Modeling of Low Pressure Plasmas in CH₄-H₂ Mixtures

António Miguel da Cruz Baptista Dias

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Juri Committee

President: Prof. Carlos Renato de Almeida Matos Ferreira
Advisor: Prof. Luís Paulo da Mota Capitão Lemos Alves
Vowel: Prof. Luís Silvino Alves Marques

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Abstract

A collisional radiative model (CRM) for CH$_4$-H$_2$ plasma in low pressure conditions is introduced. The kinetics of both CH$_4$ and H$_2$ have been reviewed and updated as well as new mechanisms were introduced when needed. The resulting code allows a wide range of input parameters (Pressure: 5 - 40 mTorr; input power 100 - 1000 W; neutral gas flow: 20 - 40 sccm ; discharge composition CH$_4$/H$_2$: 25%/75% - 75% /2%). A study of charged species transport in ambipolar electric fields is made and a method of calculating edge to center ratios of charged species’ densities is proposed. This thesis was made in partnership with Institut des Matériaux Jean Rouxel (IMN/CNRS, Nantes, France), which provided experimental data for comparison as well as a first version of the code that was developed.

Keywords: Collisional-radiative model, low pressure plasmas, charged species’ diffusion, methane-hydrogen plasmas
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Resumo

Um modelo colisional radiativo (CRM) para plasmas em misturas de CH$_4$/H$_2$ em condições de baixas pressão é apresentado. Foi realizada uma revisão e actualização dos mecanismos cinéticos, colocando-se novos mecanismos quando necessário. O código resultante permite correr uma vasta gama de parâmetros (Pressão: 5 - 40 mTorr; potência introduzida 100 - 1000 W; fluxo de gases neutros: 20 - 40 sccm ; composição da descarga CH$_4$/H$_2$: 25%/75% - 75% /25%). Um estudo do transporte de espécies carregadas em condições de campos elétricos ambipolares é realizado e um método de cálculo da razão entre a densidade no centro e a parede da descarga é proposto. Esta tese foi realizada em parceria com Institut des Matériaux Jean Rouxel (IMN/CNRS, Nantes, France), que forneceu dados experimentais para comparação com os valores obtidos da simulação assim como uma primeira versão do código que é apresentado.

Palavras-Chave: Modelos colisionais-radiativos, plasmas a baixa pressão. difusão especies carregadas, plasmas hidrogénio-metano
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List of Abbreviations

CRM  Collisional Radiative Model
EEDF  Electron Energy Distribution Function
OES  Optical Emission Spectroscopy
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Chapter 1

Introduction

1.1 Motivation

Low-temperature plasma discharges are widely used in the industrial medium, filling roles such as the production of light, the modification of surface properties (through etching and deposition), waste management and even providing thrust for off world spacecraft like satellites \[2,3\]. The use of CH\(_4\)-H\(_2\) mixtures has been significant in the area of material processing, especially in the process of etching InP materials \[4\], which are of promising use in the optoelectronics and the communications industry for manufacturing devices such as solar cells and laser diodes \[5\]. The study of these discharges is therefore important in order to understand which processes are dominant in its development and in the interaction with materials.

The development of a collisional-radiative model (CRM) is an invaluable tool for said study. CRMs solve a set of volume averaged conservation equations for both the mass and the energy of each species considered in the plasma. Since the equations are volume averaged, meaning this is a model for the whole discharge represented by a single point, no computational resources are lost with spatial considerations and a more thorough reactional scheme can be considered. The objective of these models is to understand which collisional and/or radiative mechanisms contribute the most to achieve and control the equilibrium of the discharge. Results are usually compared to experimental values obtained from real discharges in order to validate the model.
1.2 Experimental setup

The specific discharge being modeled is an inductively coupled plasma (ICP) on site at the partner institution *Institut des Matériaux Jean Rouxel* (IMN/CNRS, Nantes, France), equipped with Langmuir probe and optical emission spectroscopy (OES) diagnostics which will provide experimental data for electron temperature and density and for the relative densities of excited neutral species.

The reactor to be modeled is presented in figure 1.1.

![Figure 1.1: Top (a) and side (b) views of the modeled reactor.](image)

In this model the reactor will consist of two separate chambers. The first located on the top will be called the excitation chamber - where the power from the inductive source couples to the plasma. The second just below will be called the diffusion chamber - where the created plasma species diffuse towards the processing materials - as depicted in figure 1.2.

Working conditions will be those of a typical high-density discharge:

- Pressure ranging from 2 to 20 mTorr
- Neutral gas flow ranging from 20 to 40 sccm
- Coupled power of the order of 1 kW\[^{1}\]

\[^{1}\text{NOTE: This is the power provided to the discharge at the discharge chamber. It may and will surely not be the power coupled to the plasma at the diffusion chamber. Since this CRM does not take any spacial distribution into account, simulations are limited to a description of the excitation chamber.}\]
1.3 Overview of personal contributions

The objective of this work was the correction and update of an existing incomplete CRM code for a H$_2$-CH$_4$ plasma. This update included:

Improving the existing kinetic code by directly changing certain wrong reaction coefficients or by introducing a more coherent way of calculating those coefficients. Furthermore new reactions and species were added to the model in order to achieve more reliable results.

Introducing a convergence criterion to stop the simulation. The original code simulated the time evolution of the discharge to a time of 10 seconds, regardless the exact time taken by the discharge to achieve a steady-state. A convergence criterion that monitors the calculation error was introduced to evaluate if the simulation has reached a steady state in order to stop the program.

Changing the numerical local error calculation in order to speed up the simulation. Advancements were made in the convergence of the code for different working conditions.

Reviewing and correcting the neutral species’ diffusion. Introducing a periodic check for mass conservation.

Proposing an update to the theory of transport of charged species under ambipolar diffusion in a low pressure regime, based on the work of Lieberman [2] and Godyak [1].
Chapter 2

State of the art

In this chapter an overview of previous studies of \( \text{H}_2\)-\( \text{CH}_4 \) mixtures is presented with emphasis on the kinetic scheme adapted in each study. The last part of this chapter is dedicated to introducing the theory of charged particle transport in an ambipolar field at low pressures.

2.1 Previous studies in \( \text{CH}_4\text{-H}_2 \) mixtures

There have been many studies of discharge plasmas produced in \( \text{CH}_4\text{-H}_2 \) mixtures that resulted in the development of CRMs (\cite{6, 7, 8, 9}). These models, however lack completeness when it comes to defining the corresponding kinetic scheme.

- It is difficult to find a kinetic scheme with the same level of detail for \( \text{H}_2 \) (as in\cite{9}) and for \( \text{CH}_4 \) (as in \cite{10});

- Kinetic schemes with a decent description of both gases are often incomplete for \( \text{H}_2 \), since usually they do not include mechanisms involving vibrational states and/or excited atomic states;

- The kinetic mechanisms for \( \text{CH}_4 \) are scattered in through many studies. For instance, studies decide to include charge exchange reactions \cite{10}, others don’t \cite{6} and others are only interested in the creation of specific \( C_2H_y \) chains \cite{11}.

In Yoon’s work \cite{6}, a very good kinetic scheme for \( \text{CH}_4 \) is presented, including electron impact dissociation and detachment, neutral-neutral reactions and ion-neutral reactions. An electron energy distribution function (EEDF) is considered not as a standard Maxwellian but as a Druyvesteynian, which is a great improvement with respect to usual papers. However the hydrogen kinetics is not
present. One finds hydrogen in 3 reactions only: dissociation and ionization of $\text{H}_2$. All other sources of hydrogen result of hydrocarbon reactions where $\text{H}_2$ appears as a by-product.

In Denysenko’s work [7] a rather complete kinetic scheme is presented, including several more hydrogen reactions where both the $\text{H}_2$ molecule and the $\text{H}$ atom are considered. However, many mechanisms involving $\text{H}_2$ are still missing, particularly, those relative to the vibrational states of hydrogen.

In Lombardi and Hassouni’s work [9], the exact opposite happens. While the $\text{H}_2$ kinetics is well considered throughout both papers, Hassouni’s paper only considers the kinetics of neutral hydrocarbon species and Lombardi offers only a few more reactions involving argon and hydrocarbon neutrals (this paper is for Ar/CH$_4$/H$_2$ mixtures).

Alman’s work [10], while not being intended to present a model for $\text{H}_2$/CH$_4$ mixtures, is worth mentioning since it offers a very complete reactional scheme for hydrocarbons.

All the above studies also work under the assumption of a Maxwellian the EEDF. This assumption will also be considered in the present code. However, the code developed here allows using any kind of distribution function due to its generic evaluation of the electron collision rate coefficients.

### 2.2 Charged particle transport

In order to solve the CRM in 0-D a previous study of the multi-dimensional discharge must be made in order to have a priori knowledge of the density profiles with each charged species in the reactor. The correct accounting of the charged particle density profiles is important to workout meaningful loss rates for these species, and thus allow for improved estimations of the electron temperature.

In this section, the concepts that allow calculating the charged particle profile at low pressures are presented. Following [1] and [12], the calculation of the ratio of ion density in the bulk of the plasma ($n_0$) to the density at the edge of the plasma ($n_s$) is presented.

The concept of variable mobility will be introduced, derived for a 1D case following [13] and [14]. The concept of variable mobility in a multi-dimensional problem will be proposed in chapter 5. Although in the references there is no direct mention to the dimensions of the problem the results shown only apply to the 1D case, suggesting that new arguments must be introduced in order to achieve a multiple dimension description.
2.2. CHARGED PARTICLE TRANSPORT

2.2.1 Model equations

The plasma considered is constituted by:

- Singly charged ions
- Electrons
- Neutrals

The model solves the ion-particle balance equation, introducing an ion flow $\Gamma_i$, given by

$$
\Gamma_i = u_in_i,
$$

(2.1)

where $u_i$ is the mean ion drift velocity and $n_i$ is the ion density, and considering a source term due to the ionization by electron impact. The conservation equation can then be written as (in 1-D):

$$
d\frac{d}{dz}(u_in_i) = \nu_{ion}n_e,
$$

(2.2)

where $\nu_{ion}$ is the ionization frequency and $n_e$ is the electron density. The goal here is to relate the ion velocity and the ion and electron densities to the electrostatic plasma potential and then to solve for this quantity. The procedure demands introducing the concept of variable mobility.

2.2.2 Variable mobility

The usual approach to describe low pressure discharges is to make use of the concept of ‘variable mobility’ ([3, 15, 16]), which consists in the field-dependant scalar $\mu$ relating drift velocity $\vec{u}_i$ and the electrostatic field of the discharge $\vec{E}$ according to:

$$
\vec{u}_i = \mu(\vec{E})\vec{E}
$$

(2.3)

The behaviour described by 2.3 in low pressure discharges comes from the electrostatic field that maintains the discharge, which - as described by Paschen’s law depicted in figure 2.1 - is considerably higher at low pressures. We will then consider an electric field generated by a certain electrostatic potential $\phi$, such that the potential energy ($e\phi$) is much higher than the electron thermal energy ($k_BT_e$): $e\phi >> k_BT_e$\(^1\).

\(^1\) For simplicity only singly charged particles will be considered from now on.
CHAPTER 2. STATE OF THE ART

Figure 2.1: Representation of the Paschen law. Notice the steep variation of the breakdown voltage at low pressures.

The existence of a high electrostatic field allows the ions to achieve a large velocity between collisions, also because the 'mean free path' $\lambda$ will be larger at low pressures. In order for this theory to be valid, $\lambda$ must verify the following inequality: $\frac{L}{10^3} < \lambda < \frac{L}{10}$; where $L$ is the length of the reactor.

Since ions acquire larger velocities in these low-pressure scenarios, other mechanisms for transport can be speculated in these cases. Following [14], it is claimed that at these higher velocities the main collision types that influence transport come in the form of resonant charge exchange reactions. Charge exchange reactions are not in fact collisions but merely interactions between an ion and a neutral, where a fast traveling ion is neutralised by acquiring an electron from a slow traveling neutral (which in turn becomes a positive ion), hence the term 'charge exchange'. Calling the ion $A_1^+$ and the neutral $A_2$, the reaction would be as follows:

$$A_1^+(f) + A_2(s) \rightarrow A_1(f) + A_2^+(s), \quad (2.4)$$

where the $f$ stands for fast and the $s$ stands for slow. Since this is a resonant reaction, meaning that $A_1$ and $A_2$ are of the same type, an effect called Sena effect [14] occurs. The latter, named after Russian physicist L. A. Sena, is simply a form of diffusion of charged species by means of resonant charge exchange reactions. Since both ions in either side of (2.4) are of the same species and assuming there is no change in the direction of the reacting particles, if one were to consider only the ion movement in both sides of the reaction there would be an apparent diffusion of said ion due to the charge exchange reaction (figure 2.2).

Considering that these collisions happen with a certain cross section $\sigma$, and assuming they are the main source of ion scattering in low-pressure discharges, the ion mean free path between charge exchange
2.2. CHARGED PARTICLE TRANSPORT

Figure 2.2: Illustration of the Sena effect. The ion suffers an 'apparent diffusion' as a result of the charge exchange reaction. This reaction can be seen in two different ways: before and after (A. to B.) or by considering the collision of an ion with a neutral (1. to 2.)

reactions - \( \lambda \) - can be defined as:

\[
\lambda = \frac{1}{n_N \sigma},
\]

(2.5)

where \( n_N \) is the neutral gas density. For simplicity reasons this parameter will be considered constant throughout the discharge. As stated before, ions acquire high velocities in this low-pressure problem, which allows to consider the neutrals at rest when they collide with the ions. This means that when a charge exchange reaction occurs, the ion velocity drops to a small value - corresponding to the velocity of the former neutral - which will be considered as zero. This will give the ion velocity a time behaviour similar to a sawtooth waveform, as depicted in figure 2.3.

That being said, the velocity \( v \) of a given ion in the electrostatic field of the discharge between collisions, can be calculated by solving the simple equation of motion:

\[
\frac{dv}{dt} = \frac{e}{M} E,
\]

(2.6)

where \( M \) is the ion mass and \( e \) is the electron charge. One may be tempted to include in this equation a friction term due to collisions, and would be right to do so. However, as stated in the last paragraph, although the ions acquire high speeds between reactions, their velocity returns to zero immediately
after each reaction. This means that the friction term, proportional to the velocity, that should exist in (2.6) can be neglected due to its small contribution.

In order to solve (2.6) some assumption must be made about the electric field. The most simple solution, which will be the one used here, is to consider the electric field as constant (or at least with a negligible variation) between two charge exchange reactions. This allows (2.6) to be written as:

\[ v(t) = \frac{e}{M}Et. \tag{2.7} \]

We can now define the probability \( P(t) \) for a given ion not to undergo a charge exchange reaction, as a function of time. This probability will become smaller as long as time passes and the ions acquire larger velocities in the electrostatic field and thus it can be described to have a time dependence similar to the radioactive decay:

\[ \frac{dP}{dt} = -\nu(t)P, \tag{2.8} \]

where \( \nu \) represents the frequency of charge exchange reactions. Solving this equation leads to the general result:

\[ P(t) = \exp \left[ -\int_0^t \nu(t')dt' \right], \tag{2.9} \]

where the time dependence of \( \nu \) can be obtained using \( \nu = \frac{v}{\lambda} \) with \( v \) given in (2.7). Replacing in (2.9)
one gets the following form:

\[
P(t) = P_0 \exp \left[ -\frac{e E t^2}{M \lambda} \right],
\]

(2.10)

Finally, replacing \( t \) for \( v \) using (2.7), one has the probability of an ion existing, not reacting, for a certain velocity. This is the definition of the ion velocity distribution function \( f_i(u) \):

\[
f_i(v) = f_0 \exp \left[ -\frac{M v^2}{2e E \lambda} \right], \quad v > 0,
\]

(2.11)

where \( f_0 \) is a constant that can be calculated by imposing the normalization condition:

\[
\int_0^\infty f_i(v) \, dv = 1.
\]

(2.12)

Calculating for \( f_0 \) the result is \( f_0 = \sqrt{\frac{2M}{\pi e E \lambda}} \). Given the ion distribution function, the mean ion velocity can be calculated as:

\[
u = <v> = \int_0^\infty v f_i(v) \, dv,
\]

(2.13)

and using the definition of \( f_i \) given by (2.11), with normalization condition imposed by (2.12), the mean ion velocity is given by:

\[
u = \sqrt{\frac{2e E \lambda}{\pi M}}.
\]

(2.14)

Equation (2.14) corresponds to the relationship we were searching for, between the electric field and the mean ion velocity, and can be transformed to introduce a field-dependent mobility:

\[
u = \sqrt{\frac{2e \lambda}{\pi M E}} E = \mu(E) E.
\]

(2.15)

This relationship will be important to solve the 1-D model proposed in [1] and [12].

### 2.2.3 Model Solution

Having derived a relationship for the velocity of the ions in the electrostatic field of the discharge, we can now solve the particle balance equation (2.2). The electrons are considered to be in Boltzmann
equilibrium with the field, with a density profile given by:

\[ n_e = n_0 \exp \left( \frac{e\phi}{k_B T_e} \right) \]  

(2.16)

where \( n_0 \) is the bulk density, \( k_B \) the Boltzmann constant and \( T_e \) is the electron temperature.

The ions are considered to have a velocity given by the variable mobility law which was previously derived:

\[ u = \sqrt{\frac{2eE\lambda}{\pi M}} , \]  

(2.17)

being generated mainly, via the ionization of neutrals by electron impact, characterised by the collision frequency, \( \nu_{\text{ion}} \).

Finally one assumes quasineutrality, allowing the following equation for the charged species’ densities:

\[ n_i = n_e . \]  

(2.18)

Taking into account the above relations and assumptions, equation (2.2) writes:

\[ \frac{d}{dz} \left[ \sqrt{\frac{2eE\lambda}{\pi M}} \exp \left( \frac{e\phi}{k_B T_e} \right) \right] = \nu_{\text{ion}} \exp \left( \frac{e\phi}{k_B T_e} \right) . \]  

(2.19)

It is usual to introduce the following normalized quantities:

\[ \eta = -\frac{e\phi}{k_B T_e} ; \quad Z = \frac{z}{l_P} \]

where \( l_P \) is a typical length of the problem (e.g. length of the plasma). Using the normalizations equation (2.19) can be written for the normalized electrostatic potential \( \eta \) (refer to [1], [12] and [2] for more details):

\[ \frac{d^2\eta}{dz^2} - 2 \left( \frac{d\eta}{dz} \right)^2 - 2\alpha \sqrt{\frac{d\eta}{dz}} = 0 , \]  

(2.20)

where the parameter \( \alpha \) is given by:

\[ \alpha = \sqrt{\frac{\pi l_p \nu_{\text{ion}}}{2\lambda w_B}} , \]  

(2.21)
with $u_B = \sqrt{\frac{k_B T_e}{m}}$ the Bohm velocity. This equation, once solved, gives the profile of the electrostatic field in the discharge, which in turn yields the density profiles of the charged species, using (2.16) and (2.18):

$$n_i = n_e = n_0 \exp(-\eta).$$  \hspace{1cm} (2.22)

Equation 2.20 has been solved by Godyak \[1\] - details in \[2\] - imposing $\eta(Z = 0) = 0$ and $E(Z = 0) = 0$ as boundary conditions. Further calculations from Godyak claim to arrive at a result for the ratio between the edge density and the center density ($\frac{n_e}{n_0}$), which will be refered to as $h$. For both a problem with planar symmetry ($h_Z$) and radial symmetry ($h_R$) Godyak’s results are given by:

$$h_Z = 0.86 \left(3 + \frac{L}{2\lambda}\right)^{-1/2}, \quad h_R = 0.8 \left(4 + \frac{R}{\lambda}\right)^{-1/2},$$  \hspace{1cm} (2.23)

where $L$ and $R$ are respectively the length and radius of the reactor. Note that expressions 2.23 cannot be reproduced from the references and that their derivation appears to be purely heuristic. Furthermore, the derivation of these expressions considers a constant value for the parameter $\alpha$ at different pressures, regardless of the fact that this parameter has a clear dependence on the mean free path, (highly dependent on pressure as shown in figure 2.4).

Figure 2.4: Pressure dependance of the mean free path and the adimensional parameter $\alpha$. Results were derived for an ideal gas at 300 K, a Bohm velocity of $10^7 \text{ m/s}$, ionization frequency of $10^4 \text{ s}^{-1}$ and typical scale length of 0.1 m.

The previous limitations on obtaining the charged particle density profiles at low pressures show the pertinence in reviewing this classical transport theory, also in view of generalising the approach to a multi-dimensional situation.
Chapter 3

Model Formulation and solution

This chapter presents the general formulation of the model and describes its numerical solution. The different equations to solve for each species are introduced with a brief description of their terms, differentiating between transport, kinetic and flow input terms. Finally the numerical code used to solve this system of equations is presented, along with constraints that physical meaningful solutions.

3.1 Model equations

The model to solve is for a plasma 3 types of species:

- Heavy neutral species
- Heavy charged species (singly charged ions)
- Electrons

Considering that there will be $n$ heavy species (neutral and charged) in the plasma, then a set of $n$ equations is needed to calculate the density of those species. The electron temperature and density are also to calculate for two reasons, because they allow defining the rates of the electron-impact mechanisms, which play a paramount role in the plasma kinetics. This means that the model contains a total of $n + 2$ equations, namely:

- Particle conservation equations for each of the heavy species, which will be used to calculate each their densities;
- Electron energy density conservation equation, which will be used to calculate the electron tem-
perature;

- Quasineutrality condition to close the problem and to calculate the electron density.

Below is a deduction of each of the equations.

### 3.1.1 Particle conservation equations

The time-dependant particle conservation equations can be obtained from the zeroth moment of the Boltzmann equation [17] for the particle distribution function \( F(\vec{x}, \vec{v}, t) \):

\[
\frac{\partial F}{\partial t} + (\vec{v} \cdot \vec{\nabla} F) + (\vec{\nabla} \cdot \vec{a}) = \left( \frac{dF}{dt} \right)_{\text{col}},
\] (3.1)

where \( \left( \frac{dF}{dt} \right)_{\text{col}} \) represents the collision operator term. We consider the distribution function \( F \) to satisfy the following normalization condition:

\[
\int F(\vec{x}, \vec{v}, t) d^3 v = N(\vec{x}, t),
\] with \( N \) representing the time-space density profile of the species. The zeroth moment of (3.1) corresponds to:

\[
\int \frac{\partial F}{\partial t} d^3 v + \int (\vec{v} \cdot \vec{\nabla} F) d^3 v + \int (\vec{\nabla} \cdot \vec{a}) d^3 v = \int \left( \frac{dF}{dt} \right)_{\text{col}} d^3 v
\] (3.2)

The second term on the left hand side of (3.2) is zero [17] and the remaining terms lead to the following result:

\[
\frac{\partial N}{\partial t} + \vec{v} \cdot \left( N \langle \vec{v} \rangle \right) = \left( \frac{dN}{dt} \right)_{\text{coll}}
\] (3.3)

where \( \langle \vec{v} \rangle \) is the mean drift velocity, and \( \left( \frac{dN}{dt} \right)_{\text{coll}} \) is the macroscopic collision term. The latter accounts for the different collisional mechanisms responsible for the creation and loss of the particles with density \( N \), and can be written as the difference between a source and a sink rate for these particles.

\[
\left( \frac{dN}{dt} \right)_{\text{col}} = G - L
\] (3.4)
where $G$ stands for Gain and $L$ for Loss of particles. $G$ and $L$ depend on the specific types of collisions that occur but for 2 particle collisions

$$A + B \rightarrow C + D ,$$

they can be written as:

$$G_{C\text{ or }D} = N_A N_B k_{AB} .$$

Here the subscripts $A$ and $B$ refer to the particles colliding with each other, the subscripts $C$ and $D$ refer to the particles resulting from the collision, and the quantity $k_{AB}$ represents the rate coefficient of 3.5.

In order to portrait the effects of all the reactions in the model, the gain terms $G$ and $L$ in 3.4 must be a summation over all the reactions that result in a gain or in a loss of the particles of interest.

The second term on the left hand side of (3.3) is called the convection term and it takes into account the movement of the particles in the system. It can be expanded considering that the total drift velocity with each species is due to the global motion of the fluid with velocity $\vec{v}_0 \approx \text{const}$ and the individual relative motion of the particle with velocity $\vec{u} (< \vec{v} > = \vec{v}_0 + \vec{u})$

$$\vec{\nabla}_r \cdot (N < \vec{v} >) = \vec{v}_0 \cdot (\vec{\nabla}_r N) + \vec{\nabla} \cdot (N \vec{u}) .$$

This expansion effectively separates the convection term into two different contributions. The first term in the right hand side of (3.7) is the advective term, which takes into account the movement of particles by bulk motion of the entire fluid, this term will represent the pumping of particles out of the reactor in order to conserve the pressure. The remaining term in (3.7) is the diffusion term, which describes the motion of individual particles inside the plasma, namely due to collisions.

These two motions are characterized by two specific times related to bulk fluid motion, $\tau_A$, and to diffusion, $\tau_D$, whose ration defines the Péclet number ($P_e$):

$$P_e = \frac{\tau_D}{\tau_A} = \frac{v_0 L}{D} ,$$

where $L$ is a typical dimension of the plasma and $D$ is the diffusion coefficient of the particles. The advection term, as stated above, will be responsible for maintaining the pressure within the discharge.
Each species will thus be defined to have a certain residence time \( \tau^i \) - calculated from the volumetric flow injected into the plasma - \( q_0 \):

\[
\tau_A = \tau_R = \frac{V}{q_0},
\]

(3.9)

where \( V \) is the volume of the discharge. Equation (3.3) can now be written as:

\[
\frac{\partial N}{\partial t} + N \vec{\nabla}_r \cdot \vec{u} + \frac{N}{\tau_R} = G - L
\]

(3.10)

leaving only the diffusion term to be treated. In the case of the diffusion term, one must distinguish between charged species and neutral species. This is because the latter are not affected by the electric fields present in the plasma.

### 3.1.1.1 Diffusion of neutral species

The diffusion of neutral species in a plasma is described by flow from regions of higher density towards regions of lower density, given by Fick’s law:

\[
N \vec{\nabla}_r N = -D \vec{\nabla}_r N,
\]

(3.11)

where \( D \) is the corresponding diffusion coefficient. Substituting (3.11) into (3.10):

\[
\frac{\partial N}{\partial t} - D \nabla^2 N = G - L - \frac{N}{\tau_R},
\]

(3.12)

where the Laplacian term can be approximated as:

\[
\nabla^2 N = -\frac{N}{\Lambda^2},
\]

(3.13)

where \( \Lambda \) an effective diffusion length that depends on the reactor geometry and with the minus sign accounting for the negative concavity of the density profile.

So for a specific neutral species \( i \) the spatially averaged particle conservation equation can finally be written as (the subscripts 0 represent average values over the plasma volume):

\[
\frac{\partial N_{i0}}{\partial t} = G_{i0} - L_{i0} - D_i \frac{N_{i0}}{\Lambda^2} - \frac{N_{i0}}{\tau_R},
\]

(3.14)
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where the diffusion coefficient $D_i$ considers the motion of species $i$ within the various plasma constituents. This is discussed in Chapter 5.

3.1.1.2 Ion transport

The ion transport must be treated differently than the neutral transport because of the existence of self-consistent electric fields created by the charge separation inside the discharge. These fields are called *ambipolar* fields and are more important the less collisional the problem is (e.g. at low pressures, such as in the present case).

It will be assumed that the ion motion is controlled by the ambipolar electric field, meaning that the ions have a *drift velocity* towards the walls related to this electric field by a mobility $\mu$, as discussed in chapter 2.

Transport losses of ions are due to recombination at the reactor walls [2]. An analysis of the sheath region would be necessary in order to reliably calculate the ion flow towards the walls, but since the sheath region is usually considered collisionless the ion flow is conserved, keeping its value $\Gamma_{\text{Ion}}^{\text{Sheath}}$:

$$\Gamma_{\text{Ion}}^{\text{Sheath}} = N_{iS}u_B = N_{i0}u_B .$$ (3.15)

Here $N_{iS}$ is the ion density at the sheath edge (assumed to be equal to its average value in the plasma bulk) and $u_B$ is the Bohm velocity.

The amount of ions that strike the walls per unit time ($\nu_W$) can be calculated as:

$$\nu_W = \Gamma_{\text{Ion}}^{\text{Sheath}} A = N_{i0}u_B A_{\text{eff}} ,$$ (3.16)

where $A_{\text{eff}}$ is an effective area for ion collection. Therefore the loss rate of ions to the walls is given by:

$$\left(\frac{\partial N_i}{\partial t}\right)_{\text{Walls}} = N_{i0}u_B \frac{A_{\text{eff}}}{V} ,$$ (3.17)

and the volume averaged equation [3.10] for the ions can be written as:

$$\frac{\partial N_{i0}}{\partial t} = G_{i0} - L_{i0} - \frac{N_{i0}}{\tau_i} - k_i^{\text{Trans}} N_{i0} .$$ (3.18)
with $k_{i}^{\text{Trans}} = u_B \frac{A_i^L}{V}$. This term represents effectively a ballistic movement of the ions towards the walls. Ion collisions will be considered in the derivation of the effective collision area discussed in chapter 5.

Ions recombin ate at the walls, reverting back to their parent neutrals that return to the discharge volume. The ususall wall reaction may be represented by:

$$A^+ \xrightarrow{\text{wall}} A$$

This implies a transport loss of $A^+$ and a kinetic gain of $A$ to be included in its conservation equation.

### 3.1.1.3 A word on mass conservation

A volume averaged particle conservation equation has been derived for heavy species, either charged or neutral with the form:

$$\frac{\partial N_{i0}}{\partial t} = G_{i0} - L_{i0} - \frac{N_{i0}}{\tau_R} - k_{i}^{\text{Trans}} N_{i0}, \quad (3.19)$$

where the transport coefficient ($k_{i}^{\text{Trans}}$) depends on the species type: $k_{i}^{\text{Trans}} = u_B \frac{A_i^L}{V}$ for ions, $k_{i}^{\text{Trans}} = D_i \frac{A_i^L}{V}$ for neutrals.

The collisional reactions considered in the model - refer to chapter 4 - imply mass conservation. This means that even if the particles resulting from collisions are different from the initial particles, mass must be conserved. Note that this mass conservation applies only to the collisional part of the model, since the diffusion of species to the walls and the substrate can lead to a loss of particles, hence to a change in the system’s mass.

To verify mass conservation due to collisional events, one must check if the sum of all the corresponding gains and losses of mass is identically zero, i.e.

$$\sum_{i=1}^{n} m_i (G_{i0} - L_{i0}) = 0, \quad (3.20)$$

where $m_i$ is the mass of each heavy species $i$ and where the sum is over all the $n$ heavy species. In practice, the mass $m_i$ of species $C_xH_y$ is written normalized to an effective mass as:
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\[
\frac{m_i}{m_{\text{eff}}} = x \frac{m_C}{m_{\text{eff}}} + y \frac{m_H}{m_{\text{eff}}},
\]

where \(y\) is the number of hydrogen atoms (with mass \(m_H\)) and \(x\) is the number of carbon atoms (with mass \(m_C\)) in the molecule.

3.1.1.4 Gas input

A constant flow of input gas (a mixture of \(\text{CH}_4\) and \(\text{H}_2\)) is pumped into the reactor in order to create/maintain the discharge. This means that for the particle conservation equation of these precursors, another term must be added to describe gas input. The input gas density \((N_{n0})\) is calculated by the ideal gas law:

\[
N_{n0} = \frac{P}{k_B T_g},
\]

where \(P\) is the pressure, \(k_B\) is the Boltzmann constant and \(T_g\) is the gas temperature. This density flows through the reactor with a residence time \(\tau_R\) given by (3.9), corresponding to an initial mixture composition given by the partial densities:

\[
\zeta_{\text{CH}_4} = \frac{N_{\text{CH}_4}}{N_{n0}}; \quad \zeta_{\text{H}_2} = \frac{N_{\text{H}_2}}{N_{n0}}
\]

Equation (3.19) for the gaseous precursors is now written as:

\[
\frac{\partial N_{i0}}{\partial t} = G_{i0} - L_{i0} - \frac{N_{i0}}{\tau_R} - k_{i}^{\text{Trans}} N_{i0} + \frac{\zeta_i N_{n0}}{\tau_R}
\]

(3.21)

3.1.1.5 A word on particle conservation

The solution to equation (3.19) yields the densities \(N_i\) of the various species \(i\), whose sum relates to the total pressure \(P\) of the system:

\[
\sum_i N_i = N_{\text{CH}_4} + N_{\text{H}_2} = N_{n0} = \frac{P}{k_B T_g},
\]

(3.22)

which is assumed to be constant in time.

Note that this pressure conservation (or, equivalently, the conservation of the number of particles in the system) is not a priori ensured.
• because of the plasma reactivity, leading to many dissociation/association reactions in which the number of particles involved is not conserved;

• because of gains/losses of particles to and from the system, as a result of the flow regime and the different wall reactions (with losses of particles and/or return to the plasma volume)

Therefore, if the pressure value is to be kept constant, as part of the requirements imposed by the experimental working conditions, the model should tune some 'free' parameter(s) in order to ensure satisfying relation (3.22).

### 3.1.2 Electron energy conservation equation

The electron energy conservation equation can be obtained from the second moment of the Boltzmann equation for the electrons:

\[
\frac{\partial F_e}{\partial t} \frac{1}{2} m_e v^2 d^3v + \int (\vec{\nabla}_r F_e) \cdot \vec{v} \frac{1}{2} m_e v^2 d^3v + \int (\vec{\nabla}_v F_e) \cdot \vec{a} \frac{1}{2} m_e v^2 d^3v = \int \left( \frac{\partial F_e}{\partial t} \right)_{col} \frac{1}{2} m_e v^2 d^3v,
\]

(3.23)

Where \( F_e \) is the electron distribution function and \( m_e \) is the electron mass.

Equation (3.23) is a power density balance equation which measures the rate of the electron energy due to the power supplied to the plasma and lost in collisions and transport.

The first term in (3.23) is merely the time derivative of the energy density, which when averaged out over the discharge volume gives:

\[
\frac{\partial n_e \epsilon}{\partial t},
\]

where \( \epsilon = \frac{1}{2} m_e v^2 \) is the electron mean energy:

\[
\epsilon = \int \frac{1}{2} m_e v^2 F_e d^3v
\]

(3.24)

The second term in (3.23) accounts for the electron energy losses due to transport (in configuration space) and subsequent recombination at the walls. This term can be combined with the part of the third term in (3.23) representing the electron energy losses due to the action of the space-charge field,
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to yield the total power density losses at the wall.

\[
p_{w0} = (\epsilon_{\text{plasma}} + \epsilon_{\text{sheath}}) \left( \frac{\partial n_{e0}}{\partial t} \right)_{\text{wall}}.
\]

(3.25)

Here \( \epsilon_{\text{plasma}} = 2T_e(eV) \) represents the average kinetic energy carried by each electron when it leaves the plasma \(^2\); \( \epsilon_{\text{sheath}} = \frac{T_e(eV)}{2} + V_s \) is the energy lost by each electron that crosses the pre-sheath and the sheath respectively (with \( V_s = \frac{T_e}{2} \ln \left( \frac{m_e}{2\pi m_e} \right) \) the space charge potential drop) \(^2\); and \( \left( \frac{\partial n_{e0}}{\partial t} \right)_{\text{wall}} \) represents the loss rate of electrons to the walls which can be obtained by current conservation:

\[
\left( \frac{\partial n_{e0}}{\partial t} \right)_{\text{wall}} = \sum_i k^{\text{Trans}}_i N_{i0} ,
\]

(3.26)

where the sum is over all the ion species. Therefore (3.25) can be written as:

\[
p_{w0} = (\epsilon_{\text{plasma}} + \epsilon_{\text{sheath}}) \sum_i k^{\text{Trans}}_i N_{i0} = \epsilon_w \sum_i k^{\text{Trans}}_i N_{i0}
\]

(3.27)

The remainder part of the third term in (3.23) represents the action of exterior forces on the electrons, thus accounting for the average power density provided to the discharge: When volume averaged it will yield:

\[
p_{\text{Input},0} = \frac{P_{\text{Input}}}{V} ,
\]

(3.28)

where \( P_{\text{Input}} \) is the total power input and \( V \) is the discharge volume.

The final term in (3.23) integrates the collision operator, thus representing the energy density gain/loss of electrons, per unit time, in elastic/inelastic collisions with neutrals.

\[
p_{\text{coll},0} = p_{\text{el},0} + p_{\text{inel},0}
\]

\[
p_{\text{el},0} = \sum_i n_{e0} \nu_{i0}^{el} \frac{3}{2} T_e \frac{m_e}{m_i}
\]

(3.29)

\[
p_{\text{inel},0} = \sum_i n_{e0} \epsilon_i \nu_{i0}^{in}
\]

Here, \( p_{\text{el},0} \) is the averaged power lost in elastic electron-neutral collisions (with \( \nu_{i0}^{el} \) the corresponding collision frequency) and \( p_{\text{inel},0} \) is the averaged power lost in inelastic electron-neutral collisions.
(with $\epsilon_i$ the excitation/ionization energy of each species $i$ and $\nu_{i0}$ the corresponding inelastic collision frequency).

The final power balance equation for the electrons writes:

$$\frac{\partial n_{e(0)} \epsilon}{\partial t} = p_{\text{input}, 0} - p_{W0} - p_{\text{coll}, 0} ,$$  \hspace{1cm} (3.30)

with:

$$p_{\text{input}, 0} = \frac{P_{\text{input}}}{V}$$

$$p_{W0} = \epsilon W \sum i k_{\text{Trans}}^i N_{i0}$$ \hspace{1cm} (3.31)

$$p_{\text{coll}, 0} = p_{el, 0} + p_{inel, 0} = \sum i n_{e0} \nu_{i0}^{el} \epsilon T_e \frac{m_e}{m_i} + \sum i n_{e0} \epsilon_i \nu_{i0} .$$

### 3.1.3 Neutrality condition

The particle balance equations for the $n$ heavy species and the electron energy balance equation constitute a system of $n + 1$ equations to solve our problem with $n + 2$ variables. Therefore one last equation is needed to close the system, and it corresponds to the charge balance equation (or neutrality condition). Because the model considers only singly charged ions the neutrality condition writes:

$$\sum i N_{i \text{Ion}} = n_e ,$$ \hspace{1cm} (3.32)

where $N_{i \text{Ion}}$ represents the volume averaged density of the ion species $i$.

### 3.2 Numerical solution

#### 3.2.1 The DLSODE package

In the previous section, a set of equations was derived to formulate the CRM, namely the density conservation equations for the heavy species, the energy density conservation equation for the electrons
3.2. NUMERICAL SOLUTION

and the neutrality condition. Recalling those equations:

\[
\begin{align*}
\frac{dN_i}{dt} &= G_i - L_i - k_{\text{trans}} N_i \\
\frac{dn_e}{dt} &= p_{\text{input}} - p_{\text{W},0} - p_{\text{coll},0} \\
\sum_i N_{i0} &= n_{e0}
\end{align*}
\] (3.33)

In order to solve these equations a numerical Fortran code was created, using the DLSODE package from the Livermore National Laboratory [18]. As stated in its description, this package solves stiff and non-stiff systems of first-order ordinary differential equations (ODE) of the form:

\[
\frac{dy}{dt} = f(y, t)
\] (3.34)

which exactly corresponds to the system of equations presented in (3.33). In the code, the DLSODE package receives as input a subroutine (called FEX) that updates the equations and constants used in the model, the initial values of the different variables \(y\), as well as the temporary initial and final values of the independent variable, \(t_i\) and \(t_f\), respectively. As output, the package gives the value of each variable \(y\) at \(t_f\). In our case the variables \(y\) are the densities of each heavy species, the electron density and the electron temperature, which we’ll evolve in time.

Next we present an overview of the FEX routine, responsible for updating the model equations and reaction rate constants.

3.2.2 The FEX subroutine

This subroutine is used as input to the DLSODE package and is in charge of:

- Updating the electron density and temperature,
- Updating all the kinetic and transport coefficients,
- Updating the model equations,
- Consider open channels and check for mass conservation.

An overview of what the FEX subroutine actually does to fulfill these objectives is now given.
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3.2.2.1 Calculating the electron density and temperature

As stated, one objective of this code is to independently calculate the electron density and temperature, but as shown in (3.33), there is no single equation for neither of these quantities in the form of (3.34). However, using the neutrality condition, the electron density can be calculated at each iteration, if the ion densities are known.

\[ n_{\text{calc}e}^0 = \sum_i N_{\text{ion}}^{i0}. \]  (3.35)

After, the electron temperature can then be extracted from the electron energy density using the calculated electron density and assuming a maxwellian EEDF, i.e. \( \epsilon = \frac{3}{2} k_B T_e \):

\[ T_e = \frac{n_{\text{calc}e}^0 \epsilon}{n_{\text{calc}e}^0 \frac{3}{2} k_B}. \]  (3.36)

3.2.2.2 Calculating the electron rate coefficients

Since the electron temperature will change with the model iterations, so will the rate coefficients \( k_e \) associated to the different electron reactions. These coefficients are calculated as integrals of the collision cross sections \( (\sigma_e) \) over the EEDF \( f_e \) (which depends on \( T_e \)), following:

\[ k_e = \langle \sigma v \rangle = \left( \frac{2e}{m_e} \right)^{1/2} \int f_e(u) u \sigma_e(u) du , \]  (3.37)

with \( f_e(u) \) satisfying:

\[ \int_0^\infty f_e(u) \sqrt{u} du = 1. \]

Within the FEX subroutine, a code is included with 3 objectives:

- Reads the electron collision cross sections
- Performs a linear interpolation of the cross sections according to a given energy step
- Calculates the electron rate coefficients by numerically integrating over a Maxwellian EEDF, using a trapezoidal method, that adopts the previously defined energy step.

The FEX subroutine also updates the analytical expressions of other kinetic and transport coefficients (refer to chapter 4 and 5 for more details on these coefficients).
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3.2.2.3 Updating the model equations

The individual terms in equations (3.33) will depend on the rate coefficients, the heavy species’ densities, and the electron density and temperature. Since these values change at each iteration, these equations must also be updated at each call of $FEX$.

The $FEX$ subroutine receives as input a vector $Y$, which contains:

- The densities of each heavy species - $Y(i)$, $i=1, ... , n-1$
- The electron energy density in the last element - $Y(n)$

with $n$ being the dimension of the vector $Y$. Having calculated the electron density and the electron temperature, using the input values $Y(i)$ and equations (3.35) and (3.36), the particle conservation equations for the heavy species is then updated. Another vector is introduced, $YDOTT$ to store the numerical value of the conservation relation. In the case of the heavy species conservation equation, this vector is split into two other vectors, $YDOTT_{KIN}$ and $YDOTT_{TR}$ accounting for the kinetic and the transport part of the conservation equation, respectively. The particle conservation equation for a given heavy species $j$ is therefore written as:

$$YDOTT(j) = YDOTT_{KIN}(j) + YDOTT_{TR}(j), \quad (3.38)$$

with

$$YDOTT_{KIN}(j) = \sum_i \nu_{i,j} Y(i) - \sum_k \nu_{j,k} Y(j)$$

$$YDOTT_{TR}(j) = k^\text{Trans}_j Y(j) - \frac{Y(j)}{\tau_R}, \quad (3.39)$$

where $\nu_{i,j} = k_{ij} N_i$ is the collision frequency of a gain (loss) mechanism for species $j$ (i), and where the sum in $i$ is over all the gain mechanisms for species $j$ and the sum in $k$ is over all the loss mechanisms for species $j$. In the case of the precursors the source term $\zeta_i N^\text{Input}_i$ is also added to the transport vector. For the ions the recombination at the walls is represented in by a loss term in the ion transport vector of $k^\text{Trans}_i Y(i)$, since these ions fully recombine at the walls [2] the same term is considered as a gain in the parent neutral’s transport vector.

For the electron energy density conservation equation, there is no separation between kinetic terms and transport terms, and following (3.30) this equation is written in the last element of the $YDOTT$.
vector as:

\[
Y D O T(n) = \frac{2}{3} \left( \frac{P_{\text{input}}}{V} - p_{e\text{l},0} - p_{\text{inel},0} - p_{W,0} \right),
\]

(3.40)

where the different electron energy loss terms are given by:

\[
p_{e\text{l},0} = \sum_i n_{e0} Y(i) k_{el}^i 3T_e \frac{m_e}{M_i},
\]

\[
p_{\text{inel},0} = \sum_i n_{e0} \varepsilon_i \nu_{i0}
\]

\[
p_{W,0} = \sum_i \varepsilon_w k_{\text{Trans}}^i Y(i).
\]

(3.41)

In (3.41), \(k_{el}^i\) represent the electron rate coefficient of elastic scattering with heavy-species \(i\), and the sum in the wall loss term is over the different ions only.

### 3.2.2.4 Open channels and mass conservation

As stated previously, all kinetic reactions conserve mass. Therefore, when considering all resulting species the following should be verified:

\[
\sum_i m_i Y D O T.K I N(i) = 0.
\]

(3.42)

However, equation (3.42) is not directly satisfied since the species resulting from the different reactions are not all considered in the model.

These reactions where the resulting species are not considered introduce an open channel for mass loss, meaning that an alteration to (3.42) must be made in order to check the mass conservation.

Considering, as an example, the following reaction:

\[
A + B \rightarrow C + D,
\]

where species D is not considered in the model. Since mass is conserved we can write:

\[
m_A + m_B = m_C + m_D.
\]
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Now, for each species considered in the model the kinetic part of the conservation equation takes the form

\[ Y_{\text{DOT.KIN}}(A) = -\nu_{AB}N_B \]
\[ Y_{\text{DOT.KIN}}(B) = -\nu_{AB}N_B \]
\[ Y_{\text{DOT.KIN}}(C) = \nu_{AB}N_B \]

(3.43)

By summing relations (??), multiplied by the masses of species A,B,C one gets

\[-m_A\nu_{AB}N_B - m_B\nu_{AB}N_B + m_C\nu_{AB}N_B = \nu_{AB}N_B(m_C - m_A - m_B) = -m_D\nu_{AB}N_B ,\]

Which is the term missing to verify (3.42) and that would exist if species \(D\) were considered in the model. Thus in order to check for mass conservation (3.42) must be altered as follows:

\[ \sum_k M_k Y_{\text{DOT.KIN}}(k) + \sum_{i,j} M_i \nu_j N = 0 \]

(3.44)

where the first sum is over the species \(k\) in the model, the second sum is over the \(i\) species not considered in the model and over the gain mechanisms \(j\) for said species. Obviously, there are no loss mechanisms for these species, because in this case the species would have to be considered in the model with a proper conservation equation.

3.2.3 Convergence of the code

Since the code calculates the time evolution of each species density in the plasma, a parameter can be introduced to check if steady state has been achieved.

To that end, before each iteration, the original densities are stored in a vector, \(Y_{\text{prev}}\), in order to calculate the relative errors:

\[ e_i = \left| \frac{Y(i) - Y_{\text{prev}}(i)}{\frac{Y(i)}{2} + \frac{Y_{\text{prev}}(i)}{2}} \right| = 2 \left| \frac{Y(i) - Y_{\text{prev}}(i)}{Y(i) + Y_{\text{prev}}(i)} \right| . \]

(3.45)
Using (3.45) one can define the total error;

\[ e_{tot} = \frac{1}{n} \sum_{i}^{n} e_i, \tag{3.46} \]

and a convergence criterion for steady-state and program stop

\[ e_{tot} \leq 10^{-5}. \tag{3.47} \]

With this criterion each run of the code takes about 40 minutes on a 3.0 GHz CPU laptop.
Chapter 4

Kinetic scheme

This chapter presents the kinetic scheme used in the CRM, introducing all the heavy species and collisional reactions considered. The rate coefficients for each reaction or, when available, the collision cross sections are also presented. For the electron reactions, the energy thresholds are also given.

4.1 Heavy species

The heavy species considered are presented in table 4.1 together with their excitation energy and position in the density vector $Y$.

In the original model, only species 1 through 20 were considered, meaning that the updated model version further includes several excited (atomic and molecular vibrational) hydrogen species and a more complete set of methane derivates.

4.1.1 Vibrational levels of hydrogen

The model considers 15 vibrational levels of hydrogen, with energies given by the Morse oscillator expression:

$$e_v = \omega_0 \left( v + \frac{1}{2} \right) + \omega_0 \chi_e \left( v + \frac{1}{2} \right)^2,$$  \hspace{1cm} (4.1)

where $v$ is the vibrational quantum number, $\omega_0$ is the fundamental oscillating frequency and $\chi_e$ is a quantum-mechanical parameter. This expression is similar to that of the harmonic oscillator apart
Table 4.1: Heavy species considered for the model

<table>
<thead>
<tr>
<th>No.</th>
<th>Chemical symbol</th>
<th>Threshold energy (eV)</th>
<th>Density vector (Y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_4$</td>
<td>N/A</td>
<td>Y(1)</td>
</tr>
<tr>
<td>2</td>
<td>CH$_3$</td>
<td>N/A</td>
<td>Y(2)</td>
</tr>
<tr>
<td>3</td>
<td>CH$_2$</td>
<td>N/A</td>
<td>Y(3)</td>
</tr>
<tr>
<td>4</td>
<td>CH</td>
<td>N/A</td>
<td>Y(4)</td>
</tr>
<tr>
<td>5</td>
<td>C$_2$H$_5$</td>
<td>N/A</td>
<td>Y(5)</td>
</tr>
<tr>
<td>6</td>
<td>C$_2$H$_4$</td>
<td>N/A</td>
<td>Y(6)</td>
</tr>
<tr>
<td>7</td>
<td>C$_2$H$_2$</td>
<td>N/A</td>
<td>Y(7)</td>
</tr>
<tr>
<td>8</td>
<td>C$_2$H$_6$</td>
<td>N/A</td>
<td>Y(8)</td>
</tr>
<tr>
<td>9</td>
<td>C$_3$H$_8$</td>
<td>N/A</td>
<td>Y(9)</td>
</tr>
<tr>
<td>10</td>
<td>CH$_4^+$</td>
<td>N/A</td>
<td>Y(10)</td>
</tr>
<tr>
<td>11</td>
<td>CH$_3^+$</td>
<td>N/A</td>
<td>Y(11)</td>
</tr>
<tr>
<td>12</td>
<td>CH$_2^+$</td>
<td>N/A</td>
<td>Y(12)</td>
</tr>
<tr>
<td>13</td>
<td>C$_2$H$_2^+$</td>
<td>N/A</td>
<td>Y(13)</td>
</tr>
<tr>
<td>14</td>
<td>C$_2$H$_4^+$</td>
<td>N/A</td>
<td>Y(14)</td>
</tr>
<tr>
<td>15</td>
<td>C$_2$H$_5^+$</td>
<td>N/A</td>
<td>Y(15)</td>
</tr>
<tr>
<td>16</td>
<td>H$_2$(v=0)</td>
<td>N/A $^1$</td>
<td>Y(16)</td>
</tr>
<tr>
<td>17</td>
<td>H</td>
<td>N/A</td>
<td>Y(17)</td>
</tr>
<tr>
<td>18</td>
<td>H$_2^+$</td>
<td>15.4</td>
<td>Y(18)</td>
</tr>
<tr>
<td>19</td>
<td>H$^+$</td>
<td>13.61</td>
<td>Y(19)</td>
</tr>
<tr>
<td>20</td>
<td>H$_3^+$</td>
<td>N/A</td>
<td>Y(20)</td>
</tr>
<tr>
<td>21</td>
<td>H(2s)</td>
<td>10.21</td>
<td>Y(21)</td>
</tr>
<tr>
<td>22</td>
<td>H(2p)</td>
<td>10.21</td>
<td>Y(22)</td>
</tr>
<tr>
<td>23</td>
<td>H(3)</td>
<td>12.11</td>
<td>Y(23)</td>
</tr>
<tr>
<td>24</td>
<td>H(4)</td>
<td>12.76</td>
<td>Y(24)</td>
</tr>
<tr>
<td>25</td>
<td>H(5)</td>
<td>13.11</td>
<td>Y(25)</td>
</tr>
<tr>
<td>26</td>
<td>CH$_2^+$</td>
<td>N/A</td>
<td>Y(41)</td>
</tr>
<tr>
<td>27</td>
<td>CH$^+$</td>
<td>N/A</td>
<td>Y(42)</td>
</tr>
<tr>
<td>28</td>
<td>C$_2$H$_6^+$</td>
<td>N/A</td>
<td>Y(43)</td>
</tr>
<tr>
<td>29</td>
<td>C$_2$H$_3$</td>
<td>N/A</td>
<td>Y(44)</td>
</tr>
<tr>
<td>30</td>
<td>C$_2$H$_3^+$</td>
<td>N/A</td>
<td>Y(45)</td>
</tr>
</tbody>
</table>

$^1$Hydrogen vibrational states $v = 1$ through $v = 15$ are treated separately as to not tax the reader with a large amount of species with a fundamental similar behaviour.
4.2 Kinetic reactions

Kinetic reactions in this model are divided into 6 different types:

- Dissociation by electron impact,
- Ionization by electron impact,
- Neutral-neutral reactions,
- Ion-neutral reactions,
- Electron recombination reactions,
- Ionization by proton impact,

from the quadratic term which accounts for harmonicity and bond dissociation.

Each vibrational level can be identified by its energy level as listed in table 4.2.

Table 4.2: Vibrational excited states of the H\(_2\) molecule

<table>
<thead>
<tr>
<th>No.</th>
<th>Chemical symbol</th>
<th>Threshold energy (eV)</th>
<th>Density vector (Y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H(_2)(v=1)</td>
<td>0.516</td>
<td>Y(26)</td>
</tr>
<tr>
<td>2</td>
<td>H(_2)(v=2)</td>
<td>1</td>
<td>Y(27)</td>
</tr>
<tr>
<td>3</td>
<td>H(_2)(v=3)</td>
<td>1.5</td>
<td>Y(28)</td>
</tr>
<tr>
<td>4</td>
<td>H(_2)(v=4)</td>
<td>1.88</td>
<td>Y(29)</td>
</tr>
<tr>
<td>5</td>
<td>H(_2)(v=5)</td>
<td>2.28</td>
<td>Y(30)</td>
</tr>
<tr>
<td>6</td>
<td>H(_2)(v=6)</td>
<td>2.64</td>
<td>Y(31)</td>
</tr>
<tr>
<td>7</td>
<td>H(_2)(v=7)</td>
<td>2.98</td>
<td>Y(32)</td>
</tr>
<tr>
<td>8</td>
<td>H(_2)(v=8)</td>
<td>3.28</td>
<td>Y(33)</td>
</tr>
<tr>
<td>9</td>
<td>H(_2)(v=9)</td>
<td>3.56</td>
<td>Y(34)</td>
</tr>
<tr>
<td>10</td>
<td>H(_2)(v=10)</td>
<td>3.8</td>
<td>Y(35)</td>
</tr>
<tr>
<td>11</td>
<td>H(_2)(v=11)</td>
<td>4.02</td>
<td>Y(36)</td>
</tr>
<tr>
<td>12</td>
<td>H(_2)(v=12)</td>
<td>4.2</td>
<td>Y(37)</td>
</tr>
<tr>
<td>13</td>
<td>H(_2)(v=13)</td>
<td>4.36</td>
<td>Y(38)</td>
</tr>
<tr>
<td>14</td>
<td>H(_2)(v=14)</td>
<td>4.48</td>
<td>Y(39)</td>
</tr>
<tr>
<td>15</td>
<td>H(_2)(v=15)(^1)</td>
<td>4.57</td>
<td>Y(40)</td>
</tr>
</tbody>
</table>

\(^1\)This state is a temporary state used for the dissociation of the molecule.
CHAPTER 4. KINETIC SCHEME

- Excitation by electron impact,
- Elastic collisions by electron impact,
- Wall reactions.

For each reaction type, a set of rate coefficients is given, either obtained from the literature or calculated through collision cross sections. The following subsections describe each type of reaction specifically.

Reactions for the (de)excitation of the hydrogen vibrational levels will be treated separately, due to their specificity.

4.2.1 Electron impact dissociation reactions

The electron impact dissociation reactions and their respective cross sections are presented in Table B.1.

For these reactions, the collision cross section is given through the following formula [10]

\[
\sigma = \begin{cases} 
0, & E < E_{th} \\
\sigma_0 \left[1 - \left(\frac{E_{Max} - E}{E_{Max} - E_{th}}\right)^2\right], & E_{th} < E < E_{Max} \\
\sigma_0 \exp \left[\frac{E_{Max} - E}{\lambda}\right], & E > E_{Max}
\end{cases}
\]

\[(4.2)\]

where \(\sigma_0\) is given in \(10^{-16} cm^2\). For the electron energy balance equation we assume that the energies lost by electrons due to these reactions are approximated equal to the threshold \(E_{th}\).

4.2.2 Electron impact ionization reactions

The electron impact ionization reactions and their respective rate coefficients/cross sections and presented in Table B.2.

The ionization cross sections for CH\(_4\) subproducts are also given by equation \((4.2)\). The hydrogen
atom ionization cross section is given by the following equation:

\[
\sigma(E) = \begin{cases} 
0, & E \leq E_{th} \\
ARG(E) \times FH4(YK1, C1, E, G), & E_{th} < E \leq 40 \\
ARG(E) \times FH4(YK2, C2, E, G), & 40 < E \leq 150 \\
ARG(E) \times FH4(YK3, C3, E, G), & E > 150
\end{cases}
\]  

\[ (4.3) \]

where

\[
ARG(E) = \begin{cases} 
ARGH(\sqrt{VM} + ARGH(\sqrt{|V0|}) + 1.209199576, & VM * V0 < 0 \\
ARGH(max(\sqrt{|V0|}, \sqrt{VM})) - ARGH(min(\sqrt{|V0|}, \sqrt{VM})), & VM * V0 \geq 0
\end{cases}
\]  

\[ (4.4) \]

\[
FH(YK, C, E, G) = 47.826 \frac{G \times YK}{E} \log \left( \frac{C \times E}{13.6} \right)
\]  

\[ (4.5) \]

\[
ARGH(x) = \log \left[ \frac{x^2 - x + 1}{(x+1)^2} \right] + 1.154700538 \arctan \left[ \frac{2x - 1}{1.732050808} \right],
\]  

\[ (4.6) \]

with

\[
G = 2 + \frac{65}{E}; \quad V0 = -\frac{Y0}{G}; \quad VM = \frac{EM - Y0}{G}; \quad EM = \frac{E - E_{th}}{2}; \quad Y0 = 1.6 \exp \left[ -\frac{E - E_{th}}{2.2} \right].
\]

In the cases where the cross section is said to be provided, an input file is read where the respective cross section is numerically tabulated.

Again for the electron energy conservation equation, for each reaction the threshold energies are taken as a representative of the electron energy losses with each reaction.

### 4.2.3 Neutral-neutral reactions

Kinetic reactions between neutral species and their respective cross sections/ rate coefficients, are presented in table B.3.
4.2.4 Ion-Neutral reactions

Kinetic reactions between ions and neutrals, as well as their corresponding rate coefficients, are presented in table B.3.

4.2.5 Electron recombination / detachment reactions

Electron recombination and detachment reactions and their respective cross sections / rate coefficients are presented in table B.5.

Some reaction coefficients are given by the following equation:

\[
k(cm^3s^{-1}) = \begin{cases} 
3.92 \times 10^{-14} \frac{er^{1.5}}{er+0.35}, & n = 1s \\
1.235 \times 10^{-14} \frac{er^{1.5}}{er+0.12}, & n = 2s \\
3.11 \times 10^{-14} \frac{er^{1.5}}{er+0.61}, & n = 2p \\
5.197 \times 10^{-14} er^{1.5} \exp (\min(27, er)) E1(\min(27, er)), & n = 3, 4, 5 
\end{cases}
\] (4.7)

where \( er \) and \( E1 \) are given by

\[
er = 1.5 \frac{E_{th,H} - E_{th}(n)}{\epsilon} ; \quad E1(x) = \int_1^{\infty} \frac{\exp (-xt)}{t} dt 
\]

with \( \epsilon \) the electron mean energy and \( n \) the number of atomic hydrogen excited state (1 to 5).

Other reaction coefficients are given by the following equation:

\[
k(cm^3s^{-1}) = 2.13975 \times 10^{-26} n^2 \frac{\epsilon^{-3}}{er^{2.33} + 4.38er^{1.72} + 1.32er}, & n = 1, 2, 3, 4, 5
\] (4.8)

For these reactions, the electron energy loss is calculated from the change in energy of each heavy particle system.

\[
\epsilon_{loss} = E_{th}^{end} - E_{th}^{init},
\] (4.9)
with $E^{\text{init}}_{th}$ and $E^{\text{end}}_{th}$ the threshold energies of the initial and final heavy species. In cases where the threshold energy is not provided (e.g. for the $H_3^+$ ion), we take the electron mean energy $E^{H_3^+}_{th} = \frac{3}{2} k_B T_e$.

### 4.2.6 Ionization by proton impact

Proton ionization reactions, or charge exchange reactions with $H^+$ along with the corresponding rate coefficients are presented in table [B.6](#).

### 4.2.7 Electron impact excitation reactions

Excitation of neutral species by electron impact and their respective cross sections / rate coefficients are presented in table [B.7](#).

There are 5 different types of cross sections considered, the first one is given by ($\sigma$ is in $10^{-16}$ cm$^2$)

$$
\sigma(E) = \begin{cases} 
0, & E < E_{th,2s} \\
0.034E - 0.258, & E_{th,2s} < E \leq 12 \\
frac{1.8E}{12}, & 12 < E \leq 25 \\
F1(UH,EMM,CC4), & E > 25
\end{cases}
$$

with $E_{th,2s}$ is the threshold energy for the excited state $H(2s)$, $EMM = 0.03624$, $CC4 = 1.537$, $UH = \frac{E}{13.595}$ and

$$
F1 = (UH,EMM,CC4) = 3.519EMM \log \left( CC4 \times UH \right) UH.
$$

The second cross section is given by ($\sigma$ is in $10^{-16}$ cm$^2$)

$$
\sigma(E) = \begin{cases} 
0, & E < E_{th,2p} \\
F1(UH,EMMa,CC4a), & E_{th,2p} < E \leq 26 \\
F1(UH,EMMb,CC4b), & E > 26
\end{cases}
$$

with $EMMa = 0.3244$, $CC4a = 1.447$, $EMMb = 0.6768$ and $CC4b = 0.8517$. 

The third is given by (σ is in $10^{-16}$ cm$^2$):

$$\sigma(E) = \begin{cases} 0, & E < E_{th,3} \\ F1(UH,EMMc,CC4c), & E \geq E_{th,3} \end{cases}$$

(4.13)

with $EMMc = 0.0948$ and $CC4c = 1.1698$.

The fourth cross section is given by (σ is in $10^{-16}$ cm$^2$)

$$\sigma(E) = \begin{cases} 0, & E < E_{th,4} \\ F1(UH,EMMd,CC4d), & E \geq E_{th,4} \end{cases}$$

(4.14)

with $EMMd = 0.04139$ and $CC4d = 1.1026$.

And finally the fifth cross section is given by (σ is in $10^{-16}$ cm$^2$)

$$\sigma(E) = \begin{cases} 0, & E < E_{th,5} \\ F1(UH,EMMe,CC4e), & E \geq E_{th,5} \end{cases}$$

(4.15)

with $EMMe = 0.02119$ and $CC4e = 1.0417$.

The energy lost by electrons is calculated similarly to what is done in recombination reactions.

### 4.2.8 Elastic collisions by electron impact

Elastic collisions by electron impact and their rate coefficients / cross sections are presented in table B.8. These collisions are considered only in the electron energy density conservation equation, since they do not affect the nature of the particles involved.

### 4.2.9 Hydrogen vibrational reactions

Throughout the tables presented in the previous sections a certain number of vibrational reactions appeared. These reactions are listed in table 4.3 for the different vibrational levels considered, and characterized by either a rate coefficient or a cross section.
Table 4.3: Hydrogen vibrational reactions

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Cross section / Rate coefficient</th>
<th>Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$e + \text{H}_2(v) \rightarrow \text{H}_2(t) \rightarrow e + 2\text{H}$</td>
<td>$k_{49}(a-d) \times \text{prob}$</td>
<td>$k_{10a} - k_{10d}$</td>
</tr>
<tr>
<td>2</td>
<td>$e + \text{H}_2(v) \rightarrow e + \text{H}(1s) + \text{H}(n)$</td>
<td>$k_{49e} - k_{49j}$</td>
<td>$k_{10e}$</td>
</tr>
</tbody>
</table>
| 3   | $e + \text{H}_2(v) \rightarrow 2e + \text{H}_2^+$  
   (Branching ratio 0.93) | CS Provided | $k_{30}$ |
|     | $e + \text{H}_2(v) \rightarrow 2e + \text{H}^+ + \text{H}(1s)$  
   (Branching ratio 0.07) | | |
| 4   | $\text{H}(2s) + \text{H}_2(v) \rightarrow e + \text{H}_2^+$  
   (Branching ratio 0.75) | $k = 8.9105 \times 10^{-11} \sqrt{T_g}$ | $k_{95}$ |
|     | $\text{H}(2s) + \text{H}_2(v) \rightarrow e + 3\text{H}(1s)$  
   (Branching ratio 0.25) | | |
| 5   | $\text{H}(2p) + \text{H}_2(v) \rightarrow \text{H}(2p) + \text{H}_2(v)$ | $k = 1.06926 \times 10^{-10} \sqrt{T_g}$ | $k_{96}$ |
| 6   | $\text{H}_2(v) + \text{H}_2(w) \leftrightarrow \text{H}_2(v-1) + \text{H}_2(w+1)$ | Rate calculated | VV Trans. |
| 7   | $\text{H}_2(v) + \text{H}_2(w) \leftrightarrow \text{H}_2(v-1) + \text{H}_2(w)$ | Rate calculated | VT Trans. |
| 8   | $\text{H}_2(v) + \text{H}_2(v) \leftrightarrow \text{H}_2(v-1) + \text{H}_2(v)$ | Rate calculated | VT Trans.  
   with atoms |
| 9   | $\text{H}_2(v) + \text{H}(1s) \leftrightarrow \text{H}_2(v+1) + \text{H}(1s)$  
   $i=1$-$6$ | Rate calculated | Dissociation via  
   VT Trans.  
   with $v = 15$ |
| 10  | $\text{H}_2(v = 15) + \text{H}_2(w) \leftrightarrow 2\text{H}(1s) + \text{H}_2(w)$ | Rate calculated | |

If rate coefficient is provided, the same one is used for all similar reactions with different vibrational levels. If a cross section is provided, it is considered to describe the ground-state reaction with $\text{H}_2(v = 0)$.

In this case the cross sections for the different vibrational states are obtained from the ground-state cross section by shifting it in energy scale of values corresponding to the excitation energies of the vibrational states (see figure 4.1).

Mathematically, the cross section $\sigma_v$ for the vibrational level $v$ is then obtained from the corresponding ground-state cross section $\sigma_0$ by matching

$$
\sigma_v(E) = \sigma_0(E - E_{th,v}) ,
$$

where $E_{th,v}$ is the excitation energy of the vibrational state $v$. In order to calculate the rate coefficient
<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Cross section / Rate coefficient</th>
<th>Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>$H_2(v = 15) + H_2(w) \leftrightarrow 2H(1s) + H_2(w - 1)$</td>
<td>Rate calculated$^1$</td>
<td>Dissociation via VV Trans. with $v = 15$</td>
</tr>
<tr>
<td>12</td>
<td>$H^+ + 2H_2(v) \rightarrow H_2 + H_3^+$</td>
<td>$k = 3.1 \times 10^{-29} \left( \frac{\text{T}_{\text{g}}}{\text{T}} \right)^{0.5}$</td>
<td>$k_{122}$</td>
</tr>
</tbody>
</table>
| 13  | $H^+ + 2H_2(v > 3) \rightarrow H(1s) + H_2^+$  
$e + H_3^+ \rightarrow 3H(1s)$  
(Branching ratio 0.72)  
$e + H_3^+ \rightarrow H_2(v > 5) + H(2s, 2p)$  
(Branching ratio 0.28) | $k = 2.5 \times 10^{-9}$  
$\sigma(E) = 50 \left( \frac{0.1}{E} \right)\ln 2500/\ln 4000$ | $k_{123}$  
$k_{131}$ |
| 14  | $e + H_2(v) \leftrightarrow e + H_2(v + i)$  
(i = 1, 2, 3) | CS provided$^1$ | $k_{48}$ |
| 15  | $e + H_2(v) \rightarrow e + H_2(D^1\Pi_u, B^1\Sigma_u^+, D^3\Pi_u)$ | CS provided$^1$ | $k_{49a}$ |
| 16  | $e + H_2(v) \rightarrow e + H_2(B^1\Sigma_u^+)$  
$e + H_2(v')$ | CS provided$^1$ | $k_{49b}$ |
| 17  | $e + H_2(v) \rightarrow e + H_2(C^1\Pi_u)$  
$e + H_2(v')$ | CS provided$^1$ | $k_{49m}$ |
| 18  | $e + H_2(v) \rightarrow e + H_2(B^1\Sigma_u^+)$  
$e + H_2(v')$ | CS provided$^1$ | $k_{49n}$ |
| 19  | $e + H_2(v) \rightarrow e + H_2(D^1\Pi_u)$  
$e + H_2(v')$ | CS provided$^1$ | $k_{49a}$ |
| 20  | $e + H_2(v) \rightarrow e + H_2(D^1\Pi_u)$  
$e + H_2(v')$ | CS provided$^1$ | $k_{49a}$ |

$k_v$, the cross section must be integrated over the EEDF

$$k_v = \langle \sigma_v v \rangle = \int \sigma_v(v) v f_v(v) \, d^3v , \quad (4.17)$$

which can be changed into an energy integral:

$$k_v = \left( \frac{2e}{m_e} \right)^{1/2} \int_0^\infty \sigma_v(E) f_v(E) E dE . \quad (4.18)$$
4.2. KINETIC REACTIONS

Figure 4.1: Illustration of the setting of cross sections $\sigma_v$ for different vibrational states from the corresponding ground state cross section $\sigma_0$. $E_{th,v}$ refers to the excitation energy of vibrational state $v$.

Using relation (4.16) in (4.18)

$$k_v = \left( \frac{2e}{m_e} \right)^{1/2} \int_0^\infty \sigma_0(E - E_{th,v})f_e(E)EdE ,$$

and changing the energy variable to, $E' = E - E_{th,v}$, one obtains

$$k_v = \left( \frac{2e}{m_e} \right)^{1/2} \int_0^\infty (E' + E_{th,v})\sigma_0(E')f_e(E' + E_{th,v})dE'$$

Relation (4.20) can be easily worked out for a Maxwellian EEDF, using the numerical method described in chapter 3.

4.2.9.1 V-T transitions

V-T transitions correspond to reactions 8 and 10 in table 4.3 where two reacting hydrogen molecules collide to transfer the kinetic (translational) energy of one molecule into vibrational energy of the other. The change in the vibration level is assumed always of 1 quantum state, but the transition can happen for all vibrational states. These rate coefficients are given by [19]:

$$k_{v,v-1} = k_{1,0}v \exp [\delta_{VT}(v - 1)] ,$$
where

\[ k_{1,0} = 10^C \quad \text{and} \quad \delta_{VT} = 2a_3 \left( \frac{1.571357 \times 10^6}{T_g} \right)^{1/3}, \]

where \( T_g \) is in K, \( C = -9.28733 - \frac{44.56918}{T_g^{1/3}} \) and \( a_3 \) is given by

\[ a_3 = \frac{a_2}{a_1}; \quad a_1 = 4401.21; \quad a_2 = 121.336 \]

This assures that the rate coefficient for the VT transition to ground-state gives \( k_{1,0} = 4.66 \times 10^{-16} \text{cm}^3\text{s}^{-1} \) at \( T_g = 400K \) \[19\]

When the VT reactions proceed via the pseudo-level \( \nu = 15 \) they result in the dissociation of the molecule (see reaction 9 in table \[4.3\])

Both direct and reverse VT transitions are possible. The rate coefficients for those reactions relate via the Klein-Rosseland formula:

\[ k_{i,j} = k_{j,i} \exp \left( \frac{E_i - E_j}{k_B T_g} \right) \] (4.22)

### 4.2.9.2 V-V Transitions

V-V transitions correspond to reactions 7 and 11 in table \[4.3\] where the collision of two vibrational states of the hydrogen molecule changes the levels of both molecules. Again, we assume only mono-quantum excitations/excitations, with rate coefficients given by \[19\]

\[ k^{w-1,w}_{v,v-1} = \begin{cases} P^{0,1}_{1,0} \left[ \frac{3}{2} - \frac{1}{2} \exp (-\delta_{VV} |v - w|) \right] \exp (-\delta_{VV} |v - w|) \quad & \text{if } w \leq v \\ P^{0,1}_{1,0} \left[ \frac{3}{2} - \frac{1}{2} \exp (-\delta_{VV} |v - w|) \right] \exp (-\delta_{VV} |v - w|) \exp \left[ \frac{2E_I x_e}{k_B T_g} (w - v) \right] \quad & \text{if } w > v \end{cases} \]

(4.23)

where \( E_I = 05457eV, x_e = 0.028 \) and

\[ k^{0,1}_{1,0} = 10^D \quad \text{and} \quad \delta_{VV} = \frac{2}{3}a_3 \left( \frac{2.661025 \times 10^6}{2T_g} \right)^{1/2} \]

where \( T_g \) is in K; \( D \) is given by
The rate coefficient for the VV transition from/to ground-state assures that \( P_{1,0}^{0,1} = 3.9 \times 10^{-13} \, \text{cm}^3 \, \text{s}^{-1} \) at \( T_g = 400 \, \text{K} \) [19].

Similarly to the VT reactions the VV excitation of the pseudo-level \( v = 15 \) results in the dissociation of hydrogen molecules (see reaction 11 in table 4.3).

Also, the rate coefficients for the direct and reverse VV transitions relate via the Klein-Rosseland formula (4.22).

### 4.2.9.3 V-T transitions with atoms

VT transitions with hydrogen atoms (see reaction 9 in table 4.3) are also considered for the excitations \( v \longrightarrow v + 1 \) (with \( i = 1 - 6 \)) and the corresponding deexcitations. The rate coefficients for these mechanisms, with dependence on the gas temperature, are read and interpolated from a data file.

### 4.2.9.4 EV transitions

EV transitions correspond to reactions 17 to 20 in table 4.3 and consist in a two stage reaction where a \( \text{H}_2(v) \) molecule reaches an electronically excited Rydberg to drop back to a ground-state vibrational state \( \text{H}_2(v') \) with \( v' \neq v \). The cross sections for these reactions are those of the electronic excitation of the hydrogen molecules (\( k49l \) through \( k49o \) provided in a data file), multiplied by the probability of obtaining the final vibrational level.

For example, the cross section for the reaction 17:

\[
e + \text{H}_2(v) \longrightarrow e + \text{H}_2(B^1\Sigma^+_u) \longrightarrow e + \text{H}_2(v')
\]

writes

\[\sigma_{v,v'}^{B^1} = \sigma_{v,B^1} \times P_{v,v'} \] (4.24)
4.2.9.5 Radiative Transitions

One final type of reactions must be considered. Radiative transitions from excited states of hydrogen atoms by absorption or ejection of photons. The reaction is given by:

$$H(n) \leftrightarrow H(n') + h\nu$$

Where $n$ is the initial excited state of the hydrogen atom (from $H(1s)$ to $H(5)$). Each reaction is controlled by a certain transition rate $P(n, n - i)$ given by a data file.

4.2.9.6 Wall reaction coefficients

Wall reactions and their respective coefficients are presented in tables B.9 and B.10. For more details on the general outlines of the reactions refer to chapter 5. Charged species are considered to fully recombine to the wall and return to the volume as parent neutrals. A percentage of the neutrals striking the wall are considered to be lost (they are embedded on, or recombined at the walls), this percentage is given by the sticking factor $\gamma$. 


Chapter 5

Transport Scheme

This chapter addresses the transport schemes that were used for the different (neutral and charged) heavy species. For each species either a diffusion coefficient or a transport rate coefficient is determined in order to be used in the particle and energy density conservation equations. For the ion species, a review of the classical low-pressure transport theory is presented and a different method of calculating the two dimensional axial and radial edge-to-center density ratios is proposed.

5.1 Neutral species transport

As was derived in (3.14), neutral species experience a diffusion according to Fick’s law, and when used in a global model particle conservation equation writes

\[ k_{\text{Trans,Neutral},i} = \frac{D_i}{\Lambda^2} \],

(5.1)

where \( D_i \) is the diffusion coefficient of species \( i \) and \( \Lambda \) is an effective scale length of the problem. In the case of a cylindrical setup, with radius \( R \) and height \( L \), \( \Lambda \) can be written as [17]:

\[ \frac{1}{\Lambda^2} = \left( \frac{2.405}{R} \right)^2 + \left( \frac{\pi}{L} \right)^2 \].

(5.2)

The diffusion coefficient \( D_i \) describes the transport of species \( i \) through the whole gas, and it relates
with the so-called binary diffusion coefficients $D_{ij}$ of species $i$ on $j$ through Blanc’s Law \[20\]

$$\frac{1}{D_i} = \sum_j \frac{1}{D_{ij}} . \quad (5.3)$$

In the present case, the dominant species are considered to be the mixture precursors CH$_4$ and H$_2$ and the (effective) diffusion coefficient for species $i$ is given by:

$$\frac{1}{D_i} = \frac{1}{D_{i,CH_4}} + \frac{1}{D_{i,H_2}} . \quad (5.4)$$

The binary diffusion coefficients, $D_{A,B}$ (in cm$^2$s$^{-1}$) are given by the Chapman-Enskog approximation \[20\]:

$$D_{A,B} = 0.0018583 \sqrt{T} \left( \frac{1}{M_A} + \frac{1}{M_B} \right) \frac{1}{p\sigma_{AB}^2 \Omega_{AB}} , \quad (5.5)$$

where $T$ and $p$ is the gas temperature (in K) and pressure (in atm), $M_A$ and $M_B$ are the masses (in kg) of species $A$ and $B$,

$$\sigma_{AB} = \frac{1}{2} (\sigma_A + \sigma_B) ,$$

with $\sigma_A$ and $\sigma_B$ (in Å) the reference distances with the Lennard-Jones potentials for $A$ and $B$, and finally $\Omega_{AB}$ is the collision integral, given approximately by \[20\]:

$$\Omega = \frac{1.06036}{T^* A} + \frac{0.193}{\exp B T^*} + \frac{1.03587}{\exp C T^*} + \frac{1.76474}{\exp D T^*} , \quad (5.6)$$

with $A = 0.1561$, $B = 0.47635$, $C = 1.52996$, $D = 3.89411$ and $T^* = \frac{kT}{\epsilon_{AB}}$ and where

$$\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B} ,$$

with $\epsilon_A$ and $\epsilon_B$ (in K) the temperatures equivalent to the Lennard-Jones characteristic energies of species $A$ and $B$. 
5.2. CHARGED SPECIES TRANSPORT

5.1.1 Wall loss probability

In order to account for the reactivity of the gas with the walls we introduce a probability \( \gamma \) for the losses of neutrals to the walls. These losses can be of two different types:

- Sticking on the walls.
- Recombination/reassociation/deexcitation on the walls.

The wall loss probability represents the percentage of particles lost to the walls by the mechanisms introduced above, which means that \((1 - \gamma_i)\) of the diffusion rate of species \( i \) returns to the discharge. By adding this new creation term to the particle conservation equation for neutrals, given by (3.14), one gets:

\[
\frac{\partial N_{i0}}{\partial t} = G_{i0} - L_{i0} - \frac{N_{i0}}{\tau_R} - \frac{D_i}{\Lambda^2} N_{i0} + (1 - \gamma_i) \frac{D_i}{\Lambda^2} N_{i0} ,
\]

where the last term accounts for the incoming particles that have not been lost at the walls of the reactor. Simplifying the last two terms in the equation one finally gets:

\[
\frac{\partial N_{i0}}{\partial t} = G_{i0} - L_{i0} - \frac{N_{i0}}{\tau_R} - \gamma_i \frac{D_i}{\Lambda^2} N_{i0} .
\]

In general, the order of magnitude of the wall loss probability was taken as \(10^{-2}\). Section 4.2.9.6 provides more detailed information on the values of these coefficients.

5.2 Charged species transport

As stated in chapter 3, the loss rate of ions (singly charged) to the walls is given by

\[
k_{\text{trans,ion}}^i = u_B \frac{A_{\text{eff}}}{V} ,
\]

where the effective area \( A_{\text{eff}} \) for ion collection is, for a cylindrical reactor,

\[
A_{\text{eff}} = h_R 2\pi R^2 + h_L 2\pi RL ,
\]

with \( R \) and \( L \) the reactor radius and height, respectively. The area \( A_{\text{eff}} \) is basically that of a cylinder whose top and bottom surfaces were weighted by the radial edge-to-center ion density ratio, \( h_R \), and
the lateral surface was weighted by the axial edge-to-center ion density ratio, $h_L$ (see section 2.2.3). The loss rate of ions can then be written as

$$k_{\text{trans,ion}}^i = 2u_B \left( \frac{h_R}{L} + \frac{h_L}{R} \right).$$  \hspace{1cm} (5.10)

As stated at the end of chapter 2, the calculation of the ion density ratios is sketchy and justifies a more thorough study.

For a plasma with singly charged positive ions and electrons at low pressures, Godyak writes \[ h_Z = 0.86 \left( 3 + \frac{l_p}{\lambda} \right)^{-1/2}, \quad h_R = 0.8 \left( 4 + \frac{r_p}{\lambda} \right)^{-1/2}. \]

The axial result depends on the assumption that the quantity $\alpha$ given by (2.21)

$$\alpha = \sqrt{\frac{\pi l_p}{2\lambda u_B}}$$ \hspace{1cm} (5.11)

is constant, which is not true due to the fact that this parameter depends on the mean free path, hence on the pressure. The radial result could not be reproduced - the available bibliography refers to a paper from a Russian journal, which was not available at the time - but since the end result is similar, it is reasonable to assume that the radial equivalent of $\alpha$ was again made constant.

In order to attempt correcting these results, a different approach is presented. A two dimensional model of the discharge is introduced to solve the ion-particle conservation equation. A separation of variables is assumed in order to calculate the new density ratios:

- The ion densities are split in the product of their radial and axial parts;
- The square of the mean free path is split into the sum of three components relative to the different spacial directions.

The result is a set of differential equations to calculate the density profile of the ions. Since this is a multi dimensional model, the definition of variable mobility must be extended to a three dimensional space, where a velocity vector is now introduced.
5.2. CHARGED SPECIES TRANSPORT

5.2.1 Model equations

Generalizing the one-dimensional solution to the problem (see section 2.2.2), the ion-particle conservation equation is written using the ion flux ($\vec{\Gamma}_i$) and assuming that the main source of ions is given by ionization due to electron impact:

$$\nabla \cdot \vec{\Gamma}_i = \nu_i n_e .$$

(5.12)

Here $\vec{\Gamma} = N_i \vec{u}$, where $N_i$ is the ion density, $\vec{u}$ is the mean ion drift velocity, $\nu_i$ is the ionization frequency and $n_e$ is the electron density. Much like the 1D model equation (5.12) can be solved if the ion velocity and density are related to the electrostatic potential of the discharge, but this time the different components of the ion velocity must be known.

Since this is a cylindrical reactor, the electric field can be written assuming no angular dependence:

$$\vec{E} = E_r(r,z)\vec{e}_r + E_z(r,z)\vec{e}_z ,$$

(5.13)

and equation (5.12) can be written in cylindrical coordinates

$$\frac{\partial}{\partial z} \left[ N_i^{\text{ion}} u_{z,i} \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[ r N_i^{\text{ion}} u_{r,i} \right] = \nu_i n_e ,$$

(5.14)

or considering all plasma ions

$$\frac{\partial}{\partial z} \left[ \sum_i N_i^{\text{ion}} u_{z,i} \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[ r \sum_i N_i^{\text{ion}} u_{r,i} \right] = \nu_{\text{total}} n_e ,$$

(5.15)

where the sum is over all the ions and $\nu_{\text{total}} = \sum_i \nu_{\text{ion},i}$. The ion density and the ion velocity vector must now be calculated.

5.2.1.1 The ion density

The electrons in this problem are considered in Boltzmann equilibrium, hence quasineutrality, writes:

$$\sum_i N_i^{\text{ion}} = n_0 \exp \left[ \frac{e\phi}{k_B T_e} \right] ,$$

(5.16)
where \( \phi \) is the electrostatic potential and the sum is over all ion species \( i \). Since the sum of all ion densities is equal to an exponential in the potential we will assume that each ion density exhibits this same dependence writing

\[
N_{ion}^i = N_{ion}^{i0} \exp \left[ \frac{e\phi}{k_B T_e} \right],
\]

and thus, to ensure neutrality in the plasma volume,

\[
\sum_i N_{ion}^i = n_{e0}.
\]

In order to solve the problem, we now assume each ion density to be written as the product of an axial profile with a radial profile:

\[
N_{ion}^i(r, z) = n_r^i(r) \times n_z^i(z),
\]

and using (5.18) in (5.17) it is clear that this implies the electrostatic potential to have following form:

\[
\phi(r, z) = \phi_r(r) + \phi_z(z)
\]

### 5.2.1.2 Redefining Variable Mobility

When introducing multiple dimensions into the problem the implications go as deep as the definition of the variable mobility. Thus, closer attention has to be payed to the derivation followed in [13] and [14].

In a multi-dimensional situation, the vector-equation of motion that describes the low pressure transport of ions subjected to an electrostatic field, \( \vec{E} \), between charge exchange reactions is given by

\[
\frac{d\vec{v}}{dt} = \frac{e}{m} \vec{E}.
\]

Now, in principle, the relationship between the mean free path, \( \lambda \), and the charge exchange frequency \( \nu \) should involve the norm of the velocity vector, writing

\[
\lambda = \frac{|\vec{v}|}{\nu}.
\]
Therefore in order to define the variable mobility, equation (5.20) has to relate the norm of the velocity with the norm of the electric field which results in untreatable equations when it comes to using them in the CRM (refer to appendix A for details).

An alternative, more manageable, derivation can be achieved by introducing a directed mean free path, \( \lambda_i \), relating the \( v_i \) components of the velocity vector with the collision frequency

\[
\lambda_i = \frac{v_i}{\nu} .
\]  

With this definition, in order to recover (5.21) one concludes that, in cartesian coordinates,

\[
\lambda^2 = \lambda_x^2 + \lambda_y^2 + \lambda_z^2 ,
\]  

which will allow calculating the ion velocity distribution function as the product of three one-dimensional distributions. Again following [14], we define the probabilities of non-collision in each dimension, \( P_i \), using the same type radioactive decay law for each one:

\[
\frac{dP_i}{dt} = -\nu P_i = -\frac{v_i}{\lambda_i} P_i \Rightarrow P_i(t) = P_0 \exp \left( -\int_0^t \frac{v_i}{\lambda_i} \, dt \right) .
\]  

The different velocity components are obtained from equation (5.20), assuming that the electric field has negligible variations between collisions

\[
\frac{dv_i}{dt} = \frac{e}{m} E_i \Rightarrow v_i = \frac{e}{m} E_i t .
\]  

Substituting \( v_i \) in (5.24) and integrating, yields:

\[
P_i(t) = P_0 \exp \left( -\frac{eE_i t^2}{2m\lambda_i} \right)
\]  

Finally, replacing \( t \) by the corresponding component of the velocity, the ion velocity distribution function in a single dimension is found

\[
f_i(v_i) = f_{0i} \exp \left( -\frac{mv_i^2}{2eE_i\lambda_i} \right) , \quad v_i > 0 .
\]  

The full distribution function is obtained considering each spatial direction to be independent from
each other, i.e. in cartesian coordinates

\[ f(v_x, v_y, v_z) = f_x(v_x) \times f_y(v_y) \times f_z(v_z) \]  \hspace{1cm} (5.28)

or

\[ f(v_x, v_y, v_z) = f_0 \exp \left[ -\frac{m}{2e} \left( \frac{v_x^2}{E_x \lambda_x} + \frac{v_y^2}{E_y \lambda_y} + \frac{v_z^2}{E_z \lambda_z} \right) \right] , \quad \vec{v} > 0 . \]  \hspace{1cm} (5.29)

In order to use the previous results in solving the multidimensional problem, we will assume isotropic scattering corresponding to

\[ \lambda_i = \lambda^* , \quad \forall i , \]

and we will write the ’cylindrical electric field’ in cartesian coordinates

\[ \vec{E} = E_r \vec{e}_r + E_z \vec{e}_z ; \quad \vec{E} = E_r \cos \theta \vec{e}_x + E_r \sin \theta \vec{e}_y + E_z \vec{e}_z . \]

Substituting the last two relations into (5.29), the ion distribution function now reads

\[ f(r, z, \theta) = f_0 \exp \left[ -\frac{m}{2e \lambda^*} \left( \frac{v_r^2}{E_r} (\cos \theta + \sin \theta) + \frac{v_z^2}{E_z} \right) \right] , \quad \vec{v} > 0 . \]  \hspace{1cm} (5.30)

Notice that the previous expression, i.e. for positive velocity components \( v_i \)

The factor \( f_0 \) is a normalization factor calculated by the condition:

\[ \int f(\vec{v}) d^3v = 1 , \]  \hspace{1cm} (5.31)

which in this case writes (see figure 5.1)

\[ \int_0^\infty \int_0^{\pi/2} f_0 \exp \left[ -\frac{m}{2e \lambda^*} \left( \frac{v_r^2}{E_r} (\cos \theta + \sin \theta) + \frac{v_z^2}{E_z} \right) \right] v_r \, d\theta \, dv_z \, dv_r = 1 . \]  \hspace{1cm} (5.32)

Integration in \( v_r \) yields:

\[ \int_0^{\pi/2} f_0 \frac{e E_r \lambda^*}{m} \exp \left( -\frac{mv_z^2}{2eE_r \lambda^*} \right) \cos \theta + \sin \theta \, d\theta \, dv_z = 1 . \]
5.2. CHARGED SPECIES TRANSPORT

Figure 5.1: Representation of the polar part of the velocity vector in cylindrical coordinates. Only the first quadrant \((\theta \in [0, \frac{\pi}{2}])\) allows for positive components of the velocity.

Integration in \(\theta\) yields

\[
\sqrt{2} \text{Atanh} \left( \frac{1}{\sqrt{2}} \right) \int_0^\infty f_0 eE_r \lambda^* \frac{m}{2eE_z \lambda^*} \exp \left( \frac{-mv_z^2}{2eE_z \lambda^*} \right) dv_z = 1 .
\]

Finally, integration in \(v_z\) yields:

\[
f_0 E_r \sqrt{E_z} \sqrt{\pi} \text{Atanh} \left( \frac{1}{\sqrt{2}} \right) \left( \frac{e \lambda^*}{m} \right)^{3/2} = 1 .
\]

This last equation allows \(f_0\) to be calculated

\[
f_0 = \frac{\left[ \text{Atanh} \left( \frac{1}{\sqrt{2}} \right) \right]^{-1}}{E_r \sqrt{E_z} \sqrt{\pi}} \left( \frac{m}{e \lambda^*} \right)^{3/2} , \tag{5.33}
\]

and the ion velocity distribution function writes

\[
f(v_r, v_z, \theta) = \begin{cases} 
\frac{\left[ \text{Atanh} \left( \frac{1}{\sqrt{2}} \right) \right]^{-1}}{E_r \sqrt{E_z} \sqrt{\pi}} \left( \frac{m}{e \lambda^*} \right)^{3/2} \exp \left[ -\frac{m}{2e \lambda^*} \left( \frac{v^2_r}{E_r} (\cos \theta + \sin \theta) + \frac{v^2_z}{E_z} \right) \right] , & \vec{v} > 0 \\
0 , & \text{Otherwise} \ . \tag{5.34}
\end{cases}
\]

We can now calculate the mean ion velocity vector in cylindrical coordinates
\[ \langle \vec{v} \rangle = \vec{u} = \langle v_r \rangle \vec{e}_r + \langle v_z \rangle \vec{e}_z = u_r \vec{e}_r + u_z \vec{e}_z \],

calculating each of its components by integration over the distribution function

\[
\begin{align*}
    u_z &= \int_0^\infty \int_0^{\pi/2} v_z f_0 \exp \left[ -\frac{m}{2\varepsilon_r} \left( \frac{v_r^2}{E_r} \cos \theta + \frac{v_z^2}{E_z} \right) \right] v_r d\theta dv_z \\
    u_r &= \int_0^\infty \int_0^{\pi/2} v_r f_0 \exp \left[ -\frac{m}{2\varepsilon_r} \left( \frac{v_r^2}{E_r} \cos \theta + \frac{v_z^2}{E_z} \right) \right] v_r d\theta dv_z,
\end{align*}
\]

with \( f_0 \) given by (5.33). Integrating in \( v_r \) yields:

\[
\begin{align*}
    u_z &= \int_0^\infty \int_0^{\pi/2} v_z e^{-\frac{m v_z^2}{2 \varepsilon_z E_z}} \sqrt{\frac{2}{\pi}} \text{Atanh} \left( \frac{1}{\sqrt{2}} \right) (\sin(\theta) + \cos(\theta)) \sqrt{\frac{2}{e E_r m \lambda}} d\theta dv_z \\
    u_r &= \int_0^\infty \int_0^{\pi/2} v_r e^{-\frac{m v_z^2}{2 \varepsilon_z E_z}} \sqrt{\frac{2}{\pi}} \text{Atanh} \left( \frac{1}{\sqrt{2}} \right) \sqrt{\frac{2}{e E_r m \lambda}} d\theta dv_z,
\end{align*}
\]

Integrating in \( \theta \) yields:

\[
\begin{align*}
    u_z &= \int_0^\infty \sqrt{\frac{2}{\pi} m v_z e^{-\frac{m v_z^2}{2 \varepsilon_z E_z \lambda}}} dv_z \\
    u_r &= \int_0^\infty \sqrt{\frac{2}{\pi} m v_z e^{-\frac{m v_z^2}{2 \varepsilon_z E_z \lambda}}} \sqrt{\frac{2}{\pi}} \text{EllipticE} \left( \frac{\pi}{8} | \frac{1}{2} \right) \sqrt{\frac{2}{e E_r m \lambda}} dv_z,
\end{align*}
\]

where \( \text{EllipticE} \) denotes the elliptic integral of the second kind\(^1\)

\[
\text{EllipticE} (\phi|m) = \int_0^\phi \sqrt{1 - m \sin^2 \theta} \ d\theta.
\]

Finally, integrating over \( v_z \) yields:

\[
\begin{align*}
    u_z &= \sqrt{\frac{2 e E_r \lambda}{\pi m}} \\
    u_r &= \sqrt{\frac{\pi}{2} \text{EllipticE} \left( \frac{\pi}{8} | \frac{1}{2} \right) \sqrt{\frac{2}{e E_r m \lambda}} \text{Atanh} \left( \frac{1}{\sqrt{2}} \right)}.
\end{align*}
\]

\(^1\)In this case the numerical value of \( \text{EllipticE} \left( \frac{\pi}{8} | \frac{1}{2} \right) \) according to Mathematica calculations, yields

\[
\text{EllipticE} \left( \frac{\pi}{8} | \frac{1}{2} \right) \approx 0.372151 - 1.66533 \times 10^{-16} i \approx 0.372151.
\]
5.2. CHARGED SPECIES TRANSPORT

The mean ion velocity is now defined:

\[ u_z = \sqrt{\frac{2eE_z\lambda^*}{\pi m}} \]

\[ u_r \approx 1.12101 \sqrt{\frac{eE_r\lambda^*}{m}} \]  

(5.36)

Equations (5.37) express the radial and axial components of the mean ion velocity-vector \( v_r \) and \( v_z \), as separate functions of the corresponding electric field components, \( E_r \) and \( E_z \). Note that these equations could be used to define field-dependent mobilities for each one of the spatial directions \( r \) and \( z \). In fact, the result for the axial mean velocity corresponds to expression (2.14) already obtained in the 1D formulation, as expected from the separation of spatial directions adopted.

The separation of the velocity components obtained in (5.37), together with the separation of the variables proposed in section 5.2.1.1 leading to the potential form of 5.19, will allow splitting the ion-particle conservation equation (5.15) into a system of equations for \( \phi_r(r) \) and \( \phi_z(z) \).

5.2.1.3 Model equations for the potential

With expressions for the ion density and velocity both related to the electrostatic potential, the ion-particle conservation equation (5.15) can be written in terms of \( \phi \). Introducing the normalized potential \( \eta = -\frac{e\phi}{k_B T_e} \), equations (5.35), for each ion species \( i \), take the form:

\[ u_{z,i} = \sqrt{\frac{2}{\pi} u_{B,i}^2 \lambda^* \frac{\partial \eta}{\partial z}} \]

\[ u_{r,i} \approx 1.12101 \sqrt{u_{B,i}^2 \lambda^* \frac{\partial \eta}{\partial r}} \]  

(5.37)

where \( u_{B,i}^2 \) is the Bohm velocity of species \( i \). Substituting this result in (5.15) and using also 5.17 one obtains

\[ \frac{\partial}{\partial z} \left[ \sum_i N_{i\,0}^{\text{ion}} \exp (-\eta) \sqrt{\frac{2}{\pi} u_{B,i}^2 \lambda^* \frac{\partial \eta}{\partial z}} \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[ \sum_i r N_{i\,0}^{\text{ion}} \exp (-\eta) 1.12101 \sqrt{u_{B,i}^2 \lambda^* \frac{\partial \eta}{\partial r}} \right] \]

\[ = \nu_{\text{total}} n_e 0 \exp (-\eta) \]  

(5.38)

where \( \nu_{\text{total}} = \sum_i \nu_{\text{ion},i} \) and we have assumed the same mean free path \( \lambda^* \) for all the ion species \( i \).
Calculating the derivatives and working out the resulting expressions yields

$$\sqrt{\frac{2}{\pi}} \left( -\frac{\partial \eta}{\partial z} \sqrt{\frac{\partial \eta}{\partial z}} + \frac{1}{2} \frac{\partial^2 \eta}{\partial \eta^2} \frac{\partial \eta}{\partial z} + 1 \right) + \frac{1.12101}{r} \left( \sqrt{\frac{\partial \eta}{\partial r} - \frac{\eta}{r} \sqrt{\frac{\partial \eta}{\partial r}} + r \frac{1}{2} \frac{\partial^2 \eta}{\partial r^2} \frac{\partial \eta}{\partial r}} \right) = \frac{\nu_{\text{total}}}{\sum_i u_i n_{i0}} \sqrt{\frac{1}{\lambda^*}} n_{e0} \cdot$$

(5.39)

The previous equation can be rewritten, noting that the normalized potential has the form \( \eta(r, z) = \eta_r(r) + \eta_z(z) \), according to (5.19):

$$\sqrt{\frac{2}{\pi}} \left( -\frac{d\eta_r}{dz} \sqrt{\frac{d\eta_r}{dz}} + \frac{d^2 \eta_r}{dz^2} \frac{d\eta_r}{dz} + \frac{1}{2} \frac{d^2 \eta_z}{dz^2} \frac{d\eta_z}{dz} + 1 \right) + \frac{1.12101}{r} \left( \frac{1}{r} \sqrt{\frac{d\eta_r}{dr} - \frac{\eta_r}{r} \sqrt{\frac{d\eta_r}{dr}} + \frac{d^2 \eta_r}{dr^2} \frac{d\eta_r}{dr}} \right) = \frac{\nu_{\text{total}}}{\sum_i u_i n_{i0}} \sqrt{\frac{1}{\lambda^*}} n_{e0} \cdot$$

(5.40)

Because the first and second terms on the left-hand side of (5.40) are exclusive functions of the \( z \) and \( r \) coordinates, respectively, this differential equation can be split into two separate equations. Equation (5.40) becomes

$$\frac{2}{R} \frac{d\eta_r}{dR} + \frac{d^2 \eta_r}{dR^2} - 2 \left( \frac{d\eta_r}{dR} \right)^2 - 2 \rho \frac{d\eta_r}{dR} = 0 \quad (5.41)$$

$$\frac{d^2 \eta_z}{dz^2} - 2 \left( \frac{d\eta_z}{dz} \right)^2 - 2 \alpha \frac{d\eta_z}{dz} = 0 \quad (5.42)$$

(5.43)

where we have introduced the normalized spatial positions

$$Z = \frac{z}{z_p}; \quad R = \frac{r}{r_p},$$

with \( z_p \) and \( r_p \) representing the plasma length and radius, respectively, and where we have defined the constants

$$\rho = 0.892 \frac{2 \nu_{\text{total}} r_p}{3 \sum_i u_i n_{i0}} n_{e0} \sqrt{\frac{r_p}{\lambda^*}}; \quad \alpha = \frac{\nu_{\text{total}} z_p}{3 \sum_i u_i n_{i0}} n_{e0} \sqrt{\frac{\pi z_p}{2 \lambda^*}}$$

The solution to equations (5.41) and (5.43) yields \( \eta_r(r) \) and \( \eta_z(z) \), from which one can reconstruct the plasma potential.
\[ \phi(r, z) = -\frac{k_B T_e}{e} \left[ \eta_p(r) + \eta_z(z) \right] . \]

This potential can then be used in equations (5.17) (5.18) to obtain the \((r,z)\) profiles of the ion densities, and ultimately the radial and the axial edge-to-center density ratios

\[ h_R = \frac{N_{iS}^r}{N_{i0}^r} ; \quad h_L = \frac{N_{iS}^z}{N_{i0}^z} . \]

Note that the edge densities are taken at the plasma-sheath boundary

\[ N_{iS}^z = N_{iS}^z(z_p) ; \quad N_{iS}^r = N_{iS}^r(r_p) , \]

corresponding to the positions where we will stop the integration of equations (5.41) and (5.43). In fact, the latter equations are the result of a formulation describing the ion transport within a low-pressure plasma, under neutrality assumptions (thus not accounting for the charge separation phenomenon occurring within the space-charge sheaths).

### 5.2.2 Numerical solution

In order to numerically solve equations (5.41) and (5.43), a differential solver is implemented using a 4th order explicit Runge-Kutta method with fixed step. Runge-Kutta methods solve differential equations of the form:

\[ \frac{dy}{dx} = f(y(x), x) , \]

where \(y\) is the function to be calculated, \(x\) is the independent variable, and \(f\) is a given function of both these quantities. The particular Runge-Kutta method adopted, calculates the value of the function on the next step \((y_{n+1})\) from its value on the previous step \((y_n)\) by the following formula:

\[ y_{n+1} = y_n + \frac{1}{6} (k_1 + k_2 + k_3 + k_4) \]

\[ x_{n+1} = x_n + h , \]

where \(x_n\) is the value of the independent variable at step \(n\) and \(h\) is the step size. The values \(k_1\)
through $k_4$ are calculated as follows:

$$k_1 = hf (x_n, y_n)$$

$$k_2 = hf (x_n + \frac{1}{2}h, y_n + \frac{1}{2}k_1)$$

$$k_3 = hf (x_n + \frac{1}{2}h, y_n + \frac{1}{2}k_2)$$

$$k_4 = hf (x_n + h, y_n + k_3) \ .$$

To prepare the differential equations (5.41) and (5.43) for solution we introduce

$$\frac{d\eta_r}{dR} = \chi_r \ ; \quad \frac{d\eta_z}{dZ} = \chi_z \ ,$$

where $\chi_z$ and $\chi_r$ are, respectively, the axial and radial components of the normalized electric field, writing

$$\frac{d\chi_r}{dR} = 2\chi_r^2 + 2\rho\sqrt{\chi_r} - 2\frac{1}{R}\chi_r$$

$$\frac{d\chi_z}{dz} = 2\chi_z^2 + 2\alpha\sqrt{\chi_z} \quad (5.47)$$

The radial equation presents a singularity for $R = 0$. In order to solve this problem, it is assumed that the electric field $\chi_r$ goes to zero faster than $R$ so that a physical solution can be found by expanding this equation for small values of $R$.

Reordering the radial part of (5.47) we get

$$2\sqrt{\chi} \frac{1}{R} \frac{d}{dR} (R\sqrt{\chi}) = 2\chi^2 + 2\rho\sqrt{\chi}$$

We can now integrate this equation from 0 to $\epsilon$, which is a small value of $R$

$$\int_0^\epsilon 2\sqrt{\chi} \frac{1}{R} \frac{d}{dR} (R\sqrt{\chi}) R \ dR = \int_0^\epsilon 2\chi^2 R \ dR + \int_0^\epsilon 2\rho\sqrt{\chi} R \ dR$$

(5.49)

Considering that at $R = 0$ the electric field should be null and that $\chi$ has is practically constant from 0 to $r$ (with $\chi_r|_{R=0} = \chi_r(0)$), by solving the integrals on the right-hand side and integrating by parts in
5.2. CHARGED SPECIES TRANSPORT

the left-hand side we get:

\[ \chi_r(\epsilon) = \frac{1}{2} \left( \chi_{r0}^2 + \rho \sqrt{\chi_{r0}} \right) \epsilon \]  \hspace{1cm} (5.50)

Finally deriving with respect to \( \epsilon \) we get a new differential equation for the radial electric field that is valid for small values of \( R \)

\[ \frac{d\chi_r}{d\epsilon} = \frac{1}{2} \left( \chi_{r0}^2 + \rho \sqrt{\chi_{r0}} \right) \]  \hspace{1cm} (5.51)

One last issue to address for the solution of the equations presented in (5.51) is the fact that the independent variables, \( R \) and \( Z \) are normalized to certain scale lengths, \( r_p \) and \( l_p \), signaling the end of the neutral region via the constants \( \alpha \) and \( \rho \):

\[ \rho = 0.892 \frac{2\nu_{total}r_p}{3} \sum_i u_{B,i} N_{i0} n_{i0} \sqrt{\frac{r_p}{\pi \lambda^*}} \] \hspace{1cm} ; \hspace{1cm} \alpha = \frac{\nu_{total}z_p}{\sum_i u_{B,i} N_{i0} n_{i0} \sqrt{\frac{\pi z_p}{\lambda^*}}} \]  \hspace{1cm} (5.52)

To calculate the plasma-sheath boundary positions \( r_p \) and \( z_p \), we will relate the velocity of the ions with the Bohm velocity. First remembering that the ion velocity for each ion species is given by (5.37):

\[ u_{z,i} = \sqrt{\frac{2 e E_z \lambda^*}{\pi M_i}} = \sqrt{\frac{2}{\pi} u_{B,i} \frac{\lambda^*}{z_p} \chi_r} \] 

\[ u_{r,i} \approx 1.12101 \sqrt{\frac{E_z}{M_i}} = 1.12101 \sqrt{\frac{E_z}{z_p u_{B,i} \chi_r}} \]

If we now assume equal components for the ion velocity at the sheath edge, such that

\[ u_{z,i}(z_p) \approx u_{r,i} \approx \frac{u_{B,i}}{\sqrt{2}} \] ,

to ensure

\[ u_i(r_p, z_p) = \sqrt{u_{r,i}(r_p)^2 + u_{z,i}(z_p)^2} \approx u_{B,i} \] ,

one obtains

\[ u_{z,i}(z_p) = \frac{u_{B,i}}{\sqrt{2}} = \sqrt{\frac{2}{\pi} u_{B,i} \frac{\lambda^*}{z_p} \chi_z |z=z_p} \implies \chi_z |z=z_p = \frac{\pi z_p}{\lambda^*} \] 

\[ u_{r,i}(r_p) = \frac{u_{B,i}}{\sqrt{2}} = 1.12101 \sqrt{\frac{\lambda^*}{z_p u_{B,i} \chi_r |r=r_p} \implies \chi_r |r=r_p = 0.398 \frac{r_p}{\lambda^*} } \]
The last expressions provide a universal relationship (valid for ALL ions) between the plasma-sheath boundaries and the components of the normalized electric field at these positions:

\[
\chi_z|z=z_p = \frac{\pi}{4} \frac{L_p}{X} \\
\chi_r|r=r_p \approx 0.398 \frac{r_p}{X} 
\]

Equations (5.53) are used to iteratively calculate \(z_p\) and \(r_p\), knowing \(\chi_z|z=z_p\) and \(\chi_r|r=r_p\). The iterative process used works as follows:

1. All the ionization frequencies for the different ions are summed in order to calculate \(\sum_i \nu_{i,ion} \).
2. The term \(\sum_i \frac{1}{u_{B,i} n_i} \) is also calculated numerically.
3. The ionization frequency is separated into its different radial and axial components by degrees of freedom \((\nu_{ion}^Z = \frac{1}{3} \nu_{ion}; \nu_{ion}^R = \frac{2}{3} \nu_{ion})\).
4. The constants \(\alpha\) and \(\rho\) are calculated.
5. A certain small value is given to the scale lengths \(l_p\) and \(r_p\).
6. The radial and axial differential equations are then solved using the described Runge-Kutta method with \(Z, R \in [0, 1]\).
7. The value of the radial and axial electric field calculated at \(Z = 1\) and \(R = 1\) are compared to (5.53).
8. If the calculated values are smaller than the theoretical values, it means that the predicted neutral discharge length does not allow the electric field to reach the theoretical value and thus the neutral discharge must occupy a larger volume. \(l_p\) and \(r_p\) are then incremented to a larger value and the process is repeated from step 4.
9. If instead the calculated values are larger than the theoretical ones, this means that the neutral length of the discharge is too large and allows an incorrect development of the electric field. In this case \(l_p\) and \(r_p\) are incremented to a smaller value and the process is repeated from step 4.
10. If the error between the calculated and the theoretical values of the electric field is lower than 1%, the discharge length has been correctly predicted.

Considering that \(l_p\) and \(r_p\) start from a small value and iterate to higher values, this process will calculate the smallest length of the neutral zone of the discharge and also of the electric field in that
zone. The potential $\eta$ can then be calculated by integrating the electric field:

$$
\eta^R(R) = \int_0^1 \chi^R dR ; \quad \eta^Z(Z) = \int_0^1 \chi^Z dZ
$$

(5.54)

The ratio of densities $h$ can then be calculated by:

$$
h_R = e^{-\eta^R(R=1)} ; \quad h_Z = e^{-\eta^Z(Z=1)}
$$

(5.55)

Finally, as the discharge reaches steady-state, a check is made in order to assure that these ratios remain roughly constant. The process described above is repeated in order to assure that these ratios remain roughly under margin of 10% of their initial values, if not then new values are calculated and new equilibrium must be reached. This check will lead to transient results that are not proper representations of the evolution of the discharge but steady-state results will become more accurate.
Chapter 6

Results and Discussion

In this chapter we present and discuss the results of model and the program described in chapters 3-5. The direct output of the program gives the time evolution of the different of the species in the discharge at typical working conditions. We also focus on steady-state results, obtained at different values of pressure, power, neutral gas flow and gas composition. The dissociation degree for both precursor species and the rates for the main gain and loss mechanisms for the most relevant plasma species are also studied for different working conditions.

6.1 Typical time-evolution output

As direct output, the code gives the time evolution of the various species considered in the model, as illustrated in figures C.1 to C.7 for

- hydrocarbon species,
- hydrocarbon ionic species,
- hydrogen atomic species,
- hydrogen molecular species,
- hydrogen ionic species.

The sudden jump depicted roughly at the same time instant in all the graphics has no physical meaning. This is the direct result of updating the \( h_R \) and \( h_L \) factors, calculated as described in chapter 5. The time evolution of these ratios is presented in figure 6.1 for a single run of the code at typical working
conditions (10 mTorr, 1000 W, 36 sccm, 28% CH₄: 72% H₂ initial concentrations). The steady-state values of hₗ and hᵣ, as a function of pressure, are also shown in this figure and compared with Godyak’s calculations.

Figure 6.1: Edge-to-center density ratio of charged species as a function of time during a discharge simulation (a) and as a function of pressure at steady-state (b). For comparison, figure (b) also shows the pressure dependence calculated by Godyak and Maximov [1].

From figure 6.1 one observes that the new hₗ and hᵣ ratios overestimate those of Godyak at low pressures (p < 30 mTorr), agreeing with them as the pressure increases. The behaviour of the new ratios have a similar behaviour with pressure, as is the case for the values calculated by Godyak. The self-consistent calculation of these factors with our code gives a fast convergence: after a single iteration the relative errors \( \frac{\Delta h_{\text{hr}}}{h_{\text{hr}}} \) and \( \frac{\Delta h_{\text{hl}}}{h_{\text{hl}}} \) are already below the 10% margin.

The actual pressure in steady-state is calculated by summing the densities of all considered species, applying the ideal gas law:

\[
\sum_{i} n_i(t \to \infty) = \frac{p_{\text{final}}}{k_{\text{B}}T_{\text{g}}} .
\]

We have observed a general tendency to obtain lower pressures at steady-state (despite the significant dissociation of the precursors), which is minimized by adjusting the residence time of non-precursor species. Overall, the initial to final pressure ratio was found to be of the order or smaller than a factor of 3. This discrepancy in the initial and final pressure values may come from (i) a lack of knowledge of the surface kinetics, which may lead to a higher estimated loss rates, note that the absence of some species, not considered in the kinetic scheme, may as well be the cause of the lower pressures at steady-state; (ii) an underestimation of the residence times for certain plasma species. For the results presented here, the residence time of the non-precursor species is taken to be a factor of 10 above that
of the precursor species.

6.2. Steady state densities

In this section, steady-state results are presented for different work conditions. These results could not be compared with the experimental data available since, as previously stated, the model was applied to the excitation chamber while the measurements were taken in the diffusion chamber.

The next sections will briefly analyze the changes in the simulation results with variations in the pressure, power, neutral gas flow and distribution of initial pressure concentrations.

When one of the working parameters changes, all others are kept as in the standard working point defined as follows:

- 10 mTorr pressure,
- 1000 W of applied power,
- 36 sccm of neutral gas flow,
- 28% CH$_4$ and 72% H$_2$ of initial neutral gas concentrations.

6.2.1 Variation with the pressure

The discharge is simulated for pressures ranging from 5 to 40 mTorr. The densities of the most relevant species are presented in figure 6.2.

The electron temperature and density are presented in figure 6.3 along with the dissociation degree of the precursor species.
CHAPTER 6. RESULTS AND DISCUSSION

Figure 6.2: Variation with the pressure of the most relevant plasma species densities.

Figure 6.3: Variation with the pressure of $n_e$ and $T_e$ (a) and of the dissociation degree of the precursor species (b).
6.2. STEADY STATE DENSITIES

The dissociation degree ($\delta$) for the different precursor species is calculated for methane as:

$$\delta_{\text{CH}_4} = 1 - \frac{[\text{CH}_4] + [\text{CH}_3^+]}{[\text{CH}_4] + [\text{CH}_3] + [\text{CH}_2] + [\text{CH}] + [\text{CH}_3^+] + [\text{CH}_2^+] + [\text{CH}^+]}, \quad (6.1)$$

and for hydrogen as:

$$\delta_{\text{H}_2} = 1 - \frac{\sum_i [\text{H}_2(v = i)] + [\text{H}_3^+]}{\sum_i [\text{H}_2(v = i)] + [\text{H}(1s)] + [\text{H}(2s)] + [\text{H}(2p)] + [\text{H}(3)] + [\text{H}(4)] + [\text{H}(5)] + [\text{H}_2^+] + [\text{H}_3^+] + [\text{H}^+]}, \quad (6.2)$$

where $[i]$ represents the density of species $i$. The observation of figures 6.2 and 6.3 reveals the following.

- The densities of hydrocarbon neutral species decreases with the pressure, with the exception of CH (the dominant species) and $\text{C}_2\text{H}_3$, whose densities increase with $p$ at lower pressures.

- The density of $\text{H}_2$ decreases with the pressure, whereas the density of H increases with $p$.

- The previous observations are coherent with the results obtained for the dissociation degree: both $\delta_{\text{CH}_4}$ and $\delta_{\text{H}_2}$ increase with $p$, thus leading to decreasing CH$_4$ and H$_2$ concentrations with the pressure. In general, the dissociation degree of hydrogen remains low ($< 20\%$ at low pressures) when compared to that of methane ($\sim 70 - 95\%$). At higher pressures $\delta_{\text{H}_2}$ increases to more than 80%, probably due to the increased dissociation of the methane and its derivatives.

- The distribution of species densities shows that CH$_4$ and H$_2$ are not dominant (several species have densities in the range $10^{12} - 10^{13}$ cm$^{-3}$). Therefore, the simplified treatment adopted for the transport of neutral species in chapter 5 lacks justification.

- In general, the ion densities increase with the pressure and the same is also observed for the electron density ($n_e \sim 10^{11} - 10^{13}$ cm$^{-3}$). The dominant hydrocarbon ion is CH$^+$, whereas the dominant hydrogen ions are H$_3^+$ and H$^+$ contrary to what is usually observed in the H$_2$ kinetics. This result can be associated with an enhanced influence of the electron kinetic mechanisms in the present case.

- As expected, the electron temperature decreases with the pressure. However, its values are too high ($T_e \sim 18 - 40$ eV), which may indicate the need for a revision of (i) the particle loss mechanisms due to diffusion and at the walls; (ii) the discharge power balance equation.
6.2.2 Variation with the power

The discharge is simulated for powers ranging from 100 to 1000 W. The variation in the densities of the most relevant neutral and ion species are represented in figure 6.4.

Figure 6.4: Variation with power of the most relevant plasma species densities.

The electron temperature and density as well as the dissociation degree of the precursor species, are shown in figure 6.5.
6.2. **STEADY STATE DENSITIES**

![Graphs showing variation with power of $n_e$ and $T_e$ (a) and of the dissociation degree of the precursor species (b)](image)

Figure 6.5: Variation with power of $n_e$ and $T_e$ (a) and of the dissociation degree of the precursor species (b)

Figures 6.4 and 6.5 show the following.

- The dissociation of the precursor species increases with power. This is coherent with the decrease in the densities of CH$_4$, CH$_3$ and H$_2$ when the power is increased.

- The electron density and temperature increase with power, as the ion densities also do. This expected result confirms the enhancement in the electron kinetic mechanisms as the power is increased, which relates also with the observed increase in $\delta_{\text{CH}_4}$ and $\delta_{\text{H}_2}$.

- Overall, power variations have an impact in results smaller than pressure variations.

### 6.2.3 Variation with the neutral gas flow

The neutral gas flow is varied from 25 to 45 sccm. As expected an increase in the neutral gas flow allows the existence of more neutral species to suffer both ionization and dissociation. The increase observed in the densities of the most relevant plasma species with the flow is shown in figure 6.6.

The electron density and temperature behaviour for an increase in the flow is similar to that of an increase in pressure. This is expected, since in both cases there is a higher amount of particles being injected onto the discharge. Figure 6.7 represents the $n_e$ and $T_e$ as well as the dissociation degree of the precursor species, as a function of the flow.
Figure 6.6: Variation with the neutral gas flow of the most relevant plasma species densities.

Figure 6.7: Variation with the neutral gas flow of \( n_e \) and \( T_e \) (a) and of the dissociation degree of the precursor species (b).
6.2.4 Variation with the initial gas composition

Simulations analyzed the plasma behaviour for initial concentrations of methane satisfying $\zeta_{\text{CH}_4} = 28\% - 90\%$ (hence, initial concentrations of hydrogen $\zeta_{\text{H}_2} = 72\% - 10\%$). Results are represented in figure 6.8 for the densities of the most relevant plasma species, and in figure 6.9 for the electron temperature and density as well as for the dissociation degree of the precursor species.

Figure 6.8: Densities of the most relevant plasma species, as a function of the initial percentage of CH$_4$ in the discharge.
An observation of these figures shows the following:

- With the introduction of more CH\textsubscript{4} (less H\textsubscript{2}) in the discharge there is an expected increase in the densities of the hydrocarbon neutral species and ions, and a simultaneous decrease in the densities of the H\textsubscript{2} molecules and the H\textsuperscript{+}\textsubscript{2} and H\textsuperscript{+}\textsubscript{3} ions.

- The densities of the H atoms and ions increase slightly as the initial concentration of CH\textsubscript{4} (H\textsubscript{2}) increases (decreases). Similarly to what is observed when the pressure varies, this result can be partially explained by an enhancement in the dissociation reactions of hydrocarbon species that create atomic hydrogen, which is confirmed by figure 6.9 (b). Note, however, that the dissociation degree of CH\textsubscript{4} remains approximately constant with the increase in the initial concentration of methane (see figure 6.9 (b)), which may indicate that H\textsubscript{2} is being directly used in the production of heavier species (such as C\textsubscript{2}H\textsubscript{3}, see figure 6.8 (a)) as \(\zeta_{CH_4}\) increases.

- The electron density increases with the initial concentration of CH\textsubscript{4} in the discharge, similarly to what is observed for the densities of the most representative neutral and ion species. Simultaneously with the rise in \(n_e\), the electron temperature decreases in order to maintain the value of the electron energy density (at constant power applied to the discharge).

Note finally that the code experienced convergence problems for very low methane concentrations, thus revealing some limitations in the description of (almost) pure hydrogen plasmas.
Chapter 7

Conclusions and future work

7.1 Conclusions

In this thesis, a CRM code to simulate plasmas produced in CH$_4$-H$_2$ mixtures was improved. The collisional scheme was updated and several new mechanisms were introduced, including a whole new class of hydrogen reactions, in coherency with state-of-the-art models. A total of ten new species (not including the hydrogen vibrational levels) were added to the model, two of which (CH$^+$ and CH$_2^+$) have shown to be relevant in the working conditions considered.

Regarding the numerical implementation of the model, a significant improvement was achieved allowing to enlarge the window of input parameters (power, pressure, neutral gas flow and initial plasma composition) for which the code converges. A convergence criterion was introduced to monitor the discharge evolution towards steady-state. The calculation of the electron collision rate coefficients was extended to allow using generic (non-Maxwellian) EEDFs, and a periodic check of mass conservation was introduced to more easily detect implementation errors in the kinetic scheme.

The charged species transport under low-pressure ambipolar conditions was revised. The resulting set of differential equations is coupled to the CRM-code, and it calculates the electrostatic field and potential of the plasma in its neutral region, as well as the densities and subsequent edge-to-center density ratio of charged species.

Although results were obtained for a range of input parameters wider than the one authorized by the original model, there were some cases where the numerical output returned unsatisfactory results (such as in simulations for initial CH$_4$ percentages lower than 20%).

The experimental results available were obtained in the diffusion chamber, whereas the model was
applied to the excitation chamber. Therefore no direct comparison could be made between the measurements and calculations. Despite this fact, one can compare the evolution trend of the H(5) species with the pressure, as shown in figure 7.1 to conclude that its behaviour is not well described by the model at low $p$.

![Figure 7.1: Density of the H(5) species, as a function of the pressure, calculated by the model (a) and measured by OES (b).](image)

The results obtained with the model confirm CH$_3$ as one of the most important hydrocarbon radicals, revealing an important influence of the atomic hydrogen in the plasma kinetics at high CH$_4$ initial concentrations, due to the methane dissociation.

In general, model results show that the plasma is highly dissociative and that the creation/destruction of species is controlled by wall losses and by electron collision mechanisms. The latter are strongly dependent on the electron temperature, which was found overestimated by the model, thus introducing the need for future corrections and confirmations on the dominant particle gain/loss channels.

### 7.2 Future work

Regardless of the progress made here, the present model requires further development and improvement.

#### 7.2.1 Electron temperature

The unusually high electron temperatures calculated suggest that there may be other energy transfer mechanisms that are not considered in the model. One possibility is that, since working pressures are
low and the subsequent electric fields are high, the energy acquired by the ions and released at the walls should be considered in the energy conservation equation [15]. Therefore rather than using the electron energy conservation equation, a discharge energy balance equation should be written instead, accounting for the energy exchanges involving both electrons and ions.

Moreover, the use of a general energy balance equation can also enhance the influence of the surface kinetics on the energy description, similarly to what is observed in the particle gains/losses.

### 7.2.2 Surface kinetics

The surface kinetics of this particular discharge is widely unknown. In the case of hydrogen, values for the wall loss probabilities of high pressure discharges were used. In the case of the wall reactions for hydrocarbon species, an unique wall loss factor $\gamma = 10^{-2}$ was used. A more comprehensive study of the surface kinetics for this particular mixture must be made, in order to more successfully calculate the wall recombination/reassociation rates for each neutral/-ion.

### 7.2.3 Model validation. Comparison with the experiment

The IMN Jean Rouxel of Nantes is currently carrying out measurements of the electron density and temperature (using probes) and of the densities of several radicals (using OES), in the excitation chamber of the ICP reactor. This new test of experimental data should be used in the validation of the model, revealing missing mechanisms and suggesting the rate coefficients to be tuned. Model validation should extend to low methane concentrations, for which the current version of the code has convergence problems.

### 7.2.4 Transport of neutral species

The calculated densities of neutral species show that CH$_4$ and H$_2$ have concentrations similar to hydrocarbon radicals and hydrogen atoms. Therefore a generalized multi-component diffusion theory should be used to describe the transport of neutral species in the plasma.

### 7.2.5 EEDF

In this thesis, a Maxwellian EEDF was used to calculate the electron rate coefficients. Usually, at low pressures, the EEDF deviates equilibrium becoming (at least) a Druyvesteynian distribution function.
A self-consistent calculation of the EEDF should be performed, by coupling a Boltzmann solver to the CRM-code.

### 7.2.6 Transient analysis

The results of this thesis were merely on steady-state ones. This discharge is to be operated in a pulsed regime, therefore a study of the transient regime is required.

### 7.2.7 Negative ions

The model can be completed with the inclusion of negative ions, resulting from attachment reactions with CH$_4$. 
Appendix A

Conventional calculation of the variable mobility

As was stated in section 5.2.1.2, there is a more conventional way of calculating the variable field-dependent mobility and of obtaining equivalent differential equations for the three dimensional transport problem.

A.1 Defining the variable mobility from the norm of the velocity vector

Consider the norm of the vector equation (5.21) to integrate it assuming negligible variations of the electric field between charge exchange reactions. The resulting equation writes

\[ |\vec{v}| = \frac{e}{m} |\vec{E}| t. \] (A.1)

With (A.1) and (5.21), our analysis will closely follow that of section 5.2.1.2. Again the probability \( P \) of non-collision (or non-interaction) for each ion has a time variation similar to a radioactive decay law:

\[ \frac{dP}{dt} = -\nu P \Rightarrow P(t) = P_0 \exp \left[-\int_0^t \nu dt\right]. \] (A.2)
Using (5.21) along with (A.1) the explicit time dependence of $P(t)$ can be found:

$$P(t) = P_0 \exp \left[ -\frac{e|\vec{E}| t^2}{m\lambda} \right], \tag{A.3}$$

and using (A.1) once more we obtain the ion velocity distribution function

$$f(|\vec{v}|) = f_0 \exp \left[ -\frac{M|\vec{v}|^2}{2e|E|\lambda} \right], \quad \vec{v} > 0. \tag{A.4}$$

Notice that this will only apply for $\vec{v} > 0$ as in the one dimensional case and the one defined in section 5.2.1.2. The factor $f_0$ is calculated from the normalization condition:

$$\int f(|\vec{v}|) d^3v = 1, \tag{A.5}$$

using the same limits as the ones discussed in chapter 5.2.1.2

$$\int_0^{+\infty} \int_0^{+\infty} \int_0^{\frac{\pi}{2}} f(|\vec{v}|) \, d\theta \, dv_r \, dv_z. \tag{A.6}$$

Solving for $f_0$ one gets

$$f_0 = \left( \frac{2 \cdot M}{\pi \cdot e|E|\lambda} \right)^{3/2},$$

and the ion velocity distribution function writes

$$f(|\vec{v}|) = \begin{cases} 
\left( \frac{2 \cdot M}{\pi \cdot e|E|\lambda} \right)^{3/2} \exp \left[ -\frac{M|\vec{v}|^2}{2e|E|\lambda} \right], & \vec{v} > 0 \\
0, & \text{Otherwise} \end{cases} \tag{A.7}$$

To obtain the field dependent mobility, one needs to relate the mean ion velocity with the electric field. The electric field is axis-symetric, and thus writes in cylindrical coordinates

$$\vec{E} = E_r \vec{e}_r + E_z \vec{e}_z. \tag{A.8}$$
A.2. USING (??) IN THE ION-PARTICLE CONSERVATION EQUATION

In the same cylindrical coordinates the mean ion velocity writes

\[ \langle \vec{v} \rangle = \vec{u} = \langle v_r \rangle \vec{e}_r + \langle v_z \rangle \vec{e}_z = u_r \vec{e}_r + u_z \vec{e}_z , \quad (A.9) \]

with

\[ \langle v_i \rangle = \int_0^\infty v_i f(|\vec{v}|)d^3v . \]

Calculating for each component of the velocity

\[ u_z = \int_0^\infty \int_0^\infty \int_0^{\pi/2} v_z f_0 \exp \left[ -\frac{M(v_r^2 + v_z^2)}{2e|\vec{E}|} \right] v_r d\theta dv_r dv_z = \sqrt{\frac{\pi e|\vec{E}|}{2M}} \]
\[ u_r = \int_0^\infty \int_0^\infty \int_0^{\pi/2} v_r f_0 \exp \left[ -\frac{M(v_r^2 + v_z^2)}{2e|\vec{E}|} \right] v_r d\theta dv_r dv_z = \sqrt{\frac{\pi e|\vec{E}|}{2M}} \frac{\pi}{2} \quad (A.10) \]

A relation between each component of the velocity and the norm of the electric field has thus been calculated to be

\[ u_z = \sqrt{\frac{\pi e\lambda}{2M|\vec{E}|}} |\vec{E}| \]
\[ u_r = \sqrt{\frac{\pi e\lambda}{2M|\vec{E}|}} \frac{\pi}{2} |\vec{E}| \quad (A.11) \]

with \(|\vec{E}| = \sqrt{E_R^2 + E_Z^2}.

A.2 Using \([A.11]) in the ion-particle conservation equation

Considering \(\vec{E} = -\nabla\phi\) and introducing the normalized quantity \(\eta\)

\[ \eta = -\frac{e\phi}{k_BT_e} , \]
Equation (5.14) for the ion species $i$ becomes, after substituting the relations A.11

$$\frac{\partial}{\partial z} \left[ N_{i0}^{\text{ion}} \exp(-\eta) \left\{ \frac{2\nu_{\text{Bi}}}{\pi} \left( \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right) \right\}^{1/2} \right]$$

$$+ \frac{1}{r} \frac{\partial}{\partial r} \left[ r N_{i0}^{\text{ion}} \exp(-\eta) \left( \frac{2\nu_{\text{Bi}}}{\pi} \left( \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right) \right)^{1/2} \right] = n_{i0} \nu_i \exp(-\eta)$$

(A.12)

Where $u_{Bi} = \sqrt{\frac{k_B T_i}{M_i}}$ is the Bohm velocity of the $i$ ion. Expanding the derivatives and passing all possible constants to the right-hand side:

$$-\frac{\partial \eta}{\partial z} \left[ \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right]^{1/4} + \frac{1}{r} \frac{\partial}{\partial r} \left[ \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right]^{1/4} + \frac{1}{\pi} \left[ \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right]^{1/4}$$

$$-r \frac{\partial \eta}{\partial r} \left[ \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right] + \frac{r}{\pi} \left[ \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right] = \frac{\nu_i}{u_{Bi}} \frac{n_{i0}}{N_{i0}} \sqrt{2\pi} \left[ \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right]^{3/4}.$$

Multiplying both sides by $\left[ \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right]^{3/4}$:

Finally, assuming that the potential satisfies the separate form (5.19)

$$-\frac{\partial \eta}{\partial z} \left[ \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right] + \frac{1}{r} \frac{\partial}{\partial r} \left[ \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right] + \frac{1}{\pi} \left[ \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right]$$

$$-r \frac{\partial \eta}{\partial r} \left[ \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right] + \frac{r}{\pi} \left[ \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right] = \frac{\nu_i}{u_{Bi}} \frac{n_{i0}}{N_{i0}} \sqrt{2\pi} \left[ \left( \frac{\partial \eta}{\partial z} \right)^2 + \left( \frac{\partial \eta}{\partial r} \right)^2 \right]^{3/4}.$$

(A.13)

Equation (A.13) is a nonlinear partial differential equation for the electrostatic plasma potential, which can be written for the total collision frequency $\nu_{\text{total}} = \sum \nu_i$, similarly to what was done in section 5.2.1.2 for equation (5.40). However, and contrary to (5.40), this is not a separable equation meaning that it must be numerically solved in a two-dimension integration domain, for example using a finite difference or a finite element technique. Because this treatment is beyond the scope of the present dissertation, we have chosen to solve equation (5.40), thus adopting the alternative approach described in chapter 5.
Appendix B

Tables for kinetic reactions

B.1 Electron impact Dissociation Reactions

The following table contains the cross sections for electron impact dissociation reactions.

Table B.1: Electron impact dissociation reactions
(E_{th}, E_{Max} and $\lambda$ are in eV; $\sigma_0$ is in $10^{-16}$ cm$^2$)

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Cross section / Rate coefficient</th>
<th>Representation</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| 1   | $e + CH_4 \rightarrow e + CH_3 + H$ | eq. 4.2; $\sigma_0 = 1.4$
$E_{th} = 10 E_{Max} = 25 \lambda = 77$ | $k1$ | [10] |
| 2   | $e + CH_4 \rightarrow e + CH_2 + 2H$ | eq. 4.2; $\sigma_0 = 0.73$
$E_{th} = 10 E_{Max} = 18 \lambda = 114$ | $k2$ | [10] |
| 3   | $e + CH_3 \rightarrow e + CH_2 + H$ | eq. 4.2; $\sigma_0 = 1.25$
$E_{th} = 10 E_{Max} = 25 \lambda = 77$ | $k3$ | [10] |
| 4   | $e + CH_3 \rightarrow e + CH + 2H$ | eq. 4.2; $\sigma_0 = 0.633$
$E_{th} = 10 E_{Max} = 18 \lambda = 114$ | $k4$ | [10] |
| 5   | $e + CH_2 \rightarrow e + CH + H$ | eq. 4.2; $\sigma_0 = 0.733$
$E_{th} = 10 E_{Max} = 25 \lambda = 77$ | $k5$ | [10] |
| 6   | $e + C_2H_4 \rightarrow e + C_2H_2 + 2H$ | eq. 4.2; $\sigma_0 = 1.56$
$E_{th} = 10 E_{Max} = 18 \lambda = 114$ | $k6$ | [10] |
Table B.1 continued

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Cross section / Rate coefficient</th>
<th>Representation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>(e + C_2H_5 \rightarrow e + C_2H_4 + H)</td>
<td>eq. (4.12): (\sigma_0 = 3.28) (E_{th} = 10\ E_{Max} = 25\ \lambda = 77)</td>
<td>(k7)</td>
<td>[10]</td>
</tr>
<tr>
<td>8</td>
<td>(e + C_2H_6 \rightarrow e + C_2H_4 + 2H)</td>
<td>eq. (4.12): (\sigma_0 = 1.67) (E_{th} = 10\ E_{Max} = 18\ \lambda = 114)</td>
<td>(k8)</td>
<td>[10]</td>
</tr>
<tr>
<td>9</td>
<td>(e + C_2H_6 \rightarrow e + C_2H_5 + H)</td>
<td>eq. (4.12): (\sigma_0 = 3.34) (E_{th} = 10\ E_{Max} = 25\ \lambda = 77)</td>
<td>(k9)</td>
<td>[10]</td>
</tr>
<tr>
<td>10a - 10d</td>
<td>(e + H_2(v) \rightarrow H_2(l) \rightarrow e + 2H)</td>
<td>CS provided</td>
<td>(k10a - k10d)</td>
<td>[10]</td>
</tr>
<tr>
<td>10e</td>
<td>(e + H_2(v) \rightarrow e + H(1s) + H(n))</td>
<td>Refer to reaction k49a in table B.7</td>
<td>(k10e)</td>
<td>[10]</td>
</tr>
</tbody>
</table>

1These reactions are the result of the excitation of dissociative triplet states of \(H_2\) (\(H_2(l)\)), by electron impact on vibrational states.

2These reactions are the result of the excitation of singlet states of \(H_2\), by electron impact on vibrational states, with a branching ratio for the dissociation of the molecule.

### B.2 Table for Electron Impact Ionization Reactions

The following table contains the cross sections for electron ionization reactions.

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Cross section / Rate coefficient</th>
<th>Representation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(e + CH_4 \rightarrow 2e + CH_4^+)</td>
<td>eq. (4.12): (\sigma_0 = 1.4) (E_{th} = 10\ E_{Max} = 25\ \lambda = 77)</td>
<td>(k20)</td>
<td>[10]</td>
</tr>
<tr>
<td>2</td>
<td>(e + CH_4 \rightarrow 2e + CH_3^+ + H)</td>
<td>eq. (4.12): (\sigma_0 = 0.73) (E_{th} = 10\ E_{Max} = 18\ \lambda = 114)</td>
<td>(k21)</td>
<td>[10]</td>
</tr>
<tr>
<td>3</td>
<td>(e + CH_3 \rightarrow 2e + CH_3^+)</td>
<td>eq. (4.12): (\sigma_0 = 1.8) (E_{th} = 12.6\ E_{Max} = 95\ \lambda = 767)</td>
<td>(k22)</td>
<td>[10]</td>
</tr>
<tr>
<td>4</td>
<td>(e + CH_3 \rightarrow 2e + CH_2^+ + H)</td>
<td>eq. (4.12): (\sigma_0 = 1.0) (E_{th} = 15\ E_{Max} = 85\ \lambda = 832)</td>
<td>(k32)</td>
<td>[10]</td>
</tr>
<tr>
<td>5</td>
<td>(e + CH_2 \rightarrow 2e + CH_2^+)</td>
<td>eq. (4.12): (\sigma_0 = 1.8) (E_{th} = 12.6\ E_{Max} = 95\ \lambda = 767)</td>
<td>(k23)</td>
<td>[10]</td>
</tr>
<tr>
<td>6</td>
<td>(e + C_2H_2 \rightarrow 2e + C_2H_2^+)</td>
<td>eq. (4.12): (\sigma_0 = 2.96) (E_{th} = 12\ E_{Max} = 87\ \lambda = 634)</td>
<td>(k24)</td>
<td>[10]</td>
</tr>
<tr>
<td>7</td>
<td>(e + C_2H_4 \rightarrow 2e + C_2H_4^+)</td>
<td>eq. (4.12): (\sigma_0 = 1.15) (E_{th} = 10\ E_{Max} = 90\ \lambda = 668)</td>
<td>(k25)</td>
<td>[10]</td>
</tr>
<tr>
<td>No.</td>
<td>Reaction</td>
<td>Cross section / Rate coefficient</td>
<td>Representation</td>
<td>Ref.</td>
</tr>
<tr>
<td>-----</td>
<td>----------</td>
<td>----------------------------------</td>
<td>----------------</td>
<td>-----</td>
</tr>
<tr>
<td>8</td>
<td>$e + C_2H_5 \rightarrow 2e + C_2H_4^+ + H$</td>
<td>$\sigma_0 = 0.811$; $E_{th} = 10$ $E_{Max} = 89 \lambda = 717$</td>
<td>$k26$</td>
<td>[10]</td>
</tr>
<tr>
<td>9</td>
<td>$e + C_2H_5 \rightarrow 2e + C_2H_5^+$</td>
<td>$\sigma_0 = 1.24$; $E_{in} = 10$ $E_{M} = 89 \lambda = 717$</td>
<td>$k27$</td>
<td>[10]</td>
</tr>
<tr>
<td>10</td>
<td>$e + C_2H_6 \rightarrow 2e + C_2H_5^+ + H$</td>
<td>CS provided</td>
<td>$k28a$</td>
<td>[21]</td>
</tr>
<tr>
<td>11</td>
<td>$e + C_2H_6 \rightarrow 2e + C_2H_4^+ + 2H$</td>
<td>CS provided</td>
<td>$k28b$</td>
<td>[21]</td>
</tr>
<tr>
<td>12</td>
<td>$e + C_2H_6 \rightarrow 2e + C_2H_3^+ + 3H$</td>
<td>CS provided</td>
<td>$k28c$</td>
<td>[21]</td>
</tr>
<tr>
<td>13</td>
<td>$e + C_2H_6 \rightarrow 2e + C_2H_2^+ + 4H$</td>
<td>CS provided</td>
<td>$k28d$</td>
<td>[21]</td>
</tr>
<tr>
<td>14</td>
<td>$e + C_2H_6 \rightarrow 2e + C_2H_6^+$</td>
<td>CS provided</td>
<td>$k29$</td>
<td>[21]</td>
</tr>
<tr>
<td>15</td>
<td>$e + H_2(v) \rightarrow 2e + H_2^+$ (Branching ratio 0.93)</td>
<td>$YK1 = 0.08135$, $C1 = 1.1841$ $YK2 = 0.1733$, $C2 = 0.5985$ $YK3 = 0.1175$, $C3 = 1.4658$</td>
<td>$k30$</td>
<td>[10]</td>
</tr>
<tr>
<td>16</td>
<td>$e + H(1s) \rightarrow 2e + H^+$</td>
<td>$E_{th} = 17.9$ $E_{Max} = 95 \lambda = 800$</td>
<td>$k31$</td>
<td>[22], [23]</td>
</tr>
<tr>
<td>17</td>
<td>$e + CH_2 \rightarrow 2e + CH^+ + H$</td>
<td>$\sigma_0 = 0.65$; $E_{th} = 17.9$ $E_{Max} = 95 \lambda = 800$</td>
<td>$k33$</td>
<td>[10]</td>
</tr>
<tr>
<td>18</td>
<td>$e + CH \rightarrow 2e + CH^+$</td>
<td>$\sigma_0 = 1.8$; $E_{th} = 12.6$ $E_{Max} = 95 \lambda = 746$</td>
<td>$k34$</td>
<td>[10]</td>
</tr>
<tr>
<td>19</td>
<td>$e + C_2H_3 \rightarrow 2e + C_2H_3^+$</td>
<td>$\sigma_0 = 1.07$; $E_{th} = 10$ $E_{Max} = 86 \lambda = 646$</td>
<td>$k35$</td>
<td>[10]</td>
</tr>
<tr>
<td>20</td>
<td>$e + C_2H_6 \rightarrow 2e + C_2H_4^+ + H_2$</td>
<td>$\sigma_0 = 4.37$; $E_{th} = 12$ $E_{Max} = 86 \lambda = 742$</td>
<td>$k27$</td>
<td>[10]</td>
</tr>
</tbody>
</table>
### B.3 Table for Neutral-Neutral Reactions

The following table contains reaction rate coefficients for kinetics between neutrals.

#### Table B.3: Neutral-neutral reactions

(k is in cm$^3$ s$^{-1}$; T$_g$ is in K)

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Rep.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H + CH$_4$ $\rightarrow$ CH$_3$ + H$_2$</td>
<td>$k = 2.2 \times 10^{-20} T_g^3 \exp\left(\frac{-4045}{T_g}\right)$</td>
<td>70</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>2</td>
<td>H + CH$_3$ $\rightarrow$ CH$_2$ + H$_2$</td>
<td>$k = 10^{-10} \exp\left(\frac{-7500}{T_g}\right)$</td>
<td>71</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>3</td>
<td>H + CH$_2$ $\rightarrow$ CH + H$_2$</td>
<td>$k = 10^{-11} \exp\left(\frac{900}{T_g}\right)$</td>
<td>72</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>4</td>
<td>H + C$_2$H$_6$ $\rightarrow$ C$_2$H$_5$ + H$_2$</td>
<td>$k = 2.4 \times 10^{-15} T_{1.5} \exp\left(\frac{-3730}{T_g}\right)$</td>
<td>73</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>5</td>
<td>H + C$_2$H$_5$ $\rightarrow$ 2CH$_4$</td>
<td>$k = 6 \times 10^{-11}$</td>
<td>74</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>6</td>
<td>H + C$_2$H$_5$ $\rightarrow$ C$_2$H$_4$ + H$_2$</td>
<td>$k = 5 \times 10^{-11}$</td>
<td>75</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>7</td>
<td>H + C$_2$H$_4$ $\rightarrow$ C$_2$H$_3$ + H$_2$</td>
<td>$k = 9 \times 10^{-10} \exp\left(\frac{-7500}{T_g}\right)$</td>
<td>76</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>8</td>
<td>H + C$_2$H$_2$ $\rightarrow$ C$_2$H + H$_2$</td>
<td>$k = 10^{-10} \exp\left(\frac{-14000}{T_g}\right)$</td>
<td>77</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>9</td>
<td>CH$_3$ + CH$_3$ $\rightarrow$ C$_2$H$_6$</td>
<td>$k = 6 \times 10^{-11}$</td>
<td>78</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>10</td>
<td>CH$_3$ + CH$_3$ $\rightarrow$ C$_2$H$_5$ + H</td>
<td>$k = 5 \times 10^{-11} \exp\left(\frac{-6800}{T_g}\right)$</td>
<td>79</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>11</td>
<td>CH$_3$ + CH$_3$ $\rightarrow$ C$_2$H$_4$ + H$_2$</td>
<td>$k = 1.7 \times 10^{-8} \exp\left(\frac{-16000}{T_g}\right)$</td>
<td>80</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>12</td>
<td>CH$_3$ + CH$_2$ $\rightarrow$ C$_2$H$_4$ + H</td>
<td>$k = 7 \times 10^{-11}$</td>
<td>81</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>13</td>
<td>CH$_3$ + CH $\rightarrow$ C$_2$H$_3$ + H</td>
<td>$k = 5 \times 10^{-11}$</td>
<td>82</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>14</td>
<td>CH$_2$ + CH$_2$ $\rightarrow$ C$_2$H$_4$</td>
<td>$k = 1.7 \times 10^{-12}$</td>
<td>83</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>15</td>
<td>CH$_2$ + CH$_2$ $\rightarrow$ C$_2$H$_2$ + H$_2$</td>
<td>$k = 2 \times 10^{-10} \exp\left(\frac{-400}{T_g}\right)$</td>
<td>84</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>16</td>
<td>CH + CH$_4$ $\rightarrow$ C$_2$H$_4$ + H</td>
<td>$k = 10^{-10}$</td>
<td>85</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>17</td>
<td>CH + CH$_2$ $\rightarrow$ C$_2$H$_2$ + H</td>
<td>$k = 6.6 \times 10^{-11}$</td>
<td>86</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>18</td>
<td>CH + CH $\rightarrow$ C$_2$H$_2$</td>
<td>$k = 2 \times 10^{-10}$</td>
<td>87</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>19</td>
<td>C$_2$H$_5$ + CH$_3$ $\rightarrow$ C$_3$H$_8$</td>
<td>$k = 4.2 \times 10^{-12}$</td>
<td>88</td>
<td>[7], [24]</td>
</tr>
<tr>
<td>20</td>
<td>CH$_2$ + C$_2$H$_6$ $\rightarrow$ C$_3$H$_8$</td>
<td>$k = 4 \times 10^{-10}$</td>
<td>89</td>
<td>[7], [24]</td>
</tr>
</tbody>
</table>
Table B.3 continued

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Cross section / Rate coefficient</th>
<th>Rep.</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| 21  | $\text{H}(2s) + \text{H}_2(v) \rightarrow e + \text{H}_2^+$  
     (Branching ratio 0.75)  
     $\text{H}(2s) + \text{H}_2(v) \rightarrow e + 3\text{H}(1s)$  
     (Branching ratio 0.25) | $k = 8.9105 \times 10^{-11} \sqrt{T_g}$ | $k95$ | [22], [26] |
| 22  | $\text{H}(2s) + \text{H}_2(v) \rightarrow \text{H}(2p) + \text{H}_2(v)$ | $k = 1.06926 \times 10^{-10} \sqrt{T_g}$ | $k96$ | [22], [27] |
| 23  | $\text{H}(2p) + \text{H}_2(v) \rightarrow \text{H}(2s) + \text{H}_2(v)$ | $k = 5.3463 \times 10^{-10} \sqrt{T_g}$ | $k97$ | [22], [9] |
| 24  | $\text{H}_2(v) + \text{H}_2(w) \leftrightarrow \text{H}_2(v-1) + \text{H}_2(w+1)$ | Rate calculated$^1$ | VV Trans. | [22], [9] |
| 25  | $\text{H}_2(v) + \text{H}_2(w) \leftrightarrow \text{H}_2(v-1) + \text{H}_2(w)$ | Rate calculated$^1$ | VT Trans. | [22], [9] |
| 26  | $\text{H}_2(v) + \text{H}(1s) \leftrightarrow \text{H}_2(v+1) + \text{H}(1s)$  
     i=1-6 | Rate calculated$^1$ | VT Trans.  
     with atoms | [22], [9] |
| 27  | $\text{H}_2(v = 15) + \text{H}_2(w) \leftrightarrow 2\text{H}(1s) + \text{H}_2(w)$ | Rate calculated$^1$ | Dissociation via  
     VT Trans.  
     with $v = 15$ | [22], [9] |
| 28  | $\text{H}_2(v = 15) + \text{H}_2(w) \leftrightarrow 2\text{H}(1s) + \text{H}_2(w - 1)$ | Rate calculated$^1$ | Dissociation via  
     VV Trans.  
     with $v = 15$ | [22], [9] |

$^1$These reactions are part of the vibrational scheme of $\text{H}_2$ and are treated separately (refer to 4.2.9).
B.4 Tables for ion-neutral reactions

The following tables contain the reaction rate coefficients for interactions between ions and neutrals.

Table B.4: Ion-neutral reactions

(k is in cm$^3$ s$^{-1}$; T is in K)

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Cross section / Rate coefficient</th>
<th>Representation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH$_4^+$ + CH$_4$ → CH$_5^+$ + CH$_3$</td>
<td>$k = 1.5 \times 10^{-9}$</td>
<td>k100</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>2</td>
<td>CH$_4^+$ + H$_2$ → CH$_5^+$ + H</td>
<td>$k = 3.3 \times 10^{-11}$</td>
<td>k101</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>3</td>
<td>CH$_3^+$ + CH$_4$ → CH$_4^+$ + CH$_4$</td>
<td>$k = 1.36 \times 10^{-10}$</td>
<td>k102</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>4</td>
<td>H$_2^+$ + H$_2$(v) → H(1s) + H$_3^+$</td>
<td>$k = 2.11 \times 10^{-9}$</td>
<td>k103</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>5</td>
<td>CH$_3^+$ + CH$_4$ → C$_2$H$_5^+$ + H$_2$</td>
<td>$k = 1.2 \times 10^{-9}$</td>
<td>k104</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>6</td>
<td>H$_3^+$ + C$_2$H$_6$ → C$_2$H$_5^+$ + 2H$_2$</td>
<td>$k = 2 \times 10^{-9}$</td>
<td>k105</td>
<td>[7], [28]</td>
</tr>
<tr>
<td>7</td>
<td>H$_3^+$ + CH$_4$ → CH$_5^+$ + H$_2$</td>
<td>$k = 1.6 \times 10^{-9}$</td>
<td>k106</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>8</td>
<td>H$_3^+$ + C$_2$H$_4$ → C$_2$H$_5^+$ + H$_2$</td>
<td>$k = 1.9 \times 10^{-9}$</td>
<td>k107</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>9</td>
<td>H$_3^+$ + C$_2$H$_2$ → C$_2$H$_5^+$ + H$_2$</td>
<td>$k = 1.94 \times 10^{-9}$</td>
<td>k108</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>10</td>
<td>C$_2$H$_2^+$ + CH$_4$ → C$_2$H$_5^+$ + CH$_3$</td>
<td>$k = 4.1 \times 10^{-9}$</td>
<td>k109</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>11</td>
<td>C$_2$H$_2^+$ + CH$_4$ → C$_3$H$_4^+$ + H$_2$</td>
<td>$k = 6.25 \times 10^{-10}$</td>
<td>k110</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>12</td>
<td>C$_2$H$_2^+$ + CH$_4$ → C$_2$H$_5^+$ + H</td>
<td>$k = 1.44 \times 10^{-9}$</td>
<td>k111</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>13</td>
<td>C$_2$H$_2^+$ + C$_2$H$_4$ → C$_3$H$_5^+$ + CH$_3$</td>
<td>$k = 3.9 \times 10^{-10}$</td>
<td>k112</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>14</td>
<td>C$_2$H$_2^+$ + C$_2$H$_4$ → C$_4$H$_8^+$</td>
<td>$k = 4.3 \times 10^{-10}$</td>
<td>k113</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>15</td>
<td>CH$_5^+$ + C$_2$H$_6$ → C$_2$H$_5^+$ + H$_2$ + CH$_4$</td>
<td>$k = 5 \times 10^{-10}$</td>
<td>k114</td>
<td>[7], [28]</td>
</tr>
<tr>
<td>16</td>
<td>C$_2$H$_5^+$ + C$_2$H$_6$ → C$_3$H$_6^+$ + CH$_4$</td>
<td>$k = 2.03 \times 10^{-13}$</td>
<td>k115</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>17</td>
<td>C$_2$H$_5^+$ + C$_2$H$_6$ → C$_3$H$_7^+$ + CH$_3$</td>
<td>$k = 1.32 \times 10^{-11}$</td>
<td>k116</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>18</td>
<td>C$_2$H$_5^+$ + C$_2$H$_2$ → C$_3$H$_7^+$</td>
<td>$k = 6.7 \times 10^{-10}$</td>
<td>k117</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>19</td>
<td>C$_2$H$_5^+$ + C$_2$H$_4$ → C$_3$H$_5^+$ + CH$_4$</td>
<td>$k = 3.1 \times 10^{-10}$</td>
<td>k118</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>20</td>
<td>C$_2$H$_5^+$ + C$_2$H$_4$ → C$_4$H$_8^+$</td>
<td>$k = 3 \times 10^{-10}$</td>
<td>k119</td>
<td>[7], [27]</td>
</tr>
<tr>
<td>21</td>
<td>H$_2^+$ + H(1s) → H$_2$ + H$^+$</td>
<td>$k = 6.4 \times 10^{-10}$</td>
<td>k121</td>
<td>[22], [29]</td>
</tr>
<tr>
<td>22</td>
<td>H$^+$ + 2H$_2$(v) → H$_2$ + H$_3^+$</td>
<td>$k = 3.1 \times 10^{-29} \left(\frac{200}{T}\right)^{0.5}$</td>
<td>k122</td>
<td>[22], [29]</td>
</tr>
<tr>
<td>23</td>
<td>H$^+$ + 2H$_2$(v &gt; 3) → H(1s) + H$_3^+$</td>
<td>$k = 2.5 \times 10^{-9}$</td>
<td>k123</td>
<td>[22], [29]</td>
</tr>
</tbody>
</table>

B.5 Tables for electron recombination reactions

Electron recombination reactions are presented in the following table:
Table B.5: Electron recombination reactions

\[ (k \text{ is in } \text{cm}^3 \text{s}^{-1} \text{ or in } \text{cm}^6 \text{s}^{-1} \text{ for } 3\text{-body reactions}; E, \epsilon \text{ and } T_e \text{ are in eV}; \sigma \text{ is in } 10^{-16} \text{ cm}^2) \]

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Cross section / Rate coefficient</th>
<th>Representation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( e + H_3^+ \to 3H(1s) ) (Branching ratio 0.72) ( e + H_3^+ \to H_2(v &gt; 5) + H(2s, 2p) ) (Branching ratio 0.28)</td>
<td>( \sigma(E) = 50 \left( \frac{E}{\text{eV}} \right)^{\ln 2500} / \ln 4000 )</td>
<td>( k_{131} )</td>
<td>[7], [29]</td>
</tr>
<tr>
<td>2</td>
<td>( 2e + H_3^+ \to e + H_2 + H(1s) )</td>
<td>( k = 8.75 \times 10^{-27} \left( \frac{\epsilon}{\text{eV}} \right)^{-4.5} )</td>
<td>( k_{131} )</td>
<td>[7], [29]</td>
</tr>
<tr>
<td>3</td>
<td>( e + H_2^+ \to H(1s) + H(n &gt; 1s) )</td>
<td>( \sigma(E) = 100 \left( \frac{\epsilon}{\text{eV}} \right)^{4/\ln 4000} )</td>
<td>( k_{132} )</td>
<td>[7], [29]</td>
</tr>
<tr>
<td>4</td>
<td>( 2e + H_2^+ \to e + 2H(1s) )</td>
<td>( k = 8.75 \times 10^{-27} \left( \frac{\epsilon}{\text{eV}} \right)^{-4.5} )</td>
<td>( k_{133} )</td>
<td>[7], [29]</td>
</tr>
<tr>
<td>5</td>
<td>( e + H^+ \to H(n) + h\nu )</td>
<td>Equation (4.7)</td>
<td>( k_{134} )</td>
<td>[7], [29]</td>
</tr>
<tr>
<td>6</td>
<td>( 2e + H_2^+ \to e + H(n) )</td>
<td>Equation (4.8)</td>
<td>( k_{135} )</td>
<td>[7], [29]</td>
</tr>
<tr>
<td>7</td>
<td>( e + CH_3^+ \to CH_3 + H ) (Branching ratio 0.25) ( e + CH_4^+ \to CH_2 + H_2 ) (Branching ratio 0.75)</td>
<td>( k = \begin{cases} 5.4 \times 10^{-8}T_e^{-0.84}, &amp; T_e &lt; 1\text{eV} \ 5.4 \times 10^{-8}T_e^{1.05}, &amp; T_e &gt; 1\text{eV} \end{cases} )</td>
<td>( k_{136} )</td>
<td>[10]</td>
</tr>
<tr>
<td>8</td>
<td>( e + CH_3^+ \to CH_2 + H )</td>
<td>( k = \begin{cases} 6.8 \times 10^{-8}T_e^{-0.77}, &amp; T_e &lt; 1\text{eV} \ 6.8 \times 10^{-8}T_e^{0.979}, &amp; T_e &gt; 1\text{eV} \end{cases} )</td>
<td>( k_{137} )</td>
<td>[10]</td>
</tr>
<tr>
<td>9</td>
<td>( e + CH_2^+ \to CH + H )</td>
<td>( k = \begin{cases} 10^{-8}T_e^{-0.544}, &amp; T_e &lt; 1\text{eV} \ 10^{-8}T_e^{1.21}, &amp; T_e &gt; 1\text{eV} \end{cases} )</td>
<td>( k_{138} )</td>
<td>[10]</td>
</tr>
<tr>
<td>10</td>
<td>( e + C_2H_4^+ \to C_2H_2 + H_2 ) (Branching ratio 0.5) ( e + C_2H_3^+ \to C_2 + H_3 + H ) (Branching ratio 0.5)</td>
<td>( k = 10^{-9}T_e^{-0.5} )</td>
<td>( k_{139} )</td>
<td>[10]</td>
</tr>
</tbody>
</table>

These reactions are part of the vibrational scheme of \( H_2 \) and are treated separately (refer to 4.2.9).

### B.6 Tables for Proton Ionization Reactions

Table B.6 presents the expressions for the rate coefficients that represent proton ionization reactions.
Table B.5 continued

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Cross section / Rate coefficient</th>
<th>Representation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>$e + C_2H_5^+ \rightarrow C_2H_3 + H_2$ (Branching ratio 0.5) $e + C_2H_5^+ \rightarrow C_2 + H_4 + H$ (Branching ratio 0.5)</td>
<td>$k = 9.65 \times 10^{-8}T_e^{-0.5}$</td>
<td>$k140$</td>
<td>[10]</td>
</tr>
<tr>
<td>12</td>
<td>$e + C_2H_2^+ \rightarrow CH + CH$ (Branching ratio 0.33) $e + C_2H_2^+ \rightarrow C_2 + H + H$ (Branching ratio 0.33) $e + C_2H_2^+ \rightarrow 2C + 2H$ (Branching ratio 0.33)</td>
<td>$k = 6.81 \times 10^{-8}T_e^{-0.5}$</td>
<td>$k142$</td>
<td>[10]</td>
</tr>
<tr>
<td>13</td>
<td>$e + CH^+ \rightarrow C + H$</td>
<td>$k = \begin{cases} 7 \times 10^{-8}T_e^{-0.553}, T_e &lt; 1eV \ 7 \times 10^{-8}T_e^{1.18}, T_e &gt; 1eV \end{cases}$</td>
<td>$k143$</td>
<td>[10]</td>
</tr>
</tbody>
</table>

Table B.6: Charge exchange reactions with $H^+$

($k$ in cm$^3$ s$^{-1}$)

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Cross section / Rate coefficient</th>
<th>Representation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$H^+ + CH_4 \rightarrow CH_4^+ + H$ (Branching ratio 0.5) $H^+ + CH_4 \rightarrow CH_3^+ + H_2$ (Branching ratio 0.5)</td>
<td>$k = 3.8 \times 10^{-9}$</td>
<td>$k170$</td>
<td>[10]</td>
</tr>
<tr>
<td>2</td>
<td>$H^+ + CH_3 \rightarrow CH_3^+ + H$ (Branching ratio 0.5) $H^+ + CH_3 \rightarrow CH_2^+ + H_2$ (Branching ratio 0.5)</td>
<td>$k = 3.6 \times 10^{-9}$</td>
<td>$k171$</td>
<td>[10]</td>
</tr>
<tr>
<td>3</td>
<td>$H^+ + CH_2 \rightarrow CH_2^+ + H$ (Branching ratio 0.5) $H^+ + CH_2 \rightarrow CH^+ + H_2$ (Branching ratio 0.5)</td>
<td>$k = 3.4 \times 10^{-9}$</td>
<td>$k172$</td>
<td>[10]</td>
</tr>
</tbody>
</table>
### Table B.6 continued

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Representation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>$H^+ + CH \rightarrow CH^+ + H$</td>
<td>$k = 3.8 \times 10^{-9}$</td>
<td>$k_{173}$</td>
<td>[10]</td>
</tr>
<tr>
<td>5</td>
<td>$H^+ + C_2H_6 \rightarrow C_2H_5^+ + H_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Branching ratio 0.33)</td>
<td>$k = 5 \times 10^{-9}$</td>
<td>$k_{174}$</td>
<td>[10]</td>
</tr>
<tr>
<td></td>
<td>$H^+ + C_2H_6 \rightarrow C_2H_4^+ + H_2 + H$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Branching ratio 0.33)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$H^+ + C_2H_6 \rightarrow C_2H_3^+ + H_2 + H_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Branching ratio 0.33)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$H^+ + C_2H_5 \rightarrow C_2H_5^+ + H$</td>
<td>$k = 4.9 \times 10^{-9}$</td>
<td>$k_{175}$</td>
<td>[10]</td>
</tr>
<tr>
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<td>(Branching ratio 0.33)</td>
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</tr>
<tr>
<td></td>
<td>$H^+ + C_2H_5 \rightarrow C_2H_4^+ + H_2 + H$</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>(Branching ratio 0.33)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$H^+ + C_2H_5 \rightarrow C_2H_3^+ + H_2 + H_2$</td>
<td></td>
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<tr>
<td></td>
<td>(Branching ratio 0.33)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>$H^+ + C_2H_4 \rightarrow C_2H_4^+ + H$</td>
<td>$k = 4.8 \times 10^{-9}$</td>
<td>$k_{176}$</td>
<td>[10]</td>
</tr>
<tr>
<td></td>
<td>(Branching ratio 0.33)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$H^+ + C_2H_4 \rightarrow C_2H_3^+ + H_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Branching ratio 0.33)</td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td>$H^+ + C_2H_4 \rightarrow C_2H_2^+ + H_2 + H$</td>
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</tr>
<tr>
<td></td>
<td>(Branching ratio 0.33)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>$H^+ + C_2H_2 \rightarrow C_2H_2^+ + H$</td>
<td>$k = 4.5 \times 10^{-9}$</td>
<td>$k_{178}$</td>
<td>[10]</td>
</tr>
<tr>
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<td>(Branching ratio 0.5)</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>$H^+ + C_2H_2 \rightarrow C_2H^+ + H_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Branching ratio 0.5)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### B.7 Tables for Electron Excitation Reactions

The following table presents electron excitation reactions

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Cross section / Rate coefficient</th>
<th>Rep.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$e + CH_4 \rightarrow e + CH_4^*$(^{2, 4})</td>
<td>CS provided</td>
<td>$k$-40a</td>
<td>[30], [31]</td>
</tr>
<tr>
<td>2</td>
<td>$e + CH_4 \rightarrow e + CH_4^*$(^{1, 3})</td>
<td>CS provided</td>
<td>$k$-40b</td>
<td>[30], [31]</td>
</tr>
<tr>
<td>3</td>
<td>$e + CH_3 \rightarrow e + CH_3^*$</td>
<td>$k = 5 \times 10^{-8}$</td>
<td>$k$-41</td>
<td>N/A</td>
</tr>
<tr>
<td>4</td>
<td>$e + CH_2 \rightarrow e + CH_2^*$</td>
<td>$k = 10^{-12}$</td>
<td>$k$-42</td>
<td>N/A</td>
</tr>
<tr>
<td>5</td>
<td>$e + C_2H_2 \rightarrow e + (C_2H_2)_{vib}$</td>
<td>CS provided</td>
<td>$k$-43a</td>
<td>[30], [32]</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow e + (C_2H_2)<em>{e2} \ ; e + (C_2H_2)</em>{e(3,1)}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>$e + C_2H_2 \rightarrow e + (C_2H_2)_{elec1}$</td>
<td>CS provided</td>
<td>$k$-43b</td>
<td>[30], [32]</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow e + (C_2H_2)<em>{e2} \ ; e + (C_2H_2)</em>{e3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>$e + C_2H_4 \rightarrow e + (C_2H_4)_{vib1}$</td>
<td>CS provided</td>
<td>$k$-44a</td>
<td>[30], [32]</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow e + (C_2H_2)_{e2}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>$e + C_2H_4 \rightarrow e + (C_2H_4)_{elec1}$</td>
<td>CS provided</td>
<td>$k$-44b</td>
<td>[30], [32]</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow e + (C_2H_4)<em>{e2} \ ; e + (C_2H_4)</em>{e3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>$e + C_2H_5 \rightarrow e + C_2H_5^*$</td>
<td>$k = 10^{-12}$</td>
<td>$k$-45</td>
<td>N/A</td>
</tr>
<tr>
<td>10</td>
<td>$e + C_2H_6 \rightarrow e + (C_2H_6)_{vib(2,4)}$</td>
<td>CS provided</td>
<td>$k$-46a</td>
<td>[30], [32]</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow e + (C_2H_6)_{vib(1,3)}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>$e + C_2H_6 \rightarrow e + (C_2H_6)_{elec1}$</td>
<td>CS provided</td>
<td>$k$-46b</td>
<td>[30], [32]</td>
</tr>
<tr>
<td></td>
<td>$\rightarrow e + (C_2H_2)<em>{e2} \ ; e + (C_2H_2)</em>{e3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>$e + H_2(v) \leftrightarrow e + H_2(v + i)$</td>
<td>CS provided</td>
<td>$k$-48</td>
<td>[22], [19], [33], [34], [35]</td>
</tr>
<tr>
<td></td>
<td>$(i = 1, 2, 3)$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>$e + H_2(v) \rightarrow e + H_2(D^1\Pi_u, B'^1\Sigma_u^+, D^3\Pi_u)$</td>
<td>CS provided</td>
<td>$k$-49a</td>
<td>[22], [19], [33], [34], [35]</td>
</tr>
</tbody>
</table>
Table B.7 continued

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Cross section / Rate coefficient</th>
<th>Representation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>$e + H_2(v) \rightarrow e + H_2(B_1^1 \Sigma_u^+ \rightarrow e + H_2(v')$</td>
<td>CS provided$^1$</td>
<td>$k49l$</td>
<td>[22], [19], [33]</td>
</tr>
<tr>
<td>15</td>
<td>$e + H_2(v) \rightarrow e + H_2(C^1 \Pi_u \rightarrow e + H_2(v')$</td>
<td>CS provided$^1$</td>
<td>$k49m$</td>
<td>[22], [19], [33]</td>
</tr>
<tr>
<td>16</td>
<td>$e + H_2(v) \rightarrow e + H_2(B_1^1 \Sigma_u^+ \rightarrow e + H_2(v')$</td>
<td>CS provided$^1$</td>
<td>$k49n$</td>
<td>[22], [19], [33]</td>
</tr>
<tr>
<td>17</td>
<td>$e + H_2(v) \rightarrow e + H_2(D_1^1 \Pi_u \rightarrow e + H_2(v')$</td>
<td>CS provided$^1$</td>
<td>$k49o$</td>
<td>[22], [19], [33]</td>
</tr>
<tr>
<td>18</td>
<td>$e + H(1s) \leftrightarrow e + H(2s)$</td>
<td>Equation (4.10)</td>
<td>$k50a$</td>
<td>[22], [23]</td>
</tr>
<tr>
<td>19</td>
<td>$e + H(1s) \leftrightarrow e + H(2p)$</td>
<td>Equation (4.12)</td>
<td>$k50b$</td>
<td>[22], [23]</td>
</tr>
<tr>
<td>20</td>
<td>$e + H(1s) \leftrightarrow e + H(3)$</td>
<td>Equation (4.13)</td>
<td>$k50c$</td>
<td>[22], [23]</td>
</tr>
<tr>
<td>21</td>
<td>$e + H(1s) \leftrightarrow e + H(4)$</td>
<td>Equation (4.14)</td>
<td>$k50d$</td>
<td>[22], [23]</td>
</tr>
<tr>
<td>22</td>
<td>$e + H(1s) \leftrightarrow e + H(5)$</td>
<td>Equation (4.15)</td>
<td>$k50e$</td>
<td>[22], [23]</td>
</tr>
</tbody>
</table>

$^1$These reactions are part of the vibrational scheme of $H_2$ and are treated separately (refer to 4.2.9).

B.8 Tables for elastic colisions by electron impact

The rate coefficients and the cross sections for elastic collisions by electron impact are represented in table B.8.
Table B.8: Elastic collisions by electron impact

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Cross section / Rate coefficient</th>
<th>Representation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$e + CH_4 \rightarrow e + CH_4$</td>
<td>CS Provided</td>
<td>$k_{60}$</td>
<td>[31]</td>
</tr>
<tr>
<td>2</td>
<td>$e + CH_3 \rightarrow e + CH_3$</td>
<td>$k = 10^{-12}$</td>
<td>$k_{61}$</td>
<td>N/A</td>
</tr>
<tr>
<td>3</td>
<td>$e + CH_2 \rightarrow e + CH_2$</td>
<td>$k = 10^{-12}$</td>
<td>$k_{62}$</td>
<td>N/A</td>
</tr>
<tr>
<td>4</td>
<td>$e + C_2H_2 \rightarrow e + C_3H_2$</td>
<td>CS Provided</td>
<td>$k_{63}$</td>
<td>[37], [52]</td>
</tr>
<tr>
<td>5</td>
<td>$e + C_2H_4 \rightarrow e + C_2H_2$</td>
<td>CS Provided</td>
<td>$k_{64}$</td>
<td>[37], [32]</td>
</tr>
<tr>
<td>6</td>
<td>$e + C_2H_5 \rightarrow e + C_3H_5$</td>
<td>$k = 10^{-12}$</td>
<td>$k_{65}$</td>
<td>N/A</td>
</tr>
<tr>
<td>7</td>
<td>$e + C_2H_6 \rightarrow e + C_2H_6$</td>
<td>CS Provided</td>
<td>$k_{66}$</td>
<td>[37], [32]</td>
</tr>
<tr>
<td>8</td>
<td>$e + H_2 \rightarrow e + H_2$</td>
<td>CS Provided</td>
<td>$k_{67}$</td>
<td>[22], [19], [33]</td>
</tr>
<tr>
<td>9</td>
<td>$e + H(n) \rightarrow e + H(n)$</td>
<td>CS Provided</td>
<td>$k_{68}$</td>
<td>[22], [39], [40]</td>
</tr>
</tbody>
</table>

B.9 Tables for wall reactions

The following reactions represent the interaction of the plasma with the wall of the discharge
Table B.9: Wall reactions - neutrals

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Rep.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH\textsubscript{4} \xrightarrow{\gamma} CH\textsubscript{4}</td>
<td>$k = \frac{D}{N^2}$; $\gamma = 0$</td>
<td>N/A 1</td>
<td>Chapter 5 section 5.1</td>
</tr>
<tr>
<td>2</td>
<td>CH\textsubscript{3} \xrightarrow{\gamma} CH\textsubscript{3}</td>
<td>$k = \frac{D}{N^2}$; $\gamma = 0.01$</td>
<td>k402</td>
<td>Chapter 5 section 5.1</td>
</tr>
<tr>
<td>3</td>
<td>CH\textsubscript{2} \xrightarrow{\gamma} CH\textsubscript{2}</td>
<td>$k = \frac{D}{N^2}$; $\gamma = 0.01$</td>
<td>k403</td>
<td>Chapter 5 section 5.1</td>
</tr>
<tr>
<td>4</td>
<td>CH \xrightarrow{\gamma} CH</td>
<td>$k = \frac{D}{N^2}$; $\gamma = 0.01$</td>
<td>k404</td>
<td>Chapter 5 section 5.1</td>
</tr>
<tr>
<td>5</td>
<td>C\textsubscript{2}H\textsubscript{2} \xrightarrow{\gamma} C\textsubscript{2}H\textsubscript{2}</td>
<td>$k = \frac{D}{N^2}$; $\gamma = 0.01$</td>
<td>k407</td>
<td>Chapter 5 section 5.1</td>
</tr>
<tr>
<td>6</td>
<td>C\textsubscript{2}H\textsubscript{3} \xrightarrow{\gamma} C\textsubscript{2}H\textsubscript{3}</td>
<td>$k = \frac{D}{N^2}$; $\gamma = 0.01$</td>
<td>k444</td>
<td>Chapter 5 section 5.1</td>
</tr>
<tr>
<td>7</td>
<td>C\textsubscript{2}H\textsubscript{4} \xrightarrow{\gamma} C\textsubscript{2}H\textsubscript{4}</td>
<td>$k = \frac{D}{N^2}$; $\gamma = 0.01$</td>
<td>k406</td>
<td>Chapter 5 section 5.1</td>
</tr>
<tr>
<td>8</td>
<td>C\textsubscript{2}H\textsubscript{5} \xrightarrow{\gamma} C\textsubscript{2}H\textsubscript{5}</td>
<td>$k = \frac{D}{N^2}$; $\gamma = 0.01$</td>
<td>k405</td>
<td>Chapter 5 section 5.1</td>
</tr>
<tr>
<td>9</td>
<td>C\textsubscript{2}H\textsubscript{6} \xrightarrow{\gamma} C\textsubscript{2}H\textsubscript{6}</td>
<td>$k = \frac{D}{N^2}$; $\gamma = 0.01$</td>
<td>k408</td>
<td>Chapter 5 section 5.1</td>
</tr>
<tr>
<td>10</td>
<td>C\textsubscript{3}H\textsubscript{8} \xrightarrow{\gamma} C\textsubscript{3}H\textsubscript{8}</td>
<td>$k = \frac{D}{N^2}$; $\gamma = 0.01$</td>
<td>k409</td>
<td>Chapter 5 section 5.1</td>
</tr>
<tr>
<td>11</td>
<td>H\textsubscript{2}(v) \xrightarrow{\gamma} H\textsubscript{2}(v = 0)</td>
<td>$k = \frac{D}{N^2}$; $\gamma = 0.07$</td>
<td>k421</td>
<td>Chapter 5 section 5.1</td>
</tr>
<tr>
<td>12</td>
<td>H(n) \xrightarrow{\gamma} H(1s) \quad (n = 2s, 2p, 3, 4, 5)</td>
<td>$k = \frac{D}{N^2}$; $\gamma = 1$</td>
<td>k500</td>
<td>Chapter 5 section 5.1</td>
</tr>
<tr>
<td>13</td>
<td>2H(1s) \xrightarrow{\gamma} H\textsubscript{2}(v = 0)</td>
<td>$k = \frac{D}{N^2}$; $\gamma = 0.05$</td>
<td>k417</td>
<td>Chapter 5 section 5.1</td>
</tr>
</tbody>
</table>

\(^1\)CH\textsubscript{4} fully returns to the discharge, terms of balance there is no diffusion loss.
### Table B.10: Wall reactions - ions

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Rep.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH\textsuperscript{+} + e\textsubscript{wall} → CH\textsubscript{4}</td>
<td>( k = 2u_B \left( \frac{h\alpha}{T} + \frac{h\beta}{T} \right) )</td>
<td>Chapter 5 section 5.2</td>
<td>k410</td>
</tr>
<tr>
<td>2</td>
<td>CH\textsubscript{3}\textsuperscript{+} + e\textsubscript{wall} → CH\textsubscript{3}</td>
<td>( k = 2u_B \left( \frac{h\alpha}{T} + \frac{h\beta}{T} \right) )</td>
<td>Chapter 5 section 5.2</td>
<td>k411</td>
</tr>
<tr>
<td>3</td>
<td>CH\textsubscript{5}\textsuperscript{+} + e\textsubscript{wall} → CH\textsubscript{3} + H\textsubscript{2}(v = 0)</td>
<td>( k = 2u_B \left( \frac{h\alpha}{T} + \frac{h\beta}{T} \right) )</td>
<td>Chapter 5 section 5.2</td>
<td>k412</td>
</tr>
<tr>
<td>4</td>
<td>CH\textsuperscript{+} + e\textsubscript{wall} → CH</td>
<td>( k = 2u_B \left( \frac{h\alpha}{T} + \frac{h\beta}{T} \right) )</td>
<td>Chapter 5 section 5.2</td>
<td>k441</td>
</tr>
<tr>
<td>5</td>
<td>C\textsubscript{2}H\textsubscript{2}\textsuperscript{+} + e\textsubscript{wall} → C\textsubscript{2}H\textsubscript{2}</td>
<td>( k = 2u_B \left( \frac{h\alpha}{T} + \frac{h\beta}{T} \right) )</td>
<td>Chapter 5 section 5.2</td>
<td>k413</td>
</tr>
<tr>
<td>6</td>
<td>C\textsubscript{2}H\textsubscript{3}\textsuperscript{+} + e\textsubscript{wall} → C\textsubscript{2}H\textsubscript{3}</td>
<td>( k = 2u_B \left( \frac{h\alpha}{T} + \frac{h\beta}{T} \right) )</td>
<td>Chapter 5 section 5.2</td>
<td>k445</td>
</tr>
<tr>
<td>7</td>
<td>C\textsubscript{2}H\textsubscript{4}\textsuperscript{+} + e\textsubscript{wall} → C\textsubscript{2}H\textsubscript{4}</td>
<td>( k = 2u_B \left( \frac{h\alpha}{T} + \frac{h\beta}{T} \right) )</td>
<td>Chapter 5 section 5.2</td>
<td>k414</td>
</tr>
<tr>
<td>8</td>
<td>C\textsubscript{2}H\textsubscript{5}\textsuperscript{+} + e\textsubscript{wall} → C\textsubscript{2}H\textsubscript{5}</td>
<td>( k = 2u_B \left( \frac{h\alpha}{T} + \frac{h\beta}{T} \right) )</td>
<td>Chapter 5 section 5.2</td>
<td>k415</td>
</tr>
<tr>
<td>9</td>
<td>C\textsubscript{2}H\textsubscript{6}\textsuperscript{+} + e\textsubscript{wall} → C\textsubscript{2}H\textsubscript{6}</td>
<td>( k = 2u_B \left( \frac{h\alpha}{T} + \frac{h\beta}{T} \right) )</td>
<td>Chapter 5 section 5.2</td>
<td>k443</td>
</tr>
<tr>
<td>10</td>
<td>H\textsubscript{2}\textsuperscript{+} + e\textsubscript{wall} → H\textsubscript{2}</td>
<td>( k = 2u_B \left( \frac{h\alpha}{T} + \frac{h\beta}{T} \right) )</td>
<td>Chapter 5 section 5.2</td>
<td>k418</td>
</tr>
<tr>
<td>11</td>
<td>H\textsuperscript{+} + e\textsubscript{wall} → H</td>
<td>( k = 2u_B \left( \frac{h\alpha}{T} + \frac{h\beta}{T} \right) )</td>
<td>Chapter 5 section 5.2</td>
<td>k419</td>
</tr>
<tr>
<td>12</td>
<td>H\textsubscript{3}\textsuperscript{+} + e\textsubscript{wall} → H\textsubscript{2}(v = 0) + H(1s)</td>
<td>( k = 2u_B \left( \frac{h\alpha}{T} + \frac{h\beta}{T} \right) )</td>
<td>Chapter 5 section 5.2</td>
<td>k420</td>
</tr>
</tbody>
</table>
Appendix C

Graphics of results

C.1 Time dependance

The time evolution of the different species considered in the model are presented in the following pictures.

![Graph of species evolution](image)

Figure C.1: Time behaviour of the hydrocarbon neutral species.
Figure C.2: Time behaviour of the hydrocarbon ionic species.

Figure C.3: Time behaviour of the hydrogen atom species’ densities.
C.1. TIME DEPENDANCE

Figure C.4: Time behaviour of the hydrogen molecule species' densities.

Figure C.5: Time behaviour of the hydrogen ions' densities.
Figure C.6: Time behaviour of the electron density.

Figure C.7: Time behaviour of the electron temperature.
Bibliography


[18] [Website](http://www.dlsode.com) for the *dlsode* package. Lawrence Livermore National Laboratory, 2010.


[32] Kinema Research and Software (click to go to site).


[34] A. V. Phelps et al. LINK NOT WORKING.


