Global modeling of low-pressure plasmas in CH_4-H_2 mixtures

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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.

1 Introduction

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 [1, 2] . 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 [3], which are of promising use in the optoelectronics and the communications industry for manufacturing devices such as solar cells and laser diodes [4]. 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 objective of this work was the development of a collisional-radiative model (CRM) for a H_2-CH_4 plasma. As a result, a number of improvements were made to the original code. 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. An update to the theory of transport of charged species under ambipolar diffusion in a low pressure regime is also proposed, based on the work of Lieberman [1] and Godyak [5].

The system to model is an inductively coupled plasma (ICP) reactor on site at the partner institution *Institut des Matériaux Jean Rouxel* (IMN/CNRS, Nantes, France) and it consits of two separate chambers.

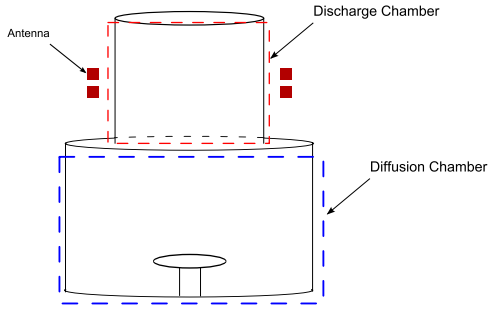


Figure 1: Illustration of the modeled reactor. The plasma is created in the excitation chamber ($R = 1.8$ cm and $L = 1.2$ cm), where the power is coupled through the antenna, and then makes its way to the substrate holder in the diffusion chamber to process the material placed there.

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

- Pressure ranging from 2 to 40 mTorr
- Neutral gas flow ranging from 20 to 40 sccm
- Coupled power ranging from 100 to 1000 W

2 Model Formulation

The code updated solves the time-dependance of each heavy species' density as well as the electron temperature and density. The set of equations used are:

- Heavy species particle balance equation
- Electron energy density equation
- Quasineutrality condition

3.1 Heavy species particle balance equation

For each heavy species, the time-dependent particle balance equation for the volume averaged density N_0 is found by calculating the zeroth moment of the Boltzmann equation [6] and averaging over the volume of the discharge

$$\frac{\partial N_0}{\partial t} = G_0 - L_0 - \frac{N_0}{\tau_R} - k^{Trans} N_0 \ , \tag{1}$$

where N_0 is the volume averaged density of the heavy species, G_0 and L_0 are the volume averaged gain and loss terms due to collisions, $\frac{N_0}{\tau_R}$ is the advective term, which takes into account the movement of particles by bulk motion of the entire fluid. This term represents the pumping of particles out of the reactor in order to conserve the pressure. It is characterized by a residence time τ_R which for precursor species is calculated by

$$\tau_R = \frac{V}{q_0}\frac{N_{n0}}{n_0} \ , \tag{2}$$

where V is the volume of the discharge, q is the input flow of the precursor gas, n_0 is the Loschmidt constant and N_{n0} is the density of the precursor gas calculated by the ideal gas law (the gas is assumed to be at room temperature - 300 K). The final term on the right-hand side of (1) is the diffusion term, where k^{Trans} is the diffusion coefficient A distinction must be made between the diffusion of neutrals and the diffusion of ions, since the former are not affected by electric fields present in the plasma.

3.1.1 Neutral species' diffusion

The diffusion of neutral species in a plasma is then described by a motion from a regions of high density, towards regions of lower density, where the flow of neutral particles is described by Fick's law:

$$N\vec{u} = -D\vec{\nabla}_r N \ , \tag{3}$$

where D is called the *diffusion coefficient*, which is a measure of how well two fluids mix with each other. Using (3) in (1) the diffusion term takes the following form $-D\nabla^2 N$, where ∇^2 is the Laplace operator. This term can be approximated as [6]:

$$\nabla^2 N = -\frac{N}{\Lambda^2} \ , \tag{4}$$

Where $\Lambda^2 = \left(\frac{\pi}{L}\right)^2 + \left(\frac{2.45}{R}\right)^2$ represents an effective diffusion lenght of the reactor. In order to calculate the diffusion coefficient the Chapman-Enskog apporximation is used to estimate the binary diffusion coefficient between the particle and other particles [7]:

$$D_{A,B} = 0.0018583\sqrt{T^3\left(\frac{1}{M_A}+\frac{1}{M_B}\right)}\frac{1}{p\sigma_{AB}^2\Omega_{AB}} \ , \tag{5}$$

where T is the gas temperature, M_i is the mass of species i, p is the pressure of the gas, σ_{AB} is the reference distance that appears in the Lennard-Jones potential for the molecule:

$$V_{A,B}(r) = 4\epsilon_{AB}\left[\left(\frac{\sigma_{AB}}{r}\right)^{12} + \left(\frac{\sigma_{AB}}{r}\right)^{6}\right] \ , \tag{6}$$

and finally Ω is the collision integral, which is given by [7]:

$$\Omega = \frac{1.06036}{T^{*\,A}} + \frac{0.193}{\exp B\,T^*} + \frac{1.03587}{\exp C\,T^*} + \frac{1.76474}{\exp D\,T^*} \ , \tag{7}$$

with $A = 0.1561$, $B = 0.47635$, $C = 1.52996$, $D = 3.89411$ and $T^* = \frac{kT}{\epsilon}$ where this last term is dependent on the gas elements.

This however only treats binary diffusion. To find the effective diffusion coefficient (D_{eff}) of a certain neutral gas inside the 2 element precursor gas one must independently calculate the binary diffusion of the gas g with each term i of the precursor gas and apply the following law in this case specific to the CH_4-H_2 gas:

$$\frac{1}{D^i_{eff}} = \frac{1}{D_{i,CH_4}} + \frac{1}{D_{i,H_2}} \tag{8}$$

In order to account for the reactivity of the gas with the walls, a wall reaction coefficient γ is introduced, which represents the losses of neutrals to the walls. This term represents the percentage of particles lost to the walls by implantation or recombination. This means that only a percentage of species is lost due to diffusion to the walls, and the rest returns to the discharge. Adding this information to the discharge means that the diffusion coefficient for neutral species must be multiplied by this factor in order to account for the return to the plasma of species.

So, finally, the neutral species diffusion term can be written as:

$$k^{Neut}_{Trans} = \gamma\frac{D_{eff}}{\Lambda^2} \ . \tag{9}$$

3.1.2 Charged species' diffusion

In the case of charged species transport, specifically ions, the transport is treated differently. This is because of the existance of self-consistent electric fields created by charge seperation inside the discharge due to the faster movement of lighter electrons. These fields are called *ambipolar* fields and are more important the less collisional the problem is (e.g. Low pressures, which is the case in the considered model).

It will then be considered that ion motion will be controlled by these ambipolar electric fields, which means that ions will have a directed *drift velocity* towards the walls related to this electric field by a mobility μ. In the case of low pressure discharges, where there are high electric fields, the mobility is no longer a constant (as is usual to assum in high pressure discharges) and has a

dependance on the electric field. The mean velocity of each ion u is found to be [8, 9, 5]:

$$u = \sqrt{\frac{2eE\lambda}{\pi M}} \ , \tag{10}$$

Where e is the electron charge, E is the electric field norm, λ is the ion mean free path and M is the mass of the ion. This concept is called *variable mobility*.

Transport loss of ions is due to recombination at the walls of the reactor [1]. This means that a given flow of ions is directed to the walls. An analysis of the sheath region would be necessary in order to reliably calculate such flow, however that study is not considered but a reasonable value can be assumed from the bulk plasma. The sheath region is usually considered collisionless, so the ion flow is conserved. This means that the ion flow that reaches the walls is the same as the flow at the entrance of the sheath region (Γ_{Ion}^{Sheath}), which is can be calculated [1]:

$$\Gamma_{Ion}^{Sheath} = N_{iS} u_B \tag{11}$$

Where N_{iS} is the ion density at the sheath edge and u_B is the Bohm velocity. For simplicty reasons, this value will be considered to be the average value of the ion density in the bulk of the discharge (N_{i0}).

The ammount of ions that strike the walls per second (ν_W) is then calculated as:

$$\nu_W = \Gamma_{Ion}^{Sheath} A = N i u_B A_{eff} \tag{12}$$

Where A_{eff} is an effective area for collection of ions. This means that per unit volume, the number of ions that hit the walls per unit of time is given by

$$\left(\frac{\partial N_i^{Ion}}{\partial t}\right)_{Walls} = N_{i0} u_B \frac{A_{eff}}{V} = N_{i0} k_{Trans} \ . \tag{13}$$

In order to account for diffusion in this otherwise ballistic approach, the effective area of collection is found to be in the case of a cylindrical reactor

$$A_{eff} = h_R 2\pi R^2 + h_L 2\pi R L \ . \tag{14}$$

Here R is the radius, L is the length and h_L and h_R are, respectively, the axial and radial ratio of edge-to-bulk density of the ion. The profile of the ions must be known in order to calculate this ratio. By solving in a quasineutral plasma the one dimensional time-independent particle balance equation for a flow of ions with velocity given by (10) and with Maxwellian electrons ($n_e = n_i = n_0 \exp\left(\frac{e\phi}{k_B T_e}\right)$, where ϕ is the electrostatic potential and T_e is the electron temperature) with a source ionization term of neutrals, Godyak offers an expression for calculation the edge-to-center density ratios ([5], more details in [10]):

$$h_Z = 0.86\left(3 + \frac{L}{2\lambda}\right)^{-1/2} \ , \ h_R = 0.8\left(4 + \frac{R}{\lambda}\right)^{-1/2} \ . \tag{15}$$

However, these expressions take into account that the constant α given by

$$\alpha = \sqrt{\frac{\pi l_p}{2\lambda}} \frac{\nu l_p}{u_B} \ , \tag{16}$$

is constant for different values of pressure. This is not true and an alternative method of solving this problem is presented. A derivation of variable mobility for a three-dimensional problem is introduced and the solution found by Godyak is revised. The density profile in this problem is assumed to be a multiplication of two independent radial and axial profiles:

$$n(r,z) = n_Z(z) n_R(r) \ . \tag{17}$$

This leads to a set of differential equations for the normalized potential ($\eta_{r,z} = -\frac{\phi_{r,z}}{k_B T_e}$) in the normalized spatial cordinates $Z = \frac{z}{z_p}$ and $R = \frac{r}{r_p}$

$$2\frac{1}{R}\frac{d\eta_R}{dR} + \frac{d^2\eta_R}{dR^2} - 2\left(\frac{d\eta_R}{dR}\right)^2 - 2\rho\sqrt{\frac{d\eta_R}{dR}} = 0 \tag{18}$$

$$\frac{d^2\eta_Z}{dZ^2} - 2\left(\frac{d\eta_Z}{dZ}\right)^2 - 2\alpha\sqrt{\frac{d\eta_Z}{dZ}} = 0. \tag{19}$$

Here z_p and r_p are length and radius of the neutral part of the plasma, and the constants ρ and α, and these constants are functions of the ionization frequency, the mean free path for charge exchange, r_p and z_p (respectively), the ratio of electron (n_{e0}) to ion (n_{i0}) densities (due to the fact that the considered discharge has multiple ion species) and the Bohm velocity.

Once solved, these equations will provide the spacial dependence of the electrostatic potential and the ratio of edge-to-bulk density can be calculated since by neutrality of the plasma $n_e(r,z) = \sum_j n_i^j(z,r) = \sum_j n_{i0}^j \exp -\eta(z,r)$:

$$h_R = e^{-\eta_R(R=1)} \ ; \quad h_Z = e^{-\eta_Z(Z=1)} \tag{20}$$

3.2 Source terms

A constant flow of input gas (mixture of CH_4 and H_2) is pumped into the reactor in order to create/maintain the discharge. This means that for the particle conservation equation of the gases that make up the input mixture, another term must be added to illustrate this 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 will move through the reactor with a residence time of τ_R given by 2, corresponding to an inital mixture composition given by the partial densities

$$\zeta_{CH_4} = \frac{N_{CH_4}}{N_{n0}} \quad ; \quad \zeta_{H_2} = \frac{N_{H_2}}{N_{n0}} \ .$$

Equation (1) for the gaseous precursors is now written as

$$\frac{\partial N_{i0}}{\partial t} = G_{i0} - L_{i0} - \frac{N_{i0}}{\tau_R} - k^{Trans} N_{i0} + \frac{\zeta_i N_{n0}}{\tau_R} \quad , \quad (21)$$

where i is to be substituted by either CH_4 or H_2.

3.3 Energy density conservation equation

The energy density equation is found by calculating the second moment of the time-dependent Boltzmann equation for the electrons [6]. Considering that the electrons are Maxwellian:

$$\frac{\partial n_e T_e}{\partial t} = \frac{2}{3} \left(p_{in,0} - p_{w,0} - p_{col,0} \right) \quad , \quad (22)$$

where p_{in} represents the input power that is coupled to the electrons, p_{wall} represents the power lost to the walls and p_{col} represents the power lost by electrons due to collisions.
The power coupled $p_{in,0}$ is calculated as an input parameter. Since this is a global model, no spatial distribution is considered and this value is calculated as ratio of input power (P_{input}) to discharge volume (V):

$$p_{in} = \frac{P_{input}}{V}$$

The power lost to the walls $p_{w,0}$ is calculated as

$$p_{w0} = (\epsilon_{\text{plasma}} + \epsilon_{\text{sheath}}) \left(\frac{\partial n_{e0}}{\partial t} \right)_{\text{wall}} \quad . \quad (23)$$

Here $\epsilon_{\text{plasma}} = 2T_e(eV)$ represents the average kinetic energy carried by each electron when it leaves the plasma [1]; $\epsilon_{\text{sheath}} = \frac{T_e(eV)}{2} + V_s$ is the energy lost by each electron that crosses the pre-sheath and the sheath respectively (with $V_s = \frac{T_e}{2} ln \left(\frac{m}{2\pi m_e} \right)$ the space charge potential drop) [1]; 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:

$$\left(\frac{\partial n_{e0}}{\partial t} \right)_{\text{wall}} = \sum_i \left(\frac{\partial N_{i0}}{\partial t} \right)_{\text{wall}} = \sum_i k_i^{\text{Trans}} N_{i0} \quad , \quad (24)$$

The power lost by collisions $p_{coll,0}$ is calculated as

$$\begin{aligned} p_{coll,0} &= p_{el,0} + p_{inel,0} \\ p_{el,0} &= \sum_i n_{e0} \nu_{i0}^{el} 3 T_e \frac{m_e}{m_i} \\ p_{inel,0} &= \sum_i n_{e0} \epsilon_i \nu_{i0} \quad . \end{aligned} \quad (25)$$

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

Quasineutrality condition

To close the problem a quasineutrality condition is assumed for the plasma and thus the electron density n_e can be calculated as:

$$n_e = \sum_i N_i^{ion} \quad , \quad (26)$$

where N_i^{ion} is the volume averaged density of ion i.

3 Kinetic Scheme

A kinetic scheme following [11] for H_2 and [12, 13] for CH_4, was introduced. A total of 162 reactions between 45 unique plasma species are included and separated into 9 different types of reactions

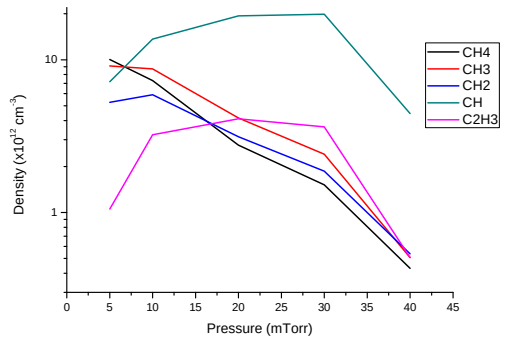
- Dissociation by electron impact,
- ionization/attachment by electron impact,
- neutral-neutral reactions,
- ion-neutral reactions,
- electron recombination reactions,
- proton ionization reactions,
- elastic collisions by electron impact,
- wall reactions for neutrals,
- wall reactions for ions.

4 Results and discussion

The code that was produced solves the time-dependent equations discussed earlier. The studies made were only for the steady-state results by changing the different operating parameters.

Variation with the pressure

The discharge is simulatedfor pressures ranging from 5 to 40 mTorr. The densities of the most relevant species are presented in the figure 2:



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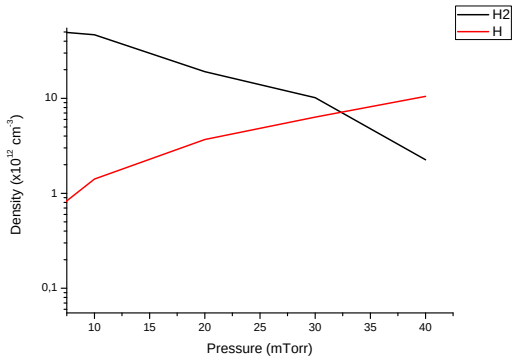

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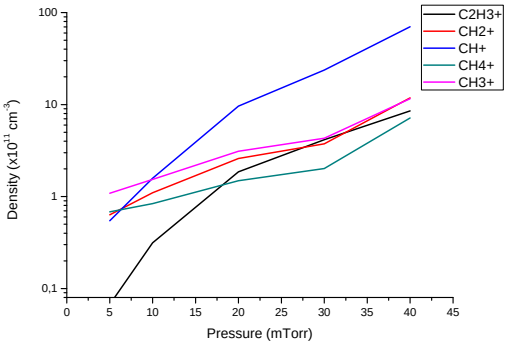

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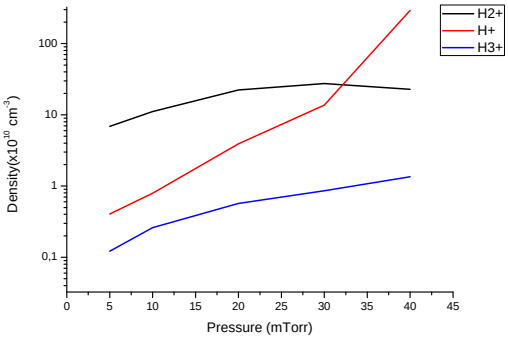

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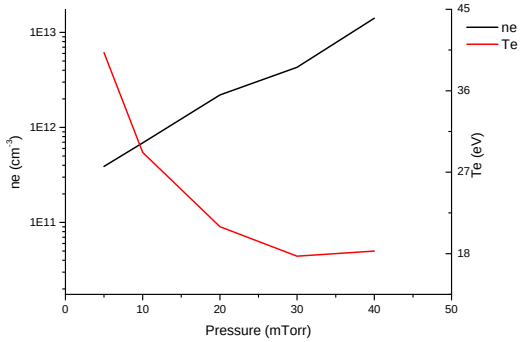
Figure 2: Variation with the pressure of the relevant plasma species.

The electron temperature and density are presented in figure 3 as well as the dissociation degree of the precursor species.



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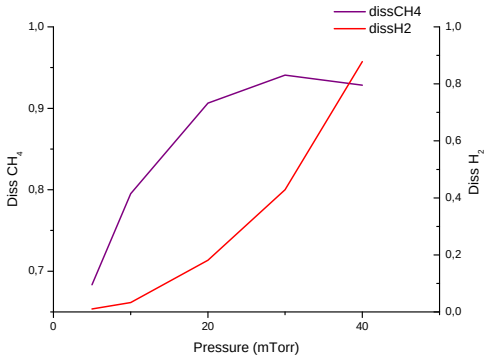


(b)

Figure 3: Variation with the pressure of n_e and T_e (a) and dissociation degree of both precursor species (b)

Observation of these figures show that the densities of hydrocarbon neutral species decreases with the pressure, with the exception of CH (the dominant species) and C_2H_3, whose densities increase with p at lower pressures. Also, the density of 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 δ_{CH_4} and δ_{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 δ_{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 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_2^+ and H^+ contrary to what is usually observed in the H_2 kinetics. This result can be associated with an enhanced in-

fluence 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.

Variation with the power

The discharge is simulated for powers ranging from 100 to 1000 W and the following conclusions can be taken.

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 δ_{CH_4} and δ_{H_2}.

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

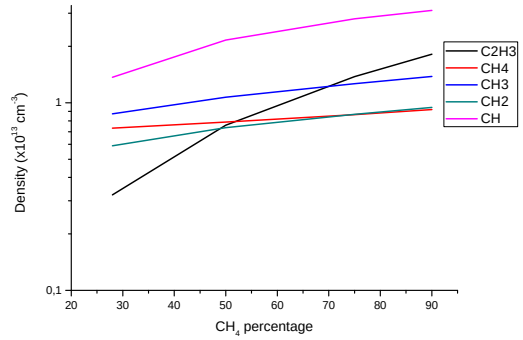
The increase in power will also directly affect the electrons due to an increase of ionization

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 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.

Variation with the initial gas composition

The discharge constitution is the measure of how much of each of the precursor species is present in the neutral gas. In the graphical representations the percentage of CH_4 (ζ_{CH_4}) will vary but since $\zeta_{CH_4} + \zeta_{H_2} = 1$, the hydrogen percentage will also vary. The density of the most relevant species is represented in figure 4.



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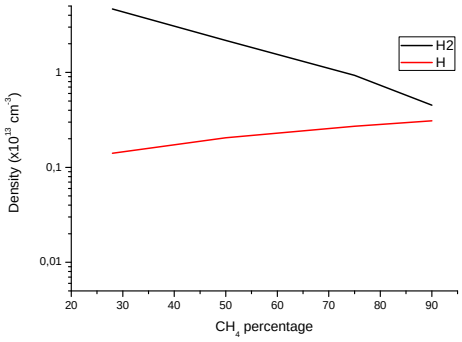

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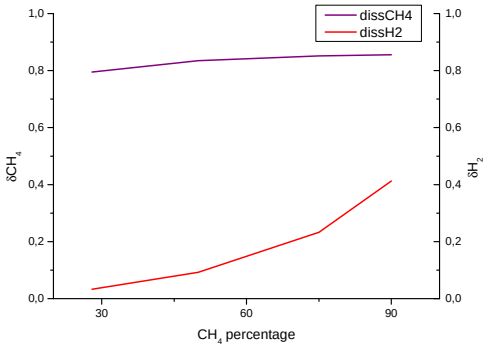

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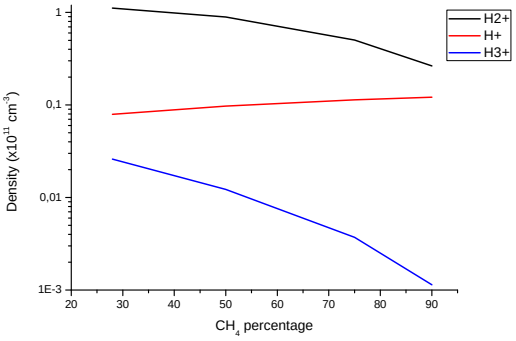

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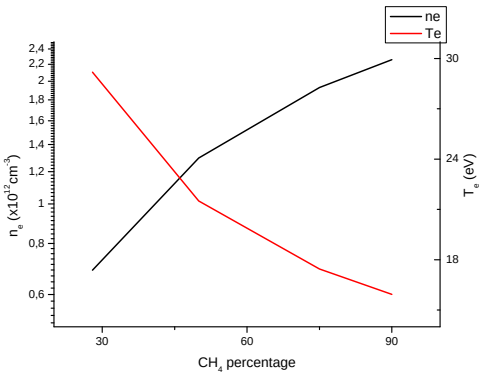
Figure 4: Densities of the relevant plasma species as a function of the initial percentage of CH_4 in the discharge.

Electron temperature and density as well as dissociation

degree of both precursor species is presented in figure 5



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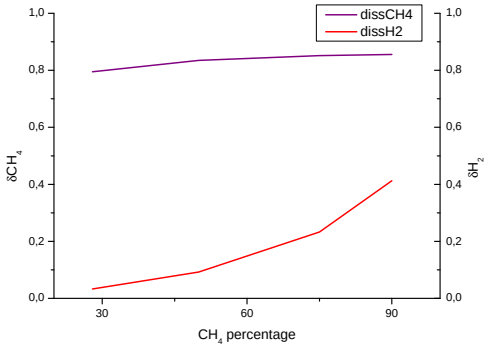

(b)

Figure 5: Electron density and temperature (a) and dissociation degree of the precursor species (b) as a function of the initial percentage of CH_4 in the discharge.

Observation of these figures show that with the introduction of more CH_4 (less H_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_2 molecules and the H_2^+ and H_3^+ ions.
Also, the densities of the H atoms and ions increase slightly as the inital concentration of CH_4 (H_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 5 (b). Note, however, that the dissociation degree of CH_4 remains approximately constant with the increase in the initial concentration of methane (see figure 5 (b)), which may indicate that H_2 is being directly used in the production of heavier species (such as C_2H_3, see figure 4 (a)) as ζ_{CH_4} increases.
The electron density increases with the inital concentration of CH_4 in the discharge, similarly to what is observed for the densitites 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).

5 Conclusions and future work

5.1 Conclusions

A CRM code to simulate a discharge with CH_4-H_2 mixtures was developed capable of providing results for the different work parameters discussed in the previous section.
A revision of the charged species transport is made and a set of differential equations is introduced to calculate the electrostatic field of the plasma in its neutral region and ultimately the edge-to-center density ratio of charged species and electrons.
Results for different input values were obtained. Experimental results, however, were not taken in the same place this code intends to model, so no direct comparison can be made between the experimental values and the simulation values.

5.2 Future work

5.2.1 Electron temperature

The unusually high electron temperatures calculated suggest that there may be other energy transfer mechnisms that are not considered in the model. One possibility is that, since working pressures are low and the and subsequent electric fields are high, the energy acquired by the ions and released at the walls should be considered in the energy conservation equation [14]. 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

5.2.2 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 successfuly calculate the wall recombination/reassociation rates for each neutral/ion.

5.2.3 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.

5.2.4 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 multicomponent diffusion theory should be used to describe the transport of neutral species in the plasma.

5.2.5 EEDF

In this work, 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.

5.2.6 Transient analysis

The results of this work 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.

5.2.7 Negative ions

The model can be completed with the inclusion of negative ions, resulting from attachment reactions with CH_4.

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