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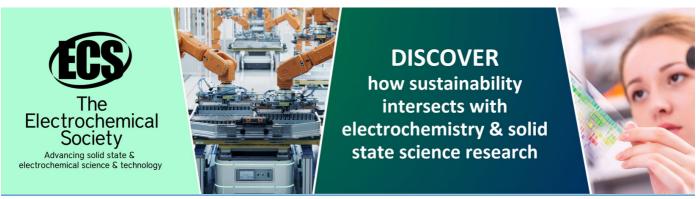
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Study on reaction rates for 2T SF₆ plasma: application to chemical kinetics of a decaying arc in high voltage circuit breakers

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Abstract. This work is devoted to the study and comparison of theories to calculate densities of chemical species in a SF₆ plasma in thermal non equilibrium conditions. The limits of the 2T law of mass action are shown. Then, the reaction rates are studied for several types of processes and they are implemented in a chemical kinetic model to access the composition of the plasma. Finally, a comparison with the densities obtained with the law of mass action is performed and the results are discussed.

1. Introduction

Design and improvement of High-Voltage Circuit Breakers (HVCB) need magneto-hydrodynamic models to understand the properties of electrical arcs [1]. However, these models are dependent on fundamental properties such as thermodynamic properties, transport coefficients and radiative properties. The determination of these parameters is well known in the scientific community in the assumption of chemical and thermal equilibrium. But the Local Thermodynamic Equilibrium (LTE) hypothesis is not valid in specific cases: near the electrodes, near the walls and in peripheral areas of the arc where turbulence and pumping phenomena are significant. Moreover, the LTE hypothesis is questionable during the arc decay. The temperature is not high enough so that scattering develops an equilibrium state. In consequence, free electrons have a kinetic temperature (T_e) higher than that of heavy particles (T_h) .

To study this type of discharge, the first step is to determine the particle densities which are necessary to obtain the others properties. There are several theoretical methods to calculate the particles densities. In the literature, we find three main methods that give the same results in LTE but present strong differences if the plasma is not in thermal equilibrium, depending on the initial assumptions [2]:

- Minimization of a thermodynamic potential (Gibbs'free enthalpy for plasma at constant pressure or Helmholtz's free energy at constant volume) [3]. This method is not easy to generalize to non-thermal conditions because it is based on thermodynamic laws (LTE implicitly assumed).
- Law of mass action (LMA) coupled with a set of equations for the conservation of pressure, electrical charge and mixture proportions [4]. The LMA is convenient to get the composition at

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chemical equilibrium on complex systems because the necessary data is reduced (only internal partition functions, masses and enthalpies of formation of each species). However, it is based on thermodynamic laws and its extension at 2T is not rigorous. Nevertheless, we will use it in two limit cases in the present work.

- Collisional-radiative (CR) or chemical kinetic (CK) models coupled with an equation for the conservation of pressure [5-6]. These models are based on a set of balance equation and are powerful to access the densities in non-equilibrium conditions. Nevertheless, we need to know the main reactions in the plasma and their reaction rates. In the literature, we found generally only the direct reaction rates. Thus we have to use a relation between reaction rates to determine the inverse reaction rates. At LTE, this relation is reduced to a law of mass action but in non-thermal condition the relation is more complex for some type of reactions involving electrons and heavy particles. We will discuss these relations for different types of reaction.

In the present work, the studied gas is SF₆ (gas most commonly used in HVCB).

2. Internal temperatures

In each model, we need to know the internal partition functions Q_{int}^i for each species i. The method used is exposed in [7]. The partition functions depend on the excitation T_{ex} , vibration T_v and rotation T_r temperatures. Rotation levels have a small gap and are thermalized at T_h by the heavy particle collisions $(T_r = T_h)$. To determine T_{ex} and T_v , we used the method developed by Gleizes $et\ al.$ [8] assuming that internal levels are populated by electronic and heavy particle collisions. These authors propose an expression giving the internal temperature T_{ex} and T_v as function of T_e , T_h , the electron densities n_e and the total densities of heavy particle n_M :

$$T_{ex,v} = -\frac{\Delta E}{k_B} \left[\ln \left(\frac{K \, n_e \, e^{\frac{\Delta E (T_e - T_h)}{k_B T_e T_h}} + n_M}{K \, n_e \, e^{\frac{\Delta E (T_e - T_h)}{k_B T_e T_h}} e^{\frac{\Delta E}{k_B T_e}} + n_M \, e^{\frac{\Delta E}{k_B T_h}} \right) \right]^{-1}$$
(1)

where ΔE is the mean energy of the gap between the vibrational or electronic levels and $K = k_e/k_h$ is the relative importance of the electronic collisions comparing to heavy particle collisions. Gleizes *et al.* give a value of $K = 10^4$ for electronic excitation and we used also this value for vibrational excitation.

This expression has two limit cases:

- If $n_e \gg n_M$, then $T_{ex} = T_e$ and $T_v = T_e$ (case 1). This case is realistic at high temperature when the electron density is significant.
- If $n_e \ll n_M$, then $T_{ex} = T_h$ and $T_v = T_h$ (case 2). This case is realistic at low temperature when the densities of heavy particles is significant.
- If $n_e \approx n_M$, then we used the expression (1) to get the internal temperatures (case 3).

As example, the transition between the case 1 and the case 2 can be observed in the figure 1 for different values of K and ΔE .

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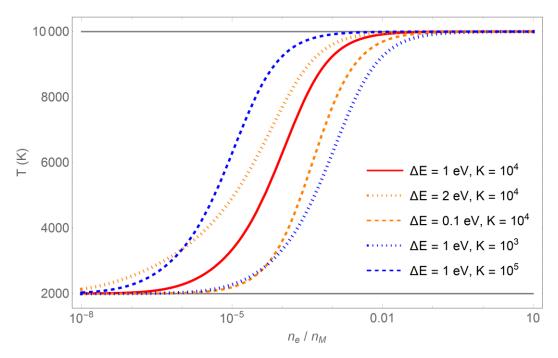


Figure 1. Examples of internal temperatures as a function of densities ratio n_e/n_M with $T_e = 10000$ K and $T_h = 2000$ K. If the electron density is greater than the density of heavy particles, the electronic collisions are dominant and $T_{ex,v} \to T_e$. Conversely, $T_{ex,v} \to T_h$.

3. 2T law of mass action

At LTE, the law of mass action is defined for an elementary reaction $\sum_{i=1}^{N_A} \nu_i A_i (\overrightarrow{\nu_{A_i}}) \overset{k_D}{\rightleftarrows} \sum_{i=1}^{N_B} \mu_i B_i (\overrightarrow{\nu_{B_i}})$ by:

$$\frac{k_{D}}{k_{I}} = \frac{\prod_{i=1}^{N_{B}} n_{B_{i}}^{\mu_{i}}}{\prod_{i=1}^{N_{A}} n_{A_{i}}^{\nu_{i}}} = \frac{\prod_{i=1}^{N_{B}} \left[\left(\frac{2\pi k_{B} m_{B_{i}} T}{h^{2}} \right)^{\frac{3}{2}} Q_{int}^{B_{i}}(T) e^{-\frac{E_{B_{i}}}{k_{B} T}} \right]^{\mu_{i}}}{\prod_{i=1}^{N_{A}} \left[\left(\frac{2\pi k_{B} m_{A_{i}} T}{h^{2}} \right)^{\frac{3}{2}} Q_{int}^{A_{i}}(T) e^{-\frac{E_{A_{i}}}{k_{B} T}} \right]^{\nu_{i}}}$$
(2)

The law of mass action can be generalized empirically at 2T in two opposite cases [7]:

- In the first case, we assumed that electrons are dominant in the plasma. We fixed the temperature of the exponential at T_e and we calculate the internal temperatures at T_e (case 1).

$$\frac{k_{D}}{k_{I}} = \frac{\prod_{i=1}^{N_{B}} n_{B_{i}}^{\mu_{i}}}{\prod_{i=1}^{N_{A}} n_{A_{i}}^{\nu_{i}}} = \frac{\prod_{i=1}^{N_{B}} \left[\left(\frac{2\pi k_{B} m_{B_{i}} T_{B_{i}}}{h^{2}} \right)^{\frac{3}{2}} Q_{int}^{B_{i}} (T_{ex} = T_{e}, T_{v} = T_{e}, T_{r} = T_{h}) e^{-\frac{E_{B_{i}}}{k_{B} T_{e}}} \right]^{\mu_{i}}}{\prod_{i=1}^{N_{A}} \left[\left(\frac{2\pi k_{B} m_{A_{i}} T_{A_{i}}}{h^{2}} \right)^{\frac{3}{2}} Q_{int}^{A_{i}} (T_{ex} = T_{e}, T_{v} = T_{e}, T_{r} = T_{h}) e^{-\frac{E_{A_{i}}}{k_{B} T_{e}}} \right]^{\nu_{i}}}$$
(3)

- In the second case, we assumed that heavy particles are dominant. We fixed the temperature of the exponential at T_h and we calculate the internal temperatures at T_h (case 2).

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$$\frac{k_{D}}{k_{I}} = \frac{\prod_{i=1}^{N_{B}} n_{B_{i}}^{\mu_{i}}}{\prod_{i=1}^{N_{A}} n_{A_{i}}^{\nu_{i}}} = \frac{\prod_{i=1}^{N_{B}} \left[\left(\frac{2\pi k_{B} m_{B_{i}} T_{B_{i}}}{h^{2}} \right)^{\frac{3}{2}} Q_{int}^{B_{i}} (T_{ex} = T_{h}, T_{v} = T_{h}, T_{r} = T_{h}) e^{-\frac{E_{B_{i}}}{k_{B} T_{h}}} \right]^{\mu_{i}}}{\prod_{i=1}^{N_{A}} \left[\left(\frac{2\pi k_{B} m_{A_{i}} T_{A_{i}}}{h^{2}} \right)^{\frac{3}{2}} Q_{int}^{A_{i}} (T_{ex} = T_{h}, T_{v} = T_{h}, T_{r} = T_{h}) e^{-\frac{E_{A_{i}}}{k_{B} T_{h}}} \right]^{\nu_{i}}}$$
(4)

In each case, the temperature in the translational term T_{B_i} or T_{A_i} is equal to T_e if the species i is an electron and T_h if it is a heavy particle.

Obviously, these two cases are arbitrary but they give two limit cases. We can expect that the first case is valid at high temperature where the electron density is high and the second case is valid at low temperature.

In this work, with the LMA method, 43 chemical species (e, S, S⁻, S⁺, S⁺⁺⁺, S⁺⁺⁺⁺, S⁺⁺⁺⁺⁺, S⁺⁺⁺⁺⁺, F, F⁻, F⁺, F⁺⁺⁺, F⁺⁺⁺⁺, F⁺⁺⁺⁺, S₂, S₂⁺, S₂⁻F₂, F₂⁺, SF₃, SF₄⁻, SF₂, SF₂⁺, SF₃, SF₂⁻, SF₃⁻, SF₃⁺, SF₄, SF₄⁺, SF₅, S₆, SF₅⁻, SF₅⁺, S₇, SF₆, SF₆⁻, S₂F₁₀, S₈, liquid and solid sulfur), are considered and the chemical composition is calculated in both cases at atmospheric pressure and for different θ values where $\theta = T_e/T_h$. As examples, the e⁻, F, SF and SF₆ number densities obtained by using the LMA approach are given in figures 2 to 5 for θ values of 2 and 5.

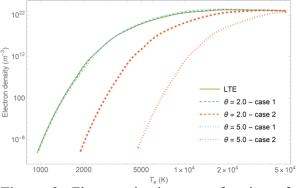
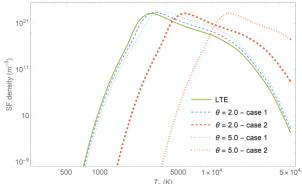
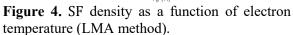


Figure 2. Electron density as a function of electron temperature (LMA method).

Figure 3. F density as a function of electron temperature (LMA method).





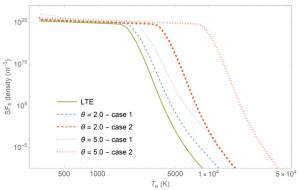


Figure 5. SF₆ density as a function of electron temperature (LMA method).

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4. Chemical kinetic model

 k_D For a reaction (elementary or not) A + B \rightleftarrows C + D where A, B, C and D are any chemical species, the

chemical balance equation for A is given by:

$$\frac{\mathrm{d}n_A}{\mathrm{d}t} = n_C n_D k_I - n_A n_B k_D \tag{5}$$

where k_D and k_I are the direct and inverse reaction rates. They characterize the chemical equilibrium of this reaction:

$$\frac{k_D}{k_I} = K_e = \frac{n_C n_D}{n_A n_B} \tag{6}$$

where K_e is the chemical equilibrium constant.

Snider and Ross [9] have shown that a system at chemical equilibrium is accurately described by the relation (6) in two cases:

- One of reactants is in large excess.
- The relaxation time of the reactions to reach an equilibrium state is high compared to the relaxation time of the translational and internal distributions: $\tau_{reac} \gg \tau_{tr,int}$.

In this work, we assumed that at least one of these conditions is valid. Thus, the reaction rates are given by [10]:

$$k_D = \int \sigma_D(\omega_{A,B}|\omega_{C,D}) \, \mathrm{d}^3\omega_{C,D} \, |\overrightarrow{v_A} - \overrightarrow{v_B}| \, f_A(\overrightarrow{v_A}) \, f_B(\overrightarrow{v_B}) \, \mathrm{d}^3v_A \, \mathrm{d}^3v_B$$
 (7)

$$k_{I} = \int \sigma_{I} \left(\omega_{C,D} | \omega_{A,B} \right) d^{3} \omega_{A,B} | \overrightarrow{v_{C}} - \overrightarrow{v_{D}} | f_{C} (\overrightarrow{v_{C}}) f_{D} (\overrightarrow{v_{D}}) d^{3} v_{C} d^{3} v_{D}$$
 (8)

where σ_D and σ_I are respectively the direct and inverse cross sections, $\overrightarrow{\omega_{A,B}} = \overrightarrow{v_A} - \overrightarrow{v_B}$ and $\overrightarrow{\omega_{C,D}} = \overrightarrow{v_C} - \overrightarrow{v_C}$ $\overrightarrow{v_D}$. $f_i(v_i)$ is the distribution function of velocity of the species i.

1. Relations between reaction rates at 2T

At LTE, electrons and heavy particles are thermalized and their distribution functions are Maxwellian at the temperature T. Using the expressions (7) and (8), we can demonstrate that the ratio k_D/k_I is equal to the law of mass action (2).

If the plasma is in thermal non-equilibrium, then the distribution functions of electrons and heavy particles are different. Therefore, the ratio k_D/k_I depends on whether the reaction involves electrons or heavy particles.

The ionization reactions have been studied by Annaloro et al. [11]. They showed that for electron impact ionization, the relation k_D/k_I is reduced to a law of mass action calculated at T_e following equation (3). On the other hand, for heavy particle impact ionization, they demonstrate that the ratio k_D/k_I depends on both T_e and T_h . We have continued this work for others types of reactions. Details on the method used are exposed in [11].

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2. Electron impact induced dissociation

For an elementary reaction $AB(\overrightarrow{v_{AB}}) + e^{-}(\overrightarrow{v_e}) \rightleftarrows A(\overrightarrow{v_A}) + B(\overrightarrow{v_B}) + e^{-}(\overrightarrow{v_e}')$ and using the definition of reaction rates (7) and (8), we obtain:

$$k_D = \int \sigma_D(\omega_{AB,e} | \omega_{e,A}, \omega_{e,B}) d^3 \omega_{e,A} d^3 \omega_{e,B} \omega_{AB,e} f_{AB}(\overrightarrow{v_{AB}}) f_e(\overrightarrow{v_{AB}}) d^3 v_{AB} d^3 v_e$$
 (9)

$$k_{I} = \int \sigma_{I}(\omega_{e,A}, \omega_{e,B} | \omega_{AB,e}) d^{3}\omega_{AB,e} \omega_{e,A}\omega_{e,B} f_{A}(\overrightarrow{v_{A}}) f_{B}(\overrightarrow{v_{B}}) f_{e}(\overrightarrow{v_{e}}) d^{3}v_{A} d^{3}v_{B} d^{3}v_{e}$$
(10)

If we consider a Maxwellian distribution f at T_e for electrons and T_h for heavy particles, using the energy conservation and a detailed balance relation [12], we can demonstrate that:

$$\frac{k_D}{k_I} = \frac{Q_{int}^A Q_{int}^B}{Q_{int}^{AB}} \left(\frac{2\pi k_B T_h}{h^2} \frac{m_A m_B}{m_A + m_B}\right)^{\frac{3}{2}} e^{-\frac{E_{diss}}{k_B T_h}} \frac{\int_0^\infty \sigma_D^{tot}(E) E e^{-\frac{E}{k_B T_e}} dE}{\int_0^\infty \sigma_D^{tot}(E) E e^{-\frac{E}{k_B T_h}} dE}$$
(11)

In the case of this reaction, the relation between direct and reverse reaction rates does not correspond to a law of mass action.

To access a general expression that is not depending on the specific cross section of the reaction, we used an approximate form for the cross section. The cross sections of dissociation can be approximated by an energy-dependent linear function with a threshold [13]:

$$\sigma_D^{tot}(E) = \begin{cases} 0 & \text{si } E < E_s \\ \alpha(E - E_s) & \text{si } E \ge E_s \end{cases}$$
 (12)

where E_s is the threshold energy of reaction. The integral terms of (11) is then equal to:

$$\frac{\int_{0}^{\infty} \sigma_{D}^{tot}(E) E e^{-\frac{E}{k_{B}T_{e}}} dE}{\int_{0}^{\infty} \sigma_{D}^{tot}(E) E e^{-\frac{E}{k_{B}T_{h}}} dE} = \frac{\theta^{3} e^{\frac{(\theta-1)E_{S}}{k_{B}T_{e}}} (E_{S} + 2k_{B}T_{e})}{\theta E_{S} + 2k_{B}T_{e}}$$
(13)

We found also in the literature the following shape of cross section for dissociation mechanisms:

$$\sigma_D^{tot}(E) = \begin{cases} 0 & \text{si } E < E_s \\ \frac{\sigma_0 \ln(E/E_s)}{E/E_s} & \text{si } E \ge E_s \end{cases}$$
 (14)

In this case, the integral term is equal to:

$$\frac{\int_0^\infty \sigma_D^{tot}(E) E e^{-\frac{E}{k_B T_e}} dE}{\int_0^\infty \sigma_D^{tot}(E) E e^{-\frac{E}{k_B T_e}} dE} = \frac{\int_{E_S}^\infty ln(E/E_S) e^{-\frac{E}{k_B T_e}} dE}{\int_{E_S}^\infty ln(E/E_S) e^{-\frac{\theta E}{k_B T_e}} dE} = \frac{\theta \Gamma\left(0, \frac{E_S}{k_B T_e}\right)}{\Gamma\left(0, \frac{\theta E_S}{k_B T_e}\right)} \tag{15}$$

where $\Gamma(a, z)$ is the incomplete gamma function defined as:

$$\Gamma(a,z) = \int_{z}^{\infty} t^{a-1}e^{-t}dt \tag{16}$$

The figure 6 shows the ratio of integral terms in equation (11) for different profiles of cross sections.

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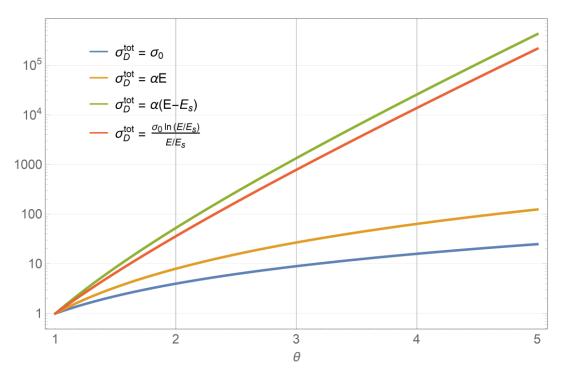


Figure 6. Amplitude of the ratio of the integral terms in equation (11) as a function of the ratio $\theta = T_e/T_h$ for several profiles of cross sections with $T_e = 5000$ K, $E_s = 1$ eV and $\alpha = 1$ m²eV⁻¹. For low θ , the integral term can be neglected but it becomes significant when θ increases.

In this work, we finally used the following relation for the calculation of the reverse reaction rate in the case of electron impact dissociation:

$$\frac{k_D}{k_I} = \frac{Q_{int}^A Q_{int}^B}{Q_{int}^{AB}} \left(\frac{2\pi k_B T_h}{h^2} \frac{m_A m_B}{m_A + m_B}\right)^{\frac{3}{2}} e^{-\frac{E_{diss}}{k_B T_h}} \frac{\theta^3 e^{\frac{(\theta - 1)E_s}{k_B T_e}} (E_s + 2k_B T_e)}{\theta E_s + 2k_B T_e}$$
(17)

3. Non elementary reactions

In the writing of the ratio k_D/k_I , we used a detailed balance to remove σ_I from the expression and simplify it. But some non-elementary reactions cannot be described by a simple detailed balance, that limits our method.

However, for these complex chemical reactions, the following assumptions were adopted for the calculation of reverse reaction rate:

- AB + CD

 AC + BD

 This reaction depends only on heavy particle at T_h. We assume that it is described by the law of mass action (4).
- $e^- + A \rightleftharpoons B^+ + C + D + \cdots + e^- + e^-$ (ex: $e^- + SF_6 \rightleftarrows F^+ + SF_4 + F + e^- + e^-$)
 The inverse reaction is slowed by the heavy particles. Therefore, we assumed that this reaction is described by the law of mass action (4).

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Table 1. Summary of rules for the relation between direct and inverse reaction rates and the temperature used to calculate the direct reaction rates.

Reaction	Type	k_D/k_I	$k_D(T_i)$
$AB + M \rightleftharpoons A + B + M$	Elementary	LMA at T_h	T_h
$A^- + M \rightleftharpoons A + e^- + M$	Elementary	LMA at T_h	T_h
$A + e^- + e^- \rightleftarrows A^- + e^-$	Elementary	LMA at T_e	T_e
$A + e^- \rightleftarrows A^+ + e^- + e^-$	Elementary	LMA at T_e	T_e
$AB + CD \rightleftharpoons AC + BD$	Non elementary	LMA at T_h	T_h
$A^+ + B \rightleftharpoons A + B^+$	Elementary	LMA at T_h	T_h
$AB + e^- \rightleftarrows A + B + e^-$	Elementary	Eq. (17)	T_e
$e^- + A \rightleftharpoons B + C + D + \cdots + e^-$	Elementary	Eq. (17) generalized	T_e
$e^{-} + A \rightleftharpoons B^{+} + C + D + \dots + e^{-} + e^{-}$	Non elementary	LMA at T_h	T_e

5. Results and discussion

A bibliographic survey has been performed to build a database of direct reaction rate coefficients. Most of them comes from the work of Haidar *et al.* [14] who gives a lot of reaction rate coefficients for a SF₆-C₂F₄ plasmas. We have completed this list with reaction rate coefficients given by Girard *et al.* [15] for pure SF₆ and the work of Lennon *et al.* [16] for the reaction rates of ionization. We found sometimes two different reaction rate coefficients for the same reaction. In this case, we chose those given by Haidar *et al.* [14] that are based on the more recent work of Christophorou and Olthoff [17].

Finally, for a pure SF_6 plasma, we have a set of 53 chemical reactions and 19 chemical species (e⁻, S, S⁻ S⁺, S⁺⁺⁺, F, F⁻, F⁺, F⁺⁺⁺, F₂, F₂, SF, SF₂, SF₃, SF₄, SF₅, SF₆). To solve the resulting 19 balance equations system, we used the subroutine DVODE library [18].

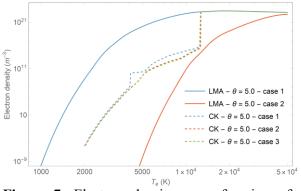


Figure 7. Electron density as a function of electron temperature (CK model).

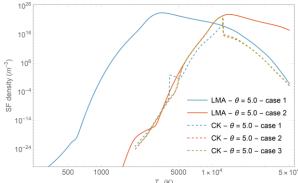


Figure 8. SF density as a function of electron temperature (CK model).

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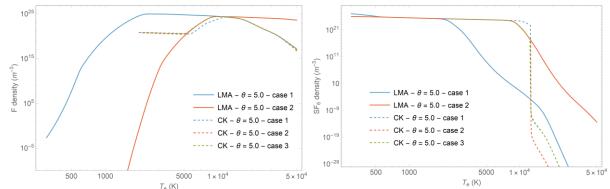


Figure 9. F density as a function of electron temperature (CK model).

Figure 10. SF₆ density as a function of electron temperature (CK model).

As examples, the number densities of the e^- , F, SF and SF₆ obtained with the CK model (for a pure SF₆ plasma at atmospheric pressure and for a ratio $\theta = 5$) are presented in figures 7 to 10. These results are compared in these figures with those obtained with the LMA method in cases 1 et 2.

With the CK model, we observed a sharp transition between both cases 1 and 2 of the LMA. As expected, we can conclude that the LMA taken in case 1 is accurate for high temperatures and in case 2 for low temperatures. On the other hand, there is an intermediate range of temperature where the LMA is not exact and the CK model is thus necessary to calculate an accurate chemical composition in this temperature range.

6. Conclusion

We performed a comparison between law of mass action and chemical kinetic model to calculate the chemical composition of a SF₆ plasma in non-thermal equilibrium condition.

At high temperatures, the reactions of ionization are preponderant. In this condition, the plasma is described by a law of mass action calculated at T_e . Conversely, at low temperature, the heavy particles processes are dominant and the plasma is described by a law of mass action at T_h .

The case of intermediate temperatures is more complex because the electrons and the heavy particles are competing with each other. The chemical kinetic model is thus necessary in this temperatures interval but it requires a study of the relations between direct and inverse reaction rates. We demonstrated that for some elementary reactions, this relation is not always equivalent to a law of mass action. Nevertheless, some complex reactions studied cannot be described by a detailed balance equation and the relation k_D/k_I for these non-elementary reactions is still an open question.

7. References

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