layer edge) and bottom (solid wall) surfaces. Now, assuming a non-ablating wall, elements are neither created or destroyed at the wall and therefore the elemental diffusion flux at the wall ④ must be identically zero. As the elemental diffusion flux through the boundary layer edge ② is generally negligible, the sum of convective fluxes ① and ④ must vanish. This conclusion will be used for the analysis of the computational
From Eq. (4.1) we can further observe that, since the diffusion term is negligible with respect to the other two convective terms, the values of the elemental fraction at the outer edge must be a weighted average of the value of the elements fraction within the boundary layer. Therefore, the difference \( X(c) - X(c)|_{\delta} \) must be a changing sign non-monotone function, which physically means that a local excess of elements is compensated by a lack somewhere else along the stagnation line.

In Fig. 4.3 the behavior of the elemental fraction is shown for different chemical regimes. Assuming absence of demixing, the elemental fractions remain of course constant and wrong values of the chemical composition are predicted, as shown in Fig. 4.1. On the other hand the calculations carried out for both the non equilibrium fully catalytic and the LTE-VEF cases satisfy the elemental balance. Indeed in Fig. 4.3 is shown that, for these conditions, the elemental fraction distributions are not in contradiction with the Eq. (4.1).

![Elemental fractions along the stagnation line](image)

**Figure 4.3: Elemental fractions along the stagnation line.**

### 4.2 Carbon Dioxide stagnation line

In this section we present the solution of the stagnation line equations for a CO\(_2\) mixture. The flow parameters considered, characteristic of Mars entry, refer to the IPG-4 plasmatron test condition defined in [75] and are recalled in Tab. 4.3.

A gas mixture, suited for Mars entry application, has been considered to be made by 5 species: CO\(_2\), CO, O\(_2\), C, and O. The same chemical regimes as previously discussed have been analyzed. In particular, for the chemical non equilibrium computation, the chemical kinetics model of Park [110] has been used and the wall has been considered fully catalytic with respect to the two following surface reactions

\[
CO + (O - s) \rightarrow CO_2 \quad O + (O - s) \rightarrow O_2
\]
Table 4.3: Flow parameters and outer edge conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{wall}}$</td>
<td>300 K</td>
</tr>
<tr>
<td>$h_\delta$</td>
<td>15.3 MJ/Kg</td>
</tr>
<tr>
<td>$p_\delta$</td>
<td>5.8·10^{-2} atm</td>
</tr>
<tr>
<td>$R_m$ [mm]</td>
<td>25</td>
</tr>
<tr>
<td>$\delta$ [mm]</td>
<td>10</td>
</tr>
<tr>
<td>$\nu_\delta \partial/\partial y (\partial u_\delta/\partial x)/(\partial u_\delta/\partial x)^2$ [-]</td>
<td>2.02</td>
</tr>
<tr>
<td>$\partial u_\delta/\partial x$ [m/s]</td>
<td>1711.2</td>
</tr>
</tbody>
</table>

The wall reaction model proposed by Rini et al. [122], described in Sec. 3.1.1.3, has been used. In Fig. 4.4, the evolution of the mass fractions along the stagnation line is shown for the three chemical regimes previously described. From the analysis of the profiles related to LTE-VEF and LTE-CEF, it appears that significant elemental fraction variations take place in the flow. Indeed in the case of elemental ratios of 2/3 : 1/3, 100% CO$_2$ at the wall is recovered as expected from the analysis of Fig. 2.5.

![Graph showing mass fraction and nondimensional temperature along the stagnation line](image-url)

Figure 4.4: Mass fraction and nondimensional temperature along the stagnation line.[0:w;1:δ]

On the other hand, when elemental demixing is accounted for, the diffusion of carbon elements is responsible of a lower carbon wall fraction than in the case of constant elemental fraction, this leading to a lower concentration of CO$_2$. On the other hand, the oxygen wall fraction increases with respect to the constant elemental fraction case, leading to a non zero amount of molecular oxygen at the surface.

From the analysis of the CNEQ-FCW results, we notice the presence of non equilibrium effects that lead to the presence of both CO$_2$ and O$_2$ at the surface. As observed for the case of an air mixture, the CNEQ-FCW composition tends toward the equilibrium one only in the case in which elemental demixing is considered. It is of interest to analyze the elements fraction
4.3 Chemical non equilibrium versus LTE regime

This section aims to discuss and clarify the relation between the chemical non equilibrium regime and the local thermodynamic equilibrium one. From the analysis of Eq. (2.5), we can identify at least three chemical regimes, depending on the relative magnitude of the convective-diffusive and chemical-source terms. To simplify the analysis, the expression used to compute the mass production term [160] due to chemical reactions is recalled in Eq. (4.2) for a set of

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...
Chapter 4. Diffusion phenomena in reacting mixtures: applications to stagnation line flows

\( N \), chemical processes of the type

\[ \sum_{i=1}^{N_{sp}} \nu_{fr,i} X_i \Rightarrow k_{fr} \sum_{i=1}^{N_{sp}} \nu_{fr,i} X_i, \]

where the backward reaction rates are computed as the ratio between the forward and the equilibrium ones. For this set of reactions, the net rate of change of the \( i \)th species concentration reads

\[ \dot{\omega}_i = \sum_{r=1}^{N_r} \omega_{fr,r} \]

where

\[ \omega_{fr,r} = M_i (\nu''_{fr,i} - \nu'_{fr,i}) k_{fr,r} \left\{ \prod_{i=1}^{N_{sp}} c_{i}^{\nu'_{fr,i}} - \frac{1}{K_{fr,r}} \prod_{i=1}^{N_{sp}} c_{i}^{\nu''_{fr,i}} \right\}. \]

When the characteristic time of the chemical processes, \( \tau_c \), is much higher than the flow characteristic time \( \tau_f \), the flow is said to be frozen.

![Figure 4.6: Air mixture: LTE-demixing vs CNEQ-NCW.](image)

This coincides with a set of very small, zero in the limit, forward reaction rates. Under these conditions, the right hand side of Eq. (2.5) is negligible with respect to the left hand one and therefore in a frozen regime the species concentrations obey to the equations

\[ \text{div}(\rho_i u + J_i) = 0. \] (4.3)

On the other hand, if \( \tau_c \ll \tau_f \), the local equilibrium conditions are approached. This is equivalent to artificially imposing very high values, infinite in the limit, of the forward reaction rates. As a consequence the convective-diffusive term in Eq. (2.5) is negligible with respect to each term of the sum expressed by Eq. (4.2). Therefore in the equilibrium regime the species continuity equations tend to the limit \( \dot{\omega}_i = 0 \), which can be satisfied only by an LTE composition.
4.3. Chemical non equilibrium versus LTE regime

\( K_{r} \), being the equilibrium constants computed from statistical thermodynamics [160]. Indeed if the condition

\[
\text{div}(\rho_i \mathbf{u} + \mathbf{J}_i) \ll \omega_{ir} \quad (\forall r)
\]

is satisfied, then from species mass conservation one has

\[
\sum_{i=1}^{N} \omega_{ir} \cdot \text{div}(\rho_i \mathbf{u} + \mathbf{J}_i) \approx \sum_{i=1}^{N} \omega_{ir} = 0.
\]

Moreover the composition satisfying the species equations in the limit of local equilibrium conditions, is actually coincident with the solution of the non linear system (3.13), as a function of local pressure, temperature and elemental fractions. The proof of the previous statement, in contrast with the observations of Ref. [56], is presented in Figs. 4.6, and 4.7 for air and carbon dioxide mixtures.

![Figure 4.7: CO₂ mixture: LTE-demixing vs CNEQ-NCW.][0:0.1:0.6]

Figure 4.7: CO₂ mixture: LTE-demixing vs CNEQ-NCW. [0:0.1:0.6]

It is worth noticing that for the CNEQ regime a non catalytic wall (NCW) has been chosen as boundary condition for the species continuity equations in order to let the bulk chemistry drive the species evolution, avoiding any interference with surface reactions. The excellent coincidence of the two computations show clearly that if the speed of chemistry is artificially increased, the local thermodynamic equilibrium conditions are achieved, provided that the variation of elemental fraction is correctly taken into account by solving elements continuity equations.

From a numerical point of view, these results show not only the robustness of the VKI Boundary Layer code [11, 12], able to solve the stiff problem of infinite rates, but also assess the correctness of the LTE-VEF formulation. The results obtained in this section will be confirmed by the analysis of inductively coupled plasma flows to be presented in chapter 5.
4.4 CO₂/N₂ stagnation line

In the previous section, we performed an investigation of elemental demixing along stagnation lines for both air and CO₂ mixtures. This analysis allowed to establish the existence and the importance of elemental diffusion phenomena. However, even if the previous results represent an original and pioneering attempt to the investigation of elemental diffusion, a clear description of the physical mechanism leading to elemental diffusion is still missing in the results presented until now. To answer the need of a deeper understanding of the physical mechanisms leading to the variation of the elemental fraction along the stagnation line we propose to apply the theory presented in chapter 2. Although stagnation line flows are often under chemical non-equilibrium conditions, our previous analysis [121] showed that for a CO₂ mixture, assuming a fully catalytic wall provides an estimation of wall heat flux close to the one obtained by assuming LTE conditions to be established along the stagnation line, provided that elemental demixing is taken into account [Tab. 4.4]. In addition, the elemental fraction profiles obtained under chemical non equilibrium follow closely those under chemical equilibrium [Figs. 4.5]. Thus we will present the solution of the LTE stagnation line problem formulated following the equations presented in Sec. 3.1.2.1 plus the mass formulation of the closed form of the elemental and energy equations [Eqs. (3.30)-(3.31)].

To present our analysis of the stagnation line flow we will start defining a working mixture suited for the analysis of martian entry problems. Further on, we will define the test case to be investigated and finally the solution of the stagnation line flow will be presented with strong emphasis on the description of diffusion phenomena.

4.4.1 Mixture definition

Several models for the description of the Martian atmosphere are available in the literature. In Ref. [106], Noll and McElroy present detailed information on the atmospheric composition and local information obtained from computations with climatological models are presented by Justus et al. and Lewis in Refs. [68], respectively [85]. As stated by Owen et al. [108], the atmosphere of Mars is mainly composed of CO₂, plus some N₂, O₂, Ar and minor species. In this work, by neglecting minor species and Ar, the Martian atmosphere is modeled with CO₂, N₂, and O₂. This choice was also adopted by Chen and Candler in Ref. [31], where hypersonic flow simulations are presented to predict the heat flux on a fore-body heat-shield. We therefore consider a 8 species mixture containing CO₂, CO, O₂, N₂, NO, C, N, and O. In Fig. 4.8 we present the equilibrium composition of such a mixture for the reference elemental fractions \( X_{\delta}^{C} = 0.32 \), \( X_{\delta}^{O} = 0.04 \), and \( X_{\delta}^{N} = 0.64 \) and for a pressure of 7000 Pa used later on for the stagnation line flow solution.

4.4.2 Test case definition

The flow conditions considered, characteristic of Martian entry [131], are presented in Table 4.5. The presented outer edge conditions and geometrical parameters, have been determined from a
4.4.2. Test case definition

![Equilibrium mole fractions as a function of temperature (7000 Pa) [13].](image)

Table 4.5: Operating Conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_w$ [K]</td>
<td>300</td>
</tr>
<tr>
<td>$T_δ$ [K]</td>
<td>5827</td>
</tr>
<tr>
<td>$p_δ$ [Pa]</td>
<td>7000</td>
</tr>
<tr>
<td>$R_m$ [mm]</td>
<td>25</td>
</tr>
<tr>
<td>$δ$ [mm]</td>
<td>9</td>
</tr>
<tr>
<td>$ν_δ ∂/∂y(∂u_δ/∂x)/(∂u_δ/∂x)^2$ [-]</td>
<td>1.77</td>
</tr>
<tr>
<td>$∂u_δ/∂x$ [s$^{-1}$]</td>
<td>913</td>
</tr>
</tbody>
</table>

detailed numerical [66] study of the flowfield inside the inductively coupled plasma generator and test chamber of the VKI’s plasmatron wind tunnel [15][Fig. (3.1)]. This allows for the computation of some non-dimensional parameters related to the stagnation line edge in terms of the boundary layer thickness, the axial velocity, and the velocity gradient and further details about their definition are available in previous publications [36].

In the following a single chemical regime is considered, corresponding to LTE with variable elemental fraction (LTE-VEF), where the flow is in thermochemical equilibrium and the composition is computed as a function of pressure, temperature, and local elemental fractions, obtained from the solution of the set of elemental continuity equations. Two formulations have been used.

**LTE-VEF (1)** we obtain the elemental concentration by solving Eqs. (3.27), where the element diffusive fluxes are computed as a linear combination of the species ones obtained as the solution of the Stefan-Maxwell equations [Eq. (2.7)]. The computed species diffusive fluxes are then used in the energy equation to evaluate the diffusive transport of enthalpy [121] ($∑ J_i h_i$).

**LTE-VEF (2)** we obtain the elemental concentration by solving Eqs. (3.30), where the ther-
mal demixing and multicomponent diffusion coefficients are used to compute the element diffusive fluxes. Moreover, the alternative form of the energy balance, presented in Eq. (3.31) is used, introducing the correction to $\lambda_R$ as well as the elemental heat transfer coefficients.

### 4.4.3 A priori estimation of the elemental fraction profiles

Before presenting the solution of the stagnation line problem, we analyze the evolution of the multicomponent and thermal demixing diffusion coefficients computed as a function of temperature for a fixed pressure and several elemental compositions. This is done independently from the solution of the stagnation line flow equations, with the purpose of showing how the knowledge of these transport coefficients can help to predict a priori the effect of multicomponent diffusion on the elemental concentration profiles. To this end, we present, in Fig. 4.9, the elemental thermal demixing coefficients and, in Figs. 4.10-4.12, the elemental multicomponent diffusion coefficients.

![Elemental thermal demixing coefficients as a function of temperature (7000 Pa).](image)

In both figures, we present results for different elemental compositions to investigate their sensitivity to elemental fraction variations. Three sets of elemental composition have been selected for this purpose perturbing by $\pm 5\%$ the reference oxygen and carbon elemental molar fractions. This leads to the following elemental concentrations:

- $X_C = 0.352$, $X_N = 0.072$, $X_O = 0.576$,
- $X_C = 0.320$, $X_N = 0.040$, $X_O = 0.640$,
- $X_C = 0.288$, $X_N = 0.008$, $X_O = 0.704$.
The results presented in Fig. 4.9 show the influence of elemental fraction variations on the $D_T^e$. There, we notice some differences between the results obtained with the three different elemental compositions even though the profile evolution as a function of temperature is analogous.

Figure 4.10: Elemental multicomponent diffusion coefficients as a function of temperature (7000 Pa, $X_C = 0.352$, $X_N = 0.072$, $X_O = 0.576$).

Figure 4.11: Elemental multicomponent diffusion coefficients as a function of temperature (7000 Pa, $X_C = 0.320$, $X_N = 0.040$, $X_O = 0.640$).

This is even more evident for the multicomponent diffusion coefficients presented in Fig. 4.10-4.12. There we observe a very similar behavior for the $D_{eq}$ as a function of temperature for
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Figure 4.12: Elemental multicomponent diffusion coefficients as a function of temperature (7000 Pa, $X_C = 0.288$, $X_N = 0.008$, $X_O = 0.704$).

each elemental composition. From the definition of the stagnation line problem we know that the temperature increases from its wall value (set to a typical value $\sim 300$ K for cold wall) until the outer edge is reached where $T_\delta$ is $\sim 6000$ K. As a consequence, $\partial T/\partial y$ is a positive function of $y$. As shown in Fig. 4.9, the thermal demixing coefficients are not a positive function of $T$ and present a change in sign in the temperature range $[T_w, T_\delta]$. This will obviously induce a similar change in sign in the demixing source terms $-\rho D^e \nabla T$. On the other hand, from Figs. 4.10-4.12 we notice how the elemental multicomponent diffusion coefficients do not change sign in the temperature range of interest. A further investigation of the multicomponent elemental diffusion coefficients reveals a particular structure of the diffusion matrix $D_{eq}$.

Indeed, to respect mass conservation ($\mathbf{J}_e = 0$) the following conditions must be satisfied

\[
\sum_{q \in E} D_{eq} = \sum_{q \in E} D_{qN} = \sum_{q \in E} D_{qO} \tag{4.6}
\]

for the multicomponent diffusion coefficients, and

\[
\sum_{e \in E} D^e \approx 0 \tag{4.7}
\]

for the thermal demixing ones. From the analytical definition of the $D_{eq}$ [Eq. (A.19)] we moreover observe that the rows of the multicomponent diffusion coefficients matrix must sum up to zero ($\sum_{q \in E} D_{eq} = 0$). This property is reflected by the results presented in Figs. 4.10-4.12 where we notice that the off diagonal coefficients have values around minus half of the diagonal ones. In addition the diagonal elements of the matrix follow approximately the same evolution as a function of temperature. Inspired by the previous two observations about the structure of the matrix of the $D_{eq}$ we propose the following simplification of the multicomponent diffusion matrix

\[
\begin{pmatrix}
\rho D_{eq}
\end{pmatrix} \approx \rho \frac{1}{2} \begin{pmatrix}
2D & -D & -D \\
-D & 2D & -D \\
-D & -D & 2D
\end{pmatrix} \tag{4.8}
\]
A rapid analysis of Eq. (4.8) reveals how both the physical mass constraint (4.6) and the mathematical property \( \sum_{\mathbb{E}} D_{eq} = 0 \) are satisfied.

Eq. (4.8), together with the identity \( \sum \nabla Y^e = 0 \), allows for a substantial simplification of the mixing term of the elemental diffusive fluxes, i.e.:

\[
\sum \rho D_{eq} \nabla Y^e \approx \rho \frac{3}{2} D \nabla Y^e. \tag{4.9}
\]

Eq. (4.9) represents an important result which shows that for CO\(_2\)/N\(_2\) mixtures the mixing term (\( \sum \rho D_{eq} \nabla Y^e \)) can be simplified to a Fick’s law form which drops the coupling between the elemental continuity equations. Indeed, using Eq. (4.9) and considering steady flow conditions, the elemental continuity equations [Eqs. (2.18)] simplify to

\[
\frac{\rho \mathbf{u} \cdot \nabla Y^e - \nabla \left( \rho \frac{3}{2} D \nabla Y^e \right)}{1} = \nabla \cdot (\rho D_e^{mix} \nabla T). \tag{4.10}
\]

Eq. (4.10), together with the profiles presented in Figs. 4.9-4.12, allows for the following qualitative prediction of the elemental fraction evolution along the stagnation line. Indeed, since at sufficiently low temperatures no chemical reactions take place, the \( D_e^{mix} \) are zero and demixing of elements should not be induced in the region close to the surface. On the other hand, as temperature is sufficiently high, the demixing source terms \( -\rho D^{mix} \nabla T \) will differ from zero and, below \( \sim 4000 \) K, induce a decrease of oxygen concentration (\( D^{mix}_{O} > 0 \)) and an increase of N and C (\( D^{mix}_{N}, D^{mix}_{C} < 0 \)). For higher temperatures the opposite effect will be observed. As soon as elemental concentrations vary, the terms \( -\rho \sum D_{eq} \nabla Y^s \) will play a role trying to re-establish a uniform elemental composition. Moreover since the \( D_e^{mix} \) change sign, while the \( D_{eq} \) do not, elemental fraction profiles should have a non-monotone behavior to produce zones where \( \nabla Y^e > 0 \) and others where \( \nabla Y^e < 0 \). In this way the terms \( -\rho \sum D_{eq} \nabla Y^s \) try to counteract the demixing effect \( -\rho D^{mix} \nabla T \).

In the remaining part of this section we propose an easy and fast method to estimate the elemental fraction evolution along the stagnation line. To this end, we further simplify Eq. (4.10) neglecting the convective term \( \circledast \) with respect to the mixing term \( \circledR \). While exact for a Couette flow, in the present case the accuracy of this approximation depends on the position along the stagnation line. The non-dimensional parameter on which an accuracy analysis should be based is the Peclet number resulting from the dimensional analysis of the ratio \( \frac{[\circledast]}{[\circledR]} \). Indeed

\[
\frac{[\circledast]}{[\circledR]} = \frac{v_0 \delta}{D} = Pe, \tag{4.11}
\]

where we introduced a reference velocity \( v_0 \), a reference length \( \delta \), and a reference average diffusion coefficient \( D = 3/2D_{eq} \). For the operating conditions defined in Tab. 4.5 we find a \( Pe = 2 \) which leads to a convective term \( [\circledast] \) around the double of the mixing one \( [\circledR] \). This clearly states that neglecting convection is not a good approximation in the zone around the outer edge. Indeed, the discussion presented in Sec. 4.1 to interpret Eq. (4.1) is based on neglecting diffusion with respect to convection. On the other hand, from Eq. (4.11), if the local velocity is used as a reference, we notice that, as we move towards the surface, the velocity normal to the wall decreases, inducing a consequent decrease of the Peclet number. As a consequence, there will be an interval where the proposed approximation will be valid and, from the solution of the stagnation line problem to be presented shortly, we will notice that this interval cover the first 10% of the stagnation line. The direct consequence of neglecting convection
in the Eqs. (4.10) consists in their simplification to the conditions \( \mathbf{J}_e = 0 \). Following this result we propose an ‘approximate’ approach to estimate the elemental composition along the stagnation line which consists in solving the following set of \( N_e \) decoupled first order ordinary differential equations:

\[
\frac{\partial Y_e}{\partial \hat{\eta}} = -\frac{2}{3} \rho \frac{D_T}{D} \frac{\partial T}{\partial \hat{\eta}}. \tag{4.12}
\]

As a first guess we consider a linear temperature distribution with slope \( \frac{\partial T}{\partial \hat{\eta}} = \frac{(T_\delta - T_w)}{\Delta \hat{\eta}} \). This allows for the solution of Eq. (4.12) which leads to the determination of the elemental mass fraction profiles \( Y_e(\hat{\eta}) \). To solve Eq. (4.12) we have computed the \( D_T[T(\hat{\eta})] \) and \( D = D_{CC}[T(\hat{\eta})] \) using the outer edge pressure and elemental fractions.

In Fig. 4.13 we present the solution of Eqs. (4.12) in terms of \( Y_e(\hat{\eta}) \). In this figure we present also the results obtained as the solution of Eq. (3.27) to compare the prediction of the method introduced in the previous section with the solution of the stagnation line equations. Analyzing the profiles presented in this figure, we notice that the results of Eq. (4.12) leads to a prediction which differs from the solution of Eq. (3.27) \( \sim 2\% \) at most, for oxygen near the wall. This result shows that the elemental fraction profiles can be roughly estimated a priori using a fast and easy method.

In addition, we notice that the evolution of the three profiles presented in Fig. 4.13 is in agreement with the qualitative prediction previously presented and moreover reflects the properties of the ratio \( D_T / D \) present in Eq. (4.12).

In the following section, we will show how the results obtained with the approximate method just presented are not so different from the solution of the stagnation line equations. Indeed the evolution of the \( D_T \) and the \( D_{eq} \) along the stagnation line will closely follow what has been presented in Figs. 4.9 and 4.11. This will allow researchers dealing with stagnation line problems for TPS design to estimate a priori the order of magnitude of elemental fraction variations by means of a fast and easy tool.
4.4.4 Stagnation line solution

In this section we present the solution of the stagnation line equations for the conditions specified in Tab. 4.5. We start our analysis by discussing the temperature and enthalpy profiles shown in Fig. 4.14.

Figure 4.14: Comparison of the computed results for the temperature and enthalpy profiles along the stagnation line obtained using the LTE-VEF (1) and the LTE-VEF (2) formulations.

Figure 4.15: Comparison of computed results for the species mass fractions along the stagnation line using the LTE-VEF (1) and the LTE-VEF (2) formulations.

There we present the results obtained for the LTE-VEF regime using the two formulations LTE-
VEF (1) and LTE-VEF (2) defined in the previous section. As observed, the results obtained with the two formulations are identical. The same match is observed for all flow variables along the stagnation line, supporting the correctness of the alternative formulation recalled at the beginning of this section.

In Fig. 4.15 we present the species concentration profiles. Starting from CO, O, C, and N at the outer edge, we see how their concentration decreases providing a mixture of CO\textsubscript{2}, O\textsubscript{2}, N\textsubscript{2} at the wall and a small amount of NO. From the analysis of this picture, it appears that elemental demixing tends to reduce the amount of carbon and nitrogen at the wall while it enhances the oxygen concentration. This is reflected by the presence of an excess of O\textsubscript{2} in the low temperature region, which would have been zero if the wall elemental fractions had been the same as at the outer edge [Fig. 4.8]. This behavior is confirmed by the profiles presented in Fig. 4.16, where we plot the difference between the local elemental mass fractions and their outer edge values [\(Y_c^*(y)-Y_c^*[\delta]\)]. In addition, by looking to the element concentration profiles [Fig. 4.16] we notice that the lack of carbon and nitrogen at the wall is compensated by a higher concentration around \(y/\delta = 0.4\), while for oxygen we observe a minimum in this position and a subsequent concentration rise as the wall is approached.

![Figure 4.16: Comparison of the results obtained for the difference between the elemental mass fractions and their outer edge values \(Y^*(y)-Y^*[\delta]\) obtained using the LTE-VEF (1) and the LTE-VEF (2) formulations.](image)

Going further with the analysis of the profiles presented in Fig. 4.16, we notice that they present a non-monotone behavior as already observed in Sec. 4.1-4.2 and hereunder we give an alternative explanation for this observation. To discuss the elemental mass fraction behavior we focus on the elemental continuity equations in the form of Eq. (3.27). It is clear how the knowledge of \(J_e\) will help understanding the evolution of \(Y_e^*\) knowing that \(\bar{V} < 0\).

For this purpose we present the profiles of \(J_e\) in Fig. 4.17 for the three elements contained in the mixture. As expected [Eq. (3.27)] we observe a correspondence between the local extrema of \(J_e\) and those of \(Y_e^*\). In addition, we notice that the diffusive fluxes of elements are zero.
all over the first 10% of the stagnation line and they start to grow around \( y/\delta \approx 0.1 \). This shows that over the first 10% of the stagnation line, Eq. (3.27) simplifies to \( J_e = 0 \), meaning that convection is by far negligible. Moving further towards the outer edge a local extremum is encountered, followed by an increase for C and N, while for oxygen a decrease of \( J_O \) is observed. From this we notice that in the region defined by \( y/\delta > 0.1 \), the convective term will differ from zero and will counteract [Eq. (3.27)] the derivative of the profiles presented in Fig. 4.17. At this point, it is important to observe that, although the profiles of Fig. 4.17 allow the interpretation of the elemental fraction profiles presented in Fig. 4.16, it is by no means evident to give an explanation for the behavior of the \( J_e \) if they are computed as a linear combination of the solutions of Eqs. (2.7) as done in the formulation LTE-VEF (1) \[121, 128\] on which the results presented in Sec. 4.1-4.2 are based. Now, to improve our understanding, we use the theory introduced in chapter 2 and applied in the LTE-VEF (2) formulation of the equations.

Indeed, to understand the behavior of the element diffusive fluxes we discuss now the two components of \( J_e \). The first proportional to the temperature gradient \( (\rho D_T^e \nabla T) \) and the second obtained as a linear combination of the element mass fractions gradients \( (\rho \sum D_{eq}^e \nabla Y^q) \). In Fig. 4.18, we present the first part of the element diffusive fluxes. From Fig. 4.14 we notice that \( \partial T/\partial y > 0 \) \( \forall y \) and therefore the sign of \( \rho D_T^e \nabla T \) will depend only on \( D_T^c \), \( \rho \) being obviously a positive quantity.

As shown in chapter 2 and confirmed in Fig. 4.9, the \( D_T^c \) change their sign as temperature rises, for fixed pressure and elemental fractions. In the present case, the pressure is constant along the stagnation line but the elemental fraction varies. Therefore, both temperature and elemental composition will influence the transport properties. From the analysis conducted observing the results of Figs. 4.10-4.12, we expect the influence of temperature variations to be dominant with respect to changes in elemental composition. All these effects concur to the establishment of the profiles presented in Fig. 4.18.
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Figure 4.18: First contribution to the element diffusive fluxes ($\rho D_T^e \nabla T$).

Close to the wall, the thermal demixing coefficients are zero and do not contribute to the element diffusive fluxes. As temperature rises, we observe an increase in module of all contributions until a maximum is reached. Then we notice a decrease and a subsequent change in sign typical of the thermal demixing coefficients behavior.

Figure 4.19: Thermal demixing diffusion coefficients.

Indeed, from Fig. 4.19, we see how the behavior of the thermal demixing coefficients is similar to the one of the first contribution to the element diffusive fluxes. At this point it is interesting to compare Fig. 4.9 and Fig. 4.19 remembering the non-linear behavior of $T(y)$. At first glance
we observe that the evolution of the $D_T^C$ is mainly the same except for a slight increase of $D_T^C$ observed close to the wall ($y/\delta \approx 0.05$) and absent when the elemental fraction is supposed to be constant [Fig. 4.9]. The close relation between the results presented in these two figures, together with their importance in the understanding of diffusion phenomena, clearly show the physical interest and the practical value of the computation of elemental thermal demixing coefficients.

In Fig. 4.20, we plot the second contribution to the elemental diffusive fluxes. Also this contribution starts from zero at the wall and follows a non monotone behavior passing through a change in sign for O and C.

![Figure 4.20: Second contribution to the element diffusive fluxes ($\rho \sum D_{eq} \nabla Y^q$).](image)

In Fig. 4.21, we notice how all the contributions to the sums $\rho \sum D_{eq} \nabla Y^q$ go through zero where the elemental fractions have a local minimum or maximum. The change in sign observed for the second contribution to the elemental diffusive fluxes is not due to the elemental multicomponent diffusion coefficients but to the elemental mass fractions. Indeed, as shown in chapter 2 and observed in Figs. 4.10-4.12 and 4.22, the multicomponent diffusion coefficients have the same sign in the temperature range of interest.

This allows for the following interpretation of diffusion phenomena along the stagnation line. Since temperature decreases from the outer edge towards the wall, the temperature gradient is always positive along the stagnation line. In sufficiently low temperature regions, where chemical reactions do not occur, the thermal demixing coefficients are zero and do not induce demixing. As a consequence, since elemental multicomponent diffusion coefficients are not zero at low temperatures, the elemental composition stays constant ensuring mass conservation ($\mathcal{J}_e|_w = 0$). As we move away from the wall ($y < 0.05$), the thermal demixing coefficients cause a non zero contribution to the elemental diffusion flux which tends to decrease oxygen concentration ($D_T^O > 0$), increase nitrogen concentration ($D_T^N < 0$), and slightly decrease but then increase again carbon concentration ($D_T^C > 0$ and $D_T^C < 0$). As soon as variations in elemental composition are induced ($\nabla Y^e \neq 0$), a counteracting contribution to the element diffusive fluxes appear which tends to smooth out elemental concentration profiles until the outer...
edge is reached. In the central part of the stagnation line, the two contributions to element fluxes interact until the point in which the thermal demixing coefficients change sign. There, to counteract this
demixing term, the sign of element concentration gradients needs to change since the multi-component diffusion coefficients have a constant sign [Fig. 4.22]. The counteracting character of the term $\sum \rho D_{eq} \nabla Y^q$ with respect to $\rho D_c^T \nabla T$ justify its label of ‘mixing term’ and the comparison of Figs. 4.18 and 4.20 clearly shows this behavior. The mathematical origin of this diffusive character of the mixing term has to be searched in the non negativity of the matrix containing the elemental multicomponent diffusion coefficients. To prove the latter property of the matrix $D_{eq}$ we compute its eigenvalues along the stagnation line. Since this matrix is
singular \( \sum_{q \in E} D_{eq} = 0 \), one eigenvalue is \( k_1 = 0 \) and the remaining two are presented in Fig. 4.23. There we clearly see that both \( k_2 \) and \( k_3 \) are positive \( \forall y \in [0, \delta] \), this proving the non-negative character of the matrix \( D_{eq} \).

As a summary, we wish to point out that, from the knowledge of the set of transport properties including both elemental thermal demixing and multicomponent diffusion coefficients such as those presented in Figs. 4.9-4.11, we can predict the evolution of the diffusive fluxes and therefore guess the shape of the elemental fractions profiles as well as the amount of demixing one can observe in the solution of the stagnation line problem.

We now move to the analysis of the heat and mass transfer along the stagnation line by means of conduction and diffusion. As shown in chapter 2, under the assumption of local thermodynamic equilibrium, the diffusive transport of enthalpy can be split into two parts related to \( \nabla T \) and \( \nabla Y_q \) respectively. As a consequence, as shown in Eq. (3.29), the computation of the heat flux involves the determination of two terms one proportional to the temperature gradient \(- (\lambda + \lambda_R + \lambda_D) \nabla T \) and the other proportional to the linear combination of element concentration gradients \(- \sum h^q_{EL} \nabla Y^q \). Moreover, the heat flux in a mixture of reacting gases is composed of a conductive part \( q_c = -\lambda \nabla T \), to which the diffusive transport of enthalpy needs to be added \( q_d = \sum h^q J^q \). To investigate the heat flux along the stagnation line and highlight the relative importance of the various contributions we start presenting the evolution of \( q_c \), \( q_d \), and \( q_{c_d} \) along the stagnation line in Fig. 4.24.

There we observe that the total heat flux presents an increasing monotone behavior starting from the outer edge until the wall, acting to balance the convection of enthalpy. At the same time we notice that this smooth evolution appears to be the result of a quite complex shape of the two contributions \( q_c \) and \( q_d \) presented in the same figure. This highly non-linear behavior of the two heat flux components is the result of the evolution of six transport coefficients \((\lambda, \lambda_R, \lambda_D, \lambda^q_{EL}) \) and four gradients \((\nabla T, \nabla Y^q) \). To provide an exhaustive description of the heat flux along the stagnation line, we start investigating the behavior of the three thermal \((\lambda)\), ther-
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Figure 4.24: Heat flux components.

Figure 4.25: Thermal, reactive, and demixing conductivities along the stagnation line.

As expected, we notice $\lambda_R$ to be the major contribution to the first part of the heat flux followed by $\lambda$. We also notice that $\lambda_D$ has a non-monotone behavior including changes in sign, highlighting the fact that demixing tends to increase or decrease heat flux depending on the local temperature and elemental fractions as already observed in Sec. 2.3. Moreover, in terms of heat flux intensity, we notice that around $y/\delta = 0.3$, $\lambda_D \approx \lambda$ showing how, neglecting $\lambda_D$ with respect to $\lambda$ could lead to important errors. The knowledge of the evolution of the transport coefficients presented in Fig. 4.25 helps us understanding the behavior of the various heat flux components shown in Fig. 4.25.
4.4.4. Stagnation line solution

Figure 4.26: Heat flux components \((\lambda_R \nabla T, \lambda_D \nabla T)\) along the stagnation line.

contributions. Indeed, the non-linear behavior of \(q_c\) can be easily explained. \(\lambda\) is an increasing monotone function from the wall towards the outer edge, while \(\partial T/\partial y\) starting from the outer edge increases, decreases and then increases again as shown in Fig. 4.14. Therefore \(q_c\) follows mainly the evolution of \(\partial T/\partial y\). For what concerns \(q_d\), we need to consider separately the five contributions \(-\lambda_R \nabla T\), \(-\lambda_D \nabla T\), and \(-\lambda_{EL} \nabla Y\).

Figure 4.27: Elemental heat transfer coefficients.

In Fig. 4.26, we present the evolution of the first two terms and their sum. The evolution of
these two contributions is more complex than the previous one since the two associated transport coefficients present a highly non-linear behavior with extrema in different positions than the temperature gradient. As far as the elemental heat transfer coefficients are concerned, we present their evolution in Fig. 4.27. There we notice that they all have a non-monotone behavior reflecting the highly reacting character of the flow. These transport coefficients lead to three contributions to the heat flux presented in Fig. 4.28, which are of the same order of magnitude for the three elements. The sum of these contributions is also plotted in the same figure to show the importance of this term with respect to the total heat flux. From the analysis of the profiles presented in Figs. 4.26-4.28, we can justify the evolution of \(q_d\) concurring to the determination of the final shape of the heat flux. As a final step we analyze in detail the relative importance of the various terms contributing to the heat flux. In Fig. 4.29, we present the results of this analysis showing the evolution of the four following ratios along the stagnation line: 

\[-(\lambda dT/dy)/q, -(\lambda_RdT/dy)/q, -(\lambda_DdT/dy)/q, \text{ and } -(\sum \lambda_{EL}^q dY^q / dy)/q.\]

The analysis of these profiles help us to quantify the importance of each term. Indeed, this shows that the major contribution to the heat flux comes from the thermal reactive conductivity (\(\lambda_R\)), the second comes from conduction (\(\lambda\)) and the two remaining contributions are of the same order of magnitude. The analysis of the curve \(-(\lambda_DdT/dy)/q\) reveals that the contribution related to elemental demixing is higher than the one due to thermal conductivity for \(0.1 < y/\delta < 0.3\). The two contributions \(-(\lambda_DdT/dy)\) and \(-(\sum \lambda_{EL}^q dY^q / dy)\) present almost an opposite behavior for \(y/\delta < 0.4\). On the other hand, for \(y/\delta > 0.4\) we notice that \(-(\sum \lambda_{EL}^q dY^q / dy)\) becomes higher than \(-(\lambda_DdT/dy)\) approaching the 10% of the total heat flux around \(y/\delta \sim 0.6\) and decreasing to 5% at the outer edge. The almost opposite behavior of the two latter contributions clearly shows that elemental diffusive fluxes have not a very important influence on the total heat flux. Indeed if \(J_e = 0 \forall e \in E\), the Butler and Brokaw thermal reactive conductivity is enough to compute \(q_d\). For the conditions previously analyzed, the presence of non vanishing elemental fluxes acts on the mixture energetic behavior with a heat flux contribution which is at most of the order of 5% of the total heat flux.
4.5 Summary

The effects of elemental demixing in thermochemical equilibrium mixtures have been analyzed by means of stagnation line computations. The results of this analysis lead us to the following major conclusions:

- For both air and carbon dioxide flows, non negligible elemental fractions variations have been observed, even though their effects on the heat flux are more important for CO₂ mixtures. In both cases, the wall composition for a chemical non equilibrium regime with fully catalytic wall is closer to the local thermal equilibrium one, where the local elemental fraction is computed by solving adequate advection diffusion equations.

- In addition, it has been verified that local thermal equilibrium with variable elemental fractions is the limit of a chemical non equilibrium regime where the forward reaction rates are artificially increased to sufficiently high values.

The transport coefficients presented for a 8 species mixture containing three elements (C,N,O) under conditions of LTE, allow to reduce the equations of chemically reacting flows to an elegant system consisting of the conventional Navier-Stokes equations (mass, momentum, energy), complemented by an advection-diffusion equation for the mass fraction of each chemical element in the mixture. The obtained formalism is in closed form in the sense that diffusive fluxes are directly expressed in terms of gradients of the solution unknowns, unlike other formulations in which these fluxes are obtained in an implicit manner, by solving the full system of Stefan-Maxwell equations. Several new LTE transport coefficients appear:

- The elemental advection-diffusion equations contain nine elemental multicomponent
and three thermal demixing coefficients. The thermal demixing coefficients sum up to zero and the matrix of elemental multicomponent diffusion coefficients is non symmetric and non negative.

- In the energy equation, the well-known thermal reactive conductivity coefficient (due to Butler and Brokaw) takes into account diffusive transport of species enthalpies in the absence of elemental demixing. An additional demixing thermal conductivity coefficient and a set of three elemental heat transfer coefficients correct for the additional flow of heat due to elemental demixing caused by temperature respectively elemental fraction gradients.

A quasi one-dimensional application of this formulation is proposed by means of the solution of the equations describing the flow of a mixture of reacting gases along a stagnation line. Both the theoretical description of the formulation and its application to a case of interest for Mars entry applications, lead us to the following major conclusions:

- For the first time thermal demixing and multicomponent diffusion coefficients as well as elemental heat transfer coefficients and thermal demixing conductivity have been computed for a mixture containing three elements. This proves the generality of the proposed formulation and clearly represents an improvement with respect to previous formulations available in the literature.

- The results obtained with the proposed closed form of the equations coincide with those obtained using an implicit formulation previously presented, indicating the correctness of the new formulation.

- The proposed approximate method for the estimation of the elemental fraction profiles allows to predict the elemental concentration along the stagnation line in an easy way with a maximum absolute error below 2%.

- Demixing of chemical elements gives rise to complex elemental concentration and heat flux patterns which can be easily explained by examining graphs of LTE transport coefficients that arise from the new LTE formulation.
Chapter 5

Applications to ICP flow computation

In this chapter we present a detailed analysis of chemical equilibrium and non-equilibrium plasma flows both in the torch and in the test chamber. In Sec. 5.1.1-5.1.2 we will present results concerning only the torch domain for both air and carbon dioxide plasmas respectively. In Sec. 5.2 we extend our investigation to the hot jet flowing into the chamber.

The two following mixtures will be considered in this chapter to simulate air and carbon dioxide plasmas:

**Air-11 species:** $\tilde{E} = \{O, N, e^+\}$, $\tilde{R} = \{O_2, N_2, NO, NO^+, O^+, N_2^+, O_2^+, N_2^+\}$, and $\tilde{S} = \tilde{R} \cup \tilde{E}$.

**CO$_2$-8 species:** $\tilde{E} = \{O, C, e^+\}$, $\tilde{R} = \{CO_2, O_2, CO, O^+, C^+\}$, and $\tilde{S} = \tilde{R} \cup \tilde{E}$.

The analysis presented in the first section is based on the study presented by Rini et al. in Ref. [128] whose motivation is twofold:

1. It is common practice in aerospace sciences to compute LTE flows, assuming a fixed elemental composition. Care should be taken when comparing these results with non-equilibrium calculations, for which demixing of elements does occur: are the observed differences due to non-equilibrium effects, or simply a consequence of the fact that demixing is not taken into account in the LTE model? The results to be presented clearly show that as pressure is increased and equilibrium conditions are approached, differences between the fixed elemental fraction LTE model and non-equilibrium model persist; however, when variations of elemental composition are correctly allowed for in the LTE model, excellent agreement is found.

2. In the aerospace industry, and in particular at the von Karman Institute for Fluid Dynamics, high-pressure air ICPs are used to test Thermal Protection System (TPS) materials...
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for atmospheric (re-)entry spacecraft. In these tests, the surface catalycity properties of the material undergoing testing are evaluated by means of a hybrid experimental-numerical methodology based on the Local Heat Transfer Simulation (LHTS) concept [71], which relies heavily upon the numerical simulation of the air ICP used. While we do not question the adequacy of the LTE assumption used for these simulations by the Russian specialists that originally developed this methodology, we wish to point out that, to obtain accurate results under general operating conditions, the demixing of chemical elements should be included in the LTE model.

The second section is devoted to the investigation of carbon dioxide plasma flows within the plasmatron torch. The analysis presented in this section is based on the study presented by Rini et al. in Ref. [130] where a code-to-code validation is presented for carbon dioxide plasmas in the VKI plasmatron torch. To this end the authors present the results of the simulation of CO₂ plasma flows within the VKI plasmatron torch carried out obtained independently from the two groups with the VKI-ICP and the IPM-α codes. The results of this comparison showed how the 1-D approach of the α code fails in the description of the Electric field within the torch. In addition, the importance of elemental diffusion on the behavior of CO₂ plasma flows is assessed and only this part will be presented in the following whose motivation is recalled hereafter:

1. accurate carbon dioxide plasma flow simulations are rare in the literature related to aerospace sciences. Moreover, up to the best author knowledge, no simulation is available where elemental demixing is considered under thermochemical equilibrium conditions. For this reason we investigate the phenomena of elemental diffusion in LTE carbon dioxide plasmas to evaluate its effects on the flow behavior.

The last section of this chapter (Sec. 5.2) is devoted to the physico-chemical characterization of the jet flowing in the test chamber for air plasmas, whose motivation is twofold:

1. the methodology proposed by IPM [71] to estimate the catalytic properties of thermal protection system materials supposes thermochemical equilibrium conditions to be established in the torch and in the test chamber. However, there is no proof that equilibrium conditions exist and a detailed analysis assessing the quality of this assumption is not available. To supply this need we present both chemical non equilibrium and chemical equilibrium computations to provide a range of pressure in which equilibrium computations are as accurate as those obtained under chemical non equilibrium, using two finite rate chemistry models.

2. As a result, we will be able to assess the influence of the finite rate chemistry model and operating pressure on the flow behavior both in the torch and especially in the test chamber.
5.1 Analysis of the flow within the torch

5.1.1 Air plasmas

We will now present and analyze numerical results for air ICPs inside the VKI Plasmatron torch (Fig. 3.3), obtained using

1. the full chemical non-equilibrium formulation (CNEQ),
2. the consistent LTE formulation which allows for varying element fractions (LTE-VEF) and
3. the simplified LTE model (LTE-CEF) assuming a fixed elemental volumetric composition (21% oxygen, 79% nitrogen).

In our numerical model, both the electromagnetic and flow field equations are discretized by means of a 2nd order accurate collocated finite volume method on a structured mesh of 131 by 47 cells. To assess the degree of grid convergence, for a reference set of operating conditions, additional computations have been performed on a mesh of 262 by 94 cells and the differences in the results were found to be below 2-3%.

Table 5.1: Plasmatron operating conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Ambient and wall temperature [K]</td>
<td>300</td>
</tr>
<tr>
<td>Power injected into the plasma [kW]</td>
<td>75</td>
</tr>
<tr>
<td>Frequency [MHz]</td>
<td>0.45</td>
</tr>
<tr>
<td>Inlet Swirl [deg]</td>
<td>45</td>
</tr>
<tr>
<td>Mass flow [g/s]</td>
<td>6</td>
</tr>
<tr>
<td>Operating pressures [atm]</td>
<td>.05, .1, .2, .3</td>
</tr>
</tbody>
</table>

All results presented in this section are converged at least 6 order of magnitude (based on the drop in the $L_2$ residual norm). The qualitative analysis of the obtained results will be based upon comparison of computed contours plots. To perform an accurate quantitative analysis, we will also present plots of radial variations of flow quantities in the plasma, obtained close to the inlet ($z=0.056m$), at the mid-coil position ($z=0.265m$) and at the outlet ($z=0.486m$), as indicated in Fig. 5.1(a). The operating conditions used for the simulations are listed in Tab. 5.1.

5.1.1.1 Flowfield and concentration analysis

In Figs. 5.1(a)- 5.1(c) we compare temperature, flowfield and volumetric oxygen fraction contours computed at a pressure of 0.05 atm using the CNEQ and the LTE-VEF formulations.
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Figure 5.1: Computed oxygen elemental fraction, temperature and stream function in an air ICP torch at an ambient pressure of 0.05 atm.

Inspection of the temperature fields shows that chemical non equilibrium effects have an important influence at this relatively low operating pressure. Because of the lower temperatures found in the CNEQ case, viscosity is smaller, the Reynolds number is higher and a small secondary recirculation appears near the inlet. Both the CNEQ and the LTE-VEF computations show that variations of oxygen elemental fractions are significant. The fact that variations are of similar order of magnitude for both formulations, indicates that elemental demixing in chemically reacting thermal plasma flows is not a CNEQ effect. The reason for this is, of course, that no chemistry terms appear in the elemental continuity Eqs. (3.10). Due to the strong temperature gradients in the radial direction, concentration variations and diffusion also
mainly act perpendicularly to the wall. Because the atomic oxygen contained inside the plasma ball diffuses faster than the (heavier) molecular oxygen in the low temperature zones adjacent to the wall, we observe a strong increase in the overall fraction of oxygen elements near the wall. Strong depletion of oxygen is observed on the axis at the outlet and also in the recirculation bubble near the inlet, where the flow particles have a larger residence time. When performing TPS material tests using high-pressure air ICPs, the outlet conditions of our torch simulations correspond to inlet conditions for a jet of hot plasma flowing into a test chamber and impacting on a TPS sample. In Sec. 5.2 we will assess the importance of this phenomenon in the jet and we will observe that the elemental composition of the air mixture hitting the TPS is likely to be far from the 21% oxygen/79% nitrogen composition commonly assumed by researchers performing TPS tests. It therefore appears to be desirable to take into account the demixing effect in the TPS testing methodology in the future.

5.1.1.2 Parametric study of the influence of pressure

In this section, we present results for all operating pressures specified in Tab. 5.1 for the following main reasons:

1. to provide a thorough comparison between the LTE-CEF and LTE-VEF formulations,
2. to show that the LTE-VEF formulation is as accurate as the CNEQ model for sufficiently high pressures.

In Fig. 5.2, we present radial profiles of volumetric oxygen fraction and temperature obtained in the inlet zone ($z=0.056m$). For a pressure of 0.05 atm, comparison of the temperature profiles shows that non equilibrium effects are quite high in the inlet zone, where temperatures are low. Differences in terms of temperature profiles between the LTE-CEF and LTE-VEF formulations are very low above 3 cm while they increase up to a maximum of around 1000 K on the axis. The oxygen element profiles obtained using the CNEQ and the LTE-VEF formulations show a clear peak at $r \approx 6.5cm$, while using the LTE-CEF formulation obviously the oxygen fraction is constant. As pressure is increased, the influence of demixing on temperature decreases and the results obtained with the LTE-CEF and LTE-VEF formulations tend to converge. A similar tendency is obtained for the radial profile under CNEQ, which starts far from the two corresponding to LTE-CEF and LTE-VEF at 0.05 atm and approaches the LTE results at higher pressure. For the highest pressure [Fig. 5.3] some differences are present and confined to a small region around the axis (here for $r \leq 2cm$). The analysis of the oxygen profiles shows that both the CNEQ and the LTE-VEF formulations predict the same order of magnitude for oxygen elemental diffusion; the LTE-CEF model does not provide this information.

In Fig. 5.3 we focus on the mid-coil zone ($z=0.265m$). All oxygen elemental fraction profiles start from a value of 0.21 at the quartz tube, as in the previous position [Fig. 5.2], showing that demixing is prevalent in the radial direction. Indeed, the cold zone close to the quartz tube is characterized by a mainly constant oxygen concentration, where the flow is continuously filled by an annular jet of $O_2/N_2$ in the molar ratio of 21/79. All the profiles corresponding to the CNEQ formulation present a peak at the edge of the plasma ball (here for $r \approx 6.5cm$) and then
Figure 5.2: Oxygen elemental fraction and temperature profiles for several operating pressures at $z=0.056m$.

become flat at lower radii. Again, we observe that the oxygen profiles obtained under LTE-VEF and CNEQ reasonably match for $p \geq 0.2$ atm. The analysis of temperature profiles show that, at the mid-coil section, the influence of elemental demixing on the temperature prediction is negligible. Indeed, the temperature profiles obtained with the LTE-CEF and LTE-VEF formulations are superposed for all pressures and all radii. In addition, the differences with respect to the CNEQ results decreases as pressure is increased, as expected.

In Fig. 5.4, we compare computed profiles of temperature and oxygen element fraction ob-
Figure 5.3: Oxygen elemental fraction and temperature profiles for several operating pressures at \( z = 0.265 \) m.

The general evolution of the oxygen elemental fraction follows the description presented for the mid-coil section. Some small differences are anyway visible close to the quartz tube. Indeed, we observe that the LTE-VEF and the CNEQ oxygen profiles start from a value slightly higher than 0.21 showing that demixing has the tendency to enrich the cold flow region in oxygen (element) and that some axial diffusion takes place near the outlet. From the analysis of
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Figure 5.4: Torch outlet profiles ($z=0.486$ m) of oxygen elemental fraction and temperature for increasing ambient pressures.

the temperature profiles, we observe that elemental demixing slightly affects the temperature profiles only at low pressures. Therefore, for what concerns the determination of TPS catalytic properties the only influence that demixing could have, for Earth (re)entry applications and for sufficiently high pressures, is related to different elemental and species concentration at the inlet of the chamber.

Another conclusion, important from both modeling and physical points of view, could be drawn
from Fig. 5.4. Indeed, as the ambient pressure increases, the CNEQ results clearly start to approach the LTE-VEF results, which is to be expected as chemistry becomes faster at higher pressures. Therefore, the inlet conditions for the test chamber can be accurately computed with an LTE-VEF formulation for sufficiently high pressures. This is also supported by the contour plot of oxygen nuclei fraction at 0.3 atm shown in Fig. 5.5: differences are quite small in agreement with Figs. 5.2-5.3 and especially if compared with the same plot at 0.05 atm (Fig. 5.1).

Figure 5.5: Elemental fraction in the torch at 0.3 atm (upper LTE-VEF, lower CNEQ).

Figure 5.6: Outlet species mole fraction profiles ($z=0.486m$) at 0.3 atm.

In the remaining part of this section, we discuss the effects of elemental demixing on the species profiles at the torch outlet for the 0.3 atm operating pressure. In Fig. 5.6, we compare the outlet mole fraction profiles at 0.3 atm for three physical formulations. We clearly see that differences between the CNEQ and the LTE-CEF formulations, at higher pressures, are mainly due to elemental diffusion effects, rather than chemistry. This conclusion is useful for the modeling of plasma torches. Indeed, in view of this result, for sufficiently high pressures, we can avoid the solution of a set of $N_{sp}$ species equations [Eqs. (3.8)], with stiff source terms,
in favor of a lighter, more elegant and reliable model containing only $N_{el}$ equations (two in the present case) without source terms.

A further reduction of the small discrepancies present at the torch outlet at 0.3 atm is possible by acting directly on the chemistry characteristic time under non equilibrium conditions. If we artificially increases the reaction rates in the CNEQ simulations at 0.3 atm, by multiplying $\dot{\omega}_s$ by a factor $10^3$ in Eqs. (3.8), then differences become tiny, as can be seen in Figs. 5.7, 5.8, and 5.9. This clearly shows that the CNEQ regime tends to the LTE-VEF regime as the speed of chemistry increases as observed in Ref. [121] for stagnation line flows (Sec. 4.3).
5.1.2 Carbon dioxide plasmas

We now move to the analysis of the numerical results obtained for an operating condition of the VKI plasmatron representative of Mars entry [66]. In Ref. [154, 155], the authors present a code-to-code comparison showing the effects of different modeling on the flow behavior for air plasmas within the IPG-4 torch. While in these contributions the authors showed that the 1-D approach for the treatment of the electric field is sufficiently accurate for the IPG-4, it was shown in Ref. [130] that, in the VKI plasmatron torch operating with CO$_2$, this is not the case and the simplified treatment lead to a nonphysical undulating behavior of the electric field reflected on the temperature contours. The analysis presented in this section is inspired on the study conducted by Rini et al. in Ref [130], omitting the part concerning the code-to-code comparison. Therefore, in the following, we only present the original investigation of elemental diffusion to assess the importance of the variations in carbon and oxygen elemental concentrations on the flow behavior.

5.1.2.1 Test case definition

In Tab. 5.2, we present the operating condition selected as representative of Mars entry [66] used to produce the results to be presented shortly. The flow has been simulated under LTE with both constant and variable elemental fractions and both computations have been carried out on the same mesh of 102 by 92 cells for which grid convergence is assured (Sec. 5.1.1). All results presented in the following are converged at least 10 order of magnitude (based on the drop of the $L^2$ residual norm).
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Table 5.2: Operating conditions for the VKI-Plasmatron operating with carbon dioxide.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambient and wall temperature [K]</td>
<td>300</td>
</tr>
<tr>
<td>Power injected into the plasma [kW]</td>
<td>90</td>
</tr>
<tr>
<td>Frequency [MHz]</td>
<td>0.37</td>
</tr>
<tr>
<td>Inlet Swirl [deg]</td>
<td>0</td>
</tr>
<tr>
<td>Mass flow [g/s]</td>
<td>8</td>
</tr>
<tr>
<td>Operating pressure [Pa]</td>
<td>7000</td>
</tr>
</tbody>
</table>

5.1.2.2 Influence of elemental diffusion

To investigate the influence of the elemental fraction variation on the flow behavior, we used the upgraded version of the VKI-ICP code programmed in the framework of the research conducted during this thesis to simulate both the LTE-VEF and the LTE-CEF formalisms. For that purpose, the plasma in the torch has been considered both under LTE-VEF and LTE-CEF conditions. For the operating conditions presented in Tab. 5.2 we obtain the elemental distribution presented in Fig. 5.10 in terms of carbon elemental mole fraction ($X_C$).

![Carbon elemental molar fraction contours.](image)

In Fig. 5.11, we present the temperature contours and in Fig. 5.12 the flow pattern, both within the torch, obtained under LTE-VEF conditions. In these figures, we observe the presence of a quite wide high-temperature region where the maximum temperature is around ~ 10 000 K, as expected for the specified power injected in the flow.

The mixture enters the torch with a reference elemental composition of $2/3$-$1/3$ for oxygen and carbon respectively. Entering the torch, the mixture is subject to very strong temperature gradients which produce a non zero demixing contribution ($-\rho D_T \nabla T$) to the elemental diffusion flux [126], inducing elemental composition variations. Once a non-uniform elemental composition field is established, a counteracting mixing term ($\sum \rho D_{ck} \nabla Y_k$), proportional to the elemental composition gradients, tends to re-establish a uniform elemental field. These two mechanisms act together with convection to provide the final steady elemental composition.
Figure 5.11: Temperature contours obtained for the LTE-VEF regime.

Figure 5.12: Stream function contours.

pattern. From the analysis of Fig. 5.10, at least three zones can be observed. The first one represents an almost cylindrical zone delimited by $7.5 < r < 8.0$ cm close to the inlet and $6.0 < r < 8.0$ cm at the outlet. There, we do not observe substantial variations in the elemental fraction and this is mainly due to the fact that, in that region, the flow is continuously filled by a stream coming from the inlet with the reference elemental composition. In addition, the wall temperature being fixed, the axial temperature gradient is negligible close to the wall leading to the absence of diffusion in the same direction.

A second zone is visible around the torch axis both inside and after the recirculation bubble. There, we observe that carbon has the tendency to diffuse out from hot regions towards lower temperatures, leading to an axial zone poorer in carbon than in the case where a constant elemental composition is arbitrarily imposed. A third region is visible at the intermediate radii and a bit downstream of the inlet. There, the carbon mole fraction reaches the maximum value of 0.38, i.e. $\sim 13\%$ more than the inlet value. This zone of high carbon concentration is
therefore the result of the diffusion of carbon from the high temperature region around the axis accompanied by the difficulty for carbon to diffuse towards the quartz tube where the concentration is mainly fixed by the cold mixture convected from the inlet to the torch exit.

Figure 5.13: Outlet profile of the carbon elemental mole fraction.

The previous description of the carbon elemental field is reflected by the profile depicted in Fig. 5.13 which corresponds to the torch exit. There we clearly see that the carbon profile has a non-monotone behavior. As we approach the exit, the flow field became almost axial and radial convection can be neglected as shown in Fig. 5.12.

Figure 5.14: Outlet profile of the species mole fractions.

This behavior of the outlet carbon elemental fraction, observed for nitrogen in air mixtures [128],
5.2. Characterization of the flow in the jet

could be predicted by observing the evolution of the elemental diffusion coefficients for the carbon element [122] as a function of temperature [Figs. 2.13-2.14].

![Outlet temperature profiles](image)

**Figure 5.15:** Outlet temperature profiles.

In Figs. 5.14 and 5.15, we present the influence of elemental fraction variations on the mixture composition and on the mixture temperature. From the analysis of Fig. 5.14, a big influence of elemental fraction variations on the species concentration is observed. Starting from the wall we observe that, since the carbon molar fraction is slightly smaller than 1/3, a small amount of O₂ is present close to the wall as a result of a LTE-VEF computation. Moving further towards the axis the differences between the CEF and the VEF computations become more evident. Indeed, the decrease of Xₖ up to a local minimum around 6 cm causes a slower CO₂ dissociation accompanied by the displacement to lower radii of both the O₂ and the CO peaks. Then, because of the successive CO dissociation we observe the formation of both atomic carbon and oxygen, where the second one is more affected by the elemental fraction variation because of the retardation of both O₂ and CO peaks. Finally, atomic species decrease their concentration close to the axis because of ionization due to the high temperature around 10000 K. On the axis we therefore find a carbon fraction of ~ 0.275, i.e. ~ 16% less than the reference value. The final influence of elemental demixing is observed in Fig. 5.15, where the outlet temperature profiles for both CEF and VEF are compared. We notice the temperature to be overestimated in the case of constant elemental composition starting from r < 7 cm. By comparing Fig. 5.15 with Fig. 5.4, we easily realize that the influence of elemental diffusion on the temperature profile is much higher for CO₂ than for air mixtures.

5.2 Characterization of the flow in the jet

We now move back to the analysis of air plasma flows. The results to be presented shortly concern both the investigation of the torch and the hot exhaust jet in the chamber. As discussed at the beginning of this chapter, the forthcoming results will allow to verify for which operating
conditions of the VKI plasmatron, the numerical simulation of LTE plasma flows is as accurate as the chemical non-equilibrium one, both in the torch and especially in the test chamber. The consequences of this finding will have a direct impact on the range of applicability of the methodology used for the estimation of catalytic properties of thermal protection system materials [71].

The mesh used for the solution of the flowfield equations is divided into two blocks: the first one (60 by 44 cells) is used to discretize the domain within the torch, while the second block (60 by 67 cells) reproduces a part of the test chamber. All results presented in the following are converged at least 10 order of magnitude (based on the drop in the $L_2$ residual norm).

The operating conditions, selected as representative of Earth (re)entry [109], are recalled in Tab. 5.3.

<table>
<thead>
<tr>
<th>Table 5.3: Plasmatron operating conditions.</th>
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<tbody>
<tr>
<td>Ambient and wall temperature [K]</td>
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<tr>
<td>Power injected into the plasma [kW]</td>
</tr>
<tr>
<td>Frequency [MHz]</td>
</tr>
<tr>
<td>Inlet Swirl [deg]</td>
</tr>
<tr>
<td>Mass flow [g/s]</td>
</tr>
<tr>
<td>Operating pressures [kPa]</td>
</tr>
</tbody>
</table>

For each simulation, the three chemical regimes CNEQ, LTE-CEF, and LTE-VEF, introduced in Sec. 5.1.1, have been considered. The presentation of the results is organized in two parts. Firstly, we present a qualitative analysis based on the investigation of the contour plots of the main flow properties. Then, we move to a deeper investigation of the flow behavior based on the analysis of temperature and elemental molar fraction profiles extracted in several crucial parts of the computational domain.

In the first part, we address the issue of the influence of finite rate chemistry on the results of the simulation. To this end, two models have been selected as representative of Earth’s atmosphere chemistry (Park [111] and Dunn-Kang [58]). Several numerical experiments have been conducted to assess how the operating pressure drives the flow behavior when one of the two models is used. As a result, we notice that the influence of the finite rate chemistry is only limited to low pressures (around 5000 Pa). Indeed, as the operating pressure is set to higher values, the results obtained under CNEQ with both models are in very good agreement.

In the second part of this section, we move to a deeper investigation of the air plasma behavior. To this end, we present the evolution of the main flow properties along the radial direction at four locations in the computational domain (Fig. 5.16):

- in the inlet zone ($z = 0.005m$),
- at the mid-coil position ($z = 0.268m$),
- at the outlet of the torch ($z = 0.505m$),
- within the chamber ($z = 0.800m$).
5.2.1 Qualitative analysis

In this section, we discuss the influence of the finite rate chemistry model on the flow behavior. To this end we present temperature and elements concentration both in the torch and in the chamber by means of contour plots. Two of the four operating pressures specified in Tab. 5.3 have been selected to perform this study, the lowest (5000 Pa) and the highest (30000 Pa).

Focusing on these two pressures, we will be able to easily show how the differences observed in the flow solution, due to differences in the reaction rates, are visible only in the low pressure case and disappear when the operating pressure is increased up to 30000 Pa. We therefore leave the definition of the pressure limit above which the influence of the finite rate model becomes negligible to the study performed in the next section. The results to be presented shortly have been obtained under LTE-VEF conditions and under CNEQ using two finite rate chemistry models: the Park model [111], indicated as CNEQ-P, and the Dunn-Kang model [58] named as CNEQ-D&K.

Each non equilibrium result is compared with the respective one obtained with the other finite rate model but also with the result of the simulation carried out under thermochemical equilibrium with variable elemental fraction. This, at the same time, allows for the assessment of the influence of the finite rate chemistry model and to answer the question of whether or not equi-
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Figure 5.18: Oxygen elemental molar fraction obtained with two finite rate models [5000 Pa].

Figure 5.19: Comparison of the temperature [K] contours obtained with the Dunn-Kang model (upper) and under LTE-VEF (lower) [5000 Pa].

In Figs. 5.17 and 5.18 we plot the temperature, respectively the oxygen elemental mass fraction both in the torch and in the chamber. The analysis of these figures reveals the presence of two zones in which the comparison of the results brings us to different conclusions. Indeed, within the torch, we notice that the CNEQ-P and CNEQ-D&P predictions differ considerably leading to different temperatures and, to a lesser extent, elemental fractions. From Fig. 5.17 we observe that the Dunn-Kang model predicts a slightly wider hot (T ≥ 6000 K) region in the torch acting on the structure of the plasma ball. As soon as we move towards the torch exit, we start noticing a rapid dwindling of the disparity between the two predictions which, at least from a qualitative point of view, show the same temperature field in the jet, corresponding to the most interesting part of the flowfield from the point of view of TPM testing.

For what concerns the oxygen elemental fraction, we notice that the finite rate chemistry model has little influence on the elements concentration field, showing once again that demixing is not a non equilibrium effect [Fig. 5.18].

In Figs. 5.19-5.20 and 5.21-5.22, we present a comparison between the results obtained under chemical non equilibrium with the Park and Dunn-Kang models with those obtained under chemical equilibrium with variable elemental fractions. In Figs. 5.19-5.20 we focus on the
**5.2.1. Qualitative analysis**

Figure 5.20: Comparison of the temperature [K] contours obtained with the Park model (upper) and under LTE-VEF (lower) [5000 Pa].

Figure 5.21: Comparison of the oxygen elemental molar fraction contours obtained with the Dunn-Kang model (upper) and under LTE-VEF (lower) [5000 Pa].

Figure 5.22: Comparison of the oxygen elemental molar fraction contours obtained with the Park model (upper) and under LTE-VEF (lower) [5000 Pa].

As expected, thanks to the analysis performed in Sec. 5.1.1, the temperature contours obtained under chemical non equilibrium differ considerably from those obtained with the equilibrium...
formalism and this for both finite rate chemistry models. From the oxygen elemental fraction presented in Figs. 5.21-5.22 we notice a certain difference in the prediction of the elemental concentration field between equilibrium and non equilibrium even though the order of magnitude of the oxygen variations is the same.

We now move to the analysis of the higher pressure (30000 Pa) and we start our analysis presenting, as done for the lower pressure case, the comparison between non equilibrium results. In Figs. 5.23-5.24 we present the temperature, respectively the elemental fraction contours both in the torch and in the chamber. From the analysis of the temperature contours, we notice that at an operating pressure of 30000 Pa, the results obtained with the two models are, at least from a qualitative point of view, equivalent. The same conclusion is drawn after inspection of Fig. 5.24 where attention is focused on the oxygen elemental fraction. Differences between the prediction with the Park and the Dunn-Kang models are hardly visible.

Figure 5.23: Temperature contours obtained with two finite rate models [30000 Pa].

Figure 5.24: Oxygen elemental molar fraction obtained with two finite rate models [5000 Pa].

In the following, we present the comparison between the previous results with the respective equilibrium computations. The critical analysis of these comparison will enhance the importance of the previous conclusions. In Figs. 5.25-5.26 and 5.27-5.28 we present the direct comparison between the temperature, respectively the elemental mole fraction contours obtained both under chemical non equilibrium and equilibrium with variable elemental fraction.

From Figs. 5.25-5.26 we realize that the temperature contours predicted by the simulation of equilibrium conditions coincide with those obtained under chemical non equilibrium for both
finite rate chemistry models after the last coil. Indeed, some small differences are visible within the torch until the last coil is reached. To further decrease these differences in the torch we just need to increase the operating pressure. On the other hand, at the torch exit, but most impor-
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Figure 5.28: Comparison of the oxygen elemental molar fraction obtained with the Park model (upper) and under LTE-VEF (lower) [30000 Pa].

stantly in the test chamber, a perfect match is observed. Similar conclusions can be drawn for the elemental composition after inspection of Figs. 5.27-5.28.

The results just described have a direct impact on the methodology used for the estimation of the catalytic properties of thermal protection materials. Indeed, thanks to the previous analysis we can argue that for sufficiently high pressures the equilibrium formalism allows for the determination of results, both in the torch and in the chamber, characterized by an accuracy very close to the one we can achieve with non equilibrium simulations. This conclusion will allow researchers performing inductively coupled plasma flow simulations for the characterization of TPM, to obtain accurate results using an equilibrium formulation at a fraction of the cost required to simulate the same conditions under non equilibrium.

In the next section we firstly provide a validation of the previous analysis, by means of the investigation of the local behavior of the plasma flow and secondly, we define the pressure limit above which the previous conclusion is applicable.

5.2.2 Detailed analysis

In this section, we present the local evolution of the main flow properties in the four locations specified in Fig. 5.16 for each of the four operating pressures defined in Tab. 5.3. From the qualitative analysis presented in Sec. 5.2.1, we observed that for the low pressure case some discrepancies are visible between the results obtained under chemical non equilibrium and equilibrium, while for high pressure these differences essentially disappeared. Following this result, we will divide the following analysis into two parts: the detailed analysis of the low pressure case and the parametric study of the pressure influence. In the first part, we present a detailed investigation of the low pressure case showing the results obtained for several chemical regimes in four locations. This will lead to an accurate description of the spatial evolution of the flow properties and will allow to verify whether, even at a so low operating pressure, a match between equilibrium and non equilibrium results can be found somewhere in the flow. For what concerns the parametric study of pressure influence, we focus our attention only on the outlet of the chamber. Indeed, as discussed during the previous qualitative analysis, the most interesting part of the flowfield from the point of view of TPM testing is the hot jet
5.2.2. Detailed analysis

Exiting from the torch. Therefore, for this particular location, we will discuss how the operating pressure drives the flow behavior depending on the chemical regime under investigation. In the results to be presented shortly, three chemical regimes will be considered: LTE with both constant (CEF) and variable (VEF) elemental fractions and chemical non equilibrium (CNEQ). In addition, two finite rate chemistry models (CNEQ-P and CNEQ-D&K) have been used to obtain the non equilibrium solutions.

5.2.2.1 Low pressure case

We start presenting the axial evolution of the elemental oxygen mole fraction at 5000 Pa in Fig. 5.29.

![Figure 5.29: Oxygen elemental molar fraction radial profiles at four locations [5000 Pa].](image)

Firstly, we focus our attention on the chemical non equilibrium results in the inlet zone where we notice the presence of a strong depletion of oxygen as already observed in Sec. 5.1.1. In addition, we are now able to show that the chemical non equilibrium predicts a similar oxygen profile for both finite rate models. Indeed, from the wall towards the axis we notice a rapid decrease of oxygen concentration followed by a plateau starting around $r \sim 6$ cm. The values of the plateau differ slightly for the two solutions obtained with the Park ($\sim 0.16$) and the D&K
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(~ 0.17) models. As we move forward from the inlet [Fig. 5.29(a)] to the mid-coil position [Fig. 5.29(b)], we retrieve similar results as in Sec. 5.1.1 for the equilibrium regime and we notice that the discrepancies between the predictions obtained with the two chemical kinetics models decrease with respect to the previous location and remain confined in a region close to the axis. These differences are further decreased when we move to the torch exit [Fig. 5.29(c)], where we notice a very good match between the CNEQ-P and the CNEQ-D&K predictions for \( r > 0.3 \) cm. The small differences observed in the third section vanish [Fig. 5.29(d)] during the time needed by the flow to reach the exit of the computational domain. Indeed, from the analysis of Fig. 5.29(d) we notice that the elemental fraction profiles obtained with the two models follow the same radial evolution.

Another interesting conclusion about the predictions obtained for different chemical regimes is drawn from the comparison between equilibrium and non equilibrium results. Indeed, we clearly notice that as we move from the inlet towards the chamber, the non equilibrium results follow closer and closer the equilibrium ones. Within the torch, we remark that the prediction obtained using the non equilibrium formalism is characterized by a plateau for \( r < 6 \) cm and, as we move toward the quartz tube, a peak is observed close to the wall for \( r \sim 7 \) cm. After the torch, the plateau is stretched, leading to a profile with a minimum for \( r \sim 6 \) cm from which the oxygen concentration increases towards the axis presenting a local extremum with a corresponding value slightly higher than 0.18. In particular, we notice that the prediction of the elemental molar fraction around the axis, obtained with the two formalisms (CNEQ and LTE-VEF) essentially coincide. This result is of direct application to the determination of catalytic properties of TPS materials since it shows that, even for a low operating pressure, the results obtained with an equilibrium formalism lead to the same elemental fraction around the axis as the one obtained under equilibrium conditions with the two different chemistry models. This local elemental fraction is different from the value corresponding to the inlet and will therefore influence the rebuilding procedure, at least from a conceptual point of view. The importance of this influence will in general depend on the operating conditions and especially from the mixture selected as representative of the plasma to be tested.

In Fig. 5.30, we present the radial temperature profiles in the four locations previously investigated. We start our analysis of the temperature evolution by considering the non equilibrium results. As for the oxygen elemental fraction we observe that the results obtained with the two models lead to the same temperature profiles beyond the mid-coil position. On the other hand, some differences are visible close to the inlet [Fig. 5.30(a)] and in the middle of the torch [Fig. 5.30(b)]. As soon as we move to the exit of the domain [Fig. 5.30(d)], the remaining differences gradually disappear. From the comparison between the equilibrium and non equilibrium results, we immediately draw conclusions similar to those obtained for the elemental fraction. Indeed, within the torch we observe a non negligible difference between the equilibrium and non equilibrium results, especially close to the axis where the equilibrium predictions lead to a higher temperature than what observed under non equilibrium. As shown in Sec. 5.1.1, we notice that the temperature prediction obtained under equilibrium is not strongly influenced by the elemental fraction variations both within and outside the torch. Finally, we clearly observe that, in the chamber [Fig. 5.30(d)], the prediction obtained in the four computations are very close, especially for \( r > 2 \) cm, even if small discrepancies are visible on the axis. The previous results, and in particular the analysis of Figs. 5.29(d) and 5.30(d), show that even at low pressure the prediction of the flow behavior in the chamber obtained under non equilibrium with two finite rate models, and under equilibrium with variable elemental fraction, are very close.
5.2.2. Parametric study of pressure influence

We now move to the parametric study of the pressure influence on the flow behavior in the test chamber. The main objective of this analysis is to characterize the flow in the jet at a certain distance downstream of the torch exit. For this purpose we focus on the exit of the computational domain placed 30 cm after the beginning of the chamber. This distance, even if arbitrary, lies in the range of possible locations where the heat flux probe can be placed within the test chamber.

Our analysis is based on the discussion of the results presented in Figs. 5.31-5.32, where we show the oxygen elemental mole fraction, respectively the temperature profiles, at the outlet of the domain \(z = 0.8\text{ m}\). Observing the profiles presented in Fig. 5.31, we notice that the results obtained under chemical non equilibrium with the two finite rate models are always coincident for each operating pressure. This leads us to the following observation: the use of Park and Dunn-Kang models leads to the same prediction of the radial evolution of the elemental concentration for \(z = 0.8\text{ m}\). If we consider the comparison between the equilibrium and non equilibrium results, we remark that the non equilibrium prediction approaches the equilibrium one as pressure rises. Indeed, for the first two pressures [Figs. 5.31(a)-5.31(b)], we notice some
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Figure 5.31: Oxygen elemental molar fraction for several operating pressures at \( z = 0.8 \text{m} \).

The particular radial evolution of the oxygen profiles follows from the oxygen diffusion within the torch described in detail in Sec. 5.1.1.

After the torch exit, the form of the profile inside
the jet does not change considerably in the axial direction whereas, along \( r \), after the peak \( (r \sim 8 \text{ cm}) \) the oxygen concentration tends toward the constant characteristic value of the relatively cold flow present in the chamber at higher radius \( (r > 12 \text{ cm}) \). Each of the graphs presented in Fig. 5.31 reflects the qualitative analysis presented previously showing that the defect of oxygen observed in the jet is compensated by an excess of oxygen concentrated in the volume between two cylinders. In the highest pressure case [Fig. 5.31(d)], this volume is confined between an inner radius \( \sim 7 \text{ cm} \) and an outer radius \( \sim 9 \text{ cm} \).

We now move to the analysis of the radial temperature profiles. As for the elemental concentration, the most important part of the temperature profiles corresponds to the zone close to the axis which is of direct interest for the estimation of the catalytic activity of TPS materials. For this reason, to improve the readability of the graphs to be presented shortly, we present the temperature profiles for \( r < 12.5 \text{ cm} \), knowing that the temperature is almost constant for larger radii. We start our analysis comparing the results obtained under non equilibrium with two finite rate models. For all the operating pressures, the use of the Park and Dunn-Kang
Chapter 5. Applications to ICP flow computation

models for the description of the air finite rate chemistry brings to the same radial temperature evolution. The differences between equilibrium and non equilibrium predictions visible in the lowest pressure case [Fig. 5.32(a)] gradually disappears as pressure rises. Indeed, for 10000 Pa [Fig. 5.32(b)] and to 20000 Pa [Fig. 5.32(c)] some small differences are visible, but they disappear for the highest operating pressure [Fig. 5.32(d)]. These observations lead us to conclusions similar to those drawn from the analysis of the oxygen elemental fraction. Indeed, starting from 10000 Pa the three formalisms CNEQ, LTE-VEF, and LTE-CEF predict the same temperature profile. With respect to the oxygen elemental fraction, we anyway notice that the elemental diffusion does not affect the temperature at sufficiently high pressure (> 10000 Pa), as already observed within the torch in Sec. 5.1.1.

5.3 Summary

A detailed analysis of both air and carbon dioxide inductively plasma flows for applications to Earth and Mars entry has been presented. This study was conducted considering both the equilibrium and the non equilibrium form of the governing equations presented in Sec. 3.2 and the critical analysis of the main flow features has been divided in two parts. Firstly, we discussed the flow behavior within the torch for air and CO\textsubscript{2} mixtures and then we considered an air plasma both in the torch and in the chamber. In the following, we present the main achievements of this study.

Air plasma flow within the torch

The analysis of the simulation of an existing high pressure Inductively Coupled Plasma torch operating at pressures ranging from 0.05 to 0.3 atm leads us to the following conclusions:

- in high-pressure ICP torches, the oxygen concentration varies significantly throughout the flowfield. From the large series of calculation presented, we find that for an inlet volumetric oxygen fraction of 21%,
  - the oxygen content typically decreases to ~ 15% inside the recirculation near the inlet and to ~ 17-18% at the outlet, on the axis.
  - At the edges of the plasma ball, closer to the quartz wall, the oxygen content typically reaches ~ 25%.
  - On the quartz wall, due to convection from the inlet, the oxygen content remain close to ~ 21%.
- While it significantly affects the plasma concentration, the effect of demixing on obtained temperature fields is very low, at least for the case of air ICPs.
- Demixing occurs regardless of the degree of chemical non equilibrium in the plasma. At sufficiently high pressures (0.3 atm for the torch considered here), the Local Thermodynamic Equilibrium formulation with variable elemental fraction is as accurate as the chemical non equilibrium formulation.
5.3. Summary

- Chemical equilibrium conditions do exist in viscous flows at sufficiently high pressures and chemical reaction terms based upon the law of mass action are compatible with this fact.

**Carbon dioxide plasma flow within the torch**

We presented original carbon dioxide plasma flow simulations under equilibrium considering both constant and variable elemental fraction conditions. A critical analysis of these results shows that for an inlet carbon volumetric fraction of $\sim 33\%$:

- the solution, under chemical equilibrium, of an additional set of elemental continuity equations for oxygen and carbon shows the presence of important variations in the elemental composition.
- The amount of demixing observed for the operating conditions considered is characterized by a maximum increase to $\sim 38\%$ and a decrease to $\sim 28\%$ of the carbon elemental fraction.
- The effects of these variations in the elemental fraction on the species evolution is much higher than for air flows. Indeed, at the outlet of the torch, important differences are observed between the species radial profiles obtained under equilibrium with constant and variable elemental fractions.
- The influence of demixing on the temperature prediction is much higher for CO$_2$ flows than for air. At the torch exit, neglecting elemental diffusion a maximum relative error of $\sim 40\%$ is observed for $r \sim 5.8$ cm, while on the axis it decreases sharply to $\sim 2\%$.

**Air plasma flow both in the torch and in the chamber**

In the second part of this chapter, we presented the analysis of air plasma flows both in the torch and in the chamber of the VKI plasmatron for four operating pressures ranging from 5000 Pa to 30000 Pa. The results obtained for this geometrical configuration have been produced using three formulations: chemical non equilibrium and equilibrium with both constant and variable elemental fractions. In addition, two finite rate models have been used to obtain the non equilibrium results. The analysis of these results leads us to the following conclusions:

- for the low pressure case (5000 Pa), we observe a certain influence of the finite rate chemistry model on the prediction of the flow behavior within the torch. This influence was found to decrease considerably after the torch, leading to almost negligible differences at the end of the computational domain placed $\sim 30$ cm after the torch.
- From the comparison of the equilibrium and the non equilibrium results, we notice that the flow in the torch is indeed in non equilibrium for the low pressure case (5000 Pa). The degree of non equilibrium depends on the position, decreases as we move toward the exit of the torch and is sensibly reduced in the jet. There, the non equilibrium results are rather close to the equilibrium ones, provided that elemental demixing is taken into account.
• As pressure rises, the differences between the predictions obtained with the two finite rate models sharply decrease in the whole flow field. They are very small for the low pressure case (5000 Pa) and they become negligible afterwards.

• By increasing the operating pressure, we act directly on the relation between non equilibrium and equilibrium results. Indeed, the predictions obtained in the jet using both finite rate chemistry models approach the equilibrium results already in the lowest pressure case. Then, if pressure is further increased, the differences between the equilibrium and non equilibrium predictions decrease and become negligible at 10000 Pa.

In light of the previous observations, we can therefore conclude that, for the purpose of TPM testing, for sufficiently high pressures, the prediction of the flow physico-chemical state in the jet obtained under equilibrium conditions where elemental demixing is taken into account is as accurate as the one obtained under non equilibrium conditions. In the present study, the pressure limit above which the previous conclusion is valid has been observed to be 10000 Pa.
Chapter 6

Practical application to TPM testing

The von Karman Institute has been involved since 1997 in the determination of catalytic properties of thermal protection-system materials (TPM). Recently, with the initiation of several Mars exploration projects, interest has been attracted to Mars entry problems [44, 45, 28]. The two inductively coupled plasma (ICP) facilities of the Institute (Plasmatron [Fig. 1.2] and Minitorch [Fig. 1.3]) have been equipped to work with CO$_2$ mixtures as discussed in chapter 3. The VKI high-enthalpy flow solvers are interfaced with libraries to compute thermodynamic, transport, and non-equilibrium chemistry properties. The thermodynamic and transport libraries have been recently updated to incorporate CO$_2$ mixtures. In this chapter the physico-chemical description of a CO$_2$ flow is completed, allowing for simulations in chemical non-equilibrium, characterized by both bulk and surface reactions. A critical output of the LHTS methodology is the heat load on the stagnation point of a flying body, where large gradients of temperature and mass concentrations are present. These features make this point a suitable benchmark for testing thermochemical models. The flowfield in the vicinity of the stagnation point has been analyzed by means of stagnation-line flow calculations. These computations are applied for the determination of surface catalytic efficiency in CO$_2$ mixtures, leading to the determination of so-called heat-flux maps. The analysis that ensues is based on the study presented by Rini et al. in Ref. [122] whose motivation is recalled here after:

1. The simulation of gas/surface interactions in CO$_2$ flows requires a special care because of the coupling between wall reactions sharing oxygen atoms. This is correctly described by the model presented in Sec. 3.1.1.3 which will be successfully applied to describe heterogeneous recombination in carbon dioxide mixtures.

2. The model proposed in Sec. 3.1.1.3 for the description of gas/surface interactions is compared against the one presented by Scott [137] showing that the latter one is not consistent with element mass conservation.

3. In the aerospace related literature, the usual definition of a ‘catalytic surface’ is of-
ten given as the property of a certain material to promote recombination of atoms or molecules on the surface itself. As a consequence, a fully catalytic surface is said to be the one that forces a complete recombination inducing local conditions which tend to the equilibrium limit. Following this observation, several researchers working in the field of TPS design treat the gas/surface interactions for fully catalytic materials by computing the local mixture composition as the one corresponding to equilibrium conditions defined by the local pressure and temperature but using a reference elemental fraction, usually corresponding to the free stream. Thanks to the analysis of the results to be presented shortly, we will show that to define the equilibrium conditions representing the limit toward which a fully catalytic condition should tend, the local elemental fraction should be used instead of the free stream one.

A crucial aspect of the methodology for the estimation of the catalytic properties of TPM is the heat flux map expressing the relation between wall heat flux, wall temperature and the effective recombination probability. As a final summary of the previous investigation, we will show how the outer edge elemental fraction affects the heat flux map. This will allow for the estimation of the influence that elemental demixing in the jet could have on the prediction of the effective recombination probability of thermal protection materials.

6.1 Stagnation line flow computations

In this section, we present the solution of the stagnation line equations presented in Sec. 3.1.2 for a carbon dioxide mixture under chemical non equilibrium conditions. The test case definition is based on several simulations and experiments presented by Kolesnikov in Refs. [75] and [74] referring to the 100-kW IPG-4 plasmatron (IPM). Many calculations have been carried out at VKI [120] covering a wide range of enthalpy conditions. To investigate the importance of bulk and surface chemistry, we focus our attention on two operating conditions characterized by different outer edge enthalpies presented in Tab. 6.1, where $h_0$ is the mixture enthalpy at the outer edge, $V_i$ the incoming flow velocity and $p$ the operating pressure. This will lead to different chemical compositions and temperatures at the outer edge. As a consequence, different chemical processes will be enhanced by the bulk recombination and the presence of atomic carbon at the outer edge in the second case, will influence the definition of the set of wall reactions.

<table>
<thead>
<tr>
<th>Table 6.1: Flow conditions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low enthalpy case</td>
</tr>
<tr>
<td>$h_0$ [MJ/kg]</td>
</tr>
<tr>
<td>$p_0$ [atm]</td>
</tr>
<tr>
<td>$R_m$ [mm]</td>
</tr>
<tr>
<td>$\delta$ [mm]</td>
</tr>
<tr>
<td>$v_0 \partial/\partial y(\partial u_0/\partial x)/(\partial u_0/\partial x)^2$ [-]</td>
</tr>
<tr>
<td>$\partial u_0/\partial x$ [s$^{-1}$]</td>
</tr>
</tbody>
</table>

The flow is considered to be under equilibrium conditions at the boundary layer edge. There-
fore, the outer edge temperature is the result of an iterative calculation in which the thermodynamic modeling of the flow plays an important role. The corresponding values of temperature are 5922 K and 8127 K for the low and high enthalpy cases respectively.

Table 6.2: Chemical reactions used in the Stagnation Line computations. (M=CO₂, CO, O₂, O, C)

<table>
<thead>
<tr>
<th>Dissociation reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ + M ⇌ CO + O + M</td>
</tr>
<tr>
<td>CO + M ⇌ C + O + M</td>
</tr>
<tr>
<td>O₂ + M ⇌ O + O + M</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Neutral exchange reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO+O ⇌ C+O₂</td>
</tr>
<tr>
<td>CO₂+O ⇌ CO+O₂</td>
</tr>
</tbody>
</table>

For the given flow conditions at the boundary layer edge, the heat flux at the stagnation point of the model has been computed as a function of the surface temperature $T_w$ and the surface effective catalycity $\gamma_w$, from the solution of the stagnation line equations. The analysis of the non equilibrium dissociated subsonic flow around the model is based on the assumptions discussed in Sec. 3.1.2 and the following ones:

- the gas is represented by a 5 species (CO₂, CO, O₂, O, C) viscous and heat conductive mixture.
- The reaction set describing the finite rate bulk chemistry of the flow is the one described in Tab. 6.2.
- The surface catalytic reactions proceed according to the Eley-Rideal mechanism [46] and the following models are considered for the various cases analyzed.

**2-surface reactions model:**

1. $O + (O - S) \rightarrow O_2 + S$
2. $CO + (O - S) \rightarrow CO_2 + S$

**3-surface reactions model:**

1. $O + (O - S) \rightarrow O_2 + S$
2. $CO + (O - S) \rightarrow CO_2 + S$
3. $C + 2(O - S) \rightarrow CO_2 + 2S$

Another important assumption in the present model is that all the recombining species have the same effective recombination probability, i.e. for the mentioned wall chemistry model we have

$$\gamma_{CO_w} = \gamma_{O_w} = \gamma_{C_w} = \gamma_w.$$  (6.1)
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As the result of the computations performed along the stagnation line, for a 50 mm diameter probe, several charts have been determined for the stagnation point heat flux as a function of \( T_w \) and \( \gamma_w \in [0, 1] \), and will be presented later in this section.

6.1.1 Low enthalpy case

We start our analysis considering the low enthalpy case for which only the 2-surface reactions model has been applied, using both Scott’s model [137] and the formulation introduced in Sec. 3.1.1.3. This reaction scheme is based on the recombination of atomic oxygen and carbon oxide to produce molecular oxygen, respectively carbon dioxide. The success of these two processes is based on the simultaneous presence of O and CO close to the surface. The atomic oxygen will then concur to both recombination processes while CO only to one of them. The description of the kinetics of these two reactions requires the knowledge of the rates of each chemical process. These frequencies will be computed on the basis of the effective probability that an atom of oxygen has to be involved in the \( i \)th process (\( \gamma^i_O \)) and on the probability that a molecule of CO has to be involved in the \( j \)th reaction (\( \gamma^j_{CO} \)). Obviously these effective recombination probability are related by mass conservation and constrained by Eq. (6.1). Nevertheless, a correct treatment of these issues is missed in several gas/surface interaction models [137, 71], whereas they are correctly described by the formalism presented in Sec. 3.1.1.3 which in the present case reads:

\[
\begin{align*}
\gamma^1_O + \gamma^2_O &= \gamma_O, \\
\gamma^2_{CO} &= \gamma_{CO}, \\
\gamma^2_O M^1_O &= \gamma^2_{CO} M^1_{CO},
\end{align*}
\]

where, thanks to Eq. (6.1), \( \gamma_O = \gamma_{CO} = \gamma_w \). Eqs. (6.2) constitute a 3 \( \times \) 3 system in the unknowns \( \gamma^1_O, \gamma^2_O, \gamma^2_{CO} \) which must also satisfy the inequalities \( 0 \leq \gamma^i_i \leq \gamma_w \). The solution is easily obtained

\[
\begin{align*}
\gamma^2_{CO} &= \gamma_w, \\
\gamma^2_O &= \gamma^2_{CO} \frac{M^1_{CO}}{M^1_O}, \\
\gamma^1_O &= \gamma_w - \gamma^2_O.
\end{align*}
\]

This solution is valid as long as \( \gamma^2_O \leq \gamma_w \). If it is not, then it means that one of the assumptions made does not hold (e.g. equal recombination probability for all species). In practice, \( \gamma^2_O \) was always below \( \gamma_w \) for our computations. Then, the reaction frequencies [Eq. (3.17)] are obtained as

\[
\begin{align*}
\chi_1 &= \frac{\gamma^1_O M^1_O}{2}, \\
\chi_2 &= \gamma^2_{CO} M^1_{CO}.
\end{align*}
\]
leading to the following expressions for the species production terms

\[
\frac{\dot{\omega}_{CO}}{M_{CO}} = \gamma_{CO}^2 M_{CO}^\downarrow, \quad (6.5a)
\]

\[
\frac{\dot{\omega}_{CO}}{M_{CO}} = -\gamma_{CO}^2 M_{CO}^\downarrow, \quad (6.5b)
\]

\[
\frac{\dot{\omega}_{O}}{M_{O}} = \frac{\gamma_{O}^1 M_{O}^\downarrow}{2}, \quad (6.5c)
\]

\[
\frac{\dot{\omega}_{C}}{M_{C}} = 0, \quad (6.5d)
\]

\[
\frac{\dot{\omega}_{O}}{M_{O}} = -(\gamma_{O}^1 + \gamma_{CO}^2) M_{O}^\downarrow. \quad (6.5e)
\]

We now move to the presentation of the solution of the stagnation line equations presented in Sec. 3.1.2. All the computations showed in the following are converged for a 100 points discretization of the stagnation line. A grid resolution study was conducted to obtain reliable heating predictions. Species mass fraction and non-dimensional temperature profiles along the stagnation line are shown in Fig. 6.1 for 100 and 200 equidistant point grids, for both the McKenzie [Fig. 6.1(a)] and Park [Fig. 6.1(b)] bulk chemistry models. The solutions for both mesh refinements are seen to be identical, showing the grid independence of the results. The analysis of Fig. 6.1 reveals a non negligible influence of the bulk chemistry model. The main difference in the predictions obtained with the two sets of finite rate chemical processes lies in the evolution of atomic carbon along the stagnation line. The McKenzie model does not enhance considerably C recombination, while for the Park model C is involved in the formation of CO$_2$ starting from 80% of the stagnation line and it is completely depleted when we reach the 40% of the stagnation line. As a consequence, in Fig. 6.1(a) we observe that, even if CO disappears completely, a lower amount of CO$_2$ is present at the wall with respect to the computations obtained with the Park model. In addition, since less carbon is available for recombination, a higher amount of O$_2$ is observed at the wall for the prediction obtained with the McKenzie model. The difference in the prediction of atomic carbon chemistry will be more evident for the high enthalpy case and some of the previous observations will be helpful for the definition of the set of wall reactions.

We now turn our attention to the analysis of the diffusion demixing phenomenon considering three different wall boundary conditions:

- fully catalytic wall (present wall chemistry model - FCW);
- equilibrium wall with the element fraction of the outer edge (LEW - $X_{c}^\delta$);
- equilibrium wall with the element fraction corresponding the fully catalytic case (LEW - $X_{FC}^\delta$).

The wall heat flux corresponding to these cases is summarized in Tab. 6.3. Assuming a local equilibrium wall with the outer edge elemental fraction results in an overestimation of the wall heat flux, which is explained as follows. The wall heat flux is primarily controlled by the recombination processes taking place at the wall. Due to diffusion demixing
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Figure 6.1: Species mass fraction and non dimensional temperature profiles [Surface reaction model presented in Eq. (6.5), $h_e=15.3\text{MJ/kg, } T_w=300\text{K}$], [0: wall; 1: $\delta$].

(a) McKenzie bulk chemistry model.

(b) Park bulk chemistry model.

in the boundary layer, there is more oxygen and less carbon at the wall then at the outer edge (see Fig. 6.2 which shows the mass fraction profiles for the 3 boundary conditions). As a result, fewer CO$_2$ molecules can be formed, the excess oxygen forming O$_2$ molecules. Hence, less heat is released than if C and O elements were in the $1/3 - 2/3$ proportion. These results point out the importance of diffusion demixing effects, in particular regarding their influence on wall heat flux, and clearly establishes that the local equilibrium boundary
6.1.1. Low enthalpy case

Figure 6.2: Mass fractions and non-dimensional temperature for three different boundary conditions (Park bulk chemistry model) \( h_e=15.3\text{MJ/kg}, T_w=300\text{K} \).

Table 6.3: Wall heat flux for several boundary conditions (Park chemistry model) \( h_e=15.3\text{MJ/kg}, T_w=300\text{K} \).

<table>
<thead>
<tr>
<th>Boundary Condition</th>
<th>( q_w ) [MW/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCW</td>
<td>0.856</td>
</tr>
<tr>
<td>LEW - ( X_{\delta}^c )</td>
<td>0.857</td>
</tr>
<tr>
<td>LEW - ( X_{\delta}^c )</td>
<td>0.918</td>
</tr>
</tbody>
</table>

condition based on outer edge (free stream) elemental fractions, widely used in the framework of hypersonic flows simulations, is incorrect [125, 124].

At this point, it is interesting to comment on the relation between elemental diffusion and surface chemistry. Indeed, some approximate models used to describe stagnation line flows are based on the constant elemental fraction assumption as for example in the \( \gamma \)-code developed at IPM [72]. Under chemical non equilibrium conditions, using the 2-surface reactions model, both \( \text{O}_2 \) and \( \text{CO}_2 \) should be present at the wall under fully catalytic conditions. On the other hand, if constant elemental fraction is assumed through the boundary layer, equal to the outer edge one (1/3-2/3), the co-presence of these two species is not possible. Indeed, as shown in Ref. [131], the results of the \( \gamma \)-code operating with \( \text{CO}_2 \) mixtures under non equilibrium and for a fully catalytic surface, based on the 2-surface reactions scheme, show the presence of only \( \text{CO}_2 \) on the surface for cold wall conditions. This is clearly in contradiction with the equal effective recombination probability which is one of the major assumption of the IPM methodology. We wish to stress that the model presented in this thesis is free of these inconsistency.

Another illustration of the importance of the demixing phenomenon is provided by comparing Scott’s and the present formulation for a fully catalytic wall. Computed elemental fraction profiles are presented in Fig. 6.3, always for the low enthalpy case. Elemental fractions of carbon...
(X^C) and oxygen (X^O) defined in Eq. (2.2), are related to \( \xi \) as follows.

\[
X^O = \frac{\xi_O}{\xi_C + \xi_O} \quad \text{and} \quad X^C = \frac{\xi_C}{\xi_C + \xi_O}
\]

where

\[
\xi_C = (x_{CO_2} + x_{CO} + x_C) \frac{p}{R_u T}
\]

and

\[
\xi_O = (2x_{CO_2} + x_{CO} + 2x_{O_2} + x_O) \frac{p}{R_u T}
\]

\( R_u \) being the universal gas constant. From the analysis of Fig. 6.3(a) we observe that for Scott’s formulation \( X^O > X^{O,\delta} \) throughout the boundary layer, which is in contradiction with the elemental balance [Eq. (4.1)]. Indeed, as discussed earlier, in general only convective fluxes are significant in the elemental balance (the wall diffusion flux is zero and the edge diffusion flux is negligible) so that Eq. (4.1) reduces to

\[
\xi_j \delta V_\delta + 2 \frac{\partial u_\delta}{\partial x} \frac{\delta}{\hat{\eta}_{\text{max}}} \int_0^{\hat{\eta}_{\text{max}}} \frac{\xi_j F(\hat{\eta})}{\rho} d\hat{\eta} = 0. \quad (6.6)
\]

Hence, the elemental concentration (\( \xi_j \)) distribution must be such that some weighted average of it equals the outer edge concentration, and similarly for the elemental fraction (\( X^j \)), which is not verified when \( X^O > X^{O,\delta} \) throughout the boundary layer. In contrast, the elemental fraction distributions obtained with the present wall chemistry model are compatible with this condition [Fig. 6.3(b)].

In fact, the elemental fraction distribution obtained with Scott’s wall chemistry model violates this condition because this model does not respect elemental conservation at the wall. For the present problem, it provides a source of O and a sink of C at the wall. This was verified by computing the elemental diffusion fluxes at the wall and observing that

\[
C : \quad \frac{J_{CO_2,w}}{M_{CO_2}} + \frac{J_{CO,w}}{M_{CO}} + \frac{J_{C,w}}{M_C} < 0,
\]

\[
O : \quad 2 \frac{J_{CO_2,w}}{M_{CO_2}} + \frac{J_{CO,w}}{M_{CO}} + 2 \frac{J_{O_2,w}}{M_{O_2}} + \frac{J_{O,w}}{M_O} > 0.
\]

We now analyze the calculated heat flux maps for the present flow conditions. Heat flux maps consist of curves of wall heat flux (\( q_w \)) as a function of wall temperature between 300 K and 2100 K for various values of the recombination probability \( \gamma_w \). Four different maps have been obtained for the present test case, corresponding to all possible bulk chemistry (Park/McKenzie) and wall chemistry (Scott/present) model combinations. They are displayed in Fig. 6.4.

The influence of the bulk chemistry model is clearly visible. Park’s model reaction rates being much larger than McKenzie’s, the wall heat flux is significantly larger for low wall temperatures and low recombination probabilities. The influence of the wall reaction model is also important for large recombination probabilities. For high values of catalycity, the heat flux is seen to be significantly higher with the present model, which is consistent with the fact that, because of the existence of a sink of C atoms at the wall in Scott’s model, there are fewer C atoms available for recombination.
6.1.2 High enthalpy case

Attention is now turned to the high enthalpy case. Because of the higher enthalpy level, the mass fraction of C atom at the outer edge is much higher, so that the third wall reaction

\[ C + 2(O - S) \rightarrow CO_2 \]

may become important. For this reason, we first analyze the influence of the wall reactions set using Scott’s formulation for both bulk chemistry models. Species mass fractions and non-
dimensional temperature profiles are shown in Fig. 6.5 for a fully catalytic wall. Whereas for Park’s model there is no influence of the wall reactions set because the carbon atom entirely recombines inside the boundary layer (bulk chemistry), on the contrary the wall reactions set has a large influence when using McKenzie’s model, for which bulk reactions are much slower.

In particular, if the third wall reaction is ignored, there remains an important amount of atomic carbon at the wall. As a result, the wall heat flux is considerably smaller (see Tab. 6.4 in which heat fluxes are listed for all bulk chemistry/wall reaction set combinations).
6.1.2. High enthalpy case

(a) McKenzie bulk chemistry model.

(b) Park bulk chemistry model.

Figure 6.5: Mass fractions and non-dimensional temperature profile \([h_e=39\text{MJ/kg}, T_w=300\text{K}][0: \text{wall}; 1: \delta]\).

The present formulation for the 3 wall reactions model reads as follows

\[
\begin{align*}
\gamma_o^1 + \gamma_o^2 + \gamma_o^3 &= \gamma_o, \\
\gamma_{CO}^2 &= \gamma_{CO}, \\
\gamma_c^3 &= \gamma_c, \\
\gamma_o M_{CO}^i &= \gamma_{CO} M_{CO}^i, \\
\gamma_c M_c^i &= \frac{\gamma_o^3 M_o^i}{2},
\end{align*}
\]
Table 6.4: Wall heat flux for several sets of surface reactions \( [h_e=39 \text{ MJ/kg}, T_w=300 \text{K}] \).

<table>
<thead>
<tr>
<th>Surface Stagnation Line</th>
<th>( q_w ) [MW/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scott 2WR</td>
<td>McKenzie</td>
</tr>
<tr>
<td>Scott 3WR</td>
<td>McKenzie</td>
</tr>
<tr>
<td>Scott 3WR</td>
<td>Park</td>
</tr>
<tr>
<td>Scott 2WR</td>
<td>Park</td>
</tr>
</tbody>
</table>

where \( \gamma_{CO} = \gamma_O = \gamma_C = \gamma_w \). Eqs. (6.7a) represent a system of 5 equations in 5 unknowns \( \gamma_1^t, \gamma_2^t, \gamma_3^t, \gamma_{CO}, \gamma_C \). For the present flow conditions, numerical experiments have shown that the solution does not satisfy the constraint \( \gamma_3^t \leq \gamma_w \), which implies that the hypothesis of equal recombination probabilities for all species does not hold [144]. The analysis of a suitable assumption is however left as an open subject for a further study.

We therefore switch our attention to the Park bulk chemistry/2 wall reaction model for the present high enthalpy case.

![Figure 6.6: Mass fractions and non-dimensional temperature profile (Park bulk chemistry model) \( [h_e=39 \text{ MJ/kg, } T_w=300 \text{K}] \) [0: wall; 1: \( \delta \)].](image)

Species mass fraction and non-dimensional temperature profiles for a fully catalytic wall computed using the present wall chemistry formulation are shown in Fig. 6.6. This is to be compared with Fig. 6.5(b) where Scott’s formulation was used. The same conclusion as for the low enthalpy case is obtained, i.e. for high \( \gamma_w \) Scott’s model acts as a sink of carbon atoms at the wall. As a result, the wall heat flux is smaller, as seen in Fig. 6.7 which shows the heat flux map for the high enthalpy case.

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6.2 Influence of outer edge elemental fractions on heat flux maps

As discussed in the introduction, the methodology developed at the IPM and currently used at VKI to estimate the catalycity properties of TPS materials, is based upon Navier-Stokes simulations of an ICP facility supposed to be under LTE conditions determined assuming constant elemental fractions. The purpose of the Navier-Stokes plasma flow simulation is to provide the LTE outer edge inputs for the finite thickness non equilibrium stagnation line flow computations, carried out to compute a heat flux map. Among the quantities needed, the composition is implicitly given as a function of the outer edge pressure and rebuilt-enthalpy, assuming LTE and using the torch inlet elemental fractions. In general, thanks to elements diffusion, the elemental fractions vary within the ICP facility [153], as shown in chapter 5, leading to an outer edge elemental composition different from the torch inlet one. If this difference has an influence on the heat flux map, by shifting or stretching the iso-catalycity lines, the same influence will be reflected to the estimation of TPS material catalycity.

One way to easily estimate this influence is to use the results of the constant elemental fraction ICP simulation and vary only the outer edge elemental fractions, used to determine the outer edge composition for the given enthalpy and pressure. In chapter 5 we found an oxygen elemental fraction lower than the inlet value \( X_o^M = 0.21 \) in the jet near the axis for air plasmas. On the other hand, for carbon dioxide flows the opposite behavior was observed, i.e. the oxygen elemental fraction reached values higher than at the torch inlet \( X_o^M = 2/3 \). Following this result, we have perturbed the oxygen outer edge elemental fraction by +10% and −10% of the reference inlet value, for carbon dioxide and air plasmas respectively.

The results of this analysis are presented in Figs. 6.8 and 6.9, where are shown the heat flux
maps corresponding to the conditions defined in Secs. 4.1-4.2, for both air and carbon dioxide. The results show an important influence on stagnation point heat flux for carbon dioxide mixtures. The reason of these differences can be explained from the analysis of species concentration showed in Fig. 6.10 for a fully catalytic cold wall. Indeed, the increase of oxygen outer edge fraction reduces the amount of carbon available for CO$_2$ recombination at the surface, this leading to a lower heat flux. This is more evident for high values of recombination probabilities, where almost the same effect on wall heat flux is observed in the whole temperature range considered. As the recombination probability is reduced the influence of the outer edge elemental fraction decreases as well, and a higher influence is observed for cold wall conditions, where recombination is enhanced by the bulk
chemistry owing to the low temperature.
As far as air mixtures are concerned, the effects on wall heat flux are essentially negligible. Indeed the lines of Fig. 6.9 are superposed for all values of catalycity in the temperature range investigated. The quite low influence on heat flux can be explained by the analysis of the species mass fraction profiles of Fig. 6.11. Indeed the perturbation of the elements fraction shifts slightly the concentration of N\textsubscript{2}, N, and O at the outer edge without altering too much the stagnation line chemistry.

The analysis carried out in this section shows therefore that, especially for Mars entry applica-
6.3 Summary

Several numerical solutions of the stagnation line flow of air and CO₂ reacting mixtures have been presented.

The numerical simulation of non equilibrium stagnation line flow of neutral mixtures impinging on a TPS sample, leads us to the following major conclusions:

- Two models for the description of the finite rate chemistry of a carbon dioxide mixture of neutral species have been tested to evaluate their influence on the stagnation point heat flux. From the analysis presented in this chapter, we observed an important difference in the results obtained with the Park and McKenzie models, the second leading in general to a lower recombination of C in the bulk followed by less CO₂ close to the surface. As a consequence, when using the McKenzie model a lower heat flux is observed at the stagnation point for sufficiently high recombination probabilities.

- Two models for the simulation of gas/surface interactions have been used to compute the stagnation point heat flux as a function of the effective recombination probability. Firstly, it was shown that the model of Scott does not respect elemental conservation at the wall. Then, to remedy this problem an alternative model has been proposed and successfully tested.

- Thanks to the analysis of the results obtained with the gas/surface interaction model proposed in this chapter, we firstly improved the understanding of the theoretical relation between a fully catalytic surface and the related equilibrium conditions; secondly, we showed that the constant elemental fraction assumption may contradict the hypothesis of equal effective recombination probability. Indeed, we have shown that a fully catalytic surface in CO₂ flows leads to a wall mixture composition which corresponds to the equilibrium one obtained using the local temperature, pressure, and elemental fractions. This contradicts the usual approach followed in the literature, based on the use of the reference (or free stream) elemental composition, leading always to 100% CO₂ on the surface, for cold wall conditions. The same arguments were used to show that a non equilibrium model of a carbon dioxide stagnation line flow based on the constant elemental fraction assumption, is in contrast with the equal recombination probability for CO and O involved in the formation of CO₂ and O₂ at the wall.

- Some of the numerical experiments conducted to produce the results presented in this chapter brought our attention on the validity of the equal recombination probability hypothesis, i.e. \( \gamma_{COw} = \gamma_{Ow} = \gamma_{Cw} = \gamma_w \). Indeed we observed that, depending on the local wall conditions, this assumption was not compatible with the surface reaction schemes investigated. As a consequence, we may conclude that, depending on the condition under investigation, some parts of the abacus could just be impossible to compute, leading to the determination of an heat flux map with discontinuous iso-catalycity lines or with some lines missing.
Finally, the influence of the outer edge elemental fractions on stagnation point heat flux showed the need to add them to the list of parameters of the methodology developed at the IPM, currently used at the VKI to estimate catalytic properties of TPS materials, especially for Mars entry applications.
Chapter 6. Practical application to TPM testing
Chapter 7

Related work

In the previous chapters we presented several results obtained for both chemical equilibrium and non equilibrium flow conditions involving weakly ionized plasmas and reacting mixtures of neutral components. During this thesis a parallel research topic, concerning the so called state-to-state model, has been investigated producing original results achieved thanks to the experience acquired during the studies presented in the precedent chapters, but lying a bit aside from the research path previously presented. For this reason we present the results of this research in this separate chapter in a ‘synthetic’ way.

Recent advancements of the state-to-state theory can be explained by the growing interest in different kinds of non equilibrium flows. It is well known that, in many real gas flows, strong non equilibrium conditions arise, so that widely used quasi-stationary distributions over vibrational energies are not valid. Examples of these conditions are the flows behind shock waves [104, 86, 1], expanding flows [132, 33, 138, 34] and flows in the boundary layer under (re)entry conditions [4, 24]. In the previous references the master equations for the vibrational level populations has been solved and noticeable deviations from the Boltzmann vibrational distribution have been found in some regions of the flow field.

The core of a state-to-state model consists in the solution of a set of continuity equations for each energetic level considered in the model itself. Each of the equations to be considered has a form similar to the one expressing the mass conservation of chemical species in a mixture of reacting gases [Eq. (2.5)], i.e.

\[
\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{u} + \mathbf{J}_i) = \dot{\omega}_i, \tag{7.1}
\]

where \(\rho_i\) represents the density of the ‘species’ \(i\), which should be thought as being related to a certain energetic level of a molecule or an atomic species. In the case where only vibrational non equilibrium is considered, the species \(i\) will represent a certain vibrational level of a molecule, e.g. \(N_2(i)\), or the atomic species \(N\) in the ground state. From Eq. (7.1) we observe that the design of a state-to-state model, for the description of vibrational non equilibrium phenomena, relies on two main aspects. The first aspect, related to the computation of the...
mass production term \( \dot{\omega}_i \), consists in the choice of the energy relaxation processes influencing the establishment of a certain vibrational population. The second, required to determine the species/level diffusive fluxes \( J_i \), is related to the evaluation of transport properties under vibrational non equilibrium conditions and it is of interest also for the computation of the transport coefficients present in the mixture momentum and energy conservation equations. Several ways could be followed to compute the mass production term, based on the physico-chemical mechanisms leading to variations of levels population when convection and diffusion are negligible. A brief presentation of these methods is presented in Sec. 7.1.1. For what concern the formal transport kinetic theory in the case of strong vibrational and chemical non equilibrium, a model has been developed in Ref. [81]. In more recent papers [79, 7, 25, 20], the effect of non equilibrium vibrational distributions on the heat transfer and diffusion in different flows is roughly estimated. In particular, it has been shown that the vibrational energy transport by diffusion represents a significant contribution to the total heat flux behind shock waves and in boundary layers. Recently, the modeling of vibrational non equilibrium processes attracted our attention and hereafter, we recall the main motivations of the investigation of the state-to-state model conducted in the framework of this thesis:

(1) several attempts to describe the ability of the state-to-state model to predict vibrational non equilibrium along a stagnation line, or in an expansion nozzle, are available in the literature. Many works have been published by the group of the IMIP [4, 6, 5, 7, 24] (Istituto di metodologie inorganiche e dei plasmi, Università di Bari) and by the SPU group [80, 81, 82] (Saint Petersburg University). One of the main research topics investigated in the past by the group of the IMIP, consists in the simulation of the stagnation line equations for \( \mathrm{N}_2/\mathrm{N} \) and \( \mathrm{O}_2/O \) mixtures under vibrational non equilibrium. Even though the description of the chemical processes is very accurate, several crude approximations are present in the modeling of the fluid dynamics description of stagnation line flows and of the transport properties needed to close the system of equations. These approximations are listed here below:

- Fick’s law with a constant diffusion coefficient is used for the description of the diffusion of the vibrational levels and the atomic species.
- Constant Prandtl and Schmidt numbers are assumed throughout the boundary layer.
- The ratio \( \mu \rho / \mu g \delta \) is supposed constant and equal to one even though it can increase up to 6, depending on the condition of interest.
- The momentum equation, considered in the previous works dealing with stagnation line flows, is drastically simplified. Indeed, the solution of this equation is not found numerically, but a crude polynomial fit is used to compute the stream function.
- The mixture energy equation is written in a form where a stiff source term, proportional to the mass production term \( (\dot{\omega}_i) \), is present in place of the diffusive transport of enthalpy \( (\sum h_i J_i) \). In addition, a term of the energy equation is neglected without any evident reason.

We find it odd that so many efforts are invested in the modeling of vibrational kinetics, when a rather simplified treatment of the main flow characteristics, as fluid dynamics
7.1 State-to-State thermal non equilibrium model

When dealing with thermal non equilibrium flow conditions, several models are available the most common of which are those based on the definition of several temperatures. Known as one-temperature and multi-temperature approaches, they are based on the quasi-stationary distributions of molecules over energetic levels: the equilibrium Boltzmann distribution in the first case and the non equilibrium multi-temperature distribution in the latter case. In these models, each energy mode is therefore described by a different temperature. As a consequence, the energy distribution of a single energy mode is equilibrated at its own temperature but it is not in equilibrium with the other energy modes. However, there exist conditions where the quasi-stationary distributions over vibrational energy are not valid, due to a strong vibrational-chemical coupling. Actually, the experimental data concerning the relaxation times of different processes in reacting mixtures [140] show that, in many cases of practical interest, the following relation between the relaxation times is valid:

\[ \tau_t < \tau_r \ll \tau_{vibr} < \tau_{react} \sim \theta, \]  

(7.2)
where $\tau_t$, $\tau_r$, $\tau_{vibr}$, $\tau_{react}$ are the mean times between the collisions with the translational, rotational and vibrational energy transfer and those with chemical reactions, and $\theta$ is the hydrodynamic time. Translational energy distribution is known to equilibrate fast and the rotational relaxation time is of the same order as the translational one and much smaller in comparison to the vibrational and chemical relaxation times. Therefore, processes of translational and rotational relaxation may be considered as rapid processes and, on the contrary, vibrational and chemical relaxation as the slow ones. The mean time of slow processes is comparable with the macroscopic time and these processes are in strong non equilibrium. The condition given in (7.2) lead to the so-called level approach in non equilibrium gas dynamics, which describes the simultaneous processes of the vibrational and chemical relaxation. In this case, the macroscopic conservation equations for mass, momentum and total energy should be considered together with the equations for level populations of different chemical species. This model is important for the study of vibrational-chemical coupling in the boundary layer, in the short relaxation zone behind a shock wave where steady-state vibrational distributions are unlikely to be established. From this point of view, the level approach can give the limits of the validity of the multi-temperature and one-temperature models. Indeed, under strong vibrational non equilibrium conditions, a non-Boltzmann distribution of particles among energy levels could be observed. As a consequence, it would be impossible to uniquely determine the energy distribution by means of a temperature.

In the following, we will deal with the analysis of vibrational and chemical non equilibrium only, solving continuity equations for each vibrational level. In more general models, we could envisage to account for other forms of non equilibrium, concerning for example the rotational and electronic states. In this case, additional conservation equations should be added to the set (7.1). For the solution of these equations it would be necessary to specify a collisional model needed to specify how to compute the source term $\dot{\omega}_i$. As an example, we could cite the Collisional Radiative model [84, 114, 54], which accounts for rovibrational excited states as well as electronic states of nitrogen related species. In this work, we limit ourselves to a specific subset of all possible mechanisms leading to the unique determination of $\dot{\omega}_i$. As a consequence, the model we will define shortly will represent a member of the wide family of state-to-state models.

Several hypotheses form the basis of the vibrational non equilibrium model we have used in this work and the most important are recalled hereafter. We assume that the mixture is in partial thermal equilibrium: all rotational states are fully equilibrated with the translational energy of particles at a common translational-rotational temperature. In fact, molecules rotational states are easily excited by collisions with other particles, while the vibrational states and chemical reactions have a long relaxation time. On the other hand, special consideration is given to the vibrational energy mode: molecules in the mixture with the same vibrational energy (vibrational state) are grouped together and considered as ‘species’. The evolution of vibrational levels population is described by a set of continuity equations for vibrational states analogous to the one that describes the chemical composition of a mixture under chemical non equilibrium [Eq. (7.1)].

The electronic states relaxation time is comparable with the vibrational characteristic time but, to simplify the model, the electronic states are supposed to be in equilibrium with the translational and rotational temperature. Indeed, if the translational temperature is not too high, as in our case, the electronic states have negligible influence on the global energy balance.
7.1.1 Mass production term for the level/species continuity equations

Within the state-to-state formalism the word ‘species’ is used to refer, without distinction, to a chemical species or to a particular vibrational level of a chemical species.

In the remaining part of this section, we focus on an $N_2/N$ mixture, selected as an illustrative example for the description of the main characteristics of the model. Following the state-to-state formalism we consider all the vibrational energy levels of the $N_2$ molecule [$N_2(i = 1), \ldots, N_2(i = N_v)$] in addition to the N atom.

7.1.1 Mass production term for the level/species continuity equations

The species continuity equations, equal in form to Eqs. (3.23) for the stagnation line problem, present in the state-to-state formalism contain a mass production/destruction term needed to compute the influence of vibrational quantum jumps on the establishment of non equilibrium distributions. The mass production term is divided into two parts: a first contribution due to the vibrational energy exchanges, i.e. to the transitions of molecules from one vibrational energy level to another, and a second contribution due to dissociation and recombination processes:

\[
\dot{\omega}_i = \dot{\omega}^{\text{vib}}_i + \dot{\omega}^{\text{dr}}_i. \tag{7.3}
\]

In the following two sections we discuss the way in which these two contributions can be computed.

7.1.1.1 Vibrational energy exchanges

The first step in the modeling of the vibrational energy exchanges is to select the total number of vibrational energy levels for a molecule.

Consider for example a molecule of $N_2$ in the ground vibrational state (zero vibrational energy). If we imagine to give energy to the molecule, freezing all the degrees of freedom except the vibrational one, the molecule jumps from a vibrational energy level to another and at the end, when the vibrational energy acquired is equal to the dissociation energy, the molecule dissociates into two atoms. Given the value of the dissociation energy, the number of vibrational energy levels to be included in the model, depends on the expression for the vibrational energy of the molecule as a function of the vibrational quantum number. If the molecules are represented as anharmonic oscillators, this expression consists in a series expansion and, in the literature, several forms are available, characterized by the number of terms included in the expansion, and by uncertainties on experimental values of the coefficients. In this work, the formula and the spectroscopic constants given in Ref. [64] are used:

\[
\epsilon^0_v = \hbar c \left\{ \omega_v \left( i - \frac{1}{2} \right) - \omega_x \omega_y \left( i - \frac{1}{2} \right) \left( i - \frac{1}{2} \right)^2 + \omega_x \omega_y \left( i - \frac{1}{2} \right)^3 \right\} - \epsilon^0_{\text{vib}}, \tag{7.4}
\]

\[
\epsilon^0_{\text{vib}} = \hbar c \left\{ \omega_v \left( 1 - \frac{1}{2} \right) - \omega_x \omega_y \left( 1 - \frac{1}{2} \right) \left( 1 - \frac{1}{2} \right)^2 + \omega_x \omega_y \left( 1 - \frac{1}{2} \right)^3 \right\}, \tag{7.5}
\]
where $i = 1, 2 \ldots N_v$, $c = 2.998 \cdot 10^8 \text{ m/s}$ is the speed of light, $h = 6.626 \cdot 10^{-34} \text{ J \cdot s}$ is the Planck constant and $\varepsilon_{vib}^0$ is the vibrational energy of the ground vibrational state. The spectroscopic constants appearing in Eq. (7.4) are listed in Tab. 7.1.

<table>
<thead>
<tr>
<th>$\omega_e$</th>
<th>$\omega_e x_e$</th>
<th>$\omega_e y_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>235857</td>
<td>1432.4</td>
<td>-0.226</td>
</tr>
</tbody>
</table>

Table 7.1: Spectroscopic constants for $N_2$ molecule [m$^{-1}$].

The spectrum generated from Eq. (7.4) is truncated when the value of the vibrational energy becomes greater than the molecular dissociation energy ($D_{N_2} = 1.5636 \cdot 10^{-18} \text{ J}$). This occurs when $N_v(N_2) = 48$.

The next step of the definition of the present non equilibrium model consists in the description of the transition from a vibrational energy level to another. The picture is quite simple: molecules jump from a vibrational energy level to another through collisions. A molecule can collide with another molecule or with an atom changing its vibrational energy. The energy loss or gain can be found as a difference in:

1. vibrational energy of the other colliding molecule (VV energy exchange),
2. translational-rotational or electronic energy of the other colliding molecule (VT$_M$ energy exchange),
3. translational energy of the colliding atom (VT$_A$ energy exchange).

These three kinds of reactions read as:

**VV reactions**

\[ N_2(j) + N_2(k) \Leftrightarrow N_2(i) + N_2(h), \quad (7.6) \]

**VT$_M$ reactions**

\[ N_2(j) + N_2 \Leftrightarrow N_2(i) + N_2, \quad (7.7) \]

**VT$_A$ reactions**

\[ N_2(j) + N \Leftrightarrow N_2(i) + N, \quad (7.8) \]

where the indexes $i, j, k, h$ stand for the vibrational quantum number. Focusing our attention on the $i^{th}$ vibrational energy level ($i^{th}$ species), and considering the total number of collisions taking place in the mixture, it is obvious that some collisions will increment the number density of this level (direct reactions), while other will deplete it (inverse reactions). If we focus on the VT$_A$ reactions [Eq. (7.8)], the number of jumps of a molecule from the generic vibrational energy level $j$ to the vibrational energy level $i$ is proportional to the population of the $j^{th}$ level and to the number density of colliding atoms. The coefficient of proportionality (rate of reaction) depends on translational-rotational temperature determining the frequency and the energy of collisions, and on the starting and arrival vibrational level. The VT$_M$ reactions [Eq. (7.7)] proceed in the same way, we have only to change the number density of colliding atoms with the total number density of the colliding molecules. For VV reactions [Eq. (7.6)], considering the binary collisions that make one colliding molecule jump from the generic level $j$ to the
level \( i \) and the other colliding molecule from the generic level \( k \) to the generic level \( h \), we can argue that the number of these collisions is proportional to the number densities of the levels \( j \) and \( k \).

The master equation for the mass production terms due to vibrational energy exchanges reads [26]:

\[
\dot{\omega}_{\text{vib}}^{|i \neq N_s} = m_{N_2} \sum_{j,k,h=1}^{N_v} \left( K_{j,i}^{k,h} n_j n_i - K_{i,j}^{h,k} n_h n_i \right) + n_{N_2} \sum_{j=1}^{N_v} \left( K_{j,i}^{M,j} n_j - K_{i,j}^{M,i} n_i \right) + n_N \sum_{j=1}^{N_v} \left( K_{j,i}^{A,j} n_j - K_{i,j}^{A,i} n_i \right),
\]

\[
\dot{\omega}_{\text{vib}}^{|i = N_s} = 0,
\]

where \( N_v \) is the number of vibrational energy levels and \( N_s = N_v + 1 \) is the number of species in the mixture (molecular vibrational states plus atomic species). \( m_{N_2} \) and \( m_N \) are the masses of the nitrogen molecule and atom, \( n_i = \rho_i / m_i \) is the number density of the \( i^{th} \) species, \( n_{N_2} = \sum_{i=1,N_v} n_i \) and \( n_N \) are the global number densities of nitrogen molecules and atoms and the \( K \) coefficients are the rates of reaction. Obviously, the vibrational energy exchanges do not influence the population of the atomic species, which will be affected only by the dissociation/recombination processes described in Sec. 7.1.1.2.

In order to further simplify the model, and in agreement with experimental data, another hypothesis is introduced: multiple quantum jumps in collisions between two molecules are negligible. Under this assumption, the reactions for production and depletion of the \( i^{th} \) species in a \( N_2/N \) mixture read [57] [24]:

**VV reactions**

\[
N_2 (i + 1) + N_2 (j - 1) \rightleftharpoons N_2 (i) + N_2 (j),
\]

\[
N_2 (i - 1) + N_2 (j + 1) \rightleftharpoons N_2 (i) + N_2 (j),
\]

**VT\_M reactions**

\[
N_2 (i + 1) + N_2 \rightleftharpoons N_2 (i) + N_2,
\]

\[
N_2 (i - 1) + N_2 \rightleftharpoons N_2 (i) + N_2,
\]

**VT\_A reactions**

\[
N_2 (j) + N \rightleftharpoons N_2 (i) + N.
\]

In agreement with the introduced set of reactions, and developing some terms in Eq. (7.9), the
mass production term for the species \(i\) read \[26\]:

\[
\ddot{\omega}_i^{\text{vib}} \bigg|_{i=1} = m_{N_2} \left\{ \sum_{j=2}^{N_v} \left( K_{i+j-1,i}^{j-1} n_{i+1} - K_{i,j-1}^{j-1} n_j \right) \right\} \quad (7.16)
\]

\[
+ n_{N_2} \left( K_{i+1,i}^{M} n_{i+1} - K_{i+1,i}^{M} n_j \right) \]

\[
+ n_{N_2} \sum_{j=1}^{N_v} \left( K_{i,j}^{A} n_j - K_{i,j}^{A} n_i \right) \right\},
\]

\[
\ddot{\omega}_i^{\text{vib}} \bigg|_{i \neq 1, i \neq N_v, i \neq N_s} = m_{N_2} \left\{ \sum_{j=2}^{N_v} \left( K_{i+j-1,i}^{j-1} n_{i+1} - K_{i,j-1}^{j-1} n_j \right) \right\} \quad (7.17)
\]

\[
+ n_{N_2} \sum_{j=1}^{N_v-1} \left( K_{i+j-1,i}^{j-1} n_{i+1} - K_{i,j-1}^{j-1} n_j \right) \right\},
\]

\[
\ddot{\omega}_i^{\text{vib}} \bigg|_{i=N_v} = m_{N_2} \left\{ \sum_{j=1}^{N_v} \left( K_{i+j-1,i}^{j-1} n_{i+1} - K_{i,j-1}^{j-1} n_j \right) \right\} \quad (7.18)
\]

\[
+ n_{N_2} \left( K_{i+1,i}^{M} n_{i+1} - K_{i+1,i}^{M} n_j \right) \]

\[
+ n_{N} \sum_{j=1}^{N_v} \left( K_{i,j}^{A} n_j - K_{i,j}^{A} n_i \right) \right\},
\]

\[
\ddot{\omega}_i^{\text{vib}} \bigg|_{i=N_s} = 0. \quad (7.19)
\]

The expressions for the rate coefficients \(K\) are given in Ref. [107].

### 7.1.1.2 Dissociation and recombination processes

In literature, at least two different approaches are available to describe dissociation and recombination processes. In the first approach, the dissociation rates for each vibrational energy level are calculated analytically. The second approach is based on a global rate coefficient (usually measured from experiments in equilibrium conditions) from which the rate coefficients for the vibrational states are recovered.
Concerning the first approach, some efforts have been made in order to extrapolate the dissociation rates from the rates used for vibrational transitions. A simple model that applies this philosophy is named as Ladder Climbing Model [5, 24]. According to this model, the coefficients for vibrational quantum jumps are extrapolated to the dissociation process, providing a simple starting point for calculations.

Considering only single quantum jumps in collisions between molecules, the reactions for dissociation and recombination read:

**VV reactions**

$$N_2 (N_v) + N_2 (j + 1) \rightleftharpoons 2N + N_2 (j)$$  \hspace{1cm} (7.20)

where \( j = 1, 2, \ldots N_v - 1 \).

**VT\_M reaction**

$$N_2 (N_v) + N_2 \rightleftharpoons 2N + N_2,$$  \hspace{1cm} (7.21)

**VT\_A reactions**

$$N_2 (j) + N \rightleftharpoons 2N + N,$$  \hspace{1cm} (7.22)

where \( j = 1, 2, \ldots N_v \). The contribution to the mass production term of the \( i^{th} \) species due to dissociation and recombination reactions reads:

\[
\dot{\omega}^{dr}_{i|e=N_s} = 2m_N \left\{ \sum_{j=1}^{N_v-1} \left( K_{N_v,N_s,N_v,j+1,N_{N_v}}^{j+1} n_{N_v,j+1} - K_{N_v,N_s,N_v,j,N_{N_v}}^{j} n_{N_v,j} \right) \right. \\
+ n_N \left( K_{N_v,N_s,N_v,j,N_{N_v}}^{M} n_{N_v} - K_{N_v,N_s,j,N_{N_v}}^{M} n_{N_v}^2 \right) \\
+ n_N \sum_{j=1}^{N_v-1} \left( K_{N_v,N_s,N_v,j,N_{N_v}}^{A} n_{j} - K_{N_v,N_s,j,N_{N_v}}^{A} n_{N_v,j}^2 \right) \left\} \right.,
\]

\[
\dot{\omega}^{dr}_{i|e=N_v} = m_N \left\{ \left( K_{N_v,N_s,N_v,i+1,N_{N_v}}^{N_v,N_s} n_{N_v,i+1} - K_{N_v,N_s,N_v,i,N_{N_v}}^{N_v,N_s} n_{N_v,i} \right) \right. \\
- \sum_{j=1}^{N_v-1} \left( K_{N_v,N_s,N_v,j+1,N_{N_v}}^{j+1} n_{N_v,j+1} - K_{N_v,N_s,N_v,j,N_{N_v}}^{j} n_{N_v,j} \right) \\
- n_N \left( K_{N_v,N_s,N_v,j,N_{N_v}}^{M} n_{N_v} - K_{N_v,N_s,j,N_{N_v}}^{M} n_{N_v}^2 \right) \\
+ n_N \left( K_{N_v,N_s,j,N_{N_v}}^{A} n_{j} - K_{N_v,N_s,j,N_{N_v}}^{A} n_{N_v,j}^2 \right) \left\} \right.,
\]

\[
\dot{\omega}^{dr}_{i|e=N_v,i\neq N_s} = m_N \left\{ \left( K_{N_v,N_s,N_v,i+1,j,N_{N_v}}^{N_v,N_s} n_{N_v,i+1} - K_{N_v,N_s,N_v,j,N_{N_v}}^{N_v,N_s} n_{N_v,j} \right) \right. \\
+ \left( K_{N_v,N_s,N_v,i,N_{N_v}}^{N_v,N_s} n_{N_v,i} - K_{N_v,N_s,j,N_{N_v}}^{N_v,N_s} n_{N_v,j} \right) \\
+ n_N \left( K_{N_v,N_s,j,N_{N_v}}^{A} n_{j} - K_{N_v,N_s,j,N_{N_v}}^{A} n_{N_v,j}^2 \right) \left\} \right.,
\]

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Following the Ladder Climbing Model, the expressions for rate coefficients in Eqs. (7.16)-(7.17)-(7.18)-(7.19) are given in Ref. [107]. As several authors [5, 24], we observed in our computations that the Ladder Climbing Model strongly underestimates the dissociation rates. Concerning the second approach, a global rate coefficient for dissociation reactions is used. The dissociation rate coefficients for all the vibrational levels are obtained from the global reaction coefficients. Following this approach, the reactions for dissociation and recombination processes read:

\[ \dot{\omega}_i \bigg|_{i=N} = m_{N_2} \left\{ \left( K_{j+1,i}^{N_2} n_{N_2} n_{i+1} - K_{j+1,i}^{N_2} n_{N_2} n_i \right) + n_N \left( K_{N_s,i}^{A} n_N^2 - K_{N_s,i}^{A} n_N \right) \right\} \] (7.26)

In the present study, three different models for the rate coefficients of Eqs. (7.29)-(7.30) are applied: the Marrone-Treanor model [93, 87], the Gamma model [88] and the Warnatz model [87]. The analysis presented in this section allows for the computation of the mass production term needed to solve the advection diffusion equations expressing the conservation of each level population.

### 7.1.2 Transport terms in the state-to-state approach

In this section, we briefly present the main aspects of the accurate description of transport processes in the framework of the state-to-state model. The main objective of this description is to
show how the transport coefficients, needed to solve the stagnation line equations, have been computed. To this end we need to provide expressions for the diffusive fluxes of the vibrational levels $N_2(i)$ and the atomic nitrogen $N$, the mixture viscosity and the thermal conductivity.

In this work, we benefited of the contribution of the SPU group which provided us with their transport routines that are now linked to the VKI Boundary Layer code as described in Ref. [143]. The presentation of the complete transport kinetic theory of mixtures under vibrational non equilibrium is out of the scope of this manuscript since a detailed description is already available in the literature [81]. We therefore proceed to a brief presentation of the main characteristics of this theory, referring the interested reader to the previously cited references for more details.

The expressions of the transport coefficients are based on a generalized Chapman-Enskog method [81]. Considering the time scale constraint (7.2), we observe that no quasi-stationary vibrational distribution exist and the zero order distribution function $f_{cij}^{(0)} (c, i, j$ denote chemical species, vibrational and rotational quantum numbers) is obtained under the form of Maxwell-Boltzmann distribution over velocities and rotational energy depending on the vibrational level population and chemical species concentrations. Then, the first order distribution functions $f_{cij}^{(1)}$ are computed as a function of the $f_{cij}^{(0)}$ leading to the determination of the first order transport terms. The expressions of these transport terms are given as a function of the bracket integrals introduced in Refs. [81, 32] and they depend on the cross-sections of the most frequent collisions, i.e. the elastic collisions and those leading to rotational energy exchanges. As a consequence, the form of these bracket integrals differs from the one characteristic of the ‘classical’ thermal equilibrium single temperature approach. Indeed in the latter case the bracket integrals depend also on the cross-section of vibrational energy exchanges.

The transport formalism based on the previous discussion is pretty complicated and several problems could be encountered when implementing on a computer the final expressions obtained for the transport coefficients. As we previously noticed, the determination of these coefficients is based upon the knowledge of bracket integrals for each species. This of course requires the knowledge of the cross-sections of elastic collision and TR processes for each vibrational state of the colliding partners. In addition, the size of the linear systems to be solved to compute the viscosity, the thermal conductivity and diffusion velocities can easily be very large. Moreover, these systems need to be solved in each part of the discretization domain and for each iterative step of the solution procedure, using the local thermodynamic conditions together with the local mixture composition. As an example, for a $N_2/N$ mixture defined considering 48 vibrational levels of $N_2$, we have $1225 [(N_v + 1)(N_v + 2)/2]$ independent diffusion coefficients obtained as the solution of a $49 \times 49$ linear system. At the same time, the computation of the mixture viscosity and thermal conductivity require the solution of $49 \ [N_v + 1]$, respectively $146 \ [3N_v + 2]$ algebraic equations. This can indeed cause some additional complications in the framework of the simulation of complex flow conditions by means of CFD. To maintain the advantage of the state-to-state transport theory and at the same time simplify the procedure for the computation of the transport coefficients, several assumptions are made and they are listed in the following:

- the rigid rotator model is used to describe the rotational energy mode of molecules. This avoids the roto-vibrational coupling.

- Using the assumptions of Monchick et al. [98], the bracket integrals are computed as a linear combination of the elastic collision integrals and the integrals depending on the
change of rotational energy of the inelastic collisions.

- All collision integrals depending on the variation of the rotational energy are supposed to be much smaller than the elastic collision integrals.
- The cross-sections of elastic collisions are assumed to be independent of the vibrational states of colliding particles.

These hypotheses are discussed in details in Ref. [81]. The practical consequences of these assumptions on the computation of the transport coefficients is far from being negligible. Indeed the viscosity is now obtained thanks to the solution of 2 algebraic equations instead of 49, and thermal conductivity requires the solution of 5 equations instead of 146. For what concerns the computation of the multicomponent diffusion coefficients, simplified expressions are presented in Ref. [81]. There, the multicomponent diffusion coefficients are expressed as a function of the level populations and of the binary diffusion coefficients, where the latter ones are computed considering each level \( N_2(i) \) as if it was in the ground state. In the results to be presented shortly, we have used the transport formalism based on the major assumptions previously discussed and presented in detail in Ref. [81].

### 7.2 Stagnation line flow simulation

In this section, we briefly present the numerical solution of the stagnation line equations [Sec. 3.1.2] for an \( N_2/N \) mixture under thermal non equilibrium modelled with the state-to-state approach. The stagnation line solution is obtained using:

- the complete set of governing equations presented in Sec. 3.1.2.1 complemented by 48 continuity equations for each vibrational level \( N_2(i) \) and one for the atomic nitrogen,
- the approach presented in Sec. 7.1.1.1 for the treatment of vibrational energy exchanges and the Ladder Climbing model for the description of \( N_2 \) dissociation/recombination.

A detailed presentation of the various results obtained for this mixture is available in two VKI technical reports [107, 143] and in the following, we limit our investigation to a single test case selected as an illustrative example for the presentation of the concepts introduced in the previous sections.

The stagnation line conditions, characteristic of Earth (re)entry [107], are defined in Tab. 7.2 and the surface is considered non catalytic with respect to any possible recombination.

| \( p_0 \) | \( T_0 \) | \( x_{N_2}^1 \) | \( x_N^2 \) | \( T_w \) | \( \frac{\varphi_{x_0}}{N_{\text{atm}}} \) | \( \eta_{\text{max}} \) | \( N_2 \) |
|---|---|---|---|---|---|---|
| 1000 Pa | 5000 K | 0.7131 | 0.2869 | 300 K | 5000 s^{-1} | 4 | 48 |

Table 7.2: Stagnation line conditions

To highlight the presence of vibrational non equilibrium, we base our analysis on the evolution
of the vibrational levels population of the $N_2$ molecules. To this end, in Fig. 7.1, we plot the molar fraction of each level as a function of the vibrational quantum number ($i$) for different positions along the stagnation line. $\eta = 4$ corresponds to the outer edge where the vibrational population is supposed to be under equilibrium at the outer edge temperature $T_d$.

![Figure 7.1: Vibrational distribution - Ladder Climbing Model of VKI](image)

As $\eta$ decreases, we observe that the form of the curve $n_{N_2}(i)/n$ changes with respect to the equilibrium one observed at the outer edge. In particular, we notice that already for $\eta = 2$ a plateau is visible for $i > 35$. The size of the plateau increases as we approach the wall, together with the molar fraction at which the plateau is established. At the wall ($\eta = 0$), we clearly observe a non equilibrium distribution of the vibrational levels. As a result of this analysis, we remark that vibrational non equilibrium does occur along stagnation lines under conditions of interest for atmospheric (re)entry. To correctly describe this phenomena, the solution of additional continuity equations for each vibrational level is needed. The effect of this vibrational non equilibrium on the reliability of the heat flux prediction still needs to be assessed by means of a careful study left as an open issue for a further research.

As far as the transport properties are concerned, we have computed them in two ways. Firstly, the approach described in Sec. 7.1.2 and introduced in Ref. [81] has been used. Secondly, we have considered an approximate approach. A 'fictitious' mixture of only two species ($N_2/N$) is considered defining the composition as $n_{N_2} = \sum_{i=1}^{N_v} n_{N_2}(i)$ and $n_N$, where the $n_{N_2}(i)$ and $n_N$ are the solution of $N_v + 1$ continuity equations. For this two species mixture we have then computed the viscosity and the thermal conductivity coefficients using the approach of the kinetic theory of multicomponent mixtures under thermal equilibrium. These coefficients are then used in the solution of the stagnation line equations as if they were corresponding to the mixture of the $N_v + 1$ species. In addition, the diffusion fluxes of the vibrational levels and atomic nitrogen are obtained as the solution of an extended form of the Stefan-Maxwell equations. This leads to a $(N_v + 1) \times (N_v + 1)$ linear system defined computing the binary diffusion coefficients involving the $p^{th}$ vibrational level of the $N_2$ molecule as if the molecule was in the ground state, i.e. $D_{N_2(j)} = D_{N_2,N}$ and $D_{N_2(i)} = D_{N_2,N} \forall i, j$. Using these two approaches we retrieve practically the same solution of the stagnation line equations.
7.3 Summary

In this chapter, we presented a complete and accurate model of the stagnation line problem based on the state-to-state approach. The contribution brought to the field of state-to-state modeling was based on the observation of several limits of the models on which previous studies were based. A theoretical investigation, combined with the analysis of the obtained results, leads us to the following major conclusions:

- The stagnation line modeling based on the state-to-state approach has been considerably improved with respect to previous studies, solving a formulation of the governing equations where an accurate description of the state-to-state chemistry, a consistent treatment of transport processes and a rigorous fluid dynamic model are fully coupled.

- Several models for the description of the vibrational energy exchanges and for the dissociation/recombination processes have been tested. A non negligible influence of these models on the prediction of vibrational population is observed, showing the need to assess the reliability of these models, especially comparing the numerical solution with experimental data.

- The most up to date models for the treatment of transport processes in mixtures under strong vibrational non equilibrium have been used. The results obtained with these models have been compared with those obtained following an approximate approach based on the definition of an equivalent two species mixture with concentration \( n_{N_2} = \sum_{i=1}^{N_v} n_{N_2}(i) + n_N \). Then, for this equivalent mixture, viscosity and thermal conductivity have been computed following the ‘classical’ kinetic theory for thermal equilibrium. In addition, the diffusive fluxes of vibrational levels and atomic nitrogen have been computed as the solution of an extended form of the Stefan-Maxwell equations \([Eqs. (2.7)]\). The results obtained using these two approaches are almost equivalent, showing that, for the analyzed operating conditions, from a practical point of view, the use of the kinetic theory developed for mixtures under strong non equilibrium could be avoided. This would allow researchers equipped with transport routines for the computations of transport properties based on the results of kinetic theory under thermal equilibrium, to still apply the state-to-state formalism without modifying their transport codes.
Chapter 8

Conclusions

This research was inspired by the methodology for the determination of thermal protection system materials catalytic activity, developed at the Institute for Problems in Mechanics (IPM) of Moscow. As appeared from the description presented in Chapter 1 and from the analysis of the material presented in the remaining part of this manuscript, this methodology involves many aspects of different flow models. Among all the building blocks of this methodology, we firstly focused our interest on the hypothesis of vanishing elemental fluxes assumed in each part of the original version of the IPM methodology. This investigation, as occurs in many circumstances, drove our understanding process through several challenging brain teasers, some of which were unexpected but welcome.

As a result of our understanding of diffusion phenomena in reacting mixtures, we derived the theory of LTE viscous flows with variable elemental fractions. Then, this theory has been applied to stagnation line flows to assess its performances by comparison with an implicit formulation of the flow governing equations. Furthermore, elemental diffusion has been investigated in the torch of an ICP facility for both air and carbon dioxide mixtures. Then the hot jet exiting the torch and flowing into the chamber has been also considered under both chemical equilibrium and non equilibrium. As a result, we noticed a match between non equilibrium and equilibrium results for sufficiently high pressures, provided that elemental fraction variations are accounted for. The significant oxygen depletion observed in the region near the chamber axis, encouraged our further investigation of the effects of the elemental diffusion taking place in the jet on the final computation of the heat flux map. This latter study was based on numerical simulation of chemical non equilibrium stagnation line flows of both air and carbon dioxide mixtures. The analysis of carbon dioxide flows required more efforts but led us to the proposition of a new model for the phenomenological description of gas-surface interactions. The experience acquired in the field of chemical non equilibrium modeling encouraged our further investigation of mixtures under strong vibrational non equilibrium. This last research led to the improvement of the stagnation line modeling based on the state to state approach.
8.1 Main Achievements

In this section the main achievements of the present research are recalled following the structure of this manuscript with the aim to construct the basis for the description of the future perspectives of this work.

8.1.1 Theory of reacting mixtures under Local Thermodynamic Equilibrium

A series of new elemental transport coefficients have been presented for mixtures under thermochemical equilibrium conditions. They allow to reduce the equations of chemically reacting flows in LTE to an elegant system consisting of the conventional Navier-Stokes equations (mass, momentum, energy) complemented by an advection-diffusion equation for the mass fraction of each chemical element in the mixture. The obtained formalism is in closed form in the sense that diffusive fluxes are directly expressed in terms of gradients of the solution unknowns, unlike other formulations in which these fluxes are obtained in an implicit manner, by solving the full system of Stefan-Maxwell equations. In the case of mixtures containing both neutral and charged components, assuming local neutrality and absence of current, we have introduced the following new transport properties: the elemental multicomponent ($D_{\ell k}$) and thermal demixing ($D^T_{\ell}$) diffusion coefficients, the thermal demixing conductivity ($\lambda_{D}$), the elemental heat transfer coefficients ($\lambda_{EL\ell}$), the pressure heat transfer coefficient ($\lambda_{p}$) and finally a thermal diffusion heat transfer coefficient ($\lambda_{T}$). Each of these transport coefficient is associated with a mass/heat flux as described hereafter:

$D_{\ell k}$: they express the linearity between the mass diffusive flux of element $\ell$ ($J_{\ell}$) and the gradient of the concentration of element $k$ ($\nabla Y^k$). Their knowledge allows for the computation of the mixing term $\rho \sum D_{\ell k} \nabla Y^k$. The matrix of elemental multicomponent diffusion coefficients is in general non symmetric and non negative, at least for the cases considered in the present work.

$D^T_{\ell}$: they express the linearity between the mass diffusive flux of element $\ell$ and the temperature gradient ($\nabla T$). Their knowledge allows for the computation of the demixing term $\rho D^T_{\ell} \nabla T$.

$\lambda_{D}$: it represents a correction to the Butler and Brokaw thermal reactive conductivity ($\lambda_{R}$) which correctly accounts for elemental demixing. Knowing $\lambda_{R}$ and $\lambda_{D}$ we can compute the part of the diffusive heat flux ($\sum J_s h_s$) proportional to the temperature gradient, when thermal diffusion is neglected.

$\lambda_{EL\ell}$: they express the linearity between the diffusive part of the mixture heat flux and the gradient in the concentration of element $\ell$. Their knowledge allows for the computation of the part of the diffusive heat flux due to non uniform element concentration fields.

$\lambda_{p}$: it expresses the linearity between the diffusive part of the mixture heat flux and the pressure gradient allowing for the computation of the term $\lambda_{p} \nabla p$. 

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$\lambda_T$: it represents the effect of thermal diffusion on the diffusive transport of enthalpy expressed by the term $\lambda_T \nabla T$.

If the more general case of the presence of non vanishing current is considered, the electric field ($E$) cannot be expressed by means of temperature and pressure gradients as done to define the previous transport coefficients. As a consequence, an additional electric field heat transfer coefficient ($\lambda_E$) should be included to compute the additional heat flux term $\lambda_E E$. In addition, the element mass diffusive fluxes depend linearly on the unknown electric field through suitable transport terms ($\sigma_e$). In the particular case of mixtures containing only neutral components, the effects of electric field vanish.

In this manuscript, numerical results are obtained neglecting the effects of baro-thermal diffusion. It will be certainly worth in the future to implement the expressions derived in this thesis to critically analyze the importance of these additional diffusion driving forces in the framework of high enthalpy flows modeling.

8.1.2 Elemental diffusion along the stagnation line

To verify the importance of elemental diffusion phenomena, we firstly focused our attention to the investigation of stagnation line flows of air and carbon dioxide mixtures. In both cases, non negligible elemental fractions variations have been observed, and their effects on the mixture heat flux were found to be more important for CO$_2$ mixtures. To further improve our understanding of the relation between equilibrium and non equilibrium regimes, a numerical experiment has been performed by artificially increasing the forward reaction rates to arbitrarily high values under non equilibrium. As a result, we observed that local thermal equilibrium with variable elemental fractions is the limit of a chemical non equilibrium regime.

Then, we turned our attention to more complex mixtures containing three elements. To further investigate topics of interest for Martian entry applications, we selected an 8 species CO$_2$/N$_2$ mixture. Under conditions of LTE, we analyzed the behavior of such a mixture using the formalism presented in Chapter 2. This was possible thanks to the use of the transport properties previously presented, which required the computation of nine elemental multicomponent and three thermal demixing coefficients, the demixing thermal conductivity and three elemental heat transfer coefficients, in addition to the 'standard' LTE transport properties.

The results of this study represent the first attempt to compute thermal demixing and multi-component diffusion coefficients as well as elemental heat transfer coefficients and thermal demixing conductivity for a mixture of heteronuclear components containing three elements. This proves the generality of the proposed formulation and clearly represents an improvement with respect to previous formulations available in the literature. In addition, the results obtained with the proposed closed form of the equations coincide with those obtained using an implicit formulation, indicating the correctness of the new formulation.

Finally, after a critical analysis of the results, we noticed how complex elemental concentration and heat flux patterns can be easily explained by examining graphs of LTE transport coefficients that arise from the new proposed LTE formulation.
Chapter 8. Conclusions

8.1.3 Elemental diffusion in inductive coupled plasmas

Our analysis of elemental diffusion proceeded further towards the investigation of air and carbon dioxide inductively coupled plasma flows for application to Earth and Mars entry.

To verify the validity of one of the major hypotheses of the IPM methodology, i.e. the existence of equilibrium conditions within ICP facilities, we considered both the equilibrium and the non equilibrium form of the governing equations. The numerical solution of these equations led to a detailed analysis of the flow behavior within the torch for air and CO$_2$ mixtures and then of the jet flowing into the test chamber for air mixtures.

8.1.3.1 Plasma flow simulation within the torch

The air plasma flow produced in the VKI-Plasmatron torch has been simulated using an eleven species mixture for several operating pressures ranging from 0.05 to 0.3 atm. Three regimes have been considered, all under thermal equilibrium: chemical equilibrium with constant elemental fraction, chemical equilibrium with variable elemental fraction and finally chemical non equilibrium. The comparison of the results obtained applying the formalisms related to these three regimes led us to the following major conclusions:

- in high-pressure air ICP torches, the oxygen concentration varies significantly throughout the flowfield.
- While these variations affect the plasma concentration, the effect of demixing on obtained temperature fields is very low, at least for the case of air ICPs.
- The degree of non equilibrium does not affect the amount of demixing observed in the plasma.
- If the operating pressure is sufficiently high, the Local Thermodynamic Equilibrium formulation with variable elemental fraction is as accurate as the chemical non equilibrium formulation.

As a consequence, we finally remark that the simulation of viscous flows under chemical equilibrium conditions leads to the same results as those obtained under chemical non equilibrium for sufficiently high pressures and chemical reaction terms based upon the law of mass action.

To extend the previous analysis, we have also considered the flow of carbon dioxide mixtures within the VKI-Plasmatron torch. To this end, we have selected an eight species mixture containing both charged and neutral components, as representative of the Martian atmosphere neglecting the minor components, as Nitrogen and Argon related species. As a result of our investigation we presented original carbon dioxide plasma flow simulations under equilibrium considering both constant and variable elemental fraction conditions. Some different conclusions can be drawn from the analysis of carbon dioxide flows with respect to air plasmas as observed in the following:
8.1.3. Elemental diffusion in inductive coupled plasmas

- as for air plasmas, we noticed the presence of important variations in the elemental composition.
- The effects of these variations in the elemental fraction on the species evolution is much more important than for air flows.
- The influence of demixing on the temperature prediction is much higher for CO\textsubscript{2} flows than for air.

8.1.3.2 Plasma flow simulation within both the torch and the chamber

After examination of the flow behavior within the torch, we turned our attention to the analysis of air plasma flows both in the torch and in the chamber of the VKI-Plasmatron. Several operating pressures have been investigated ranging from 5000 Pa to 30000 Pa. In addition, the three chemical regimes used to analyze air plasmas within the torch have been considered and for the description of chemical non equilibrium, two finite rate chemistry models have been selected as representative of Earth atmosphere chemistry.

The analysis of these results leads us to the following conclusions:

- for the low pressure case (5 kPa), we observe a certain influence of the finite rate chemistry model on the prediction of the flow behavior within the torch, while, as we move towards the test chamber, the flow predictions rapidly match leading to almost negligible discrepancies ∼ 30 cm after the torch.
- Non equilibrium effects are observed within the torch for the 5 kPa operating pressure. In the jet, the non equilibrium results are rather close to the equilibrium ones, provided that elemental demixing is taken into account.
- The consequence of increasing the operating pressure is to sharply decrease the differences between the equilibrium and non equilibrium predictions. These differences are very small for the low pressure case (5 kPa) and they become negligible afterwards, especially in the jet.
- For the considered plasmatron operating conditions, we select ∼10 kPa as the pressure limit above which the jet simulation obtained under chemical equilibrium with variable elemental fraction is as accurate as the one obtained under chemical non equilibrium.

The major result of this analysis consists in the fact that, for the purpose of TPM testing, the costly simulation of chemical non equilibrium ICP flows, both in the torch and in the test chamber, can be avoided for sufficiently high pressures. Indeed the same accuracy can be reached relying on the numerical simulation of a more compact thermochemical equilibrium formalism based on the solution of an additional set of elemental advection diffusion equations, free of stiff source terms. In addition, because of the important elemental fraction variations observed as a result of both air and carbon dioxide plasma flow simulation, it appears desirable to add the elemental fractions at the stagnation line outer edge to the list of non dimensional parameters defined in the framework of the IPM methodology.
Chapter 8. Conclusions

8.1.4 Determination of TPS materials catalytic activity

Following the results obtained in the previous studies, we focused our interest on the analysis of stagnation line flows for application to TPS testing. To this end, both air and carbon dioxide mixtures have been analyzed considering only neutral components.

In our simulations, two models (Park \[110\] and McKenzie \[95\]) for the description of finite rate chemistry for a carbon dioxide mixtures of neutral species have been tested and important differences in the results have been observed. Then, our attention has been attracted by the heterogeneous recombination processes taking place on the surface of TPM samples. During our investigation, some unexpected flaws of the Scott \[137\] formulation have been discovered. To overcome them, an alternative model has been proposed and successfully tested.

The main outcome of the analysis of the results obtained with this new gas/surface interaction model reads as follows :

- a deeper description of the theoretical relation between a fully catalytic surface and the related equilibrium conditions is presented;
- we have shown that the constant elemental fraction assumption may contradict the hypothesis of equal effective recombination probability;
- we have shown that a non equilibrium model of a carbon dioxide stagnation line flow based on the constant elemental fraction assumption is in contrast with the equal recombination probability for CO and O involved in the formation of CO\(_2\) and O\(_2\) at the wall;
- we have shown that the equal recombination probability hypothesis may not be compatible with the local wall conditions;
- we have verified the influence of the outer edge elemental fractions on the stagnation point heat flux. This influence, rather important for carbon dioxide mixtures, confirms the necessity to add the them to the list of parameters of the methodology developed at the IPM suited for the estimation of catalytic properties of TPS materials, especially for Mars entry applications.

8.1.5 Mixtures under strong vibrational non equilibrium conditions

As a consequence of the investigation of chemical non equilibrium flow conditions, we decided to extend our vision of high enthalpy flows towards the description of strong vibrational non equilibrium phenomena. To this end we followed the way proposed by the so called state-to-state approach, as defined by the research groups of Bari \[34, 25, 20\] and Saint-Petersburg \[104, 79, 105\]. Observing the presence of several limits within the models on which previous studies were based, we decided to invest some time and efforts to bring our contribution to the modeling of stagnation line mixtures under strong vibrational non equilibrium.
We have presented the original solution of a formulation of the governing equations, where an accurate description of the state-to-state chemistry, a consistent treatment of transport processes and a rigorous fluid dynamic model are fully coupled.

Within the proposed formalism, we have used the most up to date models for the treatment of transport processes in mixtures under strong vibrational non equilibrium. A comparison of the results obtained with these models with those obtained using an approximate approach based on the definition of an equivalent two species mixture, with concentration $n_{\text{N}_2} = \sum_{i=1}^{N_v} n_{N_i}$ and $n_N$, has been performed. The results obtained using these two approaches are almost equivalent, showing that, for the analyzed operating conditions, from a practical point of view the use of the kinetic theory developed for mixtures under strong non equilibrium could be avoided. This would allow researchers disposing of transport routines for the computations of transport properties based on the results of kinetic theory under thermal equilibrium to still apply the state-to-state formalism without modifying their transport codes.

## 8.2 Future perspectives

In this thesis, we addressed several issues concerning the modeling of reacting flows in the framework of a methodology for the determination of the catalytic properties of thermal protection materials. However, the theoretical findings and the numerical results presented in this manuscript are of application in other fields of up-to-date research. In addition, several issues are left open from the analysis we conducted, giving the opportunity for many interesting further developments, some of which are described hereafter.

### 8.2.1 Further applications of the theory of reacting mixtures under local thermodynamic equilibrium

#### 8.2.1.1 Inductively coupled plasma flows

The analysis of elemental diffusion within ICP flows has been conducted using both the equilibrium and non equilibrium formalisms and, as a result, we have shown that the equilibrium predictions are as accurate as the non equilibrium ones, provided that elemental diffusion is correctly accounted for. However, the LTE formalism used to obtain these results is based on the computation of the elemental mass diffusive fluxes as a linear combination of the species ones obtained as the solution of the Stefan-Maxwell equations. To improve our understanding of diffusion phenomena within plasma facilities we suggest to apply the theory presented in chapter 2 to the description of ICP flows under LTE. Practically, this can be easily done by linking the routines programmed to obtain the results presented in chapter 2, to the version of the ICP code developed within the framework of this thesis.
Chapter 8. Conclusions

8.2.1.2 Combustion

Recently, the impact of elemental diffusion on the prediction of the behavior of turbulent flames has been investigated by Gicquel et al. in Ref. [55]. In this reference, the authors discuss the effects of elemental diffusion on the temperature field and in particular on the occurrence of super-equilibrium temperatures. The encouraging results obtained in this study, should motivate, in our opinion, the further investigation of elemental diffusion in combustion problems. Firstly, we suggest to adapt the formalism presented in chapter 2 to the description of laminar flames, assuming thermochemical equilibrium. Practically, this can be done using the ICP code, switching off the electromagnetic field contribution and collecting the transport and thermodynamic properties of hydrocarbon-air mixtures of interest in combustion. If successful, this study would allow for the description of flame behavior at a fraction of the computational cost of the formalisms commonly used in combustion modeling, based on a very accurate and expensive description of the flow chemistry. Then, a similar investigation of turbulent flames could be envisaged. To this end, the formalism presented in chapter 2 could be adapted to turbulent codes such as the SFELES code [139]. This task would of course require the additional effort of linking a thermodynamic, transport and chemistry library to the code. Several libraries, available in the literature, could be used for this purpose: PEGASE [11, 14, 152], MUTATION [89], EGLIB [43], and finally CHEMKIN [69] if accurate chemistry needs to be modeled.

8.2.2 IPM Methodology for the determination of TPM catalycity

8.2.2.1 Further investigation of the effects of elemental diffusion

In our analysis, we observed that significant elemental fraction variations take place both in the torch and in the chamber of inductively plasma facilities. As a consequence, we suggested to include the stagnation line outer edge elemental fractions to the list of non-dimensional parameters of the IPM methodology. However, we did not include a TPS sample in the computations presented in this manuscript since our investigation was limited to the characterization of the free jet flowing into the chamber. It will be definitely worth in the future to include a heat flux probe for the purpose of evaluating how the non dimensional parameters are affected by elemental diffusion. After the computation of the non-dimensional parameters as the result of an LTE simulation with variable elemental fraction, the rebuilding process should be executed. Finally, the heat flux maps obtained with both sets of non-dimensional parameters, obtained under LTE with constant and variable elemental fractions, should be compared. The results of this comparison will allow to finally verify the practical influence of elemental diffusion in ICP flows on the output of the IPM methodology.
8.2.3 Gas-surface interactions

8.2.2 Equal surface reaction effective recombination probability

During our investigation of chemical non equilibrium stagnation line flows, we encountered several practical situations where, for high values of catalycity, the equal surface reaction probability assumption was in contrast with mass conservation. This was observed especially for carbon dioxide mixtures since the oxygen atoms are shared between the CO$_2$ and O$_2$ wall recombination processes (the same conditions could be experienced for air mixtures when NO recombination is accounted for). As a consequence, this assumption of the methodology can be cumbersome not only from the physico-chemical point of view, but also lead to practical inconsistencies in the flow description. It is therefore worth to invest time and efforts to avoid the need for this assumption. From a practical point of view, if this assumption is released, additional experimental inputs are needed to still apply the methodology. Very useful information could for example consist in the species concentrations in some points of the stagnation line. Intensive research efforts, based on spectroscopic measurements within the VKI-ICP facilities [116, 115, 151], are ongoing in this direction. The interest of the results of these contributions will certainly not be limited to the investigation of the equal recombination probability. Indeed, from the modeling point of view, we would enormously benefit from the results of this study, thanks to which, for example, we would be able to validate high enthalpy CFD codes and models versus experiments.

8.2.3 Gas-surface interactions

The approach followed for the estimation of the catalytic properties of thermal protection materials is based on a phenomenological treatment of gas-surface interactions. We believe that a different research path should be investigated in parallel in the future. It is the purpose of an ongoing international INTAS research program [66] involving VKI and several other European and Russian institutions to find a connection between the microscopic and macroscopic treatment of heterogeneous recombination. In addition, a VKI-RTO Lecture Series has been recently devoted to a similar subject [161]. From the numerical side, we suggest to proceed in this direction by considering the application of Molecular Dynamics [23] to conditions of interest for TPM testing in ICP facilities. From the experimental side, it would be of great help to investigate the relation between the measurable quantities in the neighborhood of the stagnation point of an heat flux probe held in an ICP facility and in chemical reactors [113, 112] also used to determine the catalytic activity of TPM.

8.2.4 Ablation

The particular type of thermal protection materials considered in the framework of this thesis belongs to the category of non-ablating materials. This kind of materials is of interest for a restricted range of applications where the heat transfer to the heat shield is sufficiently low [162]. To extend its capabilities, it could be of interest to VKI to devote some efforts to the development of both numerical and experimental tools focused on the design of ablating heat shields. From the experimental side, some investigations have already been performed to analyze the
ablation of graphite due to convective heat transfer in the VKI Minitorch. Thanks to the interest of the experimental results, it could be definitely worth in the future to include the simulation of ablating surfaces in the high enthalpy codes available at VKI [150]. The results of this effort would in addition be of direct application to the field of high speed missiles design.

8.2.5 Numerics

The numerical techniques used to simulate ICP flows are based on the discretization of the governing equations on structured meshes. This represents a serious limit for our approach, since it requires considerable efforts when the need comes to compute flow conditions involving complex geometries. To improve our approach we strongly recommend to use discretization methods based on unstructured grids [118]. Recently, this process began [117] with the implementation of the governing equations of reacting mixtures under thermochemical equilibrium within the COOLFluiD framework [83]. In addition, recent efforts will hopefully lead us to the implementation of the formalism presented in chapter 2 within COOLFluiD for the purpose of performing numerical studies of elemental diffusion in atmospheric (re)entry flows under local thermochemical equilibrium.
Appendix A

Mixtures of neutral components

In this section we provide detailed derivations of results derived in Sec. 2.3.2 and 2.3.3 and used to obtain the numerical values presented in Sec. 2.3.5. These derivations can also be used as guidelines for the practical implementation.

A.1 Species diffusion

The species diffusion fluxes obey the Stefan-Maxwell equations introduced in Sec. 2.3.2.1 and recalled hereafter:

$$
\frac{M}{\rho} \sum_{j \in S} \left( \frac{x_i W_j}{D_{i j f ij}} - \frac{x_j W_i}{D_{i j f ij}} \right) = \nabla x_i = d_i \quad (i \in S). \tag{A.1}
$$

In matrix form, the previous equation reads

$$
S \bar{W} = \bar{d} \tag{A.2}
$$

where

$$
S_{ij} = \begin{cases} 
  x_i M / [\rho D_{i j f ij}] & (i \neq j) \\
  \sum_{\ell \in S \setminus \{i\}} -x_\ell M / [\rho D_{\ell i f ij}] & (i = j).
\end{cases}
$$

For mathematical convenience, we split the matrix $S$ into four components, defined as follows:

$$
S = \begin{bmatrix} S_1 & S_2 \\ S_3 & S_4 \end{bmatrix} \tag{A.3}
$$

where

$$
S_{1,i,j} = S_{i,j} \quad (i, j \leq N_r), \quad S_{2,i,N_r-j} = S_{i,j} \quad (i \leq N_r; N_r < j \leq N_s), \quad S_{3,N_r-i,j} = S_{i,j} \quad (N_r < i \leq N_s; j \leq N_r), \quad S_{4,N_r-j,N_r-i} = S_{i,j} \quad (N_r < i, j \leq N_s).
$$

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A.2 Matrix assembly

The first part of the system defining the equilibrium condition for each of the $N_r$ reactions [Eqs. (2.10-2.11)] reads:

$$\sum_{s \in S} \nu_s^r \ln x_s = \ln K_p^r - \ln p \sum_{s \in S} \nu_s^r \quad (r \in \mathcal{R}).$$ \hspace{1cm} (A.4)

Taking the gradient of the previous equation, assuming constant pressure and using the van’t Hoff’s relation, we have that:

$$\sum_{s \in S} \nu_s^r x_s \nabla x_s = \Delta h^r \frac{R}{p} \nabla T \quad (r \in \mathcal{R}).$$ \hspace{1cm} (A.5)

Substituting the Stefan-Maxwell equations [Eq. (A.2)] into the matrix form of Eq. (A.5), we obtain that:

$$\begin{bmatrix} \tilde{A} & \tilde{B} \end{bmatrix} \begin{bmatrix} \tilde{A} & \tilde{B} \end{bmatrix}^T \begin{bmatrix} \begin{bmatrix} S_1 & S_2 \\ S_3 & S_4 \end{bmatrix} - \begin{bmatrix} B & I \\ -I & B \end{bmatrix} \end{bmatrix} \begin{bmatrix} \tilde{W}_R \\ \tilde{N} \end{bmatrix} = \theta,$$

where $\tilde{A}_{ij} = \delta_{ij}/x_j$ and $\tilde{B}^T = -B_{ji}/x_j$. Introducing the unit matrix $I$ and highlighting the structure of $S$, the previous relation reads:

$$\theta = \begin{bmatrix} \tilde{A} & \tilde{B} \end{bmatrix} \begin{bmatrix} S_1 - S_2B & S_2 \\ S_3 - S_4B & S_4 \end{bmatrix} \begin{bmatrix} \tilde{W}_R \\ \tilde{N} \end{bmatrix}.$$ \hspace{1cm} (A.6)

From Eq. (A.6) one easily verifies the validity of Eq. (2.25) introduced in Sec. 2.3.2.4, recalled hereafter:

$$\mathbf{Y} \tilde{W}_R + \mathbf{Z} \tilde{N} = \theta$$ \hspace{1cm} (A.7)

where $\mathbf{Y} = \tilde{A}(S_1 - S_2B) + \tilde{B}^T(S_3 - S_4B)$ and $\mathbf{Z} = \tilde{A}S_2 + \tilde{B}^TS_4$. Note that $\mathbf{Y}$ is symmetric; it may be shown that $\tilde{A}S_1$ and $\tilde{B}^TS_4B$ are symmetric and $\tilde{A}S_2B = -[\tilde{B}^T S_3]^T$.

The lower part of the equilibrium system, needed to impose the elements mass conservation [Eq. (2.12)], reads:

$$\sum_{s \in S} \phi_s^e \frac{M_e}{M_s} y_s^e = \mathbf{Y}^e \quad (e \in \mathcal{E}).$$

Taking the gradient of the previous equation, we have that:

$$M_e \sum_{s \in S} \phi_s^e \frac{\nabla y_s^e}{M_s} = \nabla \mathbf{Y}^e.$$ \hspace{1cm} (A.8)

We now introduce the matrix $\mathbf{F}$ representing the link between $\nabla (y_s/M_s)$ and $\nabla x_s$.

Species mass fractions are related to the respective mole fractions by means of the following relation:

$$y_s = \frac{\rho_s}{\sum_{i \in S} \rho_i} = \frac{M_s n_s}{\sum_{i \in S} M_i n_i} = \frac{M_s x_s}{\sum_{i \in S} M_i x_i}.$$
A.3 Linear system solution

The gradient of the previous relation reads:

\[
\frac{\nabla x_s}{M_s} = \frac{\nabla x_s}{\sum_{i \in S} M_i x_i } - \left( \frac{x_s}{\sum_{i \in S} M_i x_i } \right)^2 \sum_{i \in S} M_i \nabla x_i \\
= \frac{\nabla x_s}{M} - \frac{x_s}{M^2} \sum_{i \in S} M_i \nabla x_i \\
= \sum_{i \in S} F_{si} \nabla x_i 
\]

(A.9)

where \( M \) is the mixture molar mass, and the elements of the matrix \( F \) are defined as:

\[
F_{si} = \begin{cases} 
\frac{1 - y_s}{M} & \text{if } s = i \\
-x_sM_i/M^2 & \text{if } s \neq i 
\end{cases}
\]

(A.10)

Introducing the matrices \( \hat{B}_{eq} = B_{eq} M_e \) and \( \hat{C}_{e\ell} = \delta_{e\ell} M_e \) for \( e, \ell \in E \) and \( q \in R \), and making use of the matrix \( F \) to express Eq. (B.10) in matrix form, we have that:

\[
\begin{bmatrix} \bar{\psi} \end{bmatrix} = \begin{bmatrix} \hat{B} & \hat{C} \end{bmatrix} \begin{bmatrix} \mathcal{F}_1 & \mathcal{F}_2 \\ \mathcal{F}_3 & \mathcal{F}_4 \end{bmatrix} \begin{bmatrix} \bar{d} \end{bmatrix} = \begin{bmatrix} \hat{B} & \hat{C} \end{bmatrix} \begin{bmatrix} \mathcal{F}_1 & \mathcal{F}_2 \\ \mathcal{F}_3 & \mathcal{F}_4 \end{bmatrix} \begin{bmatrix} SW \\
\bar{W}_R \\
\bar{N} \end{bmatrix}
\]

(A.11)

where \( \mathcal{B} = \hat{B} \mathcal{F}_1 + \hat{C} \mathcal{F}_3 \) and \( \mathcal{C} = \hat{B} \mathcal{F}_2 + \hat{C} \mathcal{F}_4 \). From Eq. (A.11) one easily verifies the validity of Eq. (2.27) introduced in Sec. 2.3.2.4, recalled here after:

\[
\mathcal{T} \bar{W}_R + \mathcal{K} \bar{N} = \bar{\psi},
\]

(A.12)

where \( \mathcal{T} = \mathcal{B}(S_1 - S_2 B) + \mathcal{C}(S_3 - S_4 B) \) and \( \mathcal{K} = \mathcal{BS}_2 + \mathcal{CS}_4 \).

A.3 Linear system solution

To obtain expressions for the elemental multicomponent diffusion coefficients, we now solve Eqs. (A.7) and (A.12) using straightforward Gaussian elimination, although other techniques based upon iterative solvers are also possible.

First we solve the system (A.7) with respect to \( \bar{W}_R \) and then substitute the solution in (A.12) which will be finally solved for \( \bar{N} \) by computing \( \mathcal{Y}^{-1} \). Then the element number fluxes follow from the solution of the system (A.13):

\[
\mathcal{J} \bar{N} = -\mathcal{T} \mathcal{Y}^{-1} \bar{\theta} + \bar{\psi}
\]

(A.13)
where $\mathcal{S} = (K - T Y^{-1} Z)$. Because of the singular character of $\mathcal{S}$, inherited from the matrix $S$, the mass conservation constraint:

$$\tilde{\alpha}^T \tilde{N} = 0,$$  \hspace{1cm} (A.14)

where $\alpha_e = M_e$ for $e \in \mathcal{E}$, must still be applied to regularize $\mathcal{S}$ [63]. This can be easily done by solving the following non-singular linear system equivalent to (A.13,A.14) [41, 91]:

$$(\mathcal{S} + \zeta \tilde{\alpha} \otimes \tilde{\alpha}) \tilde{N} = \tilde{\beta}$$  \hspace{1cm} (A.15)

where $\tilde{\beta} = -T Y^{-1} \underline{\bar{\omega}} + \psi$. Indeed the matrix $\mathcal{S}$ ($N_e \times N_e$) is such that the null spaces of $\mathcal{S}$ and $\mathcal{S}^T$ are respectively spanned by the vectors $\underline{R} \in \mathbb{R}^{N_e}$ and $\underline{L} \in \mathbb{R}^{N_e}$ satisfying the conditions $\underline{R}^T \tilde{\alpha} \neq 0$ and $\underline{L}^T \tilde{\alpha} \neq 0$. Therefore, for any non zero parameter $\zeta$ (with dimensions $[\text{mole} / \text{kg s}]$), $\exists \mathcal{D} = (\mathcal{S} + \zeta \tilde{\alpha} \otimes \tilde{\alpha})^{-1}$ such that for a vector $\underline{\bar{\beta}} \in \mathbb{R}^{N_e}$ and in the range of $\mathcal{S}$, the solution of the system (A.15) is:

$$\tilde{N} = -\mathcal{D}^T Y^{-1} \underline{\bar{\omega}} + \mathcal{D} \underline{\bar{\beta}}$$  \hspace{1cm} (A.16)

where $\tilde{N}$ satisfies both Eqs. (A.13) and (A.14).

From a practical point of view we suggest to use $\zeta$ such that the regularization term has the same order of magnitude as the elements of the matrix $\mathcal{S}$, for example $\zeta = \sum_i |\mathcal{D}_{ij}| / (N_e^2 \bar{M}^2)$.

**A.4 Elemental diffusion coefficients**

To identify the elemental multicomponent and thermal demixing diffusion coefficients, we just need to extract the components of $\tilde{N}$ from Eq. (A.16) and put them in the form of Eq. (2.20), recalled hereafter:

$$f_e = M_e N_e = -\rho D_e^f \nabla T - \sum_{j \in \mathcal{E}} \rho D_{ef} \nabla Y^f.$$  \hspace{1cm} (A.17)

The elemental multicomponent coefficients $D_{ef}$ are related to the elements of the matrix $\mathcal{D}$, which are functions of $\zeta \in \mathbb{R}$. To eliminate this indeterminacy, characteristic of the solution technique used, we correct the matrix components as follows:

$$\mathcal{D}_{p,e} = \frac{\mathcal{D}_{eh}}{N_e}.$$  \hspace{1cm} (A.18)

The reader may easily verify that $\mathcal{D}_{p,e} = \mathcal{D}_{\bar{e},e}$ for any physically acceptable right hand side vector $\underline{\bar{\beta}}$ such that $\sum_{e \in \mathcal{E}} \mathcal{D}_{p,e} \bar{\beta}_e = \underline{L}^T \underline{\bar{\beta}} = 0$, $\underline{L} = [1, \ldots, 1]^T$ being the member of the null space of $\mathcal{S}^T$. In addition, we have that $\mathcal{D}_{p,L} = 0$. Any vector $k \in \mathbb{R}^{N_e}$ can be written as the sum of a part parallel to and a part normal to $\underline{L}$: $k = \tilde{k}_{\parallel} + \tilde{k}_{\perp}$. From the above, it follows that $\mathcal{D}_{p,k}$ is unique for any $k$. In particular, $\mathcal{D}_{p,\bar{e}}$ (where $\bar{\epsilon}_i = [0, \ldots, 1, \ldots, 0]^T$) is unique and hence all columns of $\mathcal{D}_p$ are independent of $\zeta$. Finally the elemental multicomponent diffusion coefficients read:

$$\rho D_{ef} = -M_e \mathcal{D}_{p,e} \quad (e, f \in \mathcal{E}).$$  \hspace{1cm} (A.19)

The elemental thermal demixing coefficients can be easily computed by assembling the following expression and extracting the following expression and extracting the $N_e$ components of the result:

$$\rho D^e = \frac{M_e}{R_a T^2} \left( \mathcal{D}_p T Y^{-1} \bar{\mathcal{M}}_e \right) \quad (e \in \mathcal{E}).$$  \hspace{1cm} (A.20)
A.5 Diffusive transport of enthalpy

The diffusive transport of enthalpy defined in Eq. (2.31) is recalled hereafter:

\[ q_d = \sum_{s \in S} W_s h_s = \overline{\Delta h}^T \tilde{W} + \bar{h}_{EL} \bar{N}. \]  \hspace{1cm} (A.21)

Substituting Eq. (A.16,A.18) into Eq. (A.12) an expression for \( \bar{W}_R \) is found:

\[ \bar{W}_R = (Y^{-1} + Y^{-1} Z \bar{D} \bar{P}^T Y^{-1} \bar{D} \bar{P}) \bar{W} \]  \hspace{1cm} (A.22)

Substituting Eqs. (A.22) and (A.16,A.18) in Eq. (A.21), the expression of the different contributions to the diffusive heat flux are retrieved. The computation of \( \lambda_R \), \( \lambda_D \) and \( \lambda_{EL} \) results from the straightforward application of the equations (A.23), (A.24) and (A.25) below, which require the computation of several matrix products:

- the thermal reactive conductivity reads

\[ \lambda_R = -\frac{1}{R_u T^2} \Delta h Y^{-1} \bar{D} \bar{P}^T Y^{-1} \bar{D} \bar{P}. \]  \hspace{1cm} (A.23)

- the thermal demixing conductivity is given by

\[ \lambda_D = -\frac{1}{R_u T^2} (\Delta h Y^{-1} Z \bar{D} \bar{P}^T Y^{-1} \bar{D} \bar{P} - \bar{h}_{EL} \bar{D} \bar{P}^T Y^{-1} \bar{D} \bar{P}). \]  \hspace{1cm} (A.24)

- the elemental heat transfer coefficients are obtained as the components of the array

\[ \bar{\lambda}^T_{EL} = \overline{\Delta h}^T Y^{-1} Z \bar{D} \bar{P} - \bar{h}^T_{EL} \bar{D} \bar{P}. \]  \hspace{1cm} (A.25)

While they may appear tedious in analytical form, these matrix products can be easily implemented in an efficient manner on a computer.
Chapter A. Mixtures of neutral components
Appendix B

Mixtures of both neutral and charged components

In this section we provide detailed derivations of results presented in Sec. 2.4 and used to obtain the numerical values presented in Sec. 2.4.8.

B.1 Matrix assembly

As for mixtures of neutral components, the species diffusion is treated using the Stefan-Maxwell equations written under matrix form as in Eq. (A.2), where the matrix \( S \) is subdivided in four components as in Eq. (A.3). On the other hand in the present case the vector of driving forces reads as follows

\[
\vec{d}_i = \vec{d}_i = k_i \vec{E} + \nabla x_i + (x_i - y_i) \nabla \ln p + k_{T_i} \nabla \ln T.
\]

(B.1)

The first part of the system defining the equilibrium condition for each of the \( N_r \) reactions [Eqs. (2.10-2.11)] reads:

\[
\sum_{s \in S} \nu_r^s \ln x_s = \ln K_p^r - \ln p \sum_{s \in S} \nu_r^s \quad (r \in \mathcal{R}).
\]

(B.2)

Taking the gradient of the previous equation using the van’t Hoff’s relation, we have:

\[
\sum_{s \in S} \frac{\nu_r^s}{x_s} \nabla x_s = \frac{\Delta h_T^r}{R_u T^2} \nabla T - \sum_{s \in S} \nu_r^s \nabla \ln p \quad (r \in \mathcal{R}),
\]

which under matrix form reads

\[
\begin{bmatrix}
\vec{A} & \vec{B}^T
\end{bmatrix}
\begin{bmatrix}
\nabla x_1 \\
\vdots \\
\nabla x_{N_{sp}}
\end{bmatrix}
=
\begin{bmatrix}
\Delta h_1 \\
\vdots \\
\Delta h_{N_r}
\end{bmatrix}
\frac{\nabla T}{R_u T^2} -
\begin{bmatrix}
\sum_{s \in S} \nu_s^1 \\
\vdots \\
\sum_{s \in S} \nu_s^{N_r}
\end{bmatrix}
\nabla \ln p,
\]

(B.3)
Chapter B. Mixtures of both neutral and charged components

where \( \tilde{A}_{ij} = \delta_{ij}/x_j \) and \( \tilde{B}^T = -B_{ji}/x_j \). Substituting the Stefan-Maxwell equations [Eq. (A.2)] into Eq. (B.3), we obtain that:

\[
\begin{bmatrix}
\tilde{A} & \tilde{B}^T
\end{bmatrix}
\begin{bmatrix}
\mathbf{S}
\mathbf{W}
\end{bmatrix}
= \begin{bmatrix}
\tilde{A} & \tilde{B}^T
\end{bmatrix}
\begin{bmatrix}
\mathbf{E} + \nabla \ln p + \nabla \ln T
\end{bmatrix}
+ \begin{bmatrix}
\Delta h_1 \\
\vdots \\
\Delta h_{N_r}
\end{bmatrix}
\begin{bmatrix}
\sum_{s \in S} \nu_s^1 \\
\vdots \\
\sum_{s \in S} \nu_s^{N_r}
\end{bmatrix}
\nabla \ln T
\]

The left hand side of Eq. (B.4) is treated exactly in the same way as done for mixtures of neutral components to derive Eq. (A.6-A.7). Therefore the definition of the matrixes \( \mathbf{Y} \) and \( \mathbf{Z} \) for the present is equal to the one presented in Sec. A.2. In addition the symmetric character of \( \mathbf{Y} \) hold true also for mixtures of both neutral and charged species. The difference with respect to the neutral case is the treatment of the right hand side. Indeed, using Eq. (B.4) one easily verifies the validity of Eq. (2.57) introduced in Sec. 2.4.5, recalled hereafter:

\[
\mathbf{Y} \bar{\mathbf{W}} \mathbf{R} + \mathbf{Z} \bar{\mathbf{N}} = \bar{\theta} + \bar{\pi}. \tag{B.5}
\]

where \( \mathbf{Y} = \tilde{A}(S_1 - S_2 B) + \tilde{B}^T(S_3 - S_4 B) \) and \( \mathbf{Z} = \tilde{A}S_2 + \tilde{B}^T S_4 \). As far as the right hand side is concerned, the two vectors \( \bar{\theta} \) and \( \bar{\pi} \) have the following components

\[
\bar{\theta}_r = \left( \bar{\theta}_r^R + \bar{\theta}_r^T \right) \nabla T, \tag{B.6}
\]

\[
\bar{\theta}_r^R = \frac{\Delta h_r}{R_a T^2}, \tag{B.7}
\]

\[
\bar{\theta}_r^T = \frac{1}{T} \sum_{s \in S} \nu_s^1 \frac{k_{Ts}}{x_s}, \tag{B.8}
\]

\[
\bar{\pi}_r = \frac{\pi_r^R}{\nabla p} = -\frac{1}{p} \sum_{s \in S} \nu_s^1 \frac{y_s}{x_s} \nabla p. \tag{B.9}
\]

The electric field is not present in Eq. (B.5) thanks to Eq. (2.56).

The same strategy is used for the lower part of the equilibrium system, needed to impose the elements mass conservation. Taking the gradient of Eq. (2.12), we have:

\[
M_e \sum_{s \in S} \phi_e^s \frac{\nabla y_s}{M_e} = \nabla \mathbf{Y}^e. \tag{B.10}
\]

To express the \( \nabla (y_s/M_e) \) as a function of \( \nabla x_s \), we use the matrix \( \mathbf{F} \) defined in Sec. A.2. In addition we use, as for neutral mixtures, the matrices \( \hat{B}_{e\ell} = B_{e\ell} M_e \) and \( \hat{C}_{e\ell} = \delta_{e\ell} M_e \) for \( e, \ell \in \mathcal{E} \).
and \( r \in \mathcal{R} \). Then we express Eq. (B.10) in matrix form:

\[
\vec{\psi} = \begin{bmatrix} \hat{B} & \hat{C} \end{bmatrix} \begin{bmatrix} \mathcal{F}_1 & \mathcal{F}_2 \\ \mathcal{F}_3 & \mathcal{F}_4 \end{bmatrix} \vec{d} = \begin{bmatrix} \mathcal{B} & \mathcal{C} \end{bmatrix} \vec{d}
\]

(B.11)

where \( \mathcal{B} = \hat{B} \mathcal{F}_1 + \hat{C} \mathcal{F}_3 \) and \( \mathcal{C} = \hat{B} \mathcal{F}_2 + \hat{C} \mathcal{F}_4 \). Substituting the Stefan-Maxwell equations into Eq. (B.11), accounting for Eq. (A.2), we have

\[
\begin{bmatrix} \mathcal{B} & \mathcal{C} \end{bmatrix} S \bar{W} = \vec{\psi} + \begin{bmatrix} \mathcal{B} & \mathcal{C} \end{bmatrix} \begin{bmatrix} k_1 \\ \vdots \\ k_{N_r} \end{bmatrix} E + \begin{bmatrix} x_1 - y_1 \\ \vdots \\ x_{N_r} - y_{N_r} \end{bmatrix} \nabla \ln p + \begin{bmatrix} k_{T_1} \\ \vdots \\ k_{T_{N_r}} \end{bmatrix} \nabla \ln T,
\]

(B.12)

where \( \vec{\psi} = \nabla Y \) for \( \ell \in \mathcal{E} \). The left hand side of Eq. (B.12) is treated as done for mixtures of neutral components to derive Eqs. (A.11)-(A.12). Therefore the definition of the matrixes \( T \) and \( K \) is equal to the one presented in Sec. A.2. As for Eq. (B.5), the difference with respect to the neutral case consist only in the right hand side. From Eq. (B.12) one easily verifies the validity of Eq. (2.59) introduced in Sec. 2.4.5, recalled here after:

\[
T \bar{W}_R + K \bar{N} = \vec{\psi} + \vec{\Theta} + \vec{\Pi} + \vec{\Gamma},
\]

(B.13)

where \( T = \mathcal{B}(S_1 - S_2 B) + \mathcal{C}(S_3 - S_4 B) \) and \( K = \mathcal{B} S_2 + \mathcal{C} S_4 \). As far as the right hand side is concerned, the three new vectors introduced have the following components

\[
\vec{\Theta}_\ell = \vec{\Theta}_\ell \nabla T = \frac{1}{T} \left( \sum_{x \in \mathcal{R}} B_{\ell,x} k_{T_x} + \sum_{x \in \mathcal{E}} C_{\ell,x-N_r} k_{T_x} \right) \nabla T
\]

(B.14)

\[
\vec{\Pi}_\ell = \vec{\Pi}_\ell \nabla p = \frac{1}{p} \left( \sum_{x \in \mathcal{R}} B_{\ell,x}(x - y_x) + \sum_{x \in \mathcal{E}} C_{\ell,x-N_r}(x - y_x) \right) \nabla p
\]

(B.15)

\[
\vec{\Gamma}_\ell = \vec{\Gamma}_\ell E = \left( \sum_{x \in \mathcal{R}} B_{\ell,x} k_x + \sum_{x \in \mathcal{E}} C_{\ell,x-N_r} k_x \right) E
\]

(B.16)

where \( \ell \in \mathcal{E} \).

### B.2 Linear system solution

The procedure followed to obtain the expressions for the elemental multicomponent diffusion coefficients is the same as the one used for mixtures of neutral components. We start solving Eqs. (B.5) and (B.13) using straightforward Gaussian elimination, although other techniques based upon iterative solvers are also possible.

First we solve the system (B.5) with respect to \( \bar{W}_R \) and then substitute the solution in (B.13)
which will be finally solved for \( \bar{N} \) by computing \( \mathcal{Y}^{-1} \). Then the element number fluxes follow from the solution of the system (B.17):

\[
\mathcal{J} \bar{N} = \mathcal{S} \bar{N} = -\mathcal{T} \mathcal{Y}^{-1} \mathcal{B} + \mathcal{S} - \mathcal{T} \mathcal{Y}^{-1} \mathcal{P} + \mathcal{P} + \mathcal{J}
\]

where \( \mathcal{J} = (\mathcal{K} - \mathcal{T} \mathcal{Y}^{-1} \mathcal{Z}) \). Because of the singular character of \( \mathcal{J} \), inherited from the matrix \( \mathcal{S} \), the mass conservation constraint:

\[
\alpha^T \bar{N} = 0, \quad (B.18)
\]

where \( \alpha_e = M_e \) for \( e \in \mathcal{E} \), must still be applied to regularize \( \mathcal{J} \) [63]. This can be easily done, as for mixtures of neutral components, by solving the following non-singular linear system equivalent to (B.17, B.18) [41, 91]:

\[
(\mathcal{J} + \zeta \widehat{\alpha} \otimes \widehat{\alpha}) \bar{N} = \bar{\eta}
\]

(B.19)

where \( \bar{\eta} = -\mathcal{T} \mathcal{Y}^{-1} \mathcal{B} + \mathcal{S} - \mathcal{T} \mathcal{Y}^{-1} \mathcal{P} + \mathcal{P} + \mathcal{J} \). For further details about the regularization procedure we refer the reader to Sec. A.3. The solution of the system (B.19) is:

\[
\bar{N} = -\mathcal{D} \mathcal{T} \mathcal{Y}^{-1} \mathcal{B} + \mathcal{D} \mathcal{S} - \mathcal{D} \mathcal{T} \mathcal{Y}^{-1} \mathcal{P} + \mathcal{D} \mathcal{P} + \mathcal{D} \mathcal{J}
\]

(B.20)

where \( \bar{N} \) satisfies both Eqs. (B.17) and (B.18). From a practical point of view we suggest to use \( \zeta \) such that the regularization term has the same order of magnitude as the elements of the matrix \( \mathcal{J} \), for example \( \zeta = \sum_{i,j \in \mathcal{E}} |\mathcal{J}_{ij}|/(N_c^2 M^2) \).

### B.3 Elemental diffusion coefficients

To identify the elemental multicomponent and thermal demixing diffusion coefficients, we proceed as for mixtures of neutral components. We extract the components of \( \bar{N} \) from Eq. (B.20) and put them in the form of Eq. (2.48), recalled hereafter:

\[
\mathcal{J}_f = \sigma_f \mathcal{E} - \rho \mathcal{D}_f(T, p, \mathcal{V}) \nabla T - \rho \mathcal{D}_f(T, p, \mathcal{V}) \nabla p - \sum_{h \in \mathcal{E}} \rho \mathcal{D}_{hf}(T, p, \mathcal{V}) \nabla Y^k \quad (f \in \mathcal{E}).
\]

(B.21)

The elemental multicomponent coefficients \( \mathcal{D}_{ef} \) are related to the elements of the matrix \( \mathcal{P} \), which are functions of \( \zeta \in \mathbb{R} \). To eliminate this indeterminacy, characteristic of the solution technique used, we proceed as done for mixtures of neutral components (Sec. A.4) and we correct the matrix components as follows:

\[
\mathcal{D}_{pf} = \mathcal{D}_{pf} - \frac{\sum_{h \in \mathcal{E}} \mathcal{P}_{ph}}{N_c}.
\]

(B.22)

Finally the elemental multicomponent diffusion coefficients read:

\[
\rho \mathcal{D}_{ef} = -M_e \mathcal{D}_{pf} \quad (f \in \mathcal{E}).
\]

(B.23)
B.4 Contribution of the electric field to the elemental diffusive fluxes

The elemental thermal demixing coefficients can be easily computed by assembling the following expression and extracting the $N_c$ components of the result:

$$\rho D^T = M_{\ell} \left[ \mathcal{D}_{\ell} T \mathbf{Y}^{-1} \mathbf{\bar{y}}^R + \mathcal{D}_{\ell} T \mathbf{Y}^{-1} \mathbf{\bar{y}}^T + \mathcal{D}_{\ell} \mathbf{\bar{Y}}^T \right] \text{ (} \ell \in \mathcal{E} \text{).}$$

(B.24)

B.4 Contribution of the electric field to the elemental diffusive fluxes

For what concern the $\sigma_{\ell}$, they can be determined as the components of the following array [see Sec.2.4.5]. Indeed from Eqs. (B.16)-(B.20), we have

$$\overline{\sigma} = \mathcal{D}_{\ell} \begin{bmatrix} B & C \end{bmatrix} \begin{bmatrix} k_1 \\ \vdots \\ k_{N_p} \end{bmatrix} = \mathcal{D}_{\ell} \bar{\Gamma}.$$  

(B.25)

B.5 Diffusive transport of enthalpy

The diffusive transport of enthalpy defined in Eq. (2.31) is recalled hereafter:

$$q_d = \sum_{s \in \mathcal{S}} W_s h_s = \Delta h^T \bar{W} + h_{EL}^T \bar{N}.$$  

(B.26)

Substituting Eq. (B.20,B.22) into Eq. (B.5) an expression for $\bar{W}_R$ is found:

$$\bar{W}_R = \mathbf{Y}^{-1} \mathbf{\bar{y}} + \mathbf{Y}^{-1} \mathbf{\bar{\pi}} - \mathbf{Y}^{-1} \mathbf{\bar{Z}} \bar{N}$$

$$= (\mathbf{Y}^{-1} + \mathbf{Y}^{-1} \mathbf{Z} \mathcal{D}_R T \mathbf{Y}^{-1} \mathbf{\bar{y}}) - \mathbf{Y}^{-1} \mathbf{Z} \mathcal{D}_R \mathbf{\bar{Y}}$$

$$+ (\mathbf{Y}^{-1} + \mathbf{Y}^{-1} \mathbf{Z} \mathcal{D}_R T \mathbf{Y}^{-1} \mathbf{\bar{\pi}}) - \mathbf{Y}^{-1} \mathbf{Z} \mathcal{D}_R \mathbf{\bar{\Pi}}$$

$$- \mathbf{Y}^{-1} \mathbf{Z} \mathcal{D}_R \mathbf{\bar{\psi}}.$$  

(B.27)

Substituting Eqs. (A.22) and (A.16,A.18) in Eq. (A.21), the expression of the different contributions to the diffusive heat flux are retrieved. The computation of $\lambda_R$, $\lambda_D$ and $\lambda_{EL}'$ results from the straightforward application of the equations (A.23), (A.24) and (A.25) below, which require the computation of several matrix products:

- the thermal reactive conductivity reads

$$\lambda_R = -\frac{1}{R_g T^2} \Delta h^T \mathbf{Y}^{-1} \Delta h,$$  

(B.28)
Chapter B. Mixtures of both neutral and charged components

- the thermal demixing conductivity is given by
  \[ \lambda_D = -\frac{1}{R_u T^2} (\Delta h_T Y^{-1} Z - \bar{h}_{EL}^T) \mathcal{D}_p T^\dagger, \]  \tag{B.29} \]

- the thermal diffusion reacting conductivity is given by
  \[ \lambda_T = (\Delta h_T Y^{-1} Z - \bar{h}_{EL}^T) \mathcal{D}_p T, \]  \tag{B.30} \]

- the pressure heat transfer coefficient is given by
  \[ \lambda_p = -\Delta h_T Y^{-1} \pi^p - (\Delta h_T Y^{-1} Z - \bar{h}_{EL}^T) \mathcal{D}_p T^\dagger \pi^p + \left( \Delta h_T Y^{-1} Z - \bar{h}_{EL}^T \right) \mathcal{D}_p \bar{\pi}^p, \]  \tag{B.31} \]

- the electric field heat transfer coefficients is given by
  \[ \lambda_E = (\Delta h_T Y^{-1} Z - \bar{h}_{EL}^T) \mathcal{D}_p \bar{\Gamma}_E, \]  \tag{B.32} \]

- the elemental heat transfer coefficients are obtained as the components of the array
  \[ \bar{\lambda}_{EL}^T = \left( \Delta h_T Y^{-1} Z - \bar{h}_{EL}^T \right) \mathcal{D}_p, \]  \tag{B.33} \]

The previous formulae are enough to compute and understand the importance of the various terms present in the diffusive transport of enthalpy [Eq. (2.66)] recalled hereafter
\[ \sum_{s \in S} W_s h_s = -\lambda_E \mathbf{E} - \lambda_p \nabla p - (\lambda_R + \lambda_D + \lambda_T) \nabla T - \sum_{\ell \in E} \lambda_{EL}^\ell \nabla Y^\ell. \] \tag{B.34} \]

B.6 Quasi neutral and current free plasmas

In this section we present the detailed derivation of the transport properties introduced in Sec. 2.4.7. The following results are based on two major assumptions, i.e. quasi neutral
\[ \sum_{s \in S} x_s q_s = 0 \]  \tag{B.35} \]
and current free plasma
\[ j = 0. \]  \tag{B.36} \]

B.6.1 Elemental diffusion coefficients

The elemental multicomponent diffusion coefficients of the mixtures elements differ from those previously defined in Eq. (B.23), since the electric field can now expressed as a linear combination of \( \nabla T, \nabla p, \nabla Y^\ell \). Indeed from Eq. (B.36) and Eq. (B.21) we easily retrieve Eq. (2.72), recalled hereafter
\[ \mathbf{E} = \frac{\rho D_q^T(T, p, \bar{Y})}{\sigma_q} \nabla T + \frac{\rho D_p^q(T, p, \bar{Y})}{\sigma_q} \nabla p + \sum_{k \in E} \frac{\rho D_{qk}(T, p, \bar{Y})}{\sigma_q} \nabla Y^k. \] \tag{B.37} \]
Thanks to Eqs. (B.37)-(B.20), in the case of a quasi neutral plasma, the elemental multicomponent, the thermal demixing and the pressure diffusion coefficients can be easily defined adding a correction to Eq. B.23 as shown in Eq. (2.75) recalled hereafter

\[
\begin{align*}
\rho D'_{\ell k} &= \rho D_{\ell k} - \rho D_{qk} \frac{\sigma_{\ell}}{\sigma_q} \tag{B.38a} \\
\rho D'_{\ell T} &= \rho D_{\ell T} - \rho D_{qT} \frac{\sigma_{\ell}}{\sigma_q} \tag{B.38b} \\
\rho D'_{\ell p} &= \rho D_{\ell p} - \rho D_{qp} \frac{\sigma_{\ell}}{\sigma_q} \tag{B.38c}
\end{align*}
\]

for \( \ell \in \mathcal{E} \setminus \{q\} \).

### B.6.2 Diffusive transport of enthalpy

As shown in Eq. (B.5), the diffusive transport of enthalpy is affected by the electric field through the term \(-\lambda_E E\). In the particular case of quasi neutral and current free plasma, the relation [Eq. (B.37)] between the electric field \( E \) and \( \nabla T, \nabla p, \nabla Y^\ell \) leads to some corrections to the expressions of the transport properties presented in Sec. B.5. Substituting Eq. (B.37) into Eq. (B.34) we have

\[
\begin{align*}
\lambda'_{D} &= \lambda_D - \frac{\lambda_E}{\sigma_q} \rho D_{qT} (T, p, \bar{Y}) \tag{B.39a} \\
\lambda'_{p} &= \lambda_p - \frac{\lambda_E}{\sigma_q} \rho D_{qT} (T, p, \bar{Y}) \tag{B.39b} \\
\lambda'^{\ell}_{EL} &= \lambda'^{\ell}_{EL} - \frac{\lambda_E}{\sigma_q} \rho D_{qT} (T, p, \bar{Y}) \quad (\ell \in \mathcal{E}) \tag{B.39c}
\end{align*}
\]

where the expressions of \( \lambda_D, \lambda_p, \lambda'^{\ell}_{EL}, \) and \( \lambda_E \) are given in Sec. B.5. In the case of quasi neutral and current free plasmas, the diffusive transport of enthalpy therefore reads

\[
\sum_{s \in \mathcal{S}} W_{s} h_{\tau} = -\lambda'_p \nabla p - (\lambda_R + \lambda'_D + \lambda_T) \nabla T - \sum_{\ell \in \mathcal{E}} \lambda'^{\ell}_{EL} \nabla Y^\ell. \tag{B.40}
\]
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