Abstract: The research on decomposition characteristics of SF$_6$ and its by-products have great significance to the operation, maintenance, condition assessment and fault diagnosis of power equipment. In this paper, the particle composition models of SF$_6$, SF$_6$/polytetrafluoroethylene (PTFE), SF$_6$/PTFE/O$_2$, SF$_6$/PTFE/H$_2$O, and SF$_6$/PTFE/O$_2$/H$_2$O were established by using Gibbs free energy minimization method, and the effects of trace H$_2$O and O$_2$ impurities and PTFE vapour on SF$_6$ by-products were studied by the models. In order to verify the correctness of the simulation results, a series of breaking experiments were carried out on a 40.5 kV SF$_6$ circuit breaker, and a gas chromatograph was used to detect and analyse the SF$_6$ by-products. It was found that when PTFE vapour is involved in the arc plasma, the main by-product after arc quenching is CF$_4$, and the molar fractions of C$_2$F$_6$ and C$_3$F$_8$ are very low. When O$_2$ is involved, the main by-products are SOF$_2$, SO$_2$ and SO$_2$F$_2$, and a small amount of CO and CO$_2$ was also produced. When H$_2$O is involved, the main by-products in simulation are SOF$_2$, SO$_2$ and HF, and a small amount of SO$_2$, CO$_2$, CO, SO$_2$F$_2$ and H$_2$ was also produced. The experimental results are in good agreement with the above results.

Keywords: SF$_6$ by-products; Gibbs free energy minimization method; breaking experiment; H$_2$O and O$_2$ impurities; PTFE vapour

1. Introduction

SF$_6$ is a greenhouse gas. It is one of the six gases included in the Kyoto Protocol aimed at reducing greenhouse gas emissions. The global warming potential (GWP) of SF$_6$ is 23,900 times greater than CO$_2$ according to the 2013 report of Intergovernmental Panel on Climate Change (IPCC), and it has a lifetime in the atmosphere of 3200 years. However, SF$_6$ has excellent insulation performance, arc quenching performance, and molecular stability. It is widely used in high voltage circuit breakers [1,2]. The high voltage SF$_6$ circuit breaker will inevitably produce a high temperature and high energy arc in the process of breaking currents. It will cause SF$_6$ to decompose and form SF$_6$ arc plasma. Many sulfur fluorides such as SF$_5$, SF$_4$, SF$_3$, SF$_2$, SF, S and F will be produced in the arc plasma. As the arc extinguishes, the arc temperature will gradually decrease, and these species will recombine into SF$_6$ molecules [3,4]. However, there are trace H$_2$O and O$_2$ impurities in the circuit breaker, and the nozzle made by polytetrafluoroethylene (PTFE) material will be ablated by arc to produce trace PTFE vapour during the breaking process. The H$_2$O, O$_2$, and PTFE impurities will participate in the reaction of SF$_6$ arc plasma to form various by-products such as SOF$_2$, SO$_2$, SO$_2$F$_2$, CF$_4$, C$_2$F$_6$, C$_3$F$_8$, CO$_2$, CO, and HF [5,6].

On the one hand, some by-products such as SOF$_2$ and HF are corrosive and toxic, thus posing considerable threat to the safe and stable operation of equipment and health of the operation and maintenance personnel [7]. On the other hand, there is a close relationship between some by-products and the discharge faults in the equipment, so the decomposition component analysis (DCA) technology can be used in fault detection.
and condition assessment of SF₆ power equipment [8,9]. Therefore, the decomposition characteristics of SF₆ under arc discharge and the effects of trace H₂O, O₂, and PTFE vapour on its by-products have attracted extensive attention.

Many scholars have carried out a lot of research on this problem and achieved rich results. In terms of the experiments, Boudene et al. studied the decomposition products in detail under the condition of voltage of 60 kV, a current of 4.5 kA and arcing time 40–80 ms. They found that the gas production rate of SOF₂ and SO₂F₂ and arc energy is almost linear [10]. Belmadani and Casanvas examined the SF₆ byproducts of power arc discharges using gas chromatography [11,12]. The maximum arc current reached 8.3 kA, and the primary byproducts were SOF₂, SO2F₂, SO₂, and CF₄. The concentrations of these byproducts decreased in the following order: SOF₂+SO₂ > CF₄ > SO₂F₂. Our previous work used a circuit breaker to study the influence of trace H₂O and O₂ on SF₆ by-products [13]. We found that the increase of the concentration of H₂O and O₂ will increase the production of SOF₂+SO₂, and the concentration of CF₄ is hardly affected by the concentration of H₂O and O₂. Andrzej pelc studied the generation of negative ions from SF₆ gas by means of hot surface ionization. He found eight ion species: SF₅⁻, F⁻, SF₆⁻, SF₄⁻, SF₃⁻, SF₂⁻, SF⁺ and F₂⁻, with ion current intensities ratios of 1000:200:100:10:5:0:5:0:5:0.05. He also found the optimal temperatures at which the maximum of the ion current intensity is observed were estimated in the 1830–2000 °C range [14].

In terms of the simulations, Brand et al. studied the particle compositions of SF₆ arc plasma at standard atmospheric pressure [15]. Chervy and Gleizes considered the influence of copper vapour on the particle compositions and proposed a particle composition model of an SF₆/Cu mixture [16]. Coufal studied the effect of PTFE ablation on particle compositions, and the Gibbs free energy minimization method was first used in the calculation [17]. Wang et al. studied the arc plasma particle compositions of an SF₆/CF₄ gas mixture [18]. Up to now, there are few reports about SF₆/PTFE/H₂O, SF₆/PTFE/O₂, and SF₆/PTFE/H₂O/O₂ gas mixture arc plasma. The arc plasma model cannot be used to study the comprehensive effects of trace H₂O, O₂, and PTFE vapour on SF₆ by-products. It seriously limits the reliability of the calculation results.

In order to solve this problem, the arc plasma models of SF₆, SF₆/PTFE, SF₆/PTFE/H₂O, and SF₆/PTFE/O₂ are established by using the Gibbs free energy minimization method in this paper. The effects of trace H₂O, O₂, and PTFE vapour on SF₆ by-products was studied by these models. On this basis, a comprehensive model of SF₆/PTFE/H₂O/O₂ gas mixture was finally established. The research on the particle composition of SF₆ arc plasma is improved. In order to verify the correctness of the calculation results, a series of breaking experiments were carried out on a 40.5 kV SF₆ circuit breaker, and a gas chromatograph was used to detect and analyse the SF₆ by-products. It was found that the simulation results are in good agreement with the experimental results.

2. Methods

Under the assumption of local thermodynamic equilibrium (LTE), the physical parameters of the system are only functions of temperature and pressure. The minimization of Gibbs free energy means that the Gibbs function of the equilibrium state is the smallest when the temperature and pressure are constant [17]. In this paper, the particle composition of SF₆ arc plasma is studied by this method. In pure SF₆ arc plasma, 12 kinds of particles such as SF₆, SF₅, SF₄, SF₃, SF₂, SF, S, S₂, F₂, S₂F₁₀, and FSSF were considered. In SF₆/PTFE arc plasma, 12 kinds of particles such as C₃F₆, C₂F₆, C₂F₂, C₂F₄, C₃F₅, C₄F₆, C₅F₇, C₆F₈, CF, CF₂, CF₃, and CF₄ were added. In SF₆/PTFE/O₂ arc plasma, 10 kinds of particles such as O, O₂, SOF₂, SO₂F₂, SO, SO₂, CO₂, CO, COF, and COF₂ were added. In SF₆/PTFE/H₂O arc plasma, 9 kinds of particles such as H₂O, OH, H, H₂, H₂ Adsorption, adsorption, and specific heat at constant pressure can be obtained in the JANAF database [19]. All calculations were completed in the Chemkin software.
In order to verify the correctness of the calculation results, a series of breaking experiments were carried out on a 40.5 kV SF₆ circuit breaker. The rated voltage was 40.5 kV, the rated current was 2.5 kA, the rated frequency was 50 Hz, the rated air pressure was 0.6 MPa, the rated short circuit breaking current was 31.5 kA, and the volume of single-phase air chamber was 30.0 L. Figure 1 shows the experimental arrangement. Before the experiment, SF₆ gases with different concentrations of H₂O and O₂ were filled into three chambers respectively. Sinusoidal current was generated by an L-C circuit with pre-charged capacitor banks. Arc current was about 10 kA. Arcing time with one current half-wave was 6.5 to 10.0 ms due to the mechanical dispersion of the actuator. Arc voltage and arc current were measured by a high voltage probe and Rogowski coil respectively, and recorded by oscilloscope. After each breaking experiment, the SF₆ by-products in the chamber were analysed by gas chromatograph.

![Figure 1. Schematic of experimental arrangement.](image)

This gas chromatograph was equipped with a hydrogen ionisation detector (FID) and a pulsed flame photometric detector (PFPD) to detect SF₆ by-products. The carrier gas was He with purity over 99.99%, the output pressure was 0.5–0.6 MPa, the injection temperature was 150 °C, the injection volume was 250 µL, the split ratio was 20:1, the column temperature was 50 °C for 5 min, and 10 °C/min is raised to 200 °C for 10 min. Figure 2 shows the test result of gas chromatograph. The detected gases in channel A were H₂, O₂, N₂, CO, CH₄, CO₂, CF₄, and C₂F₆. The detected gases in channel B were SF₆, SOF₂, SO₂F₂, SO₂, COS, C₃F₈, and CS₂. Trace H₂O content was measured using a SF₆ mirror dew point instrument. This instrument is often used in the field detection of trace H₂O content in SF₆ circuit breaker, with the advantages of fast response and high precision.

The specific experimental settings are shown in Tables 1 and 2. In order to research the effect of trace H₂O on SF₆ by-products after the arc was extinguished and verify the correctness of the simulation results, the three gas chambers of the circuit breaker were filled with SF₆ gases with different H₂O concentration. The concentration of H₂O before the breaking experiment in A, B, and C chambers were 106 ppm, 748 ppm, and 1131 ppm, respectively. The breaking current was 10 kA and the times of breaking is 5. The setting of the breaking experiment with different O₂ concentration was similar to that of H₂O.
Table 1. Setting of breaking experiment with different H$_2$O concentration.

| Phase | H$_2$O Concentration | Breaking Current | Breaking Times |
|-------|----------------------|------------------|----------------|
| A     | 106 ppm              | ~10 kA           | 5              |
| B     | 748 ppm              | ~10 kA           | 5              |
| C     | 1131 ppm             | ~10 kA           | 5              |

Table 2. Setting of breaking experiment with different O$_2$ concentration.

| Phase | O$_2$ Concentration | Breaking Current | Breaking Times |
|-------|---------------------|------------------|----------------|
| A     | 59 ppm              | ~10 kA           | 5              |
| B     | 736 ppm             | ~10 kA           | 5              |
| C     | 1202 ppm            | ~10 kA           | 5              |

3. Results and Discussion

3.1. Particle Composition of SF$_6$ and SF$_6$/PTFE

Figure 3 shows the particle composition of pure SF$_6$ arc plasma at 0.6 MPa. It can be found that SF$_6$ molecules begin to decompose at about 1000 K and forms SF$_5$, SF$_4$, and F atoms first. With the increase of arc temperature, SF$_3$, SF$_2$, and SF begin to form. It should be noted that the temperature required for the formation of SF$_5$, SF$_4$, SF$_3$, SF$_2$, and SF increases step-by-step, and the maximum mole fractions of SF$_4$ and SF$_2$ is significantly greater than that of SF$_5$, SF$_3$, and SF. The main reason is that the decomposition process of SF$_6$ is a process of gradually breaking the S-F bond to form a lower-level low fluorine sulfide, and the S-F bond energy of SF$_4$ and SF$_2$ is higher than that of SF$_5$, SF$_3$, and SF. When the arc temperature is greater than 3000 K, the mole fractions of all sulfur fluorides begin to decrease, and gradually decompose into S and F atoms. It should be noted that the arc temperature decreases gradually during the arc decay process. When the arc temperature decreases below 1000 K, all sulfur fluorides and atoms recombine into SF$_6$. The results of this part show good agreement with previous work [20], which proves the reliability of our calculation results.
Figure 3. Particle composition of SF$_6$ arc plasma at 0.6 MPa.

Figure 4 shows the particle composition of SF$_6$/PTFE arc plasma at 0.6 MPa. Compared with pure SF$_6$ arc plasma, CF$_4$, CF$_3$, CF$_2$, S$_2$F$_{10}$, etc. appear in particle composition. CF$_4$ and CF$_3$ are formed by the combination of CF$_2$ radicals produced by the decomposition of PTFE and the F atom produced by SF$_6$ decomposition. The formation of CF$_4$ will lead to the lack of F atoms in the arc plasma, so some SF$_5$ radicals cannot obtain the F atoms to form SF$_6$, and these SF$_5$ radicals will combine with each other to form S$_2$F$_{10}$. It should be noted that as the arc temperature gradually decreases to room temperature, almost all PTFE vapour is converted into CF$_4$, and C$_2$F$_6$ and C$_3$F$_8$ are hardly generated. The molar fraction of C$_2$F$_6$ and C$_3$F$_8$ are both less than 10$^{-6}$.

Figure 4 shows the particle composition of SF$_6$/polytetrafluoroethylene (PTFE) arc plasma at 0.6 MPa. (a) 90% SF$_6$ + 10% PTFE. (b) 80% SF$_6$ + 20% PTFE.

Figure 5 shows the change of CF$_4$, C$_2$F$_6$, and C$_3$F$_8$ concentrations with the breaking times. The breaking current is about 10 kA. It can be found that the concentration of CF$_4$ is much higher than that of C$_2$F$_6$ and C$_3$F$_8$, and shows an obvious increasing trend with the breaking times, while C$_2$F$_6$ and C$_3$F$_8$ have no obvious change. After five breaking
experiments, the concentration of CF₄ reached 289.6 ppm, while the concentration of C₂F₆ and C₃F₈ was only 2.1 ppm and 0.2 ppm, respectively. It can be concluded that CF₄ is the main by-product produced by the ablation of PTFE, and the concentrations of C₂F₆ and C₃F₈ are very low. The experimental results are in good agreement with the simulation results.

3.2. Particle Composition of SF₆ and SF₆/PTFE/O₂

Figures 6 and 7 show the particle composition of SF₆/PTFE/O₂ arc plasma with different O₂ concentrations. Compared with SF₆/PTFE arc plasma, a large number of particles containing O element such as SOF₂, SO₂F₂, COF₂, SO₂, CO, and CO₂ appear in arc plasma. CO appears in the temperature range of 2000 K–5000 K. CO₂ and SO₂ appear in the temperature range of >1500 K. COF₂ appears in the temperature range of 1000 K–4500 K. As the arc temperature gradually decreases to room temperature, the molar fraction of these species will be reduced to <10⁻⁶. SOF₂ and SO₂F₂ can appear in arc plasma when the temperature is less than 1000 K, and their molar fraction is much higher than that of CO₂, SO₂, and COF₂. Therefore, it can be concluded that the participation of a small amount of O₂ will promote the formation of SOF₂, SO₂F₂, COF₂, SO₂, CO, and CO₂. After the arc is extinguished, the concentration of SOF₂ and SO₂F₂ will be higher than that of COF₂, SO₂, CO, and CO₂.

Figure 8 shows the changes of SOF₂, SO₂, SO₂F₂, and CO concentrations with the breaking times under different O₂ concentrations. As shown in Figure 8a, the concentration of SOF₂ increases with the breaking times. When the O₂ concentrations are 59 ppm, 748 ppm and 1130 ppm, respectively, the concentrations of SOF₂ can reach 761 ppm, 983 ppm and 1121 ppm, respectively, after five breaking experiments. This indicates that the increase of O₂ concentration can promote the formation of SOF₂. As shown in Figure 8b, the concentration of SO₂ increases with the breaking times. The concentrations of SO₂ were 3.1 ppm, 9.0 ppm and 9.7 ppm, respectively, after five breaking experiments. As shown in Figure 8c, the concentration of SO₂F₂ increases with the breaking times. After five breaking experiments, the concentrations of SO₂F₂ are 0.4 ppm, 7.1 ppm and 9.8 ppm, respectively. This indicates that the increase of O₂ concentration can significantly promote the formation of SO₂F₂. Figure 8d shows the change of CO with the breaking times. It can be seen that the concentration of CO is very low, and the highest is only 1.0 ppm. Due to the limitation of experimental conditions and the accuracy of testing equipment, when O₂ are 736 ppm and 1202 ppm, CO has no significant regularity. When O₂ is 59 ppm, the concentration of
CO is obviously lower than the former two cases. This indicates that the increase of O₂ concentration can also promote the formation of CO, but this phenomenon is not obvious.

**Figure 6.** Particle composition of 70% SF₆ + 20% CF₂ + 10% O₂ arc plasma at 0.6 MPa. (a) SF₆, SF₅, SF₄, SF₃, SF₂, SF, S, S₂, F, F₂, FSSF, CF₄, CF₃, CF₂, CF, and C particles. (b) SOF₂, SO₂F₂, COF₂, COF, O₂, O, SO₂, SO, CO₂, and CO particles.

**Figure 7.** Particle composition of 60% SF₆ + 20% CF₂ + 20% O₂ arc plasma at 0.6 MPa. (a) SF₆, SF₅, SF₄, SF₃, SF₂, SF, S, S₂, F, F₂, FSSF, CF₄, CF₃, CF₂, CF, and C particles. (b) SOF₂, SO₂F₂, COF₂, COF, O₂, O, SO₂, SO, CO₂, and CO particles.

In comparison, the concentration of SOF₂ is much higher than that of SO₂, SO₂F₂ and CO. After five breaking experiments, the concentration of SOF₂ can reach 1000 ppm, and the concentrations of SO₂ and SO₂F₂ are both about 10 ppm, while the concentration of CO is lower than 2 ppm. This phenomenon indicates that when O₂ is involved in the arc plasma reaction, SOF₂ will be the main by-product after the arc is extinguished, and the concentrations of SO₂ and SO₂F₂ will also increase significantly.
that the concentration of CO is very low, and the highest is only 1.0 ppm. Due to the limitation of experimental conditions and the accuracy of testing equipment, when O$_2$ are 736 ppm and 1202 ppm, CO has no significant regularity. When O$_2$ is 59 ppm, the concentration of CO is obviously lower than the former two cases. This indicates that the increase of O$_2$ concentration can also promote the formation of CO, but this phenomenon is not obvious.

In comparison, the concentration of SOF$_2$ is much higher than that of SO$_2$, SO$_2$F$_2$ and CO. After five breaking experiments, the concentration of SOF$_2$ can reach 1000 ppm, and the concentrations of SO$_2$ and SO$_2$F$_2$ are both about 10 ppm, while the concentration of CO is lower than 2 ppm. This phenomenon indicates that when O$_2$ is involved in the arc plasma reaction, SOF$_2$ will be the main by-product after the arc is extinguished, and the concentrations of SO$_2$ and SO$_2$F$_2$ will also increase significantly.

Figure 8. Changes of SOF$_2$, SO$_2$, SO$_2$F$_2$, and CO concentrations with the breaking times under different O$_2$ concentration. (a) Changes of SOF$_2$ with the breaking times. (b) Changes of SO$_2$ with the breaking times. (c) Changes of SO$_2$F$_2$ with the breaking times. (d) Changes of CO with the breaking times.

3.3. Particle Composition of SF$_6$ and SF$_6$/PTFE/H$_2$O

Figures 9 and 10 show the particle composition of SF$_6$/PTFE/H$_2$O arc plasma with different H$_2$O concentrations. Compared with SF$_6$/PTFE/O$_2$ arc plasma, some particles containing H such as HF, H$_2$, CH, and H appear in arc plasma, and the molar fractions of SOF$_2$ and SO$_2$F$_2$ were significantly affected. H$_2$ appears in the temperature range of 3500 K–5000 K. H appears in the temperature range of 2500 K–5000 K. HF can appear in the whole temperature range and its molar fraction is always greater than 10$^{-1}$. SOF$_2$ can appear in the temperature range of 300 K–5000 K, and its molar fraction decreases with the decrease of arc temperature. When the temperature decreases to room temperature, the molar fraction of SOF$_2$ can reach 10$^{-1}$. SO$_2$F$_2$ can appear in the temperature range of 300 K–3000 K, and its molar fraction relatively low. It can be concluded that the participation of a small amount of H$_2$O will promote the formation of HF, H$_2$, SOF$_2$, SO$_2$F$_2$, COF$_2$, etc.
SO₂, CO, and CO₂. After the arc is extinguished, the concentration of HF and SOF₂ will be significantly higher than that of SO₂F₂, COF₂, SO₂, CO, and CO₂.

**Figure 9.** Particle composition of 70% SF₆ + 20% CF₂ + 10% H₂O arc plasma at 0.6MPa. (a) SF₆, SF₅, SF₄, SF₃, SF₂, SF, S, S₂, F, F₂, FSSF, S₂F₁₀, CF₄, CF₃, CF₂, CF, C, C₂F, and C₂F₂ particles. (b) SOF₂, SO₂F₂, COF₂, COF, O₂, O, SO₂, SO, CO₂, CO, HF, H, H₂, and CH particles.

**Figure 10.** Particle composition of 60% SF₆ + 20% CF₂ + 20% H₂O arc plasma at 0.6MPa. (a) SF₆, SF₅, SF₄, SF₃, SF₂, SF, S, S₂, F, F₂, FSSF, S₂F₁₀, CF₄, CF₃, CF₂, CF, C, C₂F, and C₂F₂ particles. (b) SOF₂, SO₂F₂, COF₂, COF, O₂, O, SO₂, SO, CO₂, CO, HF, H, H₂, and CH particles.

Figure 11 shows the changes of SOF₂, SO₂, CO₂, and CO concentrations with the breaking times under different H₂O concentration. It can be found that the concentration of SOF₂, SO₂, CO₂ and CO increase with the breaking times. The increase of H₂O concentration can promote the production of SOF₂, SO₂, CO₂, and CO. For example, when the H₂O concentrations are 106 ppm, 748 ppm and 1130 ppm, respectively, the concentrations of SOF₂ are 1097 ppm, 1130 ppm and 1253 ppm, respectively, after five breaking experi-
ments. This conclusion is consistent with the calculation results of particle composition of SF₆/PTFE/H₂O arc plasma.

In comparison, the concentration of SOF₂ is much higher than that of SO₂, CO₂ and CO. After five breaking experiments, the concentration of SOF₂ can reach 1000 ppm, while the concentration of SO₂ and CO₂ is lower than 20 ppm, and the concentration of CO is lower than 2 ppm. This phenomenon indicates that when H₂O is involved in the arc plasma reaction, SOF₂ will be the main by-product after the arc is extinguished. This conclusion also shows good agreement with the calculation result.

Contrary to the simulation results, SO₂F₂ and HF are hardly detected in this experiment. We believe the main reason is that H₂O does not promote the formation of SO₂F₂ obviously, and HF can react with the metal materials and solid insulation materials in the circuit breaker quickly, which makes it hardly detected. The particle composition model of arc plasma needs to be further improved.

![Graphs](image_url)

**Figure 11.** Changes of SOF₂, SO₂, CO₂, and CO concentrations with the breaking times under different H₂O concentration. (a) Changes of SOF₂ with the breaking times. (b) Changes of SO₂ with the breaking times. (c) Changes of CO₂ with the breaking times. (d) Changes of CO with the breaking times.
It can be found by comparing the breaking experiments under different O₂ and H₂O concentrations that both H₂O and O₂ can promote the formation of SOF₂. Under similar experimental conditions, the promotion effect of H₂O on the formation of SOF₂ is more obvious than that of O₂. For example, when the concentration of H₂O is 748 ppm, the concentration of SOF₂ can reach 1130 ppm after five breaking experiments, with an average of 226 ppm each time. When the concentration of O₂ is 736 ppm, the concentration of SOF₂ is 983 ppm after five breaking experiments, with an average of 197 ppm each time. It also can be found that both H₂O and O₂ can promote the formation of SO₂ and CO, but the concentrations are relatively low. O₂ can significantly promote the formation of SO₂F₂, while H₂O has no obvious effect on SO₂F₂.

3.4. Particle Composition of SF₆ and SF₆/PTFE/O₂/H₂O

Figure 12 shows the particle composition of 60% SF₆ + 20% CF₂ + 10% H₂O + 10% O₂ arc plasma at 0.6 MPa. A total of 43 kinds of particles are considered in this model. The molar fractions of 33 kinds of particles are more than 10⁻⁶. The SF₆ by-products detected after the breaking experiment all appeared in this model, and the molar fractions of these species are relatively high. CO appears in the temperature range of 2000 K–5000 K, and the maximum molar fraction is 4.6%. CO₂ and SO₂ appear in the temperature range of 1250 K–5000 K, and the maximum molar fraction is 0.27% and 0.19%, respectively. CF₄ appears in the temperature range of 300 K–3500 K, and the maximum molar fraction is 20.0%. SOF₂ appears in the temperature range of 500 K–4500 K, and the maximum molar fraction is 13.8%. SO₂F₂ appears in the temperature range of 300 K–2750 K, and the maximum molar fraction is 15.0%. HF appears in the whole temperature range, and the maximum molar fraction is 20.2%. It should be noted that SOF₂, SO₂F₂, CF₄, HF, O₂, and SF₆ are the main particles when the arc temperature drops below 1000 K.

![Figure 12. Particle composition of 60% SF₆ + 20% CF₂ + 10% H₂O + 10% O₂ arc plasma at 0.6 MPa. (a) SF₆, SF₅, SF₄, SF₃, SF₂, SF, S, S₂, F, F₂, FSSF, CF₄, CF₃, CF₂, CF, and C particles. (b) SOF₂, SO₂F₂, COF₂, COF, O₂, O, SO₂, SO, CO₂, CO, HF, H, H₂, and OH particles.](image)

4. Conclusions

This paper established the arc plasma models of SF₆ (12 particles are considered), SF₆/PTFE (24 particles are considered), SF₆/PTFE/O₂ (34 particles are considered), SF₆/PTFE/H₂O (43 particles are considered), and SF₆/PTFE/O₂/H₂O (43 particles are considered) by using the Gibbs free energy minimization method. The effects of trace H₂O and O₂
impurities and PTFE vapour on the SF$_6$ by-products were studied. In order to verify the correctness of the simulation results, a series of breaking experiments were carried out on a 40.5 kV SF$_6$ circuit breaker, and a gas chromatograph was used to detect and analyse the SF$_6$ by-products. It was found that the experimental results are in good agreement with the simulation results. The primary conclusions are summarized below:

(1) SF$_6$ molecules began to decompose at about 1000 K and form SF$_5$, SF$_4$, SF$_3$, SF$_2$, SF, S, and F with the increase of arc temperature. The maximum molar fractions of SF$_4$ and SF$_2$ were higher than SF$_5$, SF$_3$, and SF. As the arc temperature gradually decreases to room temperature, all low fluorine sulphides recombine into SF$_6$.

(2) When PTFE vapour was involved in the arc plasma, the main by-product after arc quenching was CF$_4$, and the molar fractions of C$_2$F$_6$ and C$_3$F$_8$ were very low. After five breaking experiments, the concentration of CF$_4$ can reach 289.6 ppm, while the concentration of C$_2$F$_6$ and C$_3$F$_8$ was only 2.1 ppm and 0.2 ppm, respectively. The simulation results were in good agreement with the experimental results.

(3) When O$_2$ was involved in the arc plasma, the main by-products were SOF$_2$, SO$_2$, and SO$_2$F$_2$. At the same time, a small amount of CO, and CO$_2$ was produced. After five breaking experiments, the concentration of SOF$_2$ can reach 1100 ppm, and the concentrations of SO$_2$ and SO$_2$F$_2$ were both about 10 ppm, while the concentration of CO was lower than 2 ppm.

(4) When H$_2$O was involved in the arc plasma, the main by-products were SOF$_2$, SO$_2$, SO$_2$F$_2$, and HF. At the same time, a small amount of CO$_2$, CO, and H$_2$ was produced. After five breaking experiments, the concentration of SOF$_2$ can reach 1200 ppm, and the concentration of SO$_2$ and CO$_2$ was lower than 20 ppm, while the concentration of CO was lower than 2 ppm. Contrary to the simulation results, SO$_2$F$_2$ and HF were hardly detected in this experiment.

(5) When H$_2$O and O$_2$ impurities and PTFE vapour were involved in the arc plasma together, the main by-products were SOF$_2$, CF$_4$, SO$_2$F$_2$, and HF. At the same time, a small amount of SO$_2$, CO$_2$, CO, and H$_2$ was be produced.

**Author Contributions:** R.Y. and J.Y. proposed the idea, established the model, and completed the experiment. M.X. and M.Y. completed the simulation, analyzed the results, and finished the original draft of this paper. Y.G. and Z.L. provided valuable opinions, and collected the data. J.W. checked the format. All authors have read and agreed to the published version of the manuscript.

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