Kinetic Study of a Decaying SF$_6$ Arc Plasma in The Presence of Impurities

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A kinetics model has been developed to study the chemical composition of a decaying SF$_6$ arc plasma in the presence of impurities such as copper, carbon and water, proceeding from electrode and nozzle erosion or desorption in real SF$_6$ circuit-breakers. The model is based on the following main assumptions: the plasma is in thermal equilibrium (only one temperature for all the species); the plasma is homogeneous; the pressure remains constant during the decay; the transient temperature evolution is previously imposed. Experimental gas analysis by chromatography, after arcing in a circuit-breaker has confirmed the main results of the calculation: proportion of SOF$_2$ is much more important than that of SO$_2$F$_2$ and very low formation of S$_2$F$_{10}$ molecules.

Keywords: arc plasma, SF$_6$, kinetic model, byproducts

1. Introduction

In SF$_6$ circuit-breakers, impurities such as water, copper vapour, carbon or CF$_2$ vapours may mix with the filled gas because of the erosion of the electrodes or the nozzle and also may provide from desorption of these elements during the arc phase. All these species may react with the SF$_6$ decomposition products during arc extinction and can form compounds (byproducts) which may decrease the interruption capability of the apparatus or which can be toxic. The aim of this work is to develop a kinetic model of an extinguishing SF$_6$ circuit-breaker arc in the presence of impurities in order to predict the formation of complex molecules.

Among the results, we will focus our attention on the evolutions of the concentrations of three products: S$_2$F$_{10}$, because of its high toxicity; SOF$_2$ and SO$_2$F$_2$, because their relative real evolutions are different from the equilibrium composition, which allows to test the validity of the kinetic model. This model is partially validated by gas phase chromatography measurements performed on a breaker prototype, the gas being analysed a long time after arcing.

2. Bases of the model

2.1 Hypothesis

The model which is composed of the conservation equations of all the species, is based on the following main assumptions: the medium is homogeneous, in thermal equilibrium and the energy distribution functions of all species are maxwellian; the temperature evolution T(t) is previously known and deduced from literature values on arc cooling; the reaction rates are only function of the mean temperature defined at time t, even if cooling is partially due to turbulence; the medium is assumed to be a perfect gas; there are no external forces; for each species we consider only one state which corresponds to the ground state; the pressure remains constant during the arc decay (calculations have been performed for 0.1 and 0.4 MPa). The latter hypothesis needs an injection of particles to the plasma to maintain the pressure during cooling. The initial conditions at high temperature (typically 12 000 K) are obtained considering an equilibrium composition of the plasma.

2.2 Species and reactions

We have considered 61 species: electrons, S, S+, F, F+, S', F', S$_2$, S$_2$+, F$_2$, F$_2$+, F$_2$-, SF, SF+, SF', SF$_2$, SF$_3$, SF$_4$, SF$_5$, SF$_5$-, SF$_6$, SF$_6$-, S$_2$F$_{10}$, Cu, Cu+, CuF, Cu$_2$F$_2$, C, C+, CF, CS, CS$_2$, CF$_2$, CF$_3$, CF$_4$, O, O', O', H, O$_2$, H$_2$, O$_2$, O$_2$-, O$_2$+, SH, SO, OF, HF, OH, O$_2$, H$_2$S, SO$_2$, S$_2$O, S$_2$F$_2$,OF$_2$, O$_2$F, OF, O$_2$O, O$_3$, SH, SF, SF$_2$, SOF$_2$, SOF$_4$ and H$_2$SO$_4$.

More than 200 chemical reactions between these species have been taken into account and have been described in [1]. One of the main difficulties of this work was to determine the reaction rates either from the literature or using general theories. The details on these reaction rates cannot be given in this paper and may be found in [1]. Most of the direct reaction rates proceed from references [2] (for pure SF$_6$) and [3], whereas the reverse rates have been computed by micropic-reversibility requiring the calculation of the partition functions.

2.3 Equations

The conservation equation for species i is given by:
\[
\frac{\partial n_i}{\partial t} = \left(\frac{\partial n_i}{\partial t}\right)_{eq} + \frac{n_i k T}{P} \sum_j \left(\frac{\partial n_j}{\partial t}\right)_{eq} - \frac{n_i k T}{T} \left(\frac{\partial n_i}{\partial T}\right),
\]

where \(n_i\) is the number density of species i, k is the collision cross section, T is the temperature, and P is the pressure.

The first term on the right hand-side represents the variations of the number density of species i (noted \(n_i\)) due to chemical reactions. The two other terms take into account the fact that the pressure remains constant [2,4]. For minority species such as copper, these two terms may be deleted if we consider that the species are only produced during the high temperature phase and not during the arc cooling.

The model starts from an initial stationary state assumed to be in Local Thermodynamic Equilibrium (LTE) at high temperature (12 000 K), and the temperature decreases down to

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300K. The rate equations (1) written for the stationary state are not linearly independent. Other relations exist to link the particle densities and will be given in part 3. In the transient state the equations (1) are solved by a program designed by Young and Boris [5] optimized for a system of stiff equations (the equations of small time constant are solved through integration by asymptotic selection and the others by the classical method).

3. Results in stationary state

In stationary state the set of equations (1) is reduced to the following equations:

\[
\frac{\partial n_i}{\partial t} = \frac{\partial n_{i+1}}{\partial t}
\]

(1b)

These equations are not independent and other relations must be added: electrical neutrality; stochiometric ratio between S and F species; impurities proportions and perfect gas law for a given pressure, which is written:

\[
p = \sum n_i kT
\]

(2)

In stationary state, taking into account the reaction microreversibility, the solutions of equations (1b) give the equilibrium composition. This equilibrium composition will be used for analysing the composition predicted by the kinetic model and to study the possible departures from equilibrium. Furthermore, the relaxation times - also called reaction time constants - can be estimated with the equilibrium composition and the reaction rates. For a reaction of the type

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

(3)

the relaxation time of the A particles is defined by

\[\tau_A = \frac{1}{K} \rho_A\]

(4)

If several reactions exist, all leading to the disappearance of species A, each with its relaxation time \(\tau_a\), an overall relaxation time \(\tau_m\) can be defined by

\[\frac{1}{\tau_m} = \sum \frac{1}{\tau_a}\]

(5)

As an example the variations of some particle densities in SF₆-H₂O mixture are shown in figure 1, for a relative proportion of water equal to 10⁻³. In this temperature range the main species due to the presence of water are O and H. At lower temperatures, hydrogen mainly forms HF and oxygen SO₂F₂. The equilibrium variations of SO₂F₂, SO₂F₁₂ and S₂F₁₀ densities are drawn in figure 2, at a very low temperature. The first comment concerns S₂F₁₀ which relative proportion remains low, with a maximum at 5x10⁻⁹. Secondly, down to 2100 K the SO₂F₂ equilibrium density is clearly higher than the SO₂F₁₂ equilibrium density whereas the contrary occurs at lower temperatures.

4. Transient evolution

4.1 Pure SF₆

The total temperature range, between 12 000 and 300 K have been decomposed into various regions, each of them corresponding to a linear variation of temperature versus time. Between 12 000 K and 3 000 K we have used two temperature variations given in figure 3. The first one, noted (1) in Fig. 3, was given by Brand and Kopainsky [2]; the second, noted (2), was deduced from a numerical calculation of the temperature evolution in a circuit-breaker prototype [6]. For temperatures

![Fig. 1: Variations of some equilibrium densities in SF₆-H₂O mixture (p=10⁵ Pa; H₂O molar proportion: 10⁻³)](image)

![Fig. 2: Equilibrium densities at very low temperature in SF₆-H₂O mixtures](image)

![Fig. 3: Temperature variations during arc decay](image)
lower than 3 000 K, various cooling rates (CR) have been chosen to study chemical kinetics. The study of the transient evolution was separated into two parts: a parametric study of the influences of the various impurities on the decaying plasma composition and the general analysis of the total mixture properties.

First of all the calculation has dealt with pure SF6 plasma. Our results confirm the evolution of the electron number density found previously with a limited number of species [4]. These variations are represented in figure 4, for a pressure of 1 atm (0.1 MPa). The comparison between the electron density values obtained by the kinetics model and the equilibrium values show that departures from equilibrium may be important around 5 000 K but decrease when the cooling rate decreases. Furthermore it must be noted that these departures vanish at high pressure (p> 4 atm) for the same temperature evolution. The disappearance of electrons in this temperature range is mainly due to dissociative attachment (with F2 and SF) and dissociation (with S2+ and SF+).

At low temperature (T<2 000 K) the results show that the F density may be higher than the equilibrium value specially when the CR is important (> 10^5 Ks^{-1}). This phenomenon may lead to an overpopulation of S2F10. The results give an S2F10 density around 5*10^{16} m^{-3} at T= 1000 K and atmospheric pressure, for a strong CR of 10^6 Ks^{-1}. In fact there exists a maximum production of S2F10 at 1700 K and when the cooling is very fast this population remains more or less constant at lower temperature due to a quenching effect. When the CR is only 10^4 Ks^{-1} the S2F10 density value at 1000 K is very close to the equilibrium value (10^{14} m^{-3}). Let us note that the total number density is about 7*10^{24} m^{-3} under these conditions.

**Fig. 4: Comparison between the equilibrium values (curve 3) and the calculated variations of the electron number density, at atmospheric pressure (curves 1 and 2 correspond to the temperature transient evolutions noted 1 and 2 respectively in figure 3)**

4.2 SF6-Cu and SF6-C mixtures
Copper vapours proceed from the contact erosion and carbon from the nozzle erosion. The presence of only copper or only carbon is not realistic because in practical conditions there are always other impurities such as water. So the calculation performed for these mixtures had two aims: the study of the general behaviour of the plasma in presence of species collecting fluorine atoms (in this case for creating CuF and CuF2 or CF4 molecules); the modification of certain conservation equations to take into account the dilution of copper or carbon species during cooling.

The main results concern the evolutions of S2F10 density at very low temperature (T < 1000 K) which are presented in figure 5, for the SF6-Cu mixture with an important copper molar proportion of 10^{-3} (the same kind of results have been obtained for SF6-C mixture). The equilibrium composition shows that the S2F10 concentration should be important in an SF6-Cu mixture: the S2F10 proportion is of the order of the copper proportion. This phenomenon is due to the fact that the presence of copper leads to the formation of CuF2 at low temperature and thus not all the SF6 molecules are reconstituted. At T = 1000 K there exists an overpopulation of SF4 and SF5 molecules and the equilibrium thermodynamics properties lead to the formation of S2F10 molecules at lower temperatures. Let us note that the high S2F10 density is not realistic because the real relative proportion of copper at low temperature never exceeds 10^{-6}.

The results of the kinetics model in figure 5 show that the formation of S2F10 molecules due to chemical reactions is slow and in general its concentration should be much more lower than the value predicted by the equilibrium composition in the SF6-Cu mixture.

4.3 SF6-H2O mixtures
Water vapour always exists in the SF6 gas injected in the circuit-breaker and is also produced by the wall desorption. At high temperature (T > 3 000 K) the calculations show that the departures from equilibrium remain weak unless for SO2 and H. The most interesting result concerning the SF6-H2O mixture is relative to the evolutions of SOF2 and SO2F2 number

**Fig. 5: Evolutions of the S2F10 density in SF6-Cu mixture**
(copper proportion: 10^{-3})
densities, for T < 3 000 K. They are represented in figure 6 for two CR values (10^4 and 10^5 Ks⁻¹) and for a molar water proportion of 10⁻³. These evolutions are very different from the equilibrium values drawn in the same figure. We can observe that the transformation of SOF₂ in SO₂F₂ at T < 2 000 K, which is predicted by the equilibrium laws, does not occur. This is due to the fact that the chemical reaction

\[ \text{SOF}_2 + \text{O} \rightarrow \text{SO}_2\text{F}_2 \]  \hspace{1cm} (6)

is very slow because of the low density of atomic oxygen. The cooling between 1 000 and 300 K does not change the relative evolution of the SOF₂ and SO₂F₂ number densities. At 300 K, in opposition to the equilibrium composition, the SOF₂ population is in general higher than the SO₂F₂ population by several orders of magnitude.

5. Comparison of experiments and discussion

The composition of the medium after a series of arcings realised with a small circuit-breaker prototype (the internal volume was 5.68 liters) has been analysed by gas chromatography. The details of the experimental set-up and of the procedure were given in [7-8]. The gas flow within the circuit-breaker prototype, through a PTFE nozzle, was self-generated, without puffer action. The arc itself created an overpressure in the upstream part of the chamber by transfer of mass and energy [9]. The filling pressure was 400 kPa. For each arcing, the duration of the current pulse was 10 ms and its amplitude 8.3 kA. Gas analysis was performed after series of 50 arcings. Additional measurements have been performed with a metallic nozzle to have a very limited injection of carbon.

The aim of this experimental study was to partially validate the kinetic model by comparing the experimental and the predicted composition evolutions obtained by changing some conditions such as the carbon or water proportions. In the calculation we assumed an homogeneous medium whereas in the experiments only a small part of the gas was heated. The reacting gas was then mixed to the remaining SF₆ by convection and diffusion. In order to have similar experimental and theoretical conditions, two operations in the procedure were systematically realised to obtain a homogenized gas: first, after each serie of arcings, several openings were made without arcing; second, the part of the gas sample taken for the analysis, was important, up to the half of the filling gas.

The calculation has been performed for the mixture containing SF₆ and all the impurities: Cu vapour, C (either under the form of carbon, CF₄ or CF₂), water and oxygen. An example of the partial composition in the temperature range between 3 000 K and 1 000 K, is given in figure 7. It must be noted that the experimental proportions of impurities depend on the interaction between the arc and the walls or electrodes, and cannot be predicted by the model. Thus the values of impurity concentrations chosen in the model were guided by the experiments. For example, depending on several conditions (nature of the nozzle, steam injection) the total relative oxygen concentration deduced from chromatography (SOF₂, SO₂F₂ and COF₂) was in the range 10⁻⁴ to 10⁻².

The comparison between the theoretical and experimental results leads to the following main comments concerning the chemical composition of SF₆ after arcing:

- The presence of oxygen (pure or due to water dissociation) leads mainly to the formation of SOF₂ and not of SO₂F₂. This fact experimentally observed and predicted by the kinetic model is contrary to the equilibrium composition. The value of the experimental ratio between SOF₂ and SO₂F₂ concentrations lies in the range 100-1000 and is in agreement with the theoretical prediction.

- The calculation shows that the remaining molar proportion of S₂F₁₀ at 300 K is very low, of the order of 10⁻¹⁰ with our values of cooling rate. With a much faster cooling this proportion could reach 10⁻⁶. The experimental concentration of S₂F₁₀ is under the sensibility threshold of our arrangement which is about 1 ppmv.
Our model shows that the presence of carbon or copper tends to increase the S\textsubscript{2}F\textsubscript{10} production whereas the presence of oxygen or water tends to decrease this production. The first effect is due to the creation of CF\textsubscript{4} or CuF\textsubscript{2} which leads to a lack of fluorine atoms (comparatively to sulphur population considering the stoichiometric ratio in SF\textsubscript{6}) favouring the production of SF\textsubscript{4} and SF\textsubscript{5} and thus of S\textsubscript{2}F\textsubscript{10} at low temperature. On the other hand oxygen leads to the formation of SOF\textsubscript{2} which acts in the opposite way, creating and overpopulation of fluorine. This overpopulation is not compensated by the formation of HF molecules.

After arcing, at T = 300 K, our model predicts that the SOF\textsubscript{2} molecules react very slowly with water molecules to create SO\textsubscript{2}, such as the SO\textsubscript{2}+SOF\textsubscript{2} density remains constant (see figure 8). This phenomenon and the associated time constant (of the order of one month) are in agreement with the measurements.

With the model, all the hydrogen proceeding from water dissociation is transformed in HF molecules. This molecule was not detected experimentally because it strongly reacts with the walls of the circuit-breaker.

Finally, the model predicts that the SOF\textsubscript{2} concentration is proportional to the initial water concentration. This was not observed in the experiments. In fact the final SOF\textsubscript{2} concentration is much higher than the initial water proportion and we think that there exists a strong water desorption during arcing which prevents any comparison between experience and theory concerning the influence of water on the decaying SF\textsubscript{6} plasma composition.

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![Figure 8: Slow variations of some species densities at ambient temperature](image)

References


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