PREDOMINANT PARTICLES IN SF6-CU MIXTURE AT TEMPERATURES OF 300-50,000 K

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ABSTRACT

The compositions of SF_6-Cu gas mixture at temperatures of 300-50,000 K are calculated based on Gibbs free energy minimization. The predominant particles with high molar fractions are determined in the cases of 1% Cu, 10% Cu, and 50% Cu. It is found that SF_6 and F are generally the predominant particles in the temperature ranges of 300 K-1000 K and 1000 K-10,000 K respectively. While at temperatures of 10,000 K-50,000 K, electrons become the predominant particle.

1. INTRODUCTION

Sulfur hexafluoride (SF_6) is widely used as an arc-quenching and an electrical-insulating gas for circuit breakers. Whatever the operating conditions, the arc does not burn in pure SF_6 but in a mixture containing non-ignorable proportions of impurities (i.e. copper vapour). The presence of these impurities must be taken into account in the modeling of arc simulation since they can modify the arc characteristics and thus exert influence over the interruption capability [1].

There are a few works concerning impurities such as copper vapour. Chervy et al. [1] calculated the thermodynamic properties and transport coefficients in SF_6-Cu mixtures. Paul et al. [2] studied the transport and thermodynamic properties of SF_6 gas under contaminated conditions with Cu and PTFE vapours. Andre et al. [4] determined the molar fractions of chemical species in PTFE, SF_6, Cu mixture for several proportions and pressures. However, all the previous works show little interest in the predominant particles in the SF_6-Cu mixture and the temperature range is limited up to 30,000 K. The object of present work is to calculate the composition of SF_6-Cu mixture at temperatures of 300 K-50,000 K and determine the predominant species. Compared with previous works, more species are taken into account.

2. CALCULATION PROCEDURE

From a thermodynamic point of view, a chemical system can be characterized by its temperature and pressure. In this case the equilibrium state is reached when the Gibbs free energy assumes a minimum [3]. In this paper, all the compounds are taken to be gaseous. The calculations are based on the assumption of local thermodynamic equilibrium (LTE). By this it is meant that at any point in the plasmas the electrons, ions, and neutral particles have the same kinetic temperature and chemical equilibrium has been achieved locally.

Assuming that the plasma contains N gaseous species, the Gibbs free energy G can be written as [4]:

$$G = \sum_{i=1}^{N} n_i \left(\mu_i^0 + RT \ln \left(\frac{n_i}{\sum_{j=1}^{N} n_j} \right) + RT \ln \left(\frac{P}{P^0} \right) \right)$$

Where n_i and μ_i^0 are the number density and the chemical potential respectively of i species at reference pressure P^0.

For an isolated system with given T and P, the trend toward an equilibrium state is described by

$dG < 0$, and the equilibrium is reached when $(dG)_{T,P} = 0$. Along with the law of mass balance, the equilibrium rule must be combined with law of electrically quasi-neutrality and Dalton's Law [3]. The Debye-Hückel correction, which is an adjustment to the usual expression for the Gibbs free energy representing the additional effect of electrostatic interactions between the charged particles, is taken into account.

In the calculation, it is assumed that the mixture of high temperature SF_6-Cu gas is composed of a total of 74 different species including relevant atoms, ions and molecules as well as electrons: F, F_2, S, S_2, S_3, S_4, S_5, S_6, S_7, S_8, SF, SF_2, SF_3, SF_4, SF_5, SF_6, FS_2F, S_2F_2, S_2F, S_2F_{10}, Cu, Cu_2, CuF, CuF_2, Cu_2F_2, Cu_3F_3, CuS, F^+, F^{2+}, F^{3+}, F^{4+}, F^{5+}, F^-, F_2^+, F_2^-, F_3^-, S^+, S^{2+}, S^{3+}, S^{4+}, S^{5+}, S^{6+}, S^-, S_2^+, S_2^-, S_3^+, S_3^-, S_4^+, S_4^-, SF^+, SF^-, SF_2^+, SF_2^-, SF_3^+, SF_3^-, SF_4^+, SF_4^-, SF_5^+, SF_5^-, SF_6^-, $S_2F_2^+$, FS_2F^-, S_2F^+, S_2F^-, Cu^+, Cu^{2+}, Cu^{3+}, Cu^{4+}, Cu^{5+}, Cu^{6+}, Cu^-, CuS^+, CuS^- and e^-. For the convenience of description, only the species having high molar fractions ($>10^{-6}$) are displayed in the following section.

3. RESULTS AND DISCUSSION

3.1 Cu concentrations of 1%

Figure (1) shows the equilibrium composition of SF_6-Cu mixture gas for Cu proportion of 1% at temperatures of 300-50,000 K and pressure of 0.1 MPa. The principal particles present at high molar fractions are found as described below:

(i) 300-1000 K: SF_6 dominates the mixture and a small proportion of SF_6 reacts with Cu mainly into SF_4 and CuF_2.

(ii) 1000-3000 K: SF_6 dissociates into some other products (i.e. SF_5 and F) and CuF_2 decomposes to CuF and F. The atomic fluoride (F) becomes the predominant particle.

(iii) 3000-10,000 K: The atomic fluoride still rules the mixture. The atomic sulfur (S) has the molar fraction of nearly 1%. CuF dissociates to Cu and F. A remarkable increase of electron concentration can be observed due to the ionizations of Cu, F and S.

(iv) 10,000-50,000 K: The ionization effect is strengthened and results in the existence of high order positive ions (i.e. F^{2+}, F^{3+}, S^{2+}, S^{3+}, Cu^{2+}, Cu^{3+} etc.). The electron becomes the predominant particle.

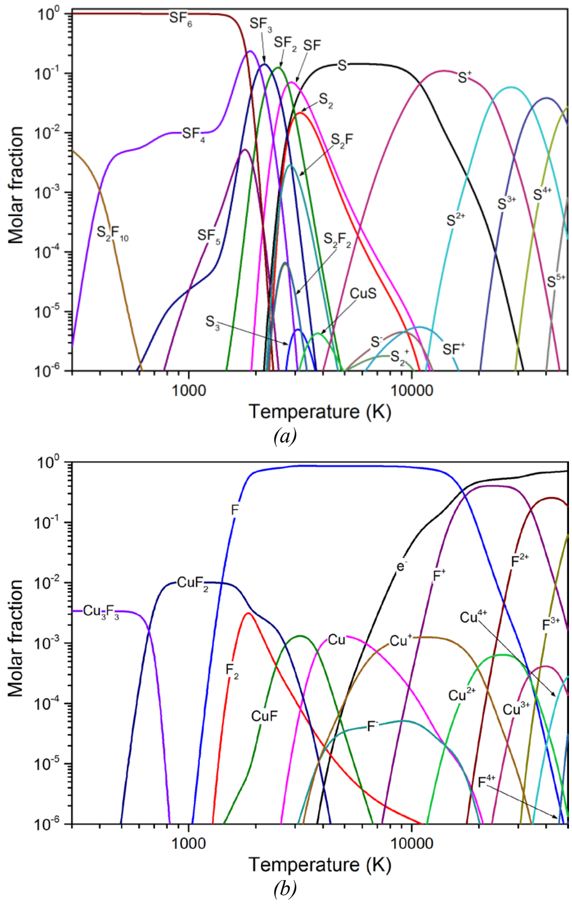

Fig. 1 Equilibrium composition of SF_6-Cu mixture gas for Cu concentration of 1% and pressure of 0.1 MPa at temperatures of 300-50,000 K

3.2 Cu concentrations of 10%

Figure (2) describes the equilibrium composition of SF_6-Cu mixture gas for Cu proportion of 10% at temperatures of 300-50,000 K and pressure of 0.1 MPa. The principal particles present at high molar fractions are found as described below:

(i) 300-1000 K: Just like the case of 1% Cu, SF_6 is still a predominant particle in the mixture. But more SF_6 reacts with Cu into SF_4 and CuF_2.

(ii) 1000-3000 K: Similar to the case of 1% Cu, SF_6 dissociates into SF_5, F and so on. CuF_2 decomposes to CuF and F. The atomic fluoride (F) rules the mixture.

(iii) 3000-10,000 K: The atomic fluoride still dominates the mixture. The atomic sulfur (S) has the molar fraction of nearly 10%. CuF decomposes to Cu and F. The ionizations of Cu, F and S cause a noticeable rise of the molar fraction of electron.

(iv) 10,000-50,000 K: The concentration of electron continues to increase and the electron becomes the predominant particle. More high order positive ions can be found, which is attributed to the stronger ionization of F, S and Cu.

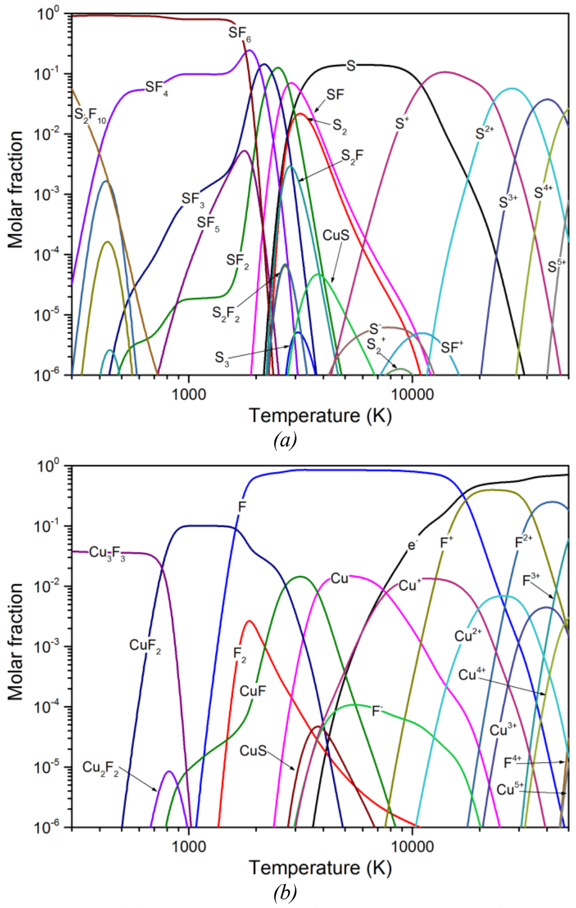

Fig. 2 Equilibrium composition of SF_6-Cu mixture gas for Cu concentration of 10% and pressure of 0.1 MPa at temperatures of 300-50,000 K

3.3 Cu concentrations of 50%

Figure (3) describes the equilibrium composition of SF_6-Cu mixture gas for Cu proportion of 50% at temperatures of 300-50,000 K and pressure of 0.1 MPa. The principal particles present at high molar fractions are found as described below:

(i) 300-1000 K: In the temperature range below 800 K, SF_6 is a predominant particle. While in the temperature range from 800 K to 1000 K, SF_4 and CuF_2 become the predominant particles.

(ii) 1000-3000 K: In the temperature range from 1000 K to 2000 K, SF_4 and CuF_2 still dominate the mixture. As the temperature is elevated above 2000 K, more CuF_2 dissociates into CuF and F. Meanwhile, the atomic fluoride (F) becomes the predominant particle.

(iii) 3000-10,000 K: The atomic fluoride still dominates the mixture. The atomic sulfur (S) and copper (Cu) both have the molar fraction of nearly 10%. Similar to the case of 10% Cu, CuF decomposes to Cu and F. The electron proportion experiences a distinct rise with the increase of temperature.

(iv) 10,000-50,000 K: Like the previous cases, the electrons rule the mixture. The high order positive ions come out due to the strong ionization of F, S and Cu.

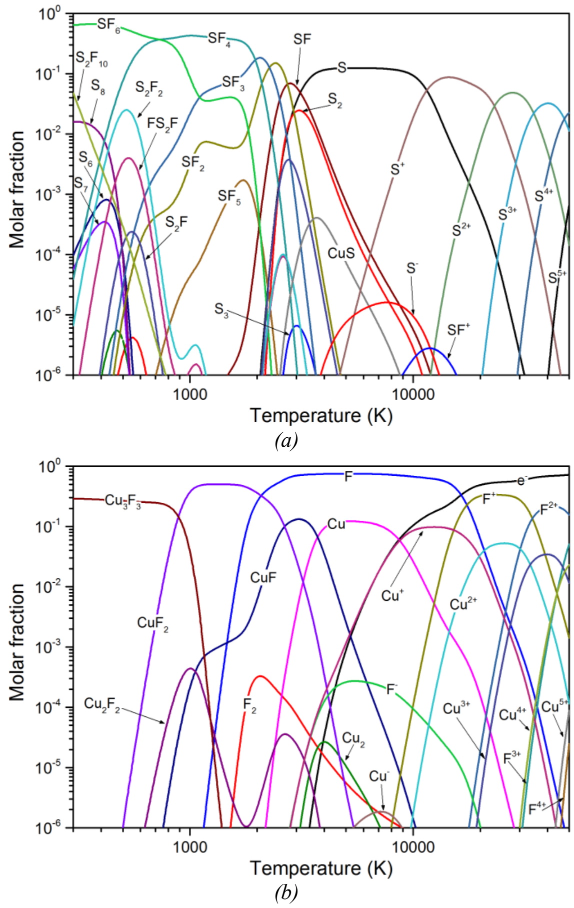

Fig. 3 Equilibrium composition of SF_6-Cu mixture gas for Cu concentration of 50% and pressure of 0.1 MPa at temperatures of 300-50,000 K

4. CONCLUSIONS

The compositions of SF_6-Cu mixture at temperatures of 300-50,000 K are calculated based on Gibbs free energy minimization. The predominant particles with high molar fractions are determined in the cases of 1% Cu, 10% Cu, and 50% Cu. Based on the present investigation, the following conclusions could be drawn:

(1) In the temperature range of 300 K-1000 K, SF_6 is generally a predominant particle. The concentrations of SF_4 and CuF_2 increase with temperature and rule the mixture above 800 K in the case of 50% Cu.

(2) In the temperature range of 1000 K-3000 K, the atomic fluoride (F) is generally a predominant particle. But in the case of 50% Cu below 2000 K, SF_4 and CuF_2 dominate the mixture.

(3) In the temperature range of 3000 K-10,000 K, the atomic fluoride still rules the mixture. The ionizations of Cu, F and S cause a noticeable rise of the molar fraction of electron.

(4) In the temperature range of 10,000 K-50,000 K, the electrons become the predominant particle. The high order positive ions come out due to the strong ionization of F, S and Cu.

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