doi:10.14311/ppt.2020.3.52
Plasma Physics and Technology **7**(3):52–58, 2020

0D KINETIC MODEL: APPLICATION TO SF_6

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Abstract. This work is related to the chemical kinetics modelling of plasma during extinction. A zero-dimensional model (0D) has been developed. Two hypotheses were used: (A) a constant pressure or (B) a constant mass density. Three initial data categories are generally required for the model: (1) the chemical reactions that govern the kinetic scheme, (2) the chemical composition at the local thermodynamic equilibrium (LTE) and (3) a law of temperature decay as a function of time representing the cooling rate. The developed model is presented and applied to SF_6, gas commonly used in high voltage circuit breakers (HVCB), in order to be validated. We present the evolution of the species during the temperature decay for several cooling rates. The results give the evolution of species densities and the departures from equilibrium according to the cooling rate. Consideration of SF_x molecules is essential in order to avoid erroneous interpretations.

Keywords: chemical kinetic, 0D model, constant pressure, constant mass density, chemical composition, SF_6.

1. Introduction

The study of chemical kinetics is essential in order to know the evolution of the species, the predominant reactions or even the differences that may exist in relation to the Local Thermodynamic Equilibrium (LTE) hypothesis. These deviations depend on the initial and operating conditions such as pressure, temperature, gases involved or the cooling rate. For example, in combustion engine [1, 2], the focus will be on the OH radical to describe the combustion front [3]. In applications related to the treatment of iron and steel industry gases, attention will be paid to the species present and the NO_x produced. Finally, in switching devices such as High Voltage Circuit Breakers (HVCB), the main interest is in the electronic densities present during the transition by the current zero in order to study the evolution of conductance as a function of time and the dielectric recovery [4]. In this last example the gas is mostly SF_6, although new filling gases are being studied [5, 6] in order to find alternative gases less harmful to the environment. In the literature, we looked at existing transient 0D kinetic models and found interesting results allowing us to compare our results for the validation of our model. These studies were applied to SF_6 gas under constant pressure [7–10]. Nevertheless, for some applications the assumption of a constant mass density seems more appropriated. A 0D model was then developed and is based on the resolution of the species conservation equations. It makes possible to carry out a calculation under the hypothesis of a constant pressure as this can be seen in the literature [7–11], or to consider a given mass density for the representativeness of an evolution in a closed medium. In this study, we present first the basic equations of the kinetic model and the methods used for the resolution. Secondly, a comparison of our results at constant pressure with the literature works is presented. The influence of the pressure and species considered is then shown on the chemical departure from equilibrium. The temperature ranges considered are chosen to be able to compare ours results with the results from the littertaure under the assumption of a constant pressure. Finally, on the same tempertaure ranges, we present the results of the 0D model with the assumption of a constant mass density for several cooling speeds. Two values of the constant mass density are considered corresponding to the tempertaures of 12 kK and 5kK. These two tempertaures values have been chosen arbitrary in the tempertaure range studied by Borge et al [9]. In thermal plasma created by electric arc like in HVCB the temperature is close to few ten thousand kelvin, so the temperature 12 kK is representative to the plasma core, as tempertaure of 5 kK is representative of an intermediate temperature close to current zero where a recovery voltage can occur. At this tempertaure, depending on the colling rate the electronic density can lead to residual electrical conductivity and so to a shutdown failure.

2. Theory

The kinetic study of a gas requires various preliminary data: the kinetic scheme containing chemical reactions of species involved in the plasma, the chemical composition at LTE, and a temperature variation, calculated or given by a law. For these data, we first relied on the work of the literature [9] in order to validate our model under the hypothesis of a constant pressure considering SF_6 gas.

2.1. Kinetic scheme Reverse rate

The chemical reactions of kinetic scheme are mainly involved in determining the rates of species creation and disappearance. These chemical reactions can be written in the form of:

$$\left[\sum_{j=1}^{N} A_j^l \underset{k_i^l}{\overset{k_d^l}{\rightleftharpoons}} \sum_{j=1}^{N^*} B_j^l\right]_{l=1}^{M} \tag{1}$$

where M represents the number of reactions, N and N^* the number of species involved in each side of the reaction l, N may be equal to or different from N^*, k_d^l and k_i^l direct and reverse reaction rates respectively, A_j^l and B_j^l the symbols of the chemical species associated with their respective concentrations. The development of the kinetic scheme depends on considered species, and on the availability of chemical reactions and data in the literature for the calculation of reaction rates. In the majority of cases, only the direct reaction rate is known for a chemical reaction [4, 9, 12]. In order to evaluate the rate of reverse reaction k_i, we based on the principle of micro-reversibility under the hypothesis of LTE [4, 9]. This allows us to write the inverse rate from equation (1):

$$k_i = \frac{\prod_{j=1}^{N} n_{A_j}}{\prod_{j=1}^{N^*} n_{B_j}}.k_d, \tag{2}$$

where n_{A_j} and n_{B_j} are the species concentration involved in the reaction. The kinetic scheme in this study involves a total of 19 species and 66 chemical reactions [9]. Direct reaction rates are evaluated from the literature [4, 9, 13].

For the determination of reverse reaction rates, species densities at LTE come from a "homemade" code developed in our team, whether for a pressure, or a given mass density [14]. For two arbitrary density values of 0.01887 and 0.05022 kg.m^{-3} which correspond to temperatures of 12 kK and 5 kK taken at 1 bar respectively, the chemical compositions of SF_6 are shown in Figure 1 for a temperature range of 300 K to 12 kK. Plasma is mainly governed by neutral species, including molecules below 2 kK and then neutral atoms beyond 12 kK. In this temperature range, charged species are present but not predominant.

2.2. Collisional radiative term and time step

The source term S_i of the species conservation equation (3) represents the collisional-radiative term:

$$\frac{\partial n_i}{\partial t} + \vec{\nabla}(n_i.\vec{v}_i) = S_i \tag{3}$$

with n_i the density of the species, t the time and v_i the velocity of the species. The source term is the difference between the number of particles created Ca_i and disappeared $n_i.Da_i$ per unit of volume and time.

$$S_i = \left(\frac{\partial n_i}{\partial t}\right)_{C.R.} = Ca_i - n_i.Da_i \tag{4}$$

The expressions of Ca_i and $n_i.Da_i$ of species i, are obtained from the set of chemical reactions of the kinetic scheme involving species densities and reaction rates (k_d and k_i). Their equations can be written as follows:

$$Ca_i = \sum_{l=1}^{M} \left(\nu_i^l.k^l.\prod_{\substack{j=1\\ i\in j}}^{N} n_j^l\right), \tag{5}$$

$$n_i.Da_i = \sum_{l=1}^{M} \left(k^l.\prod_{\substack{j=1\\ i\in j}}^{N} n_j^l\right), \tag{6}$$

where ν_i^l is the stoichiometric coefficient of the species i which has been created, and k^l a direct or reverse reaction rate depending on the direction of creation or disappearance of the species. This set of equations (1) to (6) is identical to the formulation proposed by Tanaka el al [15]. For example, considering the two chemical reactions:

$$S^+ + e^- + e^- \underset{k_{i_1}}{\overset{k_{d_1}}{\rightleftharpoons}} S + e^-, \tag{7}$$

$$F + e^- \underset{k_{i_2}}{\overset{k_{d_2}}{\rightleftharpoons}} F^+ + e^- + e^-. \tag{8}$$

The collisional-radiative term of the electron is:

$$\begin{aligned}[Ca - n.Da]_{\mathrm{e}^-} = 2[(&k_{i_1}.n_{\mathrm{S}}.n_{\mathrm{e}^-} + k_{d_2}.n_{\mathrm{F}}.n_{\mathrm{e}^-})\\ &-n_{e^-}(k_{d_1}.n_{\mathrm{S}^+} + k_{i_2}.n_{\mathrm{F}^+}.n_{\mathrm{e}^-})].\end{aligned} \tag{9}$$

From the steady state Da_i reaction frequency, we can determine the relaxation time τ_i of each species which will allow us to estimate the optimal time step for the model. This relaxation time corresponds to a quantity which roughly reflects the time interval at the end of which the density of a species deviates from its value. It is given by the following relationship:

$$\tau_i = \frac{1}{Da_i}. \tag{10}$$

For a given plasma, this time may differ by several orders of magnitude for each species as shown in Figure 2 for SF_6 at a constant mass density of 0.05022 kg.m^{-3}. The time step of the transient model should then focus on the smallest relaxation time of all the species present in the temperature range studied. However, if the density of a species is negligible over a temperature interval, whereas it has a preponderant reaction rate, its relaxation time can be ignored and its density can be considered as unchanged.

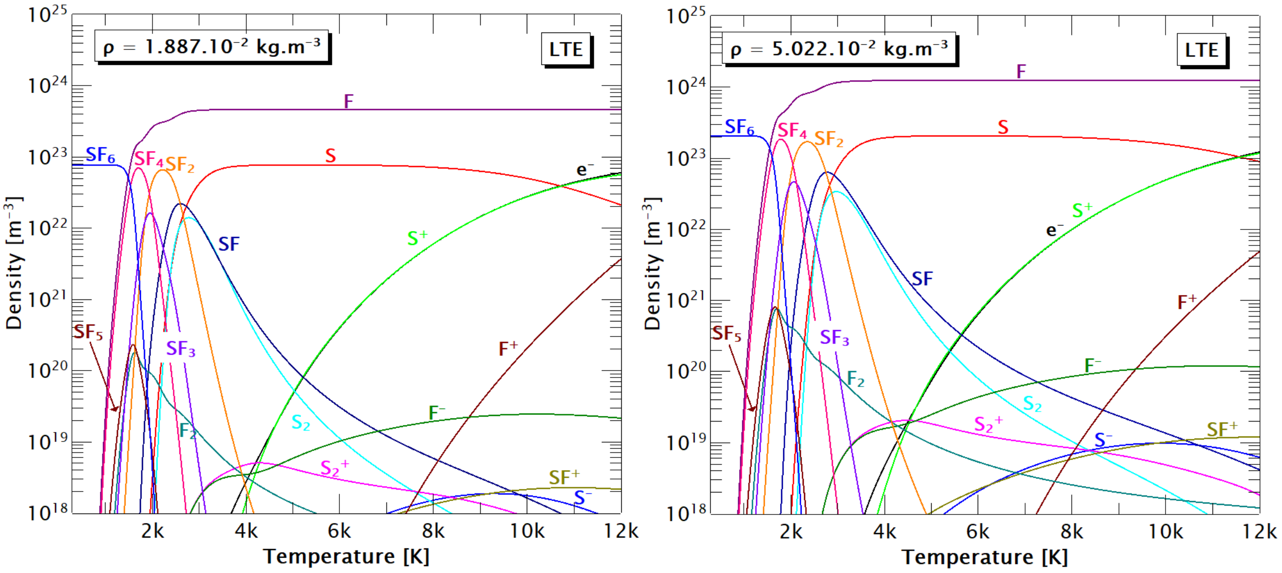

Figure 1. Chemical compositions of SF_6 at LTE for two constant values of the mass density 0.01887 kg.m^{-3} and 0.05022 kg.m^{-3} calculated by our "homemade" software [14].

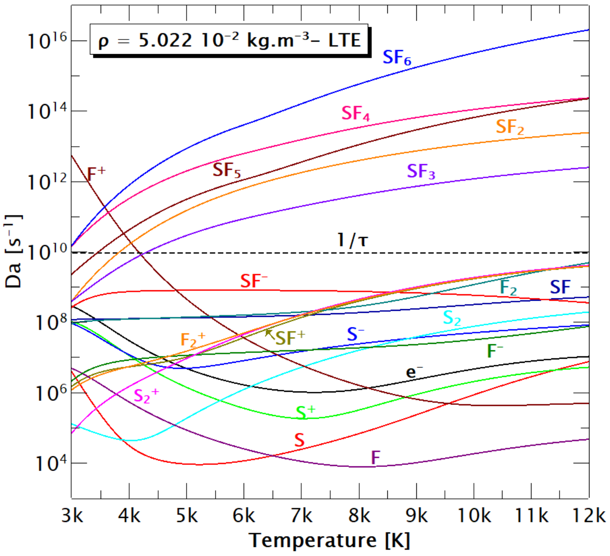

Figure 2. Disappearance frequency of SF_6 - 3 kK to 12 kK. $\rho = 0.05022\,kg.m^{-3}$ – LTE.

2.3. 0D model

The base of the chemical kinetics model consists to solve the species conservation equation (3). In 0D the convective term is generally neglected. So, the densities evolution depends mainly on the collisional-radiative term involved in the chemical reactions.

☐ Case of constant pressure: During the arc cooling, the pressure of the medium decreases, due to recombination processes. As the plasma evolves at constant pressure, two corrective terms are then added in the conservation equation of the species to compensate the pressure drop. These terms implicitly correspond to the consideration of convection by an additional contribution of particle [7–9]. The equation to be solved is then written:

$$\frac{\partial n_i}{\partial t} = \left(\frac{\partial n_i}{\partial t}\right)_{C.R.} - \frac{n_i k_b T}{P}\sum_{j=1}^{N}\left(\frac{\partial n_j}{\partial t}\right)_{C.R.} - \frac{n_i}{T}\left(\frac{\partial T}{\partial t}\right)_{P} \tag{11}$$

With k_b the Boltzmann constant, P the pressure of the chemical composition at LTE, $\sum_{j=1}^{N}(\partial n_j/\partial t)_{C.R.}$ the sum of collisional-radiative terms of all species, and $(\partial T/\partial t)$ the temporal temperature variation.

☐ Case of a constant mass density: The assumption of a constant density corresponds to configuration in a closed tank. The pressure then varies with the evolution of the species in the plasma during cooling. The species conservation equation is then written:

$$\frac{\partial n_i}{\partial t} = \left(\frac{\partial n_i}{\partial t}\right)_{C.R.} \tag{12}$$

In order to satisfy plasma neutrality, the following electric charge conservation law is integrated in the system with equation (11) or equation (12) depending on the hypothesis of the study.

$$\sum_{i=1}^{N} Z_i.n_i = 0 \tag{13}$$

Z_i represents the charge of the specie i. In the literature, the species conservation equation (11) in 0D model is solved from a suitable sub-program for differential stiff equations, and guided by the analysis of the "Chemeq" chemical reaction system [8–10]. In our developments, resolutions are carried out according to implicit Euler method.

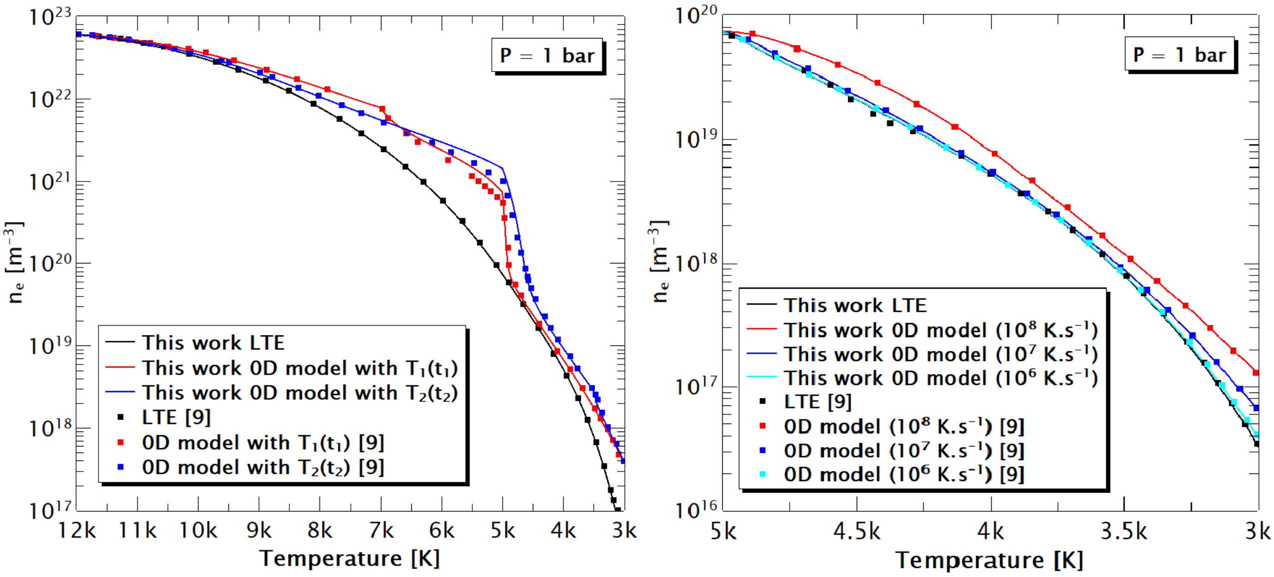

Figure 3. Evolution of electron density. The cooling rates are given in Table 1 depending on the temperatures ranges

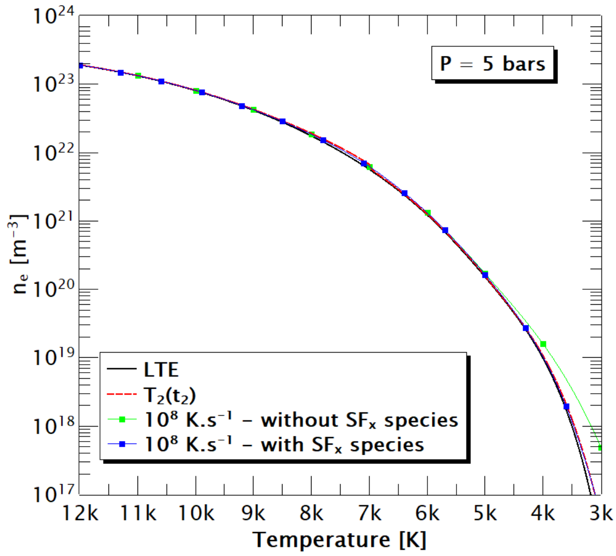

Figure 4. Evolution of electron density for a cooling rate equal to 10^8 $K.s^{-1}$ with and without taking into account SF_x species. $P = 5$ bars.

3. Results and Discussion

We present the evolution of the electronic density of the SF_6 plasma linked to the electrical conduction in the arcs of HVCB [8] and so to its breaking power when passing through the current zero. To validate our developments, the results of the constant pressure case are compared with the work of Borge [9] for different cooling speeds. The input parameters of [9] are used for the calculations, they are given in Table 1. The first column presents the species considered and the second one the cooling rates following the tempertaure ranges. These cooling rates of course strongly affect the results, they are chosen in order to be able to validate the results obtained with the model that we have developped with them obtained by the commercial software Chemkin used by Borge et al [9].

The time step considered was estimated from equation (10). As it can be seen in Figure 2, the SF_x molecules and the F^+ ion have more higher reaction rates disappearance ($Da > 10^{10}\,s^{-1}$) than other species. However, densities of these species are minority in the temperature range (3 kK< T <12 kK) of this study (Figure 1). This allows us to consider that these densities have not changed in time and can be assumed at equilibrium depending only on their tempertaure. Thus, the chosen time step is equal to $\Delta t = 10^{-10}$ s. This time step is legitimate for a given mass density of less than 0.2 kg.m^{-3} and a given pressure of less than 10 bars for a temperature between 3 kK and 12 kK.

☐ Case of constant pressure: The electronic densities at LTE and those obtained by the model 0D for a pressure of 1 bar according to the conditions of Table 1 are shown in Figure 3 and compared with the literature [9]. The calculations were initialized from the chemical composition at LTE for a temperature of 12 kK or 5 kK depending on the case. We note the influence of the cooling rate on the behavior of electronic density. When the temperature decreases slowly, n_e evolves similar to equilibrium. This means that the charged species responsible for the disappearance of the electrons evolve close to their equilibrium values, allowing the chemical reactions to satisfy the micro-reversibility.

Figure 3 (left side) shows the evolution of the electronic density using the first parameters of Table 1. SF_x molecules were not considered in this calculation. According to Borge [9], they would have only a minimal influence on the behavior of electrons. We observe the beginning of departure that appears around 10 kK, and passes through a

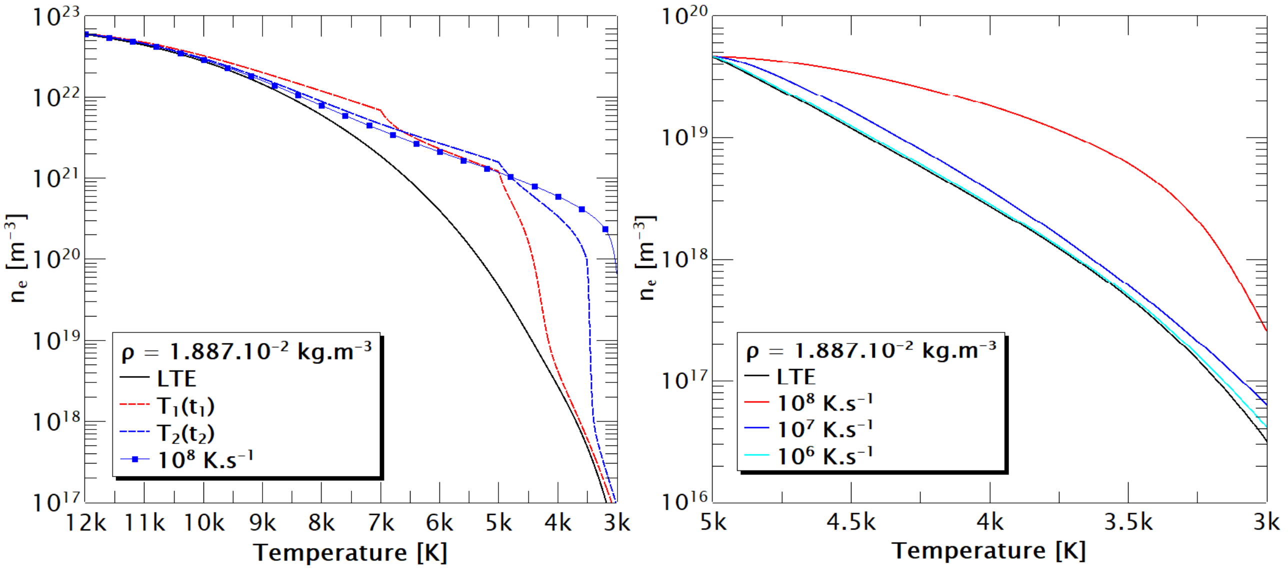

Figure 5. Evolution of electron density for several cooling rates given Table 1. $\rho = 0.01887\,kg.m^{-3}$.

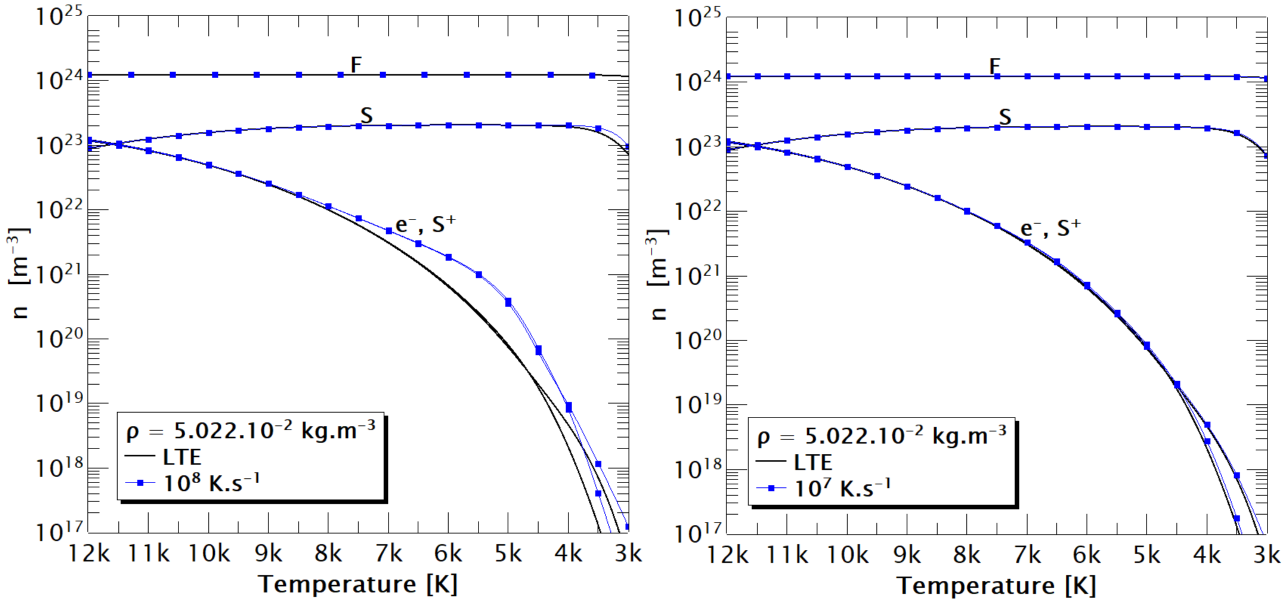

Figure 6. Evolution of F, S, S^+ *and* e^- *densities for two cooling rates* $10^8\,K.s^{-1}$ *(left side) and* $10^7\,K.s^{-1}$ *(right side).* $\rho = 0.05022\,kg.m^{-3}$.

maximum of 5 kK for the two temperature profiles $T_1(t_1)$ and $T_2(t_2)$. The departure from equilibrium subsequently decreases with the reduction in cooling speed. For each change in temperature slope as a function of time, the electronic density shows a more or less marked variation. In Figure 3 (Right side), linear temperature decay over time values are used for a temperature range of 5 kK to 3 kK, and taking now into account SF_x molecular species (Table 1). We can see that for a cooling rate value of 10^6 K.s^{-1}, the departure from equilibrium becomes negligible. According to the literature, electronic density differences in a SF_6 plasma at equilibrium should be smaller above a pressure of 4 bar [9].

Figure 4 shows the evolution of n_e for 5 bars over the temperature range from 12 kK to 3 kK. Temperature profiles $T_2(t_2)$ (Table 1) derived from an experimental measurement [7] and a typical thermal plasma cooling rate value of 10^8 K.s^{-1} [8] are used. Superposition of the electronic density curves of the 0D model and those considering LTE can be observed. However, when SF_x molecules are neglected, the evolution of n_e from a cooling rate 10^8 K.s^{-1} deviates from the equilibrium for a temperature of less than 4.5 kK. At higher pressures, species transformation processes are shifted to higher temperature, which involve the presence of molecular species. It is therefore essential to consider these molecules in order to avoid having erroneous results that will lead to misinterpretations. On the results presented for a pressure of 1 bar, we are in good agreement with those of the literature. The slight

Species	T(t)
$e^-,\ S,\ S^+,\ S^-,\ S_2,\ S_2^+,\ F,\ F^-,\ F^+,$ $F_2,\ F_2^+,\ SF,\ SF^-,\ SF^+$	$T_1(t_1)\begin{cases} \frac{\partial T}{\partial t}=-5.10^8 K.s^{-1} & 12\,kK<T<7\,kK \\ \frac{\partial T}{\partial t}=-1.10^8 K.s^{-1} & 7\,kK<T<5\,kK \\ \frac{\partial T}{\partial t}=-5.10^7 K.s^{-1} & 5\,kK<T<3\,kK \end{cases}$ $T_2(t_2)\begin{cases} \frac{\partial T}{\partial t}=-1.75.10^8 K.s^{-1} & 12\,kK<T<5\,kK \\ \frac{\partial T}{\partial t}=-3.7.10^7 K.s^{-1} & 5\,kK<T<3.5\,kK \\ \frac{\partial T}{\partial t}=-8.2.10^6 K.s^{-1} & 3.5\,kK<T<3\,kK \end{cases}$
$e^-,\ S,\ S^+,\ S^-,\ S_2,\ S_2^+,\ F,\ F^-,\ F^+,$ $F_2,\ F_2^+\ SF,\ SF^-,\ SF^+,\ SF_2,\ SF_3,$ $SF_4,\ SF_5,\ SF_6$	$\begin{cases} -10^8\ K.s^{-1} \\ -10^7\ K.s^{-1} \\ -10^6\ K.s^{-1} \end{cases}\quad 5\,kK < T < 3\,kK$

Table 1. Input parameters of the 0D model [9].

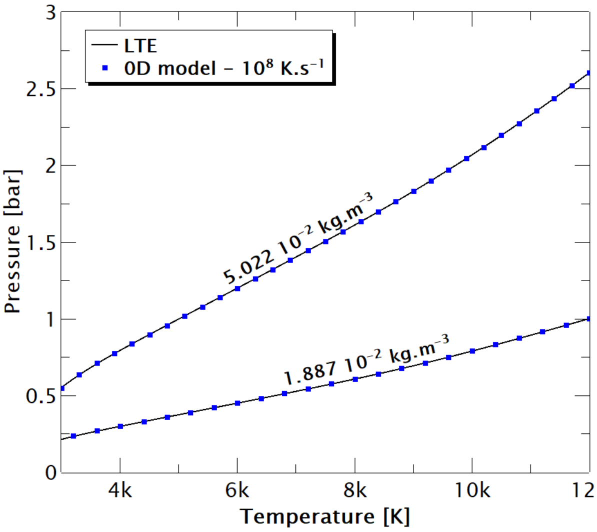

Figure 7. Variation of the pressure in SF_6 plasma at constant mass density.

differences around 5.5 kK in Figure 3 are probably due to the choice of the reaction rate values for the ionization of the Sulphur atom S and Fluorine F. The reaction rates of these processes are available in the literature, but for temperatures ranging from 8 kK to 12 kK [13]. Extrapolation is then necessary to obtain values outside this interval.

☐ Case of constant mass density: The mass densities of 0.01887 kg.m^{-3} and 0.05022 kg.m^{-3} are considered in this case for the study of the evolution of the species densities from 0D model In order to initialize the calculation and obtaining the inverse rates of chemical reactions, the LTE chemical compositions of Figure 1 related to these two mass densities are used.

Figure 5 shows the evolutions of the electronic densities for the different cooling speeds of Table 1 for a mass density of 0.01887 kg.m^{-3}. The departure from equilibrium decreases with the value of the cooling rate. We observe the presence of a marked variation of n_e which corresponds to the slope change in the temporal decrease in temperature. When the cooling speed is 10^6 K.s^{-1}, the electronic density of the 0D model deviates little from equilibrium. However, for temperature variations $T_1(t_1)$, $T_2(t_2)$ and cooling rate values above 10^7 K.s^{-1}, when considering a medium with constant density and no longer constant pressure, equilibrium deviations are more pronounced. In order to observe the departure from equilibrium which could occur by considering a greater density of 0.05022 kg.m^{-3}, we present in Figure 6 the evolutions of some predominant species (F, S, S^+ and e^-) between 12 kK and 3 kK for two cooling temperature of 10^8 K.s^{-1} (left side) and 10^7 K.s^{-1} (right side). For a cooling of 10^8 K.s^{-1} we find the presence of departures from equilibrium which mainly affect electrons and S^+ ion below 8 kK. At LTE, the densities of these two species are practically similar above 4.5 kK for the input parameters of our study (Figure 1). Thus, if one of these species deviates from equilibrium, the other is influenced. For a slower cooling of 10^7 K.s^{-1}, the differences in equilibrium over the electronic density and that of S^+ are almost negligible (Figure 6 on the right).

As the chemical composition is calculated here depending on temperature and density, the pressure changes according to their values. Figure 7 shows the evolutions in plasma pressure from SF_6 at LTE and pressure from 0D model versus temperature. The pressures rise with increasing temperature and density. The pressure deduced from the evolution of the species by the 0D model does not differ from that derived from the equilibrium calculation. This is due to the fact that the Dalton Law used for pressure determination depends mainly on the concentration of the majority species. For the temperature range of 3 kK to 12 kK, and a cooling rate of 10^8 K.s^{-1}, the differences in equilibrium over these species (F and S) are negligible.

4. Conclusion

A transient 0D kinetic model was developed. Two assumptions were used (A) a constant pressure and (B) a constant mass density. In this study only SF_6 was used but the generalized code allows studying different kinetics by adapting the input files relating to the data of the different chemical reactions. In order to have the densities at LTE according to these two hypotheses and to allow studying the departures from equilibrium, the plasma composition was calculated according to the same hypotheses. Considering SF_6, the hypothesis of constant pressure in the medium allows us to find all the results of the literature using the same cooling speeds, which confirms our results and validates our model. Departures from equilibrium are highlighted following the conditions used. On the other hand, we reviewed one of the findings in the literature which indicated that SF_x species were not predominant in the studied temperature range and could be neglected. We were able to show that taking these species into account reduced the departure from equilibrium found by the authors. We then adopted the hypothesis of a conservation of mass density. This hypothesis seems to us more legitimate especially for closed geometries. The study was carried out in SF_6 in order to remain consistent in the comparisons. With this hypothesis, departures from equilibrium are also present by considering the same cooling rates as in the previous hypothesis. We were able to show that for the same cooling conditions, the differences in equilibrium were more pronounced. The two mass density values considered correspond to temperature values of 12 kK and 5 kK taken at atmospheric pressure. With this hypothesis Dalton's law is not part of the system of equations. We have however shown under the conditions of this study that the evolution of pressure deduced from the species densities of the kinetic model evolves in equilibrium. This is explained by the densities of species F and S which remain in equilibrium over the temperature range and which are majority in the expression of Dalton's law. The kinetic module developed has been successfully tested on the 0D model considering SF_6 and the assumption of a constant pressure or a constant mass density. It can also be used for different pure gases and gas mixtures. For the next steps of our study, this module will be coupled with 1D and 2D models.

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