

DIELECTRIC PROPERTIES OF HOT SF₆ GASEOUS MIXTURE UNDER CHEMICALLY NON-EQUILIBRIUM CONDITION

W. Z. WANG^{1, 2*}, M. Z. RONG², J. D. Yan³, J. W. SPENCER³

¹ Qian Xuesen Laboratory of Space Technology, China Academy of Space Technology, 100094, Beijing, People's Republic of China

² State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, 710049, Xi'an, People's Republic of China

³ Department of Electrical Engineering and Electronics, The University of Liverpool, L69 3GJ, Liverpool, United Kingdom
*wangweizong@gmail.com

ABSTRACT

This paper calculates the critical reduced breakdown field of hot SF₆ gaseous mixture based on the solution of a two-term Boltzmann equation for the electron energy distribution function (EEDF) using improved cross section data, bearing similarities to the residual plasma in the dielectric recovery phase of a high voltage circuit breaker. The influence of species composition on the dielectric properties, in cases of departure from chemically equilibrium which takes place during the arc extinction, was analyzed considering the species evolution by a kinetic model during the decaying process of gas blast SF₆ arc. It is found that when departure from chemical equilibrium takes place, the critical breakdown field is reduced in the high temperature range.

1. INTRODUCTION

More detailed understanding of the distributions of chemical species is necessary for advanced investigation of the SF₆ arc extinction phenomena during the fault current interruption. It is possible that the departure from chemically equilibrium takes place during the arc extinction especially under strong gas blast condition due to the fact that the arc has cooled down to temperatures below 4000 K quite swiftly. The composition of such a hot gas is complex and is dependent on the temperature decay rate during thermal recovery. Additionally, in dielectric recovery phase, the electron energy distribution function influenced by the imposed recovery

voltage departs from Maxwellian and dielectric recovery depends on the production and loss of charge particle species. The physical and chemical processes responsible for the breakdown of a hot gas immediately after the thermal extinction of the arc are expected to be very different from those of SF₆ at room temperature. A careful examination of all relevant ionization, recombination and chemical reactions consistent with the time scale for dielectric breakdown is therefore required. The present study investigates the dielectric properties of hot SF₆ gaseous mixture under chemically non-equilibrium condition based on the solution of a two-term Boltzmann equation for the electron energy distribution function (EEDF) as well as a kinetic model which enables calculation of the changes occurring in particle densities.

2. KINETIC ANALYSIS OF A DECAYING SF₆ ARC PLASMA

A kinetic analysis of decaying SF₆ applied to a homogeneous medium at constant pressure, in which the variation of temperature is taken as being known, is available to investigate the influence of chemically non-equilibrium on the particle densities evolution.

2.1 Basic hypotheses

The energy distribution function of species is assumed to Maxwellian. The plasma is homogenous and its temperature is identical. The pressure remains constant during the arc decay. We assume that no recovery voltage is applied.

The reaction rates are then taken to be independent of the electric field.

2.2 Individual species

Over the temperature range studied, compared with previous work, we investigate a more wide variety of 28 species including heavy species S , S^- , S^+ , S_2 , S_2^+ , F_2 , F , F^+ , F^- , F_2^+ , SF , SF^+ , SF^- , SF_2 , SF_3 , SF_4 , SF_5 , SF_6 , SF_2^+ , SF_2^- , SF_3^+ , SF_3^- , SF_4^+ , SF_4^- , SF_5^+ , SF_5^- , SF_6^- as well as electrons and hence can bring more accurate analysis.

2.3 Chemical reactions

A kinetic model including 183 chemical reactions, of which dominant reactions are presented in table 1 from literature, are taken into account [1]. In the chemical reactions studied, only a single state is considered for each species, namely the ground state. Moreover, the radiative processes (except those involved in electron-atomic ion recombination) are irreversible. In general, for the reversible chemical reactions, results from the literature were used to determine the cross sections or rate constants of the direct reaction. The rates of reverse reactions were calculated by Detailed Balancing Law.

2.4 Governing equations

One of the governing equations is related to the species production rate equation as Eq. (1).

$$\partial Y_i / \partial t = \omega_i(t) * M_i / \rho(t) \quad (1)$$

where Y_i , ω_i and M_i are the mass fraction, molar production rate and molar weight of specie i respectively.

The variation of temperature with time $T(t)$ is known beforehand as:

$$\partial T(t) / \partial t = f(t) \quad (2)$$

Along with the governing equation describing species creation and disappearance rates, additional three relationships exist to link the particle densities: the perfect gas law, electric neutrality and the stoichiometric equilibrium. The control equations are solved by LSDOE solver which is available for numerical solution of the initial value problem for stiff and non-stiff systems [2].

Table 1 Chemical reaction scheme

$F + F \rightarrow F_2 + hv$	$F + e \rightarrow F^- + hv$
$S + e \rightarrow S^- + hv$	$F^+ + e \rightarrow F + hv$
$S^+ + e \rightarrow S + hv$	$F + e = F^+ + e + e$
$S + e = S^+ + e + e$	$SF^+ + e = S + F$
$S_2^+ + e = S + S$	$F_2^+ + e = F + F$
$F + F = F + e + F$	$S^- + F = S + e + F$
$F + e + e = F^- + e$	$F^- + F = F_2 + e$
$F^- + S = SF + e$	$SF^- + F = S + F^- + F$
$SF^- + F = F + S^- + F$	$S_2^+ + F = S + S^+ + F$
$SF^+ + F = F + S^+ + F$	$SF^+ + F = S + F^+ + F$
$F_2^+ + F = F + F^+ + F$	$F + F + F = F_2 + F$
$S + F + F = SF + F$	$S + S + F = S_2 + F$
$SF_4 + F_2 = SF_6$	$F_2 = F + F$
$SF_5 + F_2 = SF_6 + F$	$S_2 = S + S$
$SF_4 + F = SF_3 + F_2$	$SF_4 + F_2 = SF_5 + F$
$SF_4 + F = SF_5$	$SF_5 + F = SF_6$
$SF_5 + SF_5 = SF_6 + SF_4$	$S^+ + SF = S_2^+ + F$
$S^+ + F_2 = SF^+ + F$	$F_2 + e = F + F + e$
$S^- + SF = S + SF^-$	$S^+ + S_2 = S_2^+ + S$
$S^+ + SF = SF^+ + S$	$F^+ + S_2 = S_2^+ + F$
$F^+ + SF = SF^+ + F$	$F^+ + F_2 = F_2^+ + F$
$S^+ + S^- + F = S_2 + F$	$S^+ + F^- + F = SF + F$
$S_2^+ + F^- + F = S_2 + F + F$	$S_2^+ + F^- + F = SF + S + F$
$S_2^+ + F^- + F = S_2 + F_2$	$S_2^+ + F^- + F = SF + SF$
$F_2^+ + F^- = F + F + F$	$F^+ + F^- + F = F_2 + F$
$F^+ + S^- + F = SF + F$	$SF_6 + SF_2 = SF_4 + SF_4$
$SF + SF = S_2 + F_2$	$F + SF = F_2 + S$
$F + SF = SF_2$	$S + F_2 = SF_2$
$SF + F_2 = SF_2 + F$	$SF + SF = SF_2 + S$
$S_2 + F_2 = SF_2 + S$	$SF_2 + F = SF_3$
$SF_2 + F_2 = SF_3 + F$	$SF + F_2 = SF_3$
$SF_2 + SF_2 = SF_3 + SF$	$SF_3 + F = SF_4$
$SF_2 + F_2 = SF_4$	$SF_3 + SF_3 = SF_2 + SF_4$
$SF_2 + SF_2 = SF_4 + S$	$SF_3 + F_2 = SF_5$
$SF^+ + SF^- = SF + SF$	$F^+ + F^- = F + F$
$S_2^+ + F = S + F^+ + S$	$SF^+ + F^- + F = SF + F + F$
$S_2^+ + SF^- + F = SF + S_2 + F$	$SF^+ + F^- + F = SF + F_2$
$SF^+ + F^- + F = SF_2 + F$	$X^- + SF_3^+ = SF_3 + X$
$X^- + SF_2^+ = SF_2 + X$	$SF_5^+ + SF_6^- = SF_3^+ + SF_6 + F_2$
$SF_5^- + X = SF_5 + X + e$	$SF_5^- + X^+ = SF_5 + X$
$SF_3^- + X = SF_3 + X + e$	$SF_3^- + X^+ = SF_3 + X$

2.5 Species variation under different temperature cooling rates

In previous investigation [1], the plasma composition departs from equilibrium at around 12000K and we use the equilibrium molar fractions of species at 12000K as the starting point of our computation. The influence of temperature cooling rate on the electron density variation can be found in Fig. 1. With a high temperature cooling rate, the system cannot adjust to arrive at the steady equilibrium state in finite time period and have a higher electron concentration than that of equilibrium case at the same temperature because the reaction rate is

also finite. Any departures from equilibrium correspond to an electron overpopulation which tends to enhance the electrical conductivity of the plasma and thus decrease the thermal interruption capability of SF₆ obtained by the local thermodynamic equilibrium (LTE) model.

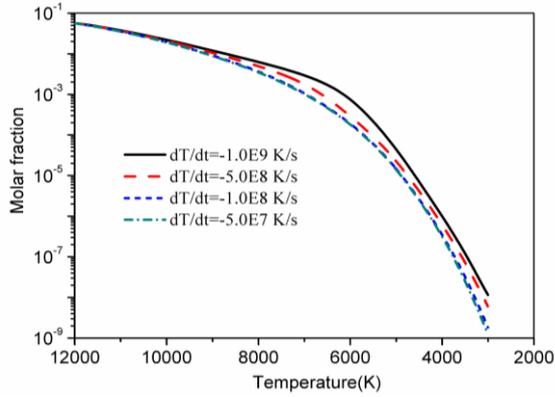


Fig.1 Evolution of electron molar fraction during SF₆ arc decay as a function of temperature at a pressure of 0.60MPa with different cooling rates.

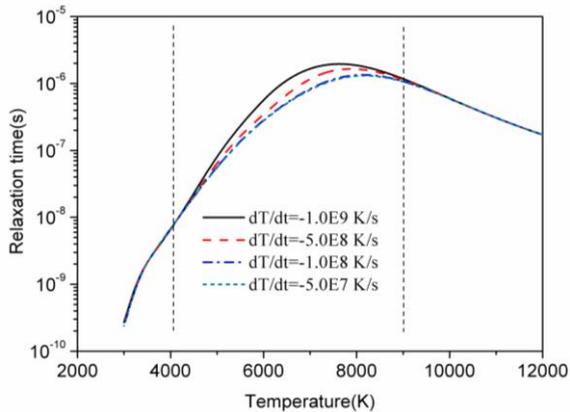


Fig.2 Evolution of overall relaxation time for electrons disappearance during SF₆ arc decay as a function of temperature at a pressure of 0.60MPa with different cooling rates.

To study the impact of departures from equilibrium on the plasma composition, we investigate the species disappearance relaxation time which is the inverse of the disappearance frequency and defined in [3]. Fig. 2 shows the influence of temperature cooling rate on overall relaxation time for electrons disappearance during SF₆ arc decay. The deviation of electron disappearance relaxation time under different temperature cooling rates mainly occurs in the intermediate temperature range from 4000K to 9000K where the dissociative recombination and dissociative attachment mechanisms especially involving diatomic molecular species are predominant. A larger temperature cooling rate leads to a higher value of electron disappearance relaxation time showing that a larger degree of

departure from equilibrium occurs and a longer time is needed to reach the equilibrium state.

3. DIELECTRIC PROPERTIES OF HOT SF₆ GASEOUS MIXTURE

A general computation procedure to determine the dielectric properties of hot gases mainly includes three steps. (1) *Calculation of species composition in the hot gases.* Successful thermal recovery requires the temperature of the arc in circuit breaker to be cooled down from high temperature to a relatively low temperature after current zero. Considering possible departure from chemically equilibrium state, the species composition is determined by adoption of a kinetic model. (2) *Evaluation of the electron energy distribution functions (EEDFs).* The critical reduced electric field strength is the field corresponding to a balance between the processes of electron generation and loss. Therefore, all the relevant processes of electron kinetics with regard to the electrons loss and generation including the electron elastic collision, the vibrational and electronic excitation, electron collision ionization and attachment should be considered. The reaction rates of these processes are derived from the electron energy distribution functions (EEDFs) which needs a priori knowledge of the collision cross section sets corresponding to all species present in the dissociated hot gas and is obtained from a two-term numerical solutions of the Boltzmann transport equation. Improved cross section data recently summarized in reference [4] has been adopted here. (3) *Determination of critical electrical breakdown field for hot gas.* The breakdown of hot gas depends on whether an electron avalanche can be formed for a given electrical field. The formation of electron avalanche is determined by the production and loss processes of electrons. The reactions which contribute to enhance the electron avalanche are ionization for electron kinetics and detachment for ion kinetics while those decreases of the electron avalanche are attachment for electron kinetics and recombination for ion kinetics.

We use the kinetic method given in section two to obtain the species composition. We assume the temperature cooling rate from 12000 K to 5000K is 5E8K/s and at the starting point, the equilibrium species composition is used. From 5000K, we perform the kinetic analysis of

species composition under different temperature cooling rates 2E8K/s, 1E8K/s, 5E7K/s and 1E7K/s. Finally the critical electron field is obtained from the solution of the following ordinary differential equation of the electron density evolution giving the balance between the electron generation and loss processes:

$$\begin{aligned} \partial n_e(t) / \partial t = & -\sum n_e n_{M_j} K_{rec-eM_j} - \sum n_e n_{M_j} K_{att-eM_j} \\ & + \sum n_e n_{M_j} K_{ion-eM_j} + \sum n_{N_j} n_{M_j} K_{det-N_jM_j} \end{aligned} \quad (3)$$

Where K_{rec-eM_j} , K_{att-eM_j} , K_{ion-eM_j} and $K_{det-N_jM_j}$ are respectively the electron-molecular ion recombination rate, the electron-neutral molecular specie attachment rate, the electron-neutral molecular specie ionization rate and detachment rate. The determination of the critical reduced breakdown field is obtained by setting the net production rate as zero.

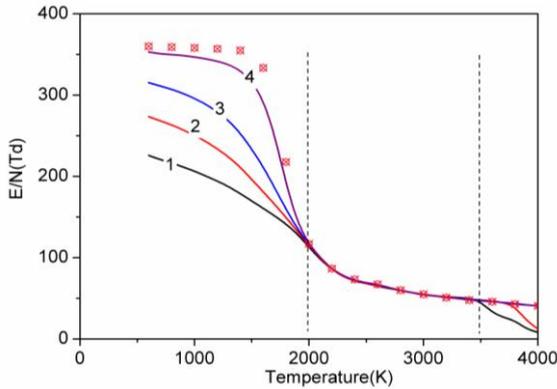


Fig.3 Calculated critical reduced electric field for hot SF₆ at a pressure of 1MPa. 1, dT/dt=-2E8 K/s; 2, dT/dt=-1E8 K/s; 3, dT/dt=-5E7 K/s; 4, dT/dt=-1E7 K/s. The data for equilibrium species composition is also given for comparison.

As the increase of the temperature cooling rate, the degree of departure from equilibrium increases. The critical breakdown field is reduced in the higher temperature range $T > 3500$ K. This is partly attributed to the contribution of increased electrons number density which can greatly increase the electron-electron collision and hence affect the electron energy distribution function. Meanwhile, regardless of the abundance of atomic fluorine, it contributes little to the dielectric strength at elevated temperatures; in contrast, the neutral diatomic and polyatomic molecular species such as SF₂, SF which own a larger dielectric strength than that of the neutral atomic species have a relatively higher concentration under the slower cooling process at the same temperature. This can increase the critical reduced breakdown field as well. In the

temperature range from 2000K to 3500K, the influence of electrons collision together with the deviation of the neutral diatomic molecular species' concentration is small under current temperature cooling rates; the discrepancy of dielectric strength is negligible as well. With the further decrease of the temperature, the simple species including atomic and diatomic species in the system has no sufficient time to compose into large molecular species. Therefore, an increase of the temperature cooling rate causes a significant reduction of the critical dielectric properties at the same gas temperature.

CONCLUSIONS

Any departures from chemically equilibrium correspond to an electron overpopulation due to the finite reaction rate which tends to enhance the electrical conductivity and thus to decrease the thermal interruption capability of SF₆ obtained by the LTE model. A larger temperature cooling rate leads to a higher value of electron disappearance relaxation time showing that a larger degree of departure from equilibrium occurs. When departure from chemical equilibrium takes place, the critical breakdown field is reduced in the high temperature range. An increase of the temperature cooling rate causes a significant reduction of the critical dielectric properties.

REFERENCES

- [1] W. Z. Wang, "Investigation of The Dynamic Characteristics and Decaying Behaviour of SF₆ Arcs In Switching Applications", PhD Thesis, The University of Liverpool, Liverpool, 2013.
- [2] R. Krishnan, A. C. Hindmarsh, Description and Use of LSODE, the Livermore Solver for Ordinary Differential Equations, NASA-RP-1327 UCRL-ID-113855, E-5843, 1993.
- [3] A. Gleizes, F. Mbolidi and A.A.M. Habibt, "Kinetic model of a decaying SF₆ plasma over the temperature range 12000 K to 3000 K", Plasma Sources Sci. Technol., 2, 173-179, 1993.
- [4] W. Z. Wang, A. B. Murphy, M. Z. Rong, et al., "Investigation on critical breakdown electric field of hot sulfur hexafluoride/carbon tetrafluoride mixtures for high voltage circuit breaker applications", J. Appl. Phys., 114, 103301, 2013.